स्वाध्याय स्वमन्थन स्वावलम्बन

UTTAR PRADESH RAJARSHI TANDON OPEN UNIVERSITY

(Established vide U.P. Govt. Act No. 10, of 1999)

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Indira Gandhi National Open University UP Rajarshi Tandon Open University

UGCHE-10

Spectroscopy

FIRST BLOCK : Basic Concepts and Rotational Spectra

SECOND BLOCK : IR and Raman Spectra

THIRD BLOCK : Electronic Spectra and Instrumentation

FOURTH BLOCK : Resonance Spectroscopy and Mass Spectrometry

Shantipuram (Sector-F), Phaphamau, Allahabad - 211013

MESSAGE

Dear Learner,

It is my proud pleasure to extend you a very warm welcome on joining the **U.P. Rajarshi Tandon Open University (UPRTOU), Allahabad.** This university which was established in 1999 is the only university of U.P. which follows the open and distance mode of education (ODE). In a short span of more than a decade, the UPRTOU with the help of its five regional centers and more than 400 study centers in UP, has made sincere efforts to reach to those remote places in UP where no other educational institution has ever reached. With its nearly 100 degree, diploma and certificate programs UPRTOU has emerged as an important alternate system of higher education in this state.

India has at present the **second largest system** of higher education in the world. However most of our universities and colleges are located in urban areas. A large population of India which lives in rural areas is, therefore, deprived of the opportunities of higher education. In order to provide access and benefits of higher education to these people in India who have been deprived of going to conventional educational institutions because of economic, social and geographical limitations/ restrictions, ODE programs have opened up a new path to nurture, build up and sustain a strong base of educational system in the country.

Distance-education courses are convenient in many ways. They are very cost effective and flexible. For example, you can get an MBA degree by studying at home. You also have an opportunity to pursue your studies simultaneously with a career. Now even you can do a Ph.D. from an open university. ODE system empowers the learners to study at their own convenience, **"Anyone. Anywhere and Anytime"**, i.e. 3A's is the main philosophy behind the development of open and distance education system.

I am very confident that you will enjoy being a part of this university and benefit a lot from this study material written by renowned experts. The UPRTOU has already initiated a large number of steps including integration with Information and Communication technology (ICT) to enhance the quality of education imparted to our students and I assure you that we will leave no stone unturned to make this university a role model for the rest of the country in high quality open and distance education.

Vice-Chancellor
U.P.Rajarshi Tandon Open University
Allahabad

Uttar Pradesh
Rajarshi Tandon Open University,

UGCHE -10
Spectroscopy

Block
1

BASIC CONCEPTS AND ROTATIONAL SPECTRA

SPECTROSCOPY

The Study of spectroscopy is of vital importance to the modern chemists. Spectroscopic techniques serve as reliable means and are being used as a routine method of identification of compounds. The main features which give it an edge over the conventional analytical techniques are given below:

- identification even with very small amounts of material
- quick analysis
- greater authenticity
- sample recovery (in most of the methods)
- finer structural details such as stereoisomer type, etc.

This course on 'Spectroscopy' has been developed keeping in mind the widespread use of this technique in modern chemistry laboratories. Both the theoretical aspects and the applications of spectroscopic methods have been dealt with in this course. You will appreciate the importance and uniqueness of each spectroscopic method, while studying this course. Besides these aspects, you will also learn about the instrumentation.

We are very much aware of the fact that the concepts dealt with in this course are slightly difficult. Therefore, they have been explained in a detailed way.

This course consists of thirteen units spread in four blocks. In order to understand spectra-structure relationship in a better way, it is suggested that you should go through (or revise) the course material of 'Atoms and Molecules' (CHE-01), 'Inorganic Chemistry' (CHE-02) and 'Organic Chemistry' (CHE-05) courses. Such a study is a pre-requisite since it would provide the bonding theories of inorganic and organic compounds and prepare you for assimilating the concepts discussed in the spectroscopy course.

As it is a four credit course, you are expected to devote 120 hours of study. But do not get disheartened as your pace of learning may vary and you may need a little more time (or little less time). You can plan your study by distributing your time as follows:

- About 7 hours of study for each unit on an average making about 90 hours for 13 units.
- 10 hours for **two tutor-marked assignments** which are to be submitted for continuous evaluation.
- remaining 20 hours can be used for attending the counselling sessions or revising the course material or doing some additional reading from the books mentioned at the end of each block. These books will be availabale at your study centre. Remember that these books are only for additional reading, i.e. if you want to study some aspects in more detail, otherwise this course material is self-sufficient.

In case of any difficulty or suggestions, send your comments to the Course Coordinator at the address given below. Your comments will give us a feed back which will further help us in improving this course.

Wishing you all the best in your studies.

Course Coordinator,
Spectroscopy (CHE-10)
School of Sciences, IGNOU
Maidan Garhi, New Delhi-110 068.

Objectives

This course familiarises the learners with both the theory and application aspects of spectroscopic methods used in the identification of compounds. After studying this course, the students should able to:

- explain the basic concepts of atomic and molecular spectra,
- use the ideas of symmetry and group theory in explaining the various types of spectroscopy,
- describe the theoretical features and applications of various types of spectroscopy i.e. rotational, vibrational, Raman and electronic etc.
- discuss the instrumentation associated with the above spectral techniques,
- explain the techniques of resonance spectroscopy such as nuclear magnetic resonance spectroscopy and electron spin resonance spectroscopy and their applications,

- state the applications of mass spectrometry, and
- correlate the spectra of simple molecules with their structure.

Study Guide

Some of the concepts explained may seem difficult to you at the first attempt, hence you are advised to read those portions again. You can plan your study time and devote 6-7 hours of study to each unit. It is suggested that you attempt the self-assessment questions given in the units to check your understanding of the concepts.

You are also advised to study the marginal remarks carefully as they will give you interesting and important information.

In case you want to read more about the topics dealt in this block, you can consult the books listed at the end of this block. Otherwise, the blocks sent to you are self-sufficient.

You will also be receiving two Tutor-Marked Assignments alongwith the course material. Assignment 1 is based on Blocks 1 and 2 and Assignment 2 is based on Blocks 3 and 4. Start doing the assignments also as you study the course material.

In case of any difficulty or suggestion, send your comments and feedback to the course coordinator.

Wishing you Good Luck in the studies.

BASIC CONCEPTS AND ROTATIONAL SPECTRA

This is the first block of the 'Spectroscopy' course. It deals with the basic concepts of spectroscopy and rotational spectra. It contains three units.

Unit 1 deals with the 'Spectra of Atoms'. It starts with the basic concepts such as how and why atomic spectrum is obtained. The atomic spectrum of hydrogen is discussed in detail whereas the spectra of some multi-electron systems such as He, C etc. have been explained briefly.

Unit 2 deals with 'Symmetry of Molecules'. The study of symmetry of molecules can help in relating the shape of a molecule to its spectrum. This unit begins with the recapitulation of the VSEPR theory which was explained in Unit 3 of 'Atoms and Molecules' (CHE-01) course. This is followed by the discussion on symmetry elements and symmetry operations. The molecules will then be classified into point groups using symmetry. This classification helps in understanding various physical properties such as dipole moment, optical rotation and spectra of molecules.

Some of the aspects of symmetry are dealt in the form of group theory in the Appendix to Unit 2. The study of group theory will help you in better understanding of advanced concepts of spectroscopy.

Unit 3 is devoted to the 'Rotational Spectra'. From this unit onwards, the study of molecular spectra begins. The study of rotational spectra of molecules helps in arriving at the values of molecular parameters such as bond length and bond angle. We will begin this unit by explaining the various types of molecular motions. The rotational spectrum of a rigid diatomic molecule will be discussed in detail followed by the applications of such a study. Then the effect of non-rigidity on rotational spectra will be explained. The rotational spectra of polyatomic molecules will also be discussed briefly.

Objectives

After studying this block, you should be able to:

- describe electromagnetic radiation,
- discuss the atomic spectrum of hydrogen in detail,
- predict the spectra of hydrogen like atoms,
- explain Zeeman effect,
- describe symmetry elements and symmetry operations,
- identify the point group of a molecule from its symmetry elements,
- state implications of molecular symmetry,
- define moment of inertia,
- discuss the rotational spectra of linear diatomic and triatomic molecules,
- give applications of study of rotational spectra,
- explain the effect of isotopic substitution and non-rigidity on the rotational spectra of molecules,
- classify various molecules on the basis of their moment of inertia, and
- relate the intensity of spectral lines with population of energy levels.

UNIT 1 SPECTRA OF ATOMS

Structure

1.1 INTRODUCTION

This is the first unit of the 'Spectroscopy' course. As suggested to you, we assume that by now you must have studied "Atoms and Molecules" (CHE-01) course. Since there must have been some time gap in-between, it will be useful to begin with by refreshing some of the concepts dealt with in the 'Atoms and Molecules' course.

This unit is devoted to the spectra of Atoms. You are aware from Unit 1 of "Atoms and Molecules" course that atomic spectra results due to the interaction of electromagnetic radiation with atoms. Hence, we will start our discussion by defining what is electromagnetic radiation and how it propagates in space. We will also enlist some characteristics of electromagnetic radiation followed by the explanation of its interaction with atoms. We will discuss the atomic spectra of hydrogen and hydrogen like atoms in detail followed by that of helium and sodium. We will also explain the spectroscopic states by taking the example of carbon. Then Zeeman effect will be discussed. Finally, two techniques such as X-ray fluorescence and photoelectron spectroscopy used in the determination of atomic spectra will be explained.

Objectives

After studying this unit, you should be able to:

- describe electromagnetic radiation,
- define and relate various parameters such as wavelength, frequency, wavenumber etc. associated with the electromagnetic radiation,
- discuss the origin of various series of spectral lines in the atomic spectrum of hydrogen,

- explain the fine structure of hydrogen atom spectrum,
- predict the spectra of hydrogen like atoms,
- discuss the possible transitions in the atomic spectrum of helium,
- write spectroscopic terms of an atom from its electron configuration,
- explain Zeeman effect and
- give importance of the x-ray flourescence and photoelectron spectroscopy.

1.2 THE ELECTROMAGNETIC RADIATION

Since atoms and molecules cannot be seen, we derive information about their structure by their interaction with electromagnetic radiation. You may recall from Units 1 and 6 of 'Atoms and Molecules' course that electromagnetic radiation consists of oscillating electric and magnetic fields directed perpendicularly to each other and also to the direction of propagation of radiation, as is shown in Fig. 1.1.

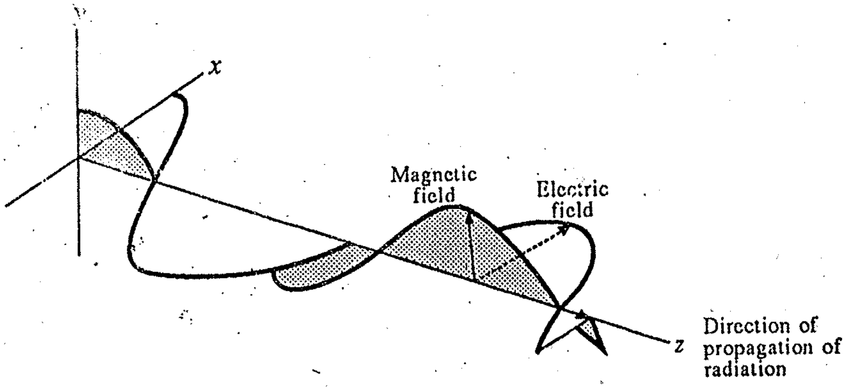


Fig. 1.1: The electric and magnetic fields of the electromagnetic radiation.

Similar to the other transverse wave motions such as that of stretched string or water wave, the electromagnetic radiation carries energy from one place to another. But unlike the other wave motions it does not require any medium for its propagation.

The electromagnetic radiation can be described in terms of certain parameters such as **wavelength, frequency, wave number** and **energy.** Although these parameters have been explained in Block 1, Unit 1, Sec. 1.4 of 'Atoms and Molecules' course, let us revise them and refresh our memory as you will be using them very often throughout this course.

Wavelength (λ) can be defined as the distance between two successive crests or troughs (see Fig. 1.2). The wavelength depends on the system through which the radiation is passing.

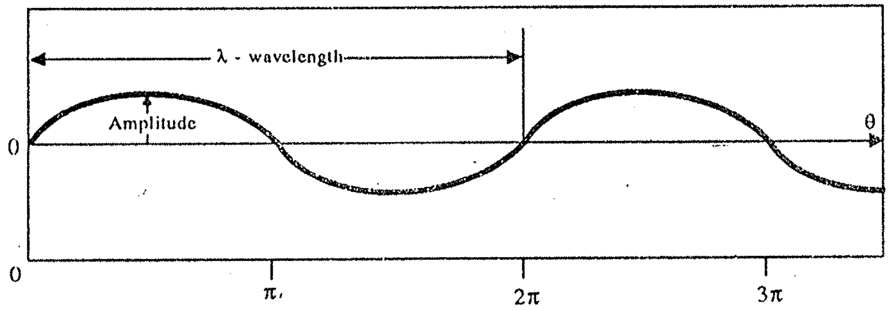


Fig. 1.2: Wavelength associated with the electromagnetic radiation.

Frequency (ν) is the number of waves per second.

Wave number ($\bar{\nu}$) is the reciprocal of wavelength and it is the number of waves per unit length.

The symbols and SI units of wavelength, frequency and wave number are listed in Table 1.1.

Table 1.1 : Some characteristics associated with electromagnetic radiation.

Parameter	Symbol	SI Unit
Wavelength	λ (lambda)	metre (m)
Frequency	ν (nu)	hertz (Hz)
Wave Number	$\bar{\nu}$ (nu bar)	metre^{-1} (m^{-1})

These parameters are related to each other by the following relations:

$$\lambda = \frac{c}{\nu} \qquad \text{...(1.1)}$$

The longer the wavelength, the **lower** is the frequency; and the **shorter** the wavelength, the **higher** is the frequency.

where c is the velocity of the radiation in the medium. However, in vacuum $c = 2.998 \times 10^8 \text{ m s}^{-1}$.

$$\text{and} \qquad \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \qquad \text{...(1.2)}$$

You may also recall from Unit 1 of 'Atoms and Molecules' course that certain phenomena like black body radiation, heat capacity variation, photoelectric effect and atomic spectra could not be explained with the help of classical mechanics. The classical mechanics puts no restrictions on the value of a dynamic variable (e.g., energy, momentum etc.). The quantum theory proposed by Max Planck in 1900, suggested that the energy can be emitted or absorbed **only by a specified amount,** called the **quanta and not continuously.** Also when we consider the interaction of radiation with matter, its wave like description fails to explain the interaction. Therefore, the particle nature of the radiation has to be considered. These particles are known as **photons**. The **energy** (E) of the photon can be related to the **frequency** (ν) of the radiation by the following expression:

You are advised to go through Unit 1, Secs. 1.5 and 1.6 for details of these phenomena.

$$E = h\nu \qquad \text{...(1.3)}$$

where h is the Planck's constant and has the value 6.626×10^{-34} J s.

From Eq. 1.1, we can say that

$$\nu = \frac{c}{\lambda}$$

Substituting the above value of υ in Eq. 1.3, we get

$$E = \frac{hc}{\lambda} \qquad \text{...(1.4)}$$

From Eq.1.2, $\bar{\nu} = \frac{1}{\lambda}$. Substituting this in Eq. 1.4, we can write

$$E = hc\bar{\nu} \qquad \text{...(1.5)}$$

Learn the above relationships by heart and do not confuse one with the other. If you do not feel confident, go through them once again.

Fig.1.3 shows the range of electromagnetic radiation in terms of the above parameters. Carefully go through the values given for various regions. Try to apply the above relationships (Eq.1.1 to Eq.1.5) to these values.

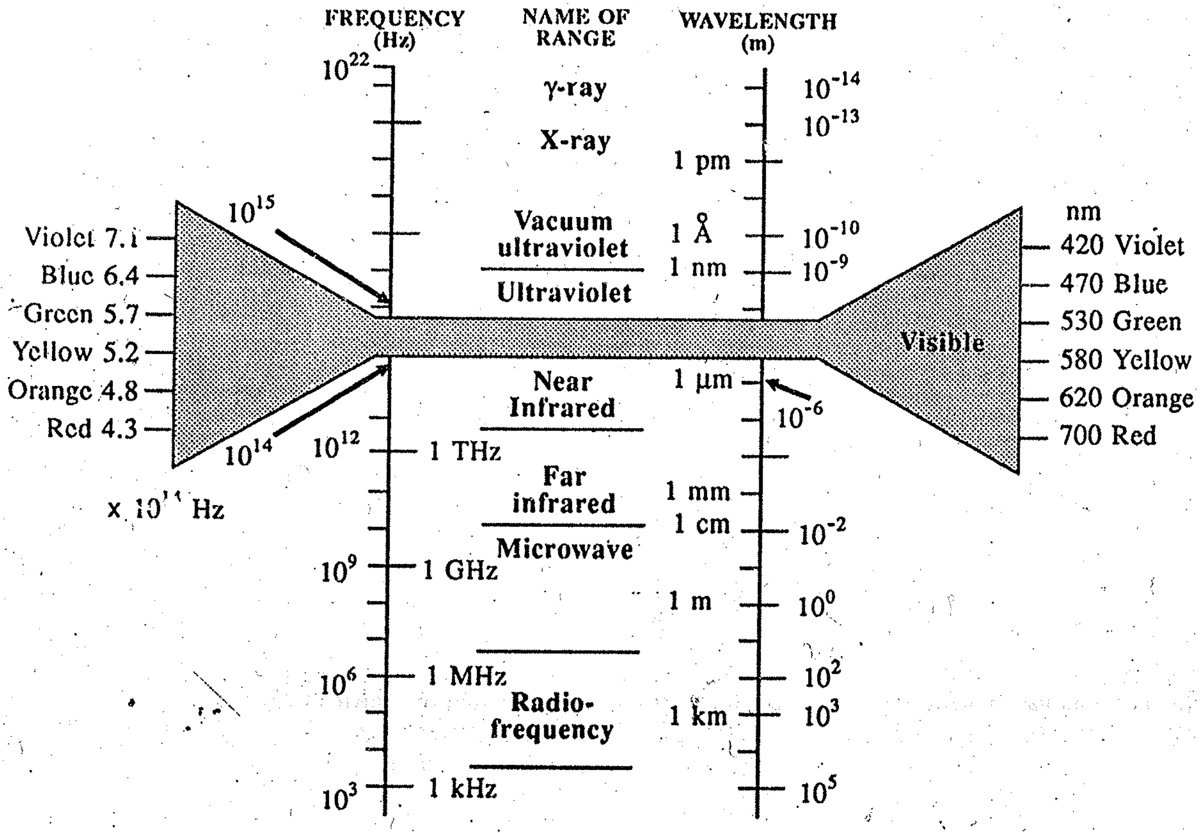


Fig. 1.3: The Range of Electromagnetic radiation.

After understanding the above section, answer the following SAQs.

Although you know the following conversions from Unit 1 of 'Atoms & Molecules' course (CHE-01), you are advised to go through them again and refresh your memory.

1 millimetre = 1 mm = 10^{-3} m
1 micrometre = 1 µm = 10^{-6} m
1 nanometre = 1 nm = 10^{-9} m
1 picometre = 1 pm = 10^{-12} m
1 Angstrom = 1 Å = 10^{-10} m

SAQ 1

Calculate the energy associated with a radiation having wavelength (λ) = 400 nm.

....

....

....

....

SAQ 2

Generally, the energy is reported per mole. How will you convert the energy value obtained above in terms of energy per mole ?

Avagadro Number = 6.022×10^{23} mol^{-1}

....

....

1.3 INTERACTION OF RADIATION WITH MATTER

From the above discussion you have an idea about what a radiation is? You are also familiar with the fact that matter consists of atoms or molecules. When electromagnetic radiation comes in contact with matter, there may be an exchange of energy between the photons and matter. As mentioned in the last section, according to Planck, energy can change only in terms of **quanta**. Thus, a system may absorb energy and go from the lower energy state E_1 to the higher energy state E_2. Alternatively, a system initially in the higher energy state E_2 can lose energy and go to the lower energy state E_1. The energy difference, ΔE, between these two states is given by the following equation.

$$\Delta E = E_2 - E_1 = h\nu \qquad \text{... (1.6)}$$

where $h\nu$ is the energy abosrbed or emitted. This is also shown in Fig. 1.4.

The lower energy state is called the **ground state** whereas the higher energy state obtained by absorption of energy is called the **excited state** for that particular system.

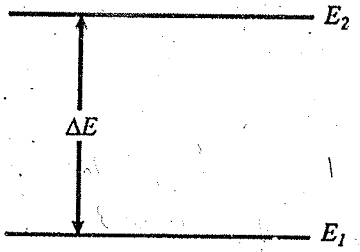


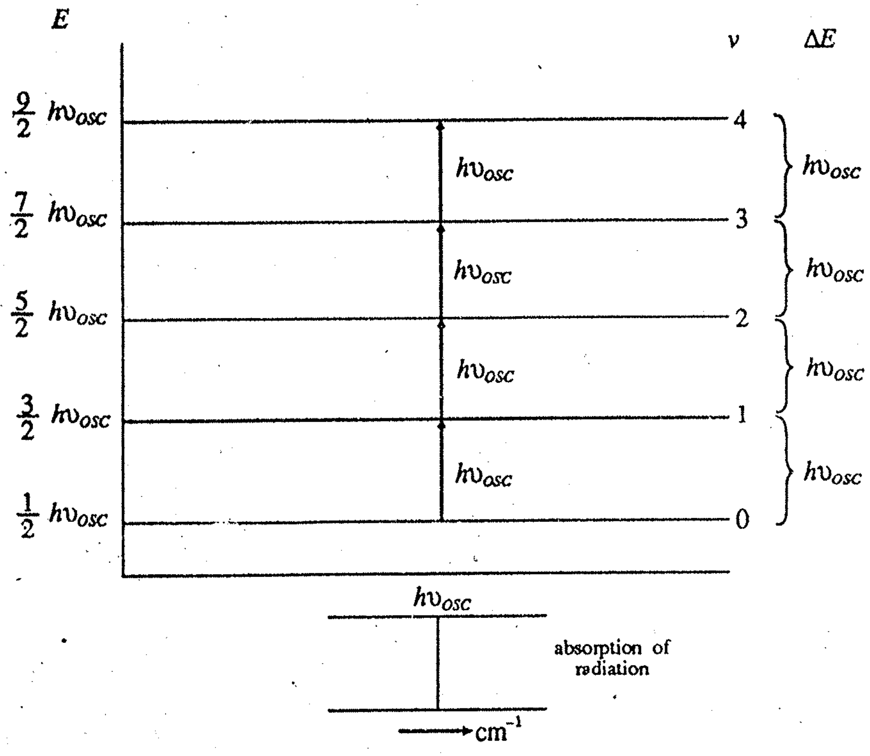
Fig.1.4: Energy levels of a system.

At this moment, can you think of the importance of the absorption or emission of energy by a system as discussed above? Obviously, by determining the energy absorbed or emitted, you can know about the energy levels present in an atom or a molecule. In other words, these energy changes can be related to the structure of the atom or the molecule.

The next question which will come to your mind is how to determine what amount of energy is absorbed or emitted? Depending upon which one of the two modes (absorption or emission) we choose for determining the energy change, we use the instrument called **absorption** or **emission spectrophotometer**. These instruments are designed to measure which frequencies of radiation are absorbed or emitted by a particular sample on irradiation. The **absorption spectrophotometer** (Fig.1.5 a) consists of a source which gives radiation of known frequency range. The radiation, thus obtained, is passed through the sample. The sample absorbs some of the frequencies and transmits the others. The transmitted radiation is then analysed, detected and the frequencies absorbed are recorded. The **emission spectrophotometer** (Fig. 1.5 b) consists of a source of excitation which energises the sample. The sample then emits a characteristic radiation which can then be resolved into its components and finally detected.

Do not worry about the details of instrumentation at this stage. You will study them in Unit 9 of Block 3 and at other appropriate places in this course.

At this stage, you may be curious to know how the absorption and emission spectra look? In absorption spectra, certain frequencies are absorbed by the sample under observation. When the transmitted radiation is analysed, these particular frequencies will be missing and if a photographic plate is used as a detector, one value of E by a quantity $h\nu_{osc}$ where ν_{osc} is the characteristic frequency of the oscillator. This shows that the energy of the oscillator cannot be changed at will but it can be only changed by a multiple of $h\nu_{osc}$. This is referred to as **quantisation of energy.** By showing the values of E for varying values of v we can build up energy levels as shown in Fig. 4.4.



Absorption of radiation

Fig. 4.4: Energy levels of a harmonic oscillator.

4.3 DIATOMIC MOLECULE AS HARMONIC OSCILLATOR

Let us now consider two particles of masses m_1 and m_2 joined together by a spring having a force constant k (Fig. 4.5a). The distance of separation between the particles is r_e. The spring can be stretched and compressed by pulling the two particles apart (Fig. 4.5b) or by pushing them to come closer (Fig. 4.5c).

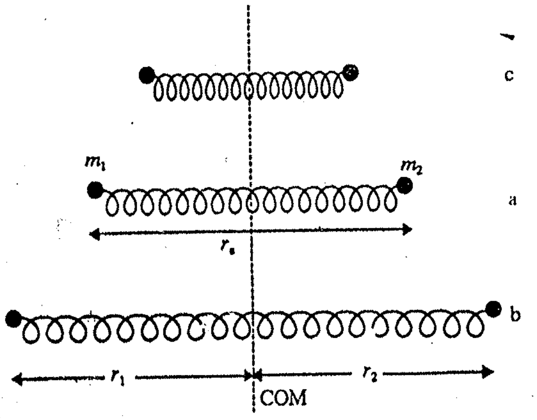


Fig. 4.5: Stretching and compression of two particles joined together by a spring.

Point O in Fig. 4.5 indicates the centre of mass and r_1 and r_2 denote distances of the particles 1 and 2, respectively, from the centre of mass O. If the new distance of separation of the two particles in Fig. 4.5 (b or c) is referred to as r, the displacement of m_1 with respect to m_2 given by $r - r_e$ (while keeping the centre of mass at O) can be employed in the equations of motion (similar to Eq. 4.4) as follows:

$$\frac{m_1 \, d^2 r_1}{d t^2} = -k(r - r_e) \qquad \text{...(4.19)}$$

and

$$\frac{m_2 \, d^2 r_2}{d t^2} = -k(r - r_e) \qquad \text{...(4.20)}$$

Since $r = r_1 + r_2$ and $m_1 r_1 = m_2 r_2$, we get

$$r_1 = \frac{m_2}{m_1 + m_2} r \text{ and } r_2 = \frac{m_1}{m_1 + m_2} r \qquad \text{..(4.21)}$$

Using these expressions for r_1 and r_2, Eqs. 4.19 and 4.20 reduce to

$$\frac{m_1 \, d^2 \left(\frac{m_2 r}{m_1 + m_2} \right)}{d t^2} = -k(r - r_e)$$

We can take out m_2 and $(m_1 + m_2)$ out of differentiation because they are constant.

Thus,
$$\frac{m_1 m_2}{(m_1 + m_2)} \frac{d^2 r}{d t^2} = -k(r - r_e) \qquad \text{...(4.22)}$$

Here $m_1 m_2/(m_1 + m_2)$ can be denoted by μ which is called the **reduced mass.**

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \text{... (4.23)}$$

Thus, Eq. 4.22 can be rewritten as

$$\mu \frac{d^2 r}{d t^2} = -k(r - r_e) \qquad \text{...(4.24)}$$

Since $\frac{d^2(r - r_e)}{d t^2} = \frac{d^2 r}{d t^2}$ because r is a constant, we substitute $\frac{d^2(r - r_e)}{d t^2}$ for $\frac{d^2 r}{d t^2}$ in Eq. 4.24 for having similarity in the variable on the two sides of the equation. Thus,

$$\mu \frac{d^2(r - r_e)}{d t^2} = -k(r - r_e) \qquad \text{... (4.25)}$$

A comparison of Eqs. 4.4 and 4.25 shows that the two expressions are similar if m of Eq. 4.4 is identified with μ of Eq. 4.25 and x of Eq. 4.4 is identified with $r - r_e$ of Eq. 4.25. This leads us to conclude that the oscillational motion for two particles joined together can be identified to the **simple harmonic vibration** of a particle of mass equal to μ and a displacement equal to $r - r_e$ (called Δr) in the above case. Going on similar analogy, therefore, we can write equations similar to Eqs. 4.2, 4.6, 4.7, 4.11 and 4.12 for oscillations of the two particles joined by a spring viz.

$$\Delta r = \Delta r_0 \cos 2\pi \nu_{osc} t \qquad \text{... (4.26)}$$

$$k = 4\pi^2 \nu_{osc}^2 \mu \qquad \text{... (4.27)}$$

Note that the potential energy is proportional to the square of relative displacement of the particle and is given by

$$V = \frac{1}{2} k (r - r_e)^2$$

and the restoring force is given as

$$F = -k(r - r_e).$$

Thus, the equations of motion for the two particles m_1 and m_2 are as given by Eqs 4.19 and 4.20, respectively.

From $m_1 r_1 = m_2 r_2$, we can write

$$r_1 = \frac{m_2 r_2}{m_1} \qquad \text{... (A)}$$

and
$$r_2 = \frac{m_1 r_1}{m_2} \qquad \text{... (B)}$$

$$\therefore \quad r = r_1 + r_2$$

$$r = \frac{m_2 r_2}{m_1} + \frac{m_1 r_1}{m_2}$$

$$r = \frac{r_2 m_2^2 + r_1 m_1^2}{m_1 m_2}$$

From $r_1 + r_2 = r$, we can say that

$$r_1 = r - r_2$$

Using this value of r_1 in Eq. A above, we get

$$r - r_2 = \frac{m_2 r_2}{m_1}$$

$$m_1 (r - r_2) = m_2 r_2$$

or

$$m_1 r - m_1 r_2 = m_2 r_2$$

or

$$m_1 r = (m_2 + m_1) r_2$$

or
$$\frac{m_1 r}{(m_2 + m_1)} = r_2$$

Similarly, from the Eq. B above, we can derive

$$r_1 = \frac{m_2 r}{(m_2 + m_1)}$$

Such a motion is described in detail in Unit 3.

The motion of a two particle system having masses m_1 and m_2 takes place around the centre of gravity. If the centre of gravity is at rest, the motion of this two particle system can be described in terms of the motion of a single (fictitious) particle around their centre of gravity having the mass μ. This mass μ is referred to as the reduced mass and is given by the following equation.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

where m_1 and m_2 are the masses of the two particles. The reduced mass of the hydrogen atom can be calculated as

$$\mu = \frac{m_n m_e}{m_n + m_e}$$

$$= m_e \frac{m_n}{m_n + m_e}$$

$$= m_e \left(\frac{1}{1 + \frac{m_e}{m_n}} \right)$$

where m_n is the mass of the nucleus and m_e is the mass of the electron.

Thus, a correction of $\left(\frac{1}{1 + \frac{m_e}{m_n}} \right)$ is to be applied to the theoretically calculated value of the Rydberg constant, R_∞. Thus the value of the Rydberg constant for hydrogen should be

$$R_H = R_\infty \left(\frac{1}{1 + \frac{m_e}{m_n}} \right) \qquad \text{... (1.11)}$$

$$= 1.09737 \times 10^7 \text{ m}^{-1} \times \left(\frac{1}{1 + \frac{9.109 \times 10^{-31} \text{ kg}}{1.6726 \times 10^{-27} \text{ kg}}} \right)$$

$$= 1.09677 \times 10^7 \text{ m}^{-1}$$

Using spectroscopic determination, ratio of the mass of proton to the mass of electron was found to be 1836.15, i.e.

$$\frac{m_p}{m_e} = 1836.15$$

Thus, Eq.1.10 for hydrogen atom rewritten as,

$$\bar{\nu}_H = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad \text{... (1.12)}$$

where R_H is given by Eq.1.11.

Therefore, we can expect that when the hydrogen atom goes from its ground state H($1s^1$) to the excited state H($1s^0 2s^1$ or $1s^0 2p^1$) i.e., when the electron in hydrogen atom goes from the first orbit ($n = 1$) to second orbit ($n = 2$), a radiation corresponding to wave number given by Eq. 1.12 should be absorbed. In the reverse process, when the atom changes from its excited state to the ground state, the radiation with $\bar{\nu}$ given by Eq.1.12 should be emitted.

But what about the higher energy levels? Let us see Fig.1.7 which shows energy levels for $n = 1$ to $n = 5$.

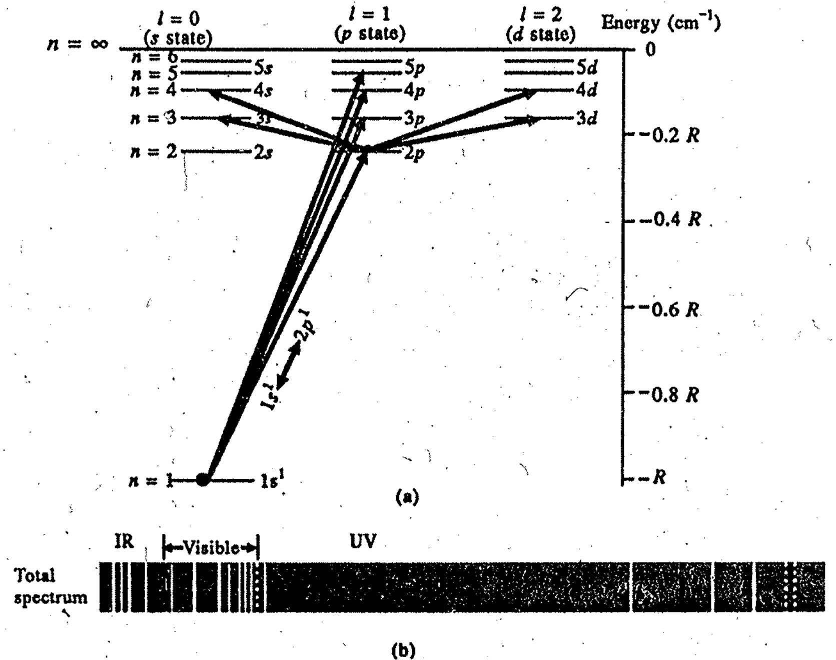


Fig. 1.7: (a) Possible transitions from ground state to excited states in hydrogen atom. (b) Hydrogen atom spectrum.

One thing which you can immediately observe in the figure is that for a particular n value, s, p and d levels are placed at the same level, i.e., they have **same energy**. This is also evident from Eq.1.7. If you see Eq.1.7 carefully, you can note that all other terms except n are constant. Thus, for a particular atom, energy is governed by n. You may also recall from Units 1 and 2 of 'Atoms and Molecules' course (CHE-01) that n was called the **principal quantum number**.

You can also see in Fig.1.7 (a) that there are various possible energy levels. But if you analyse Fig. 1.7 (b), you will find that the spectral lines appear only at discrete wavelengths (or wave numbers). Thus, we can say that all the transitions from all the levels are **not allowed**; or in other words, we say that only some transitions **are allowed** and others are not allowed. Now, to decide which transitions are allowed we can derive certain selection rules with the help of (time dependent) **Schrödinger equation.**

In this course, we will not discuss the details of how these selection rules are derived from Schrödinger equation. But we will discuss what these rules are and how they are applied in case of various atoms to understand their spectra.

The selection rules for the hydrogen atom are:

(i) Δn = any value

and (ii) $\Delta l = \pm 1$.

Using these rules, let us begin from the lowest possible level, i.e., 1s level. For this level, $n = 1$ and $l = 0$. Thus, electron from this level ($n = 1$) can go to any higher level with $n = 2, 3, 4...$ etc. but with the restriction that Δl should be equal to ± 1. Here Δl can only be $+1$. Therefore, $l = 1$ for the excited state which means that the s electron can go only to p states of higher levels. These transitions are shown in Fig. 1.7 (a). Let us also write value of $\bar{\nu}$ from Eq. 1.12 for these transitions.
Here $n_1 = 1$ and $n_2 = 2, 3, 4.....$ So we can say that

Remember that the energy levels having same energy are called **degenerate.**

Remember that the four quantum numbers about which you studied in Unit 2 of Block 1 of 'Atoms and Molecules' are principal (n), azimuthal (l), magnetic (m_l) and spin (m_s) quantum numbers. The principal quantum number (n) represents the major energy level. The azimuthal or angular momentum quantum number (l) represents the angular momentum and shape of the orbital. The magnetic quantum number (m_l) determines the possible quantised orientations of the angular momentum and the orbital in space. The spin angular quantum number (m_s) denotes the spin of an electron.

Note that according to the selection rules the transition for $1s^1 \longrightarrow 2s^1$ is **forbidden** but the transition from $1s^1 \longrightarrow 2s^0\,2p^1$ state is allowed.

You may recall that Schrödinger equation has been discussed in Unit 2 of Block 1 of 'Atoms and Molecules' course.

The Schrödinger equation can be written as

$$H\psi = E\psi \text{ where } H = \frac{-h^2}{8\pi^2 m}\nabla^2 + V$$

in which ∇^2 is $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

This form of Schrödinger equation was time independent Schrödinger equation and was used to calculate the energy of the energy levels. But, for the derivation of selection rules for spectral transitions, we have to use time-dependent Schrödinger equation. The time-dependent Schrödinger equation can be written as follows:

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\,\Psi(x,t) = \frac{h^2}{4\pi^2 i}\frac{\partial\Psi}{\partial t}$$

Note that according to the selection rules, $1s^1$ to $2s^1$ transition is forbidden.

Remember l represents the azimuthal quantum number and can take values from 0 to $n-1$.

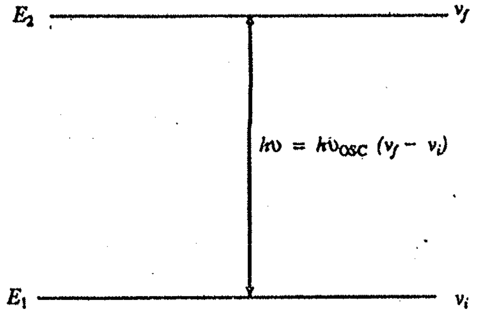


Fig. 4.7: Absorption of radiation and vibrational transition.

As you have noticed in Eq. 4.33, the harmonic oscillator with different energy levels defined by different values of v, has different wave functions. As mentioned in the appendix of Unit 2, an electric dipolar transition from energy level v_i to v_f is only allowed in case the transition moment integral given below is non-zero, i.e.

$$\int_{-\infty}^{+\infty} \psi_{v_f} \mathrm{M}\, \psi_{v_i}\, \mathrm{d}\,\tau_v \qquad \text{... (4.34)}$$

where ψ_{v_f} and ψ_{v_i} are functions for v_f and v_i levels, d t_v is volume element and M is dipole moment operator. Without giving any further derivation it can be stated that if dipole moment is a linear function of internuclear distance of the diatomic molecule, the above integral is nonzero only if $\Delta v = \pm 1$ and if the dipole moment is a non linear function of internuclear distance, the above integral is nonzero for all integral values of Δv. However, in practice only transitions with $\Delta v = \pm 1$ are allowed for harmonic oscillator model of diatomic molecules where the dipole moment is known to be a linear function of the internuclear distance. The "+" sign for Δv above refers to transitions from lower energy levels to higher levels whereas the "–" sign refers to transitions from higher energy levels to lower energy levels. The absorption of radiations thus corresponds to "+" sign and emission of radiations to "–" sign of the v values given above. Further, expansion of dipole moment operator M in Eq. 4.34 shows that fundamental transitions are allowed only if $\mathrm{d}\mu'\mathrm{d}(\Delta r)$ is non zero, i.e. the vibration should be accompanied by a change in the dipole moment to show a fundamental transition. Thus homonuclear diatomic molecules do not show any absorption in the fundamental vibrational spectrum. These rules regarding which transitions are allowed and which are forbidden, are referred to as Selection Rules.

Remember that according to the Boltzman distribution, the number of molecules present in the excited state (N_2) are related to the number of molecules in the ground state (N_1) by the following expression:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{kt}}$$

Since the frequency of the electromagnetic radiation which satisfies the condition given in Eq. 4.33 falls in the infrared region, these transitions are referred to as infrared transitions and are observed in the infrared region of the spectrum. The intensity of the band corresponds to the amount of radiation absorbed and is related to the square of the transition moment integral (Eq. 4.34). The frequency at which the maximum absorption is observed corresponds to the frequency of electromagnetic radiation responsible for transition as defined by Eq. 4.33. According to the Boltzman distribution, the number of oscillators in $v > 0$ **level** are expected to be very small at room temperature; hence only transitions from $v = 0 \longrightarrow v = 1$ are observed where the ν_{osc} for the oscillator is equal to the frequency of the electromagnetic radiation absorbed to give the fundamental transition. At higher temperatures $v = 1 \longrightarrow v = 2$ etc. transitions may also be observed. Such transitions are referred to as **hot transitions** (or hot bands in the spectrum).

4.3.3 Evaluation of Force Constant and Maximum Displacement

As we have noticed above, the frequency of electromagnetic radiation at which absorption takes place can give the value of oscillational frequency of the diatomic molecule e.g. for a transition $v_i = 0$ to $v_f = 1$.

$$\Delta E = h\nu = h\,\nu_{osc}\,, \;\; \nu = \nu_{osc} \qquad \text{... (4.35)}$$

and if we know the reduced mass of the diatomic molecule, we can calculate the value of force constant, k by using Eq. 4.27 and 4.28. Eqs. similar to 4.15 and 4.17 for diatomic molecule can be employed to evaluate maximum displacement Δr_0 for various values of v as follows:

$$\text{Total energy} = \frac{1}{2} k \Delta r_0^2 = 2 \mu \pi^2 \nu_{osc}^2 \Delta r_0^2$$

$$= \left(\mathrm{v} + \frac{1}{2}\right) h \nu_{osc} \qquad \text{... (4.36)}$$

giving

$$\Delta r_0 = \pm \sqrt{\frac{(\mathrm{v} + \frac{1}{2}) h}{2 \mu \pi^2 \nu_{osc}}} \qquad \text{... (4.37)}$$

$$\Delta E = E_f - E_i$$
$$= h\nu_{osc}(v_f + \frac{1}{2}) - h\nu_{osc}(v_i + \frac{1}{2})$$
$$= h\nu_{osc}(1 + \frac{1}{2}) - h\nu_{osc}(0 + \frac{1}{2})$$
$$= h\nu_{osc}\left(\frac{3}{2} - \frac{1}{2}\right)$$
$$= h\nu_{osc}$$

SAQ 1

HCl molecule shows an absorption at 2886 cm^{-1}. Determine its force constant and maximum displacements (changes in internuclear distance) for v = 0,1,2,3.

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4.3.4 Isotope Effect

We have noted above that the HCl molecule absorbs radiation of 2886 cm^{-1} frequency. Let us see what changes we expect in the infrared spectrum, if HCl is changed to DCl. This brings change in the reduced mass, i.e.

$$\mu_{HCl} = \frac{1 \times 35.5}{36.5 \times 6.023 \times 10^{23}} = 1.63 \times 10^{-27} \text{ kg}$$

$$\mu_{DCl} = \frac{2 \times 35.5}{37.5 \times 6.023 \times 10^{23}} = 3.14 \times 10^{-27} \text{ kg}$$

Thus, we can say that

$$\mu_{DCl} \approx 2 \mu_{HCl} \qquad \text{... (4.38)}$$

The force constant is a property of the bond which in turn depends on the number of electrons in H and D. Since number of electrons in H and D are equal it is assumed that to a good degree of approximation that the force constant for HCl and DCl are equal.

Using the above argument in Eq. 4.28, we can conclude that

$$\nu_{osc} \propto \frac{1}{\sqrt{\mu}}$$

Thus,

$$\frac{\nu_{osc}^{HCl}}{\nu_{osc}^{DCl}} = \sqrt{\frac{\mu_{DCl}}{\mu_{HCl}}} = \sqrt{\frac{\dfrac{m_D m_{Cl}}{m_D + m_{Cl}}}{\dfrac{m_H m_{Cl}}{m_H + m_{Cl}}}} = \sqrt{\frac{m_D}{m_H}} = \sqrt{2} \qquad \text{... (4.39)}$$

SAQ 3

If the ratio of mass of electron to the mass of nucleus for deuterium is 0.00027148, calculate the value of Rydberg constant for deuterium. (use the same value of R_∞ for deuterium as used for hydrogen). Also calculate the wave number for the first Balmer line for deuterium.

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1.5 FINE STRUCTURE OF HYDROGEN ATOM SPECTRUM

So far we have based our discussion on the Eq. 1.7, which relates the energy (E) of an energy level with the principal quantum number, n. But to understand the fine structure, we have to consider the effect of *other quantum numbers* as well on the energy levels.

An electron possesses an **orbital angular momentum (l)** and **spin angular momentum (s)**. The magnitude of these momenta $|\mathbf{l}|$ and $|\mathbf{s}|$ is given by the following equations:

Note that we are using $\hbar$ to represent $\frac{h}{2\pi}$.

Note that we have used modulus sign (| |) to represent the magnitude of a vector in Eqs. 1.14 (a) and 1.14(b). Thus, magnitude of **l** is represented as |**l**|. The same convention will be followed for other equations also.

Orbital angular momentum, $$|\mathbf{l}| = \sqrt{l\,(l+1)}\,.\frac{h}{2\pi} \qquad \text{.... (1.14 a)}$$

Spin angular momentum, $$|\mathbf{s}| = \sqrt{s\,(s+1)}\,.\frac{h}{2\pi} \qquad \text{... (1.14 b)}$$

Note that we are now using s to denote the *spin quantum number.*

In the above two equations l represents the *angular momentum quantum number* and can take values from 0 to $(n-1)$ and s represents the *spin quantum number.* Since these momenta are always expressed as multiples of $\frac{h}{2\pi}$ ($= 1.055 \times 10^{-34}$ J s), we can take $\frac{h}{2\pi}$ as one unit and represent it as $\hbar$. Thus, we can rewrite Eqs. 1.14a and 1.14b as given below:

$$|\mathbf{l}| = \sqrt{l\,(l+1)} \text{ in units of } \hbar = \sqrt{l\,(l+1)}\;\hbar \qquad \text{... (1.15)}$$

and $$|\mathbf{s}| = \sqrt{s\,(s+1)} \text{ in units of } \hbar = \sqrt{s\,(s+1)}\;\hbar \qquad \text{... (1.16)}$$

The **total angular momentum** of the electron, **j** has contribution from both **orbital** and **spin angular momenta** and can be expressed as,

$$\mathbf{j} = \vec{l} + \vec{s} \qquad \text{...(1.17)}$$

Conventionally, vector quantities may be represented by using an arrow on it, for example, vector **l** can be represented $\vec{l}$. But we are using bold letters to denote vector quantities.

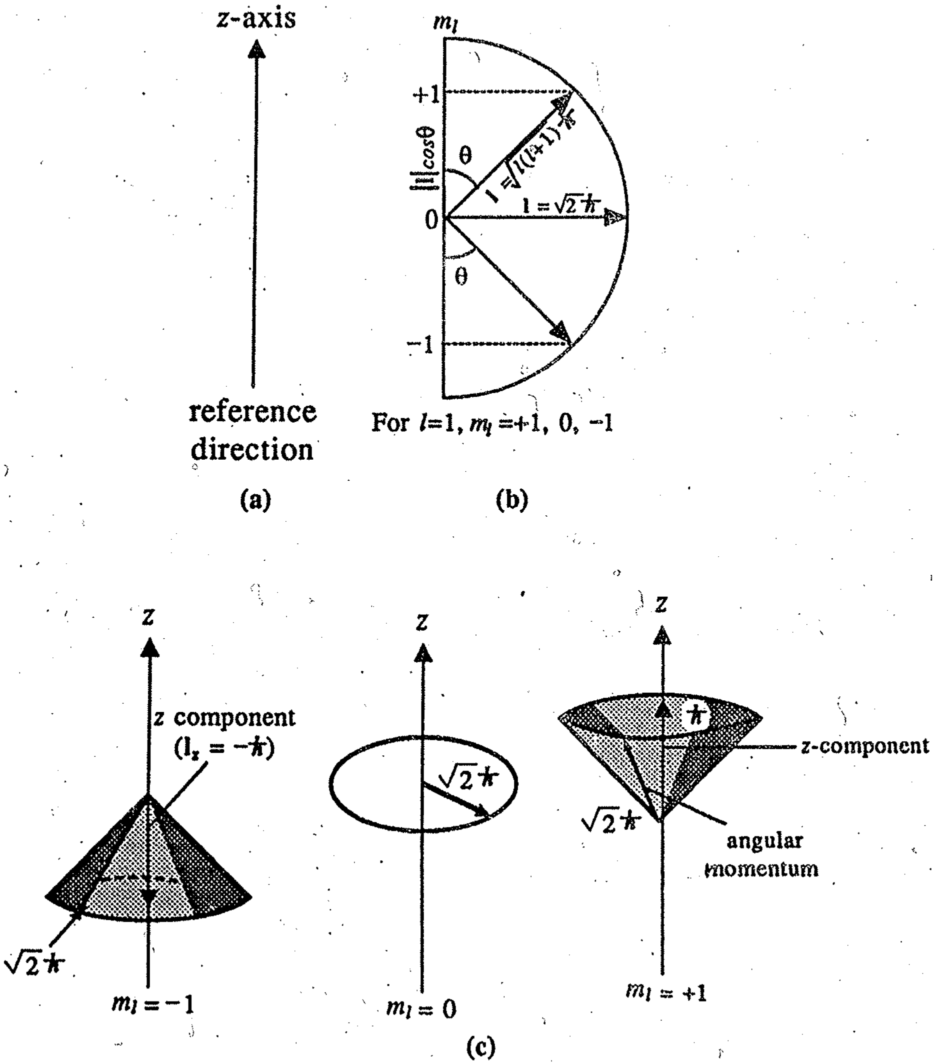
But here l and s both are vectors and their sum as given by Eq. 1.17 is a vector **addition.**

Let us now study about the vector nature of orbital angular momentum and spin angular momentum.

Vector Nature of Orbital Angular Momentum

For a *vector* quantity, e.g., orbital angular momentum of an electron, to be completely described, it is required that both its direction and magnitude should be specified. The magnitude of **l** is specified as given in Eq. 1.14a (or 1.15) and is quantised. Now what about its direction? The quantum theory says that a **reference direction** can be specified by applying the magnetic or electric field; and the angular momentum vector can have **only** those directions whose components along the reference direction are integral multiples of $\hbar$. Such a reference direction is shown **in Fig. 1.10 as pointing in vertical direction** and is conventionally used to represent z – axis, see Fig. 1.10a.

Note that for a free atom there is no preference direction. Hence, the Schrodinger equation tells us that the total angular momentum is quantised and only one component of the angular momentum out of the three components has a definite value. You may call it l_x, l_y or l_z but by convention we call it l_z. However, when the aom is placed in a magnetic field, there is a reference direction of the magnetic field (which is called z direction) and the component of the angular momentum in the direction of the field becomes quantised.



(a) (b) (c)

Fig.1.10: a) The reference direction.
b) Allowed directions for the angular momentum vector and
c) The components of angular momentum in the reference direction.

Note that the magnitude of the orbital angular momentum,

$|l| = \sqrt{l(l+1)}\,\hbar$ and the maximum value of its components in a particular direction is $l\hbar$. Since $|l| > l_z$, the angular momentum vector cannot point in the direction of the applied field. The angle between angular momentum vector and the direction of the field is given by θ.

Now, the angular momentum can point in such a way that its components in the z direction are integral multiples of $\hbar$, Fig. 1.10b. If l_z is the component of angular momentum (l) in z direction, then

$$|l_z| = m_l \hbar \qquad \dots (1.18)$$

In Fig. 1.10(b)

$$\cos\theta = \frac{l_z}{|l|} = \frac{\hbar}{\sqrt{l(l+1)}\,\hbar} = \frac{1}{\sqrt{l(l+1)}}$$

For $m_l = 1$, $\cos\theta = \frac{1}{\sqrt{l(l+1)}} = \frac{1}{\sqrt{2}}$

$\therefore \quad \theta = 45°$

$m_l = 0$, $\cos\theta = 0$

$\therefore \quad \theta = 90°$

$m_l = -1$, $\cos\theta = \frac{-1}{\sqrt{l(l+1)}} = \frac{-1}{\sqrt{2}}$

$\theta = 135°$

Here m_l is an integral number called **magnetic quantum number** and can have values as given below:

$$m_l = l, (l-1), \dots 0, \dots -(l-1), -l \qquad \dots (1.19)$$

near the equilibrium value, r_e, therefore, instead of using Morse potential, the Maclaurian series expansion of potential energy is used for inclusion of anharmonicity in the oscillator as follows:

$$V(\Delta r) = \frac{1}{2!}\left[\frac{d^2 V}{d(\Delta r)^2}\right]_{\Delta r = 0} (\Delta r)^2 \quad 9 + \frac{1}{3!}\left[\frac{d^3 V}{d(\Delta r)^3}\right]_{\Delta r = 0} (\Delta r)^3$$

$$= \frac{1}{2}k_2 (\Delta r)^2 + \frac{1}{6}k_3 (\Delta r)^3 \qquad \text{... (4.49)}$$

Maclaurian series is given as follows

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

If we include higher terms like $\frac{1}{6}k_3 (\Delta r)^3$ etc. in the potential energy expression, the oscillator is referred to as **anharmonic oscillator** and such additional terms are referred to as **anharmonicity terms** of potential energy expression. Inclusion of anharmonicity terms leads to an improved version of energy levels, transition energies and selection rules.

The vibrational energy levels of the anharmonic oscillator can be expressed as

$$G(\text{v}) = \bar{\nu}_{osc}\left(\text{v} + \frac{1}{2}\right) - X\left(\text{v} + \frac{1}{2}\right)^2 + Y\left(\text{v} + \frac{1}{2}\right)^3 + \cdots \qquad \text{... (4.50 a)}$$

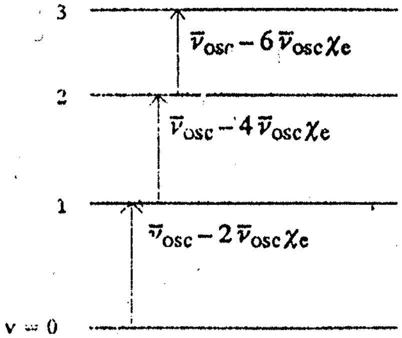
X and Y are functions of constants k_2, k_3 etc. of Eq. 4.49 and are referred to as **anharmonicity constants.** Usually the expression is turncated after two terms as Y is far lesser in value than X. However, the equation of motion obtained by using a cubic potential energy function is not easy to handle. One approximate solution to the schrödinger equation that may be formed expresses the energy in terms of the fundamental vibrational frequency, ν_{osc} and anharmonicity constant χ_e, as follows.

$$G(\text{v}) = \bar{\nu}_{osc}\left(\text{v} + \frac{1}{2}\right) - \bar{\nu}_{osc}\chi_e\left(\text{v} + \frac{1}{2}\right)^2 \qquad \text{... (4.50 b)}$$

Note that X in Eq. 4.50 a is equal to $\bar{\nu}_{osc}\chi_e$ in Eq. 4.50 b.

Even with a linear dipole moment function, the anharmonic wave functions yield selection rules $\Delta \text{v} = \pm1, \pm2, \pm3$ etc., thus overtone bands get allowed due to anharmonicity. The intensities of the overtone bands are, however, quite small in comparison to the intensity of the fundamental band (Fig. 4.6 a). Due to added terms in the energy expression (Eq. 4.50), **the energy levels are no more equidistant and they are found to converge.**

Thus, the anharmonic correction reduces the energy of every level. The reduction is greater for the higher energy levels. Thus, the spacing between the energy levels, $E_{(\text{v}+1)} - E_\text{v}$, gets smaller as v gets larger. This was shown in Fig. 4.8 and the extent of reduction is shown in the margin.



Effect of anharmonicity on the vibrational energy levels of a diatomic molecule.

4.4.3 Evaluation of Anharmonicity Constants

The **term values** G (v) for v = 0, 1, 2, 3 for anharmonic oscillator are given below:

$$G_0 = \frac{1}{2}\bar{\nu}_{osc} - \frac{1}{4}X + \frac{1}{8}Y \qquad \text{... (4.51)}$$

$$G_1 = \frac{3}{2}\bar{\nu}_{osc} - \frac{9}{4}X + \frac{27}{8}Y \qquad \text{... (4.52)}$$

$$G_2 = \frac{5}{2}\bar{\nu}_{osc} - \frac{25}{4}X + \frac{125}{8}Y \qquad \text{... (4.53)}$$

$$G_3 = \frac{7}{2}\bar{\nu}_{osc} - \frac{49}{4}X + \frac{343}{8}Y \qquad \text{... (4.54)}$$

The energies of radiation in cm^{-1} for fundamental, first and second overtones can be given as

$$\bar{\nu}_{0\to1} = \bar{\nu}_{\mathrm{osc}} - 2X + \frac{13}{4}Y \qquad \text{... (4.55)}$$

$$\bar{\nu}_{0\to2} = 2\bar{\nu}_{\mathrm{osc}} - 6X + \frac{31}{2}Y \qquad \text{... (4.56)}$$

$$\bar{\nu}_{0\to3} = 3\bar{\nu}_{\mathrm{osc}} - 12X + \frac{171}{4}Y \qquad \text{...(4.57)}$$

Thus by knowing the **frequencies** of electromagnetic radiation **absorbed** for fundamental and overtone transitions, one can evaluate the oscillational frequency and anharmonicity constants.

Also, the equilibrium dissociation energy, D_e of a molecule can be calculated from its spectroscopic dissociation energy, D_0 by using the following relation:

$$D_e = D_0 + \frac{\bar{\nu}_{\mathrm{osc}}}{2} - \frac{\bar{\nu}_{\mathrm{osc}} x_e}{4} + \frac{\bar{\nu}_{\mathrm{osc}} y_e}{8} \qquad \text{... (4.58)}$$

4.5 THE VIBRATING ROTATOR

In Unit 3, the pure rotations of diatomic molecules have been discussed and in the preceding sections of this unit we have discussed pure vibrations of diatomic molecule. The two motions have been discussed independent of each other. In reality, of course, the rotational and vibrational motions take place simultaneously. In this section, we now see how the spectrum gets modified because of this mixing.

4.5.1 Energy Levels

The total energy is given as a sum of the rotational and vibrational energies defined by the quantum numbers v and J.

$$E_{\mathrm{v},J} = G(\mathrm{v}) + F(J)$$

$$= h\nu_{\mathrm{osc}}\left(\mathrm{v} + \frac{1}{2}\right) + BhcJ(J+1) \qquad \text{... (4.59)}$$

or

$$E_{\mathrm{v},J} = h\nu_{\mathrm{osc}}\left(\mathrm{v} + \frac{1}{2}\right) + hcX\left(\mathrm{v} + \frac{1}{2}\right)^2 + \cdots$$

$$+ BhcJ(J+1) - DhcJ^2(J+1)^2 + \cdots \qquad \text{... (4.60)}$$

for v = 0, 1, 2... and J = 0, 1, 2 ... etc.

where Eq. 4.59 represents rotational vibrational energy for harmonic oscillator and rigid rotator whereas Eq. 4.60 represents the rotational vibrational energy for anharmonic oscillator and nonrigid rotator.

4.5.2 The IR Spectra and P,Q,R Branches

The selection rules for transitions in vibrating rotator are same as given for rotations and vibrations of diatomic molecules (Unit 3 and Sec 4.3.2) which state $\Delta \mathrm{v} = \pm1$ and $\Delta J = \pm1$. Thus for a fundamental vibrational transition $\Delta \mathrm{v} = +1$, we shall have a series of transitions where $\Delta J = +1$ and another series where $\Delta J = -1$. The series with $\Delta \mathrm{v} = +1$ and $\Delta J = +1$ defines the transitions (00) → (11), (01) → (12), (02) → (13), (03) → (14), ... etc; whereas the series with $\Delta \mathrm{v} = +1$ and $\Delta J = -1$ defines the transitions (01) → (10), (02) → (11), (03) → (12), (04) → (13) etc. Here, the first number in the parenthesis denotes vibrational quantum number (v) and the second

$$j = \left(2 + \frac{1}{2}\right) \quad \text{and} \quad = \left(2 - \frac{1}{2}\right)$$

$$= \frac{5}{2} \qquad\qquad = \frac{3}{2}$$

You will now learn about the nomenclature of these states using Term Symbols.

Term Symbols

The energy levels of an atom are called **terms** (or **spectral terms**). A term can be designated by a **term symbol**. A term symbol can be denoted as

J can be replaced by *j* in case of a single electron system.

$$^{2S+1}L_J$$

Here,

L is the orbital or angular momentum quantum number and can take the values 0, 1, 2, 3, 4 ... etc. and corresponding to these values L can be represented by a letter as S, P, D, F, G... etc.

Note that capital letters are used to denote various L values corresponding to the state of an atom. Similar small letters s, p, d... have been used for the states of electrons.

The superscript $^{2S+1}$ gives the **multiplicity** of the energy state and the subscript, J, *is the total angular momentum quantum number* (as expressed by Eq. 1.22).

Let us first take the example of hydrogen atom for determining the term symbol.

For the ground state of hydrogen atom, the electronic configuration is $1s^1$.

Here, $s = \frac{1}{2}$ and $l = 0$. Thus,

Note that we are representing $L = 0$ by S in the term symbol.

$$j = l + s = 0 + \frac{1}{2} = \frac{1}{2}$$

and the term symbol will be

$$^{2S+1}L_j \quad = {}^{2\times\frac{1}{2}+1}S_{1/2} \quad = {}^2S_{1/2}$$

Similarly, for a p electron, in hydrogen atom, we have

$$s = \frac{1}{2} \text{ and } l = 1$$

$$j = (l+s), (l+s-1), \ldots, (l-s)$$

$$= \left(1 + \frac{1}{2}\right), \left(1 + \frac{1}{2} - 1\right), \ldots, \left(1 - \frac{1}{2}\right)$$

$$= \frac{3}{2}, \frac{1}{2}$$

So, the term symbols for the two energy levels of a p state for hydrogen atom about which you studied above are

$$^{2S+1}L_j = {}^{(2\times\frac{1}{2}+1)}L_{\frac{1}{2}} \text{ and } {}^{2\times\frac{1}{2}+1}L_{\frac{3}{2}}$$

$$= {}^2P_{\frac{1}{2}} \text{ and } {}^2P_{\frac{3}{2}}$$

In the light of the above discussion, let us now see Fig.1.12. It shows the fine structure of energy levels of hydrogen atom.

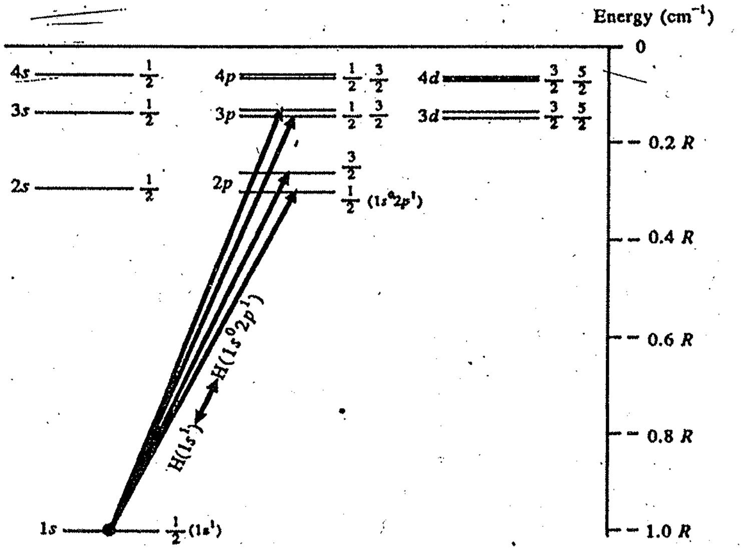


Fig. 1.12 : Splitting of p states into two energy levels corresponding to two values of j. The configuration of some lower atomic states is given in bracketts. Similarly, we can write the configuration of atomic states corresponding to higher energy levels.

The electronic configuration $1s^0 2p^1$ implies that the electron is present in p orbital and s orbital is vacant.

Note that the electron configuration $1s^0 2p^1$ of hydrogen atom gives rise to two levels with term symbols ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$. Each level is $(2j+1)$ fold degenerate. Thus, ${}^2P_{\frac{1}{2}}$ level with $j = \frac{1}{2}$ is two $(2j + 1 = 2 \times \frac{1}{2} + 1 = 2)$ fold degenerate and ${}^2P_{\frac{3}{2}}$ level with $j = \frac{3}{2}$ is four $(2j + 1 = 2 \times \frac{3}{2} + 1 = 4)$ fold degenerate. You will study in Sec. 1.10, Fig. 1.16 that these degeneracies can be removed by the application of the magnetic field.

The j values for the various p energy states are also shown in the figure. Now, if an electron in 1s energy level absorbs energy and gets excited to the 2p state; it has **two options** corresponding to **two** j levels. Here the selection rules say that in addition to the earlier restrictions of Δn = anything and $\Delta l = \pm 1$;

$$\Delta j = 0 \text{ or } \pm 1$$

By applying these selection rules to the above transitions from 1s to 2p level, we can get the following results:

$$1s\left(j = \frac{1}{2}\right) \longrightarrow 2p\left(j = \frac{1}{2}\right) \text{ and } \Delta j = 0$$

and

$$1s\left(j = \frac{1}{2}\right) \longrightarrow 2p\left(j = \frac{3}{2}\right), \text{ and } \Delta j = +1$$

So both these transitions are allowed and the spectrum of hydrogen shows one line for each of these transitions.

Thus, we can expect a doublet for the transition of an electron from an s to a p level. This is called the **fine structure of hydrogen atom spectrum.** This pattern of lines is similar to Lyman series but the difference is that each line obtained is a *doublet*. In the case of hydrogen spectrum, the spacing between the lines is very–very less and they are difficult to resolve. The spacing as shown in Fig.1.12 is many times greater than the actual splitting observed.

Actually the spacing between the lines is 0.365 cm^{-1} and requires the use of high resolution instruments for resolving these lines.

Further transitions from doublet P (2p) state to ${}^2D$ or ${}^2S$ states are possible but we will not go into details of these transitions.

In the next section, you will be studying the spectra of hydrogen like atoms.

1.6 SPECTRA OF HYDROGEN–LIKE ATOMS

The atoms of all the elements of the Ist group in the Periodic Table have a single electron in their outermost shell. The inner closed shells have zero total angular

SAQ 4

See Fig. 4.6 carefully now and note down the various features of the infrared spectrum you can explain.

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4.6 SUMMARY

In this unit, you have learnt the properties of the motion of a single particle joined by a spring fixed to a rigid wall. The motion follows Hooke's law which states that the restoring force is proportional to the displacement and acts in a direction opposite to the direction of the displacement. The displacement of the particle follows simple harmonic motion and is represented by a cosine function of time, t and characteristic frequency ν_{osc}. The expressions for the Hooke's law, Newton's second law of motion and simple harmonic motion are combined to obtain relationship between the oscillational frequency ν_{osc} and force constant of the spring, k (Eq. 4.7). The variation of the potential energy of the motion of the particle with the displacement is shown by a parabola. Expressions for the potential energy, kinetic energy and the total energy of the particle at a displacement x are then derived on the basis of the parabolic variation of the potential energy. It was shown how the use of Schrödinger wave equation for harmonic oscillator gives expression for energy of the motion which is *quantized* giving various energy levels with different values of quantum number v = 0, 1, 2, 3 ... etc. It is observed that the energy levels are equidistant with a consecutive gap of $h\,\nu_{osc}$. The motion of two particles joined by a spring was then dealt with. The mathematical derivation showed that the motion is equivalent to that of a harmonic oscillator mentioned above such that its displacement is equal to the change in internuclear distance and its mass is equal to the reduced mass of the two particles. The vibrations of the diatomic molecule were treated in a way similar to the vibrations of two particles joined by a spring, the internuclear bond made through the sharing of electrons replaces the spring. Energy levels and other expressions similar to those obtained for harmonic oscillator were used for studying the vibration of diatomic molecule.

Absorption of radiation in the infrared region led to transition of the diatomic oscillator from ground state energy level with (v = 0) to excited state. The frequency of the electromagnetic radiation at which absorption takes place is characteristic of the molecule, and is also equal to the frequency of oscillation of the diatomic harmonic oscillator. The selection rules for the vibrational transition shows that only transitions with Δ v = ±1 are allowed. Also such transitions are allowed if there is a change in the dipole moment during the vibration. These rules restrict such transitions to be possible only for heteronuclear diatomic molecules from v = 0 to v = 1 levels. Due to Boltzman's distribution, population in v > 0 is found to be very small at room temperature for most of the common diatomic molecules; therefore, transitions for v = 1 to v = 2 etc. are not observed. Evaluation of force constant and maximum displacement, effect of isotopic substitution on oscillational frequency and expression for zero point energy were discussed.

The observed behaviour of diatomic molecules regarding their dissociation at higher internuclear distances is introduced in the form of anharmonicity in the potential energy expression. This led to some correction in the quantum mechanical energy leading to a convergence in energy levels. Selection rules allow the observation of overtones in the absorption spectrum of anharmonic oscillator which can be employed to evaluate anharmonicity constants. The last section on vibrating rotator showed that simultaneous existance of vibrations and rotations in the diatomic molecules leads to observation of fine structure in the absorption bands of IR spectra in terms of P, Q, R branches.

4.7 TERMINAL QUESTIONS

1. What is the energy difference between energy levels of a harmonic oscillator?
2. Define zero point energy.
3. What are the selection rules for
   (i) a harmonic oscillator to show vibrational spectra and
   (ii) an anharmonic oscillator to show vibrational spectra?
4. Calculate D_e for H_2^+, if $D_0 = 21374.9 \text{ cm}^{-1}$

$$\nu_{osc} = 2321.7 \text{ cm}^{-1}$$

$$\nu_{osc} x_e = 66.2 \text{ cm}^{-1}$$

$$\nu_{osc} y_e = 0.6 \text{ cm}^{-1}$$

4.8 ANSWERS

Self Assessment Questions

1. $\mu = 1.627 \times 10^{-27} \text{kg}$

$k = 4\pi^2 \nu_{osc}^2 \mu$

Given $\nu = 2886 \text{ cm}^{-1}$. To get ν_{osc} from it we have to multiply it by velocity of light, c.

Thus, $k = 4\pi^2 \left(\nu_{osc}^2 \, c\right)^2 \mu$

$= 483 \text{ kg s}^{-2} = 483 \text{ N m}^{-1}$

$\Delta r_0 = 1.08 \times 10^{-9}, 1.87 \times 10^{-9}, 2.42 \times 10^{-9}, 2.86 \times 10^{-9}$ for $v = 0, 1, 2, 3$ respectively and then calculating μ and using Eq. 4.39.

2. $\text{O} - \text{D} = 2718 \text{ cm}^{-1}$.

By using $m_O = 15.9949 \times 10^{-3}$ kg

$$m_H = 1.007825 \times 10^{-3} \text{ kg}$$

$$m_D = 2.014101 \times 10^{-3} \text{ kg}$$

3. $E_0 \text{ HCl} / E_0 \text{ DCl} = \sqrt{2}$

4. Fundamental, I and II overtones at 2886, 5668 and 8346 cm^{-1}.
   (i) Overtones weaker than fundamentals
   (ii) Harmonic oscillators–only fundamental transition are allowed ($\Delta v = 0$)
   Anharmonic oscillator–Fundamental and overtones are allowed ($\Delta v = 0, 1, 2$, etc.)

1.8 ATOMIC SPECTRUM OF HELIUM

Helium represents the simplest multi–electron system. Let us first derive the term symbols for the ground state of helium atom. The electron configuration of helium is $1s^2$. Here l_1 and l_2, the quantum numbers of electrons 1 and 2, respectively have the value 0. Hence $L = l_1 + l_2 = 0$. Now, in the lowest energy state (i.e., ground state) both these electrons occupy $1s$ orbital. If the values of three quantum numbers n, l, m_l are same for the two electrons, the value of m_s should be different according to the Pauli's exclusion principle. Thus, if $m_{s_1} = +\frac{1}{2}$ then $m_{s_2} = -\frac{1}{2}$. We can calculate S by (i) the summation of m_{s_1} and m_{s_2}, to first give M_s or (ii) Eq. 1.26.

Remember that according to Pauli's Exclusion Principle no two electrons can have the same four quantum numbers.

We can write the quantum numbers of two electrons of He as given below:

	n	l	m_l	s	m_s
Ist electron	1	0	0	$\frac{1}{2}$	$+\frac{1}{2}$
IInd electron	1	0	0	$\frac{1}{2}$	$-\frac{1}{2}$

The state of an electron can further be described as α or β depending upon its s and m_s values.

For α state $(s, m_s) = \left(\frac{1}{2}, \frac{1}{2}\right)$

and for β state $(s, m_s) = \left(\frac{1}{2}, -\frac{1}{2}\right)$

(i) By summation of m_{s_1} and m_{s_2}

$$M_s = m_{s_1} + m_{s_2} = +\frac{1}{2} - \frac{1}{2} = 0$$

Since $M_s = 0$, hence $S = 0$.

Knowing L and S, we can calculate J as $J = L + S$. Thus, $J = 0 + 0 = 0$. Thus, the term symbol for the ground state of helium ${}^{2S+1}L_J$ will be ${}^{2\times 0+1}L_0 = {}^1S_0$

(Remember that $L = 0$ is denoted as S).

So we can say that for the ground state of helium ($1s^2$), the atomic state can be represented by the term symbol ${}^1S_0$.

${}^1S_0$ is pronounced as "singlet ess zero".

Note that capital italicised J is used in the term symbol ${}^{2S+1}L_J$ of an atom having more than one electron.

Let us consider the excited state of helium. If one of the electron is excited to a higher state, the electron configuration will change. The excited electron can now occupy ns^1, np^1, nd^1, ... etc. orbitals where $n \geq 2$. The corresponding electronic configurations for helium atom in excited states could be written as follows,

$$1s^1\,ns^1,\ 1s^1\,np^1,\ 1s^1\,nd^1, \ldots\text{etc.}$$

We are considering the exicitation of only one electron, since a very large amount of energy would be required to excite both the electrons simultaneously.

Corresponding to each of the above configurations, we have two possibilities:

i) the two electrons can have *opposite* spins, i.e., $m_{s_1} = +\frac{1}{2}$ and $m_{s_2} = -\frac{1}{2}$.

This will lead to $M_s = m_{s_1} + m_{s_2} = +\frac{1}{2} - \frac{1}{2} = 0$.

ii) the two electrons can have *parallel* spins; i.e., $m_{s_1} = +\frac{1}{2}$ and $m_{s_2} = +\frac{1}{2}$

leading to $M_s = m_{s_1} + m_{s_2} = \left(+\frac{1}{2}\right) + \left(+\frac{1}{2}\right) = 1$.

The component $M_s = 1$ can arise only when $S = 1$.

When the principal quantum number, n for the two electrons is different, then m_{s_1} and m_{s_2} can take values $+\frac{1}{2}$ and $+\frac{1}{2}$ leading to M_s (and S) = 1 as well as $+\frac{1}{2}$ and $-\frac{1}{2}$ yielding M_s (and S) = 0. This gives rise to states with triplet and singlet levels.

(ii) S can also be calculated using Eq. 1.26

$$S = |(s_1 + s_2)|,\ |(s_1 + s_2 - 1), \ldots\ldots,\ |(s_1 - s_2)|$$

$$\left(\frac{1}{2}+\frac{1}{2}\right), \left(\frac{1}{2}+\frac{1}{2}-1\right), \ldots\ldots\ldots, \left(\frac{1}{2}-\frac{1}{2}\right) = 1, 0$$

From the above S values (0 and 1) we can get *multiplicity* of a state which is given as $2S + 1$, as stated earlier.

Hence, when $S = 0, 2S + 1 = 2 \times 0 + 1 = 1$

and when $S = 1, 2S + 1 = 2 \times 1 + 1 = 2 + 1 = 3$

Thus, we have two spin states for each of the above configuration depending upon the value of S. For $S = 0$, when multiplicity is 1, the state is termed as a singlet state.

Table A.2: Character Table of C_{2v}

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z, x^2, y^2, z^2	
A_2	1	1	−1	−1	xy	R_z
B_1	1	−1	1	−1	x, xz	R_y
B_2	1	−1	−1	1	y, yz	R_x

The value under E represents the dimensions of a representation. In C_{2v} group, all the four representations are one-dimensional and in each case, $E = 1$. Such representations are called non-degenerate representations. In these representations, the application of a symmetry operation does not interconvert one orbital into another; for instance, p_x, p_y and p_z belong to different representations, namely B_1, B_2 and A_1. Also, A_1 representation is said to be totally symmetric representation of C_{2v} point group since the character value is 1 for all the four symmetry operations.

A_1 representation is said to be totally symmetric representation since any directional property belonging to A_1 representation of C_{2v} point group does not suffer sign change due to any of the symmetry operations.

The formation of character table for C_{3v} point group is more complicated and hence we shall only give its character table without much explanation (Table A.3).

Table A.3: Character Table for C_{3v} Group

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	$z, z^2, x^2 + y^2$	
A_2	1	1	−1		R_z
E	2	−1	0	$(x, y), (xy, x^2 - y^2), (xz, yz)$	(R_x, R_y)

The Mulliken notation of E is used for a representation, if the character value of 2 is observed for the identity operation, E. The representation E is two dimensional; this means x and y, R_x and R_y, xz and yz etc. which are all bracketed together are interconverted by a symmetry operation; i.e., those bracketed together are degenerate and hence have same energy.

Uses of Character Tables

We can make use of character tables to solve specific problems such as those given below:

1. Selection rules regarding the allowed transitions between energy levels in (atomic and) molecular spectra.
2. Symmetry species of vibrational modes in molecules.
3. Hybridisation schemes in molecules of specific geometry.

The second one will be explained in Units 5 and 6 and we shall not be discussing the third of the above. Let us now see how selection rules for transitions in the molecular spectra can be derived using character tables.

Selection Rules for the Allowed Spectral Transitions

The selection rules for the spectroscopic transitions throw light on the type of initial and final energy states for allowed spectral transitions. The selection rules specify the conditions for the allowed transitions in terms of changes in quantum numbers. Let us examine the first of the above two.

- explain the concept of group frequency and derive information about molecular structure using group frequencies,
- state how isotopic mass alters the frequencies of functional groups,
- explain how electronic factors affect the IR spectra of molecules,
- state the effect of hydrogen bonding and steric effect on the IR spectra of molecules, and
- discuss the steps involved in the analysis of IR spectra of simple molecules.

For a nonlinear molecule, six coordinates (out of 3*N* coordinates) are accounted for by translational and rotational degrees of freedom. Hence a nonlinear molecule has (3*N*–6) vibrational degrees of freedom. For a linear molecule, there are only two rotational degrees of freedom apart from three translational degrees of freedom. Hence the vibrational degrees of freedom for a linear molecule are (3*N*–5).

5.2 VIBRATIONAL DEGREES OF FREEDOM OF POLYATOMIC MOLECULES

We have already seen in Unit 4 that a diatomic molecule has only one fundamental vibration or one vibrational coordinate. This arises due to the stretching and compression of the bond connecting two atoms just like a spring (see Fig. 3.1 of Unit 3). Let us calculate the vibrational degrees of freedom of a polyatomic molecule. First let us assume that each atom is free to move in three perpendicular directions (along *x*, *y*, and *z* axes) and thus have three **degrees of freedom**. The degrees of freedom are the number of directions in which an atom can move freely independent of other atoms in the molecule. Hence, for a molecule containing *N* atoms, the total degrees of freedom is 3*N*.

We know that a molecule has translational, rotational and vibrational motions. A molecule can have only three degrees of translational motion since centre of mass of the molecule can move only along three axial directions. That is, the whole molecule can move along the three axes. In addition, when the molecule is nonlinear, there are three degrees of freedom due to rotational motions about the three axes. Therefore, there remains $3N - (3+3) = (3N-6)$ coordinates which account for vibrational degrees of freedom for nonlinear polyatomic molecules.

(Total degrees of freedom) – (translational degrees of freedom + rotational degrees of freedom) = Vibrational degrees of freedom.

For a linear molecule, there are two rotational degrees of freedom as the rotations about two axes perpendicular to internuclear bond axis only are allowed. The rotation about the internuclear axis is not possible since the moment of inertia along the internuclear axis is zero. Therefore a linear molecule possesses $3N-(3+2) = (3N-5)$ vibrational degrees of freedom. The details of the number of degrees of freedom for linear and nonlinear molecules are presented in Table 5.1

Table 5.1 : Degrees of Freedom for Polyatomic Molecules

Degrees of Freedom	Linear	Nonlinear
Total	3*N*	3*N*
Translational	3	3
Rotational	2	3
Vibrational.	(3*N*–5)	(3*N*–6)

Using Table 5.1, can you state the vibrational degrees of freedom of CO_2, H_2O and NH_3 molecules? It is worth recollecting that CO_2 is linear, H_2O is angular and NH_3 is pyramidal. CO_2 molecule has $(3 \times 3 - 5) = 4$ vibrational degrees of freedom; H_2O molecule has $(3 \times 3 - 6) = 3$ vibrational degrees of freedom and NH_3 molecule has $(3 \times 4 - 6) = 6$ vibrational degrees of freedom.

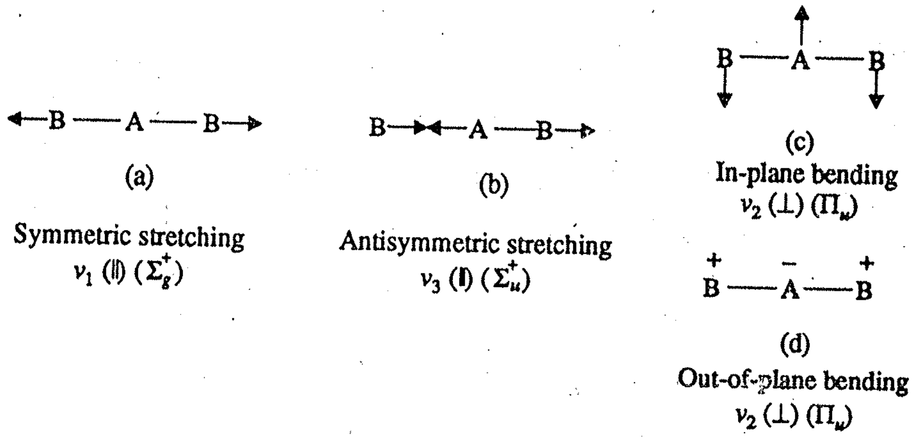
Normal Modes Vibrations

A molecule can vibrate only in certain modes, known as normal modes. Each normal mode corresponds to a vibrational degree of freedom. A normal mode is an independent simultaneous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode. **In general, a normal vibration is one in which all atoms in a molecule vibrate at the same frequency and in phase with each other.**

For a polyatomic molecule, the normal modes of vibration are of two types:

(i) stretching vibrations (ii) bending vibrations

The linear and nonlinear molecules have (N–1) stretching vibrations. The bending vibrations for linear and nonlinear molecules are (2N–4) and (2N–5), respectively.



(a) Symmetric stretching ν_1 (∥) (Σ_g^+)

(b) Antisymmetric stretching ν_3 (∥) (Σ_u^+)

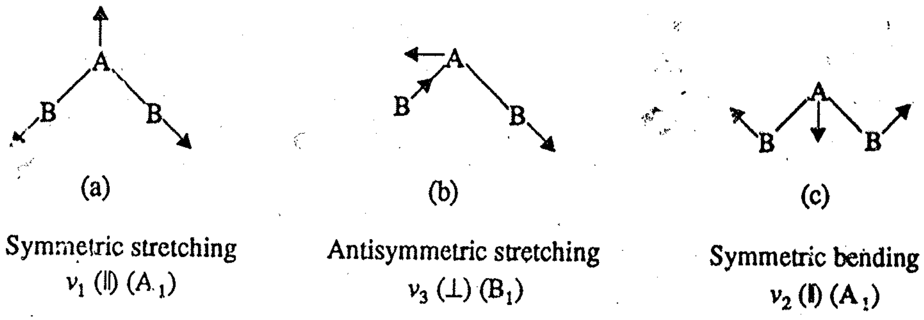
(c) In-plane bending ν_2 (⊥) (Π_u)

(d) Out-of-plane bending ν_2 (⊥) (Π_u)

Fig.5.1: Normal modes of vibration of a triatomic linear molecule, AB_2 (e.g., CO_2). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) in-plane bending and (d) out-of-plane bending; both (c) and (d) are degenerate and hence these two give rise to only one band (ν_2); (+) sign shows that the atom is going above the plane while (–) sign indicates that the atom is going below the molecular plane. The ν_1 and ν_3 vibrations are parallel (∥) vibrations whereas the degenerate vibration ν_2 is a perpendicular (⊥) vibration.

The displacement of each atom during each normal mode of vibration is such that all atoms move with the same frequency and in phase but with different amplitude. The amplitudes of vibrations of atoms are such that the centre of mass does not move. In other words, there is no translational motion of the molecule as a result of vibration and also there is no rotational motion of the molecule.

The normal mode concept can facilitate the understanding of the vibrational excitation of a particular group depending on the frequency of incident radiation; this radiation has no effect on the other part of the molecule.



(a) Symmetric stretching ν_1 (∥) (A_1)

(b) Antisymmetric stretching ν_3 (⊥) (B_1)

(c) Symmetric bending ν_2 (∥) (A_1)

Fig.5.2: Normal modes of vibrations of a triatomic angular molecule, AB_2 (e.g., H_2O). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) symmetric bending (ν_2). ν_1 and ν_2 are parallel vibrations whereas ν_3 is a perpendicular vibration.

Vibrations are classified as parallel (∥) or perpendicular (⊥) vibrations depending on whether the dipole moment change is parallel or perpendicular to the principal axis of the molecule.

In **stretching vibrations,** the atoms move along the bond axis so that the bond length increases or decreases at regular intervals. The stretching vibrations again are of two types. They are symmetric and antisymmetric stretchings. In symmetric stretching of a triatomic molecule, both the bonds connected to a common atom can simultaneously either elongate or contract. In the case of antisymmetric stretching, if one bond is lengthened, the other bond is shortened or vice versa. These stretchings are shown in Figs. 5.1a and b and Figs. 5.2a and b for linear and angular molecules of the type AB_2. **The arrows attached to each atom show the direction of its motion during half of the vibration.** In Figs. 5.1 and 5.2, we indicate the type of each vibration mode as parallel (∥) or perpendicular (⊥). In a parallel vibration, the dipole change takes place along the line of the principal axis of symmetry. In a perpendicular vibration, the dipole change takes place perpendicular to the line of the principal axis of symmetry. The nature of vibration-rotation spectra of polyatomic molecules depends on the type of vibration – parallel or perpendicular. We shall discuss this in Sec. 5.3.4.

The **bending vibrations** occur when there is a change in bond angle between bonds connected to a common atom. In some cases, the movement of a group of atoms with respect to the remaining atoms in the molecule also causes bending vibrations for a polyatomic molecule. A linear triatomic molecule has two bending vibrations (Fig.5.1 c

(i) The state of **greatest multiplicity** is the lowest energy state and

Do not worry about the details of how these allowed energy states are derived.

(ii) In case the **multiplicity is same** the state with *greatest L* value is the lowest energy state. Thus, ^3P state is of lowest energy and is the ground state. Can you predict the next higher state? It is ^1D (because it has greater L value). Then comes ^1S state. The ^3P state being a triplet has three energy levels $^3P_2$, $^3P_1$ and $^3P_0$.

(iii) For half less than filled atomic orbitals, out of the states with same L value, the state with lowest J value will be the most stable state. For more than half filled orbitals, states having higher J values have lower energy. Thus, out of $^3P_2$, $^3P_1$ and $^3P_0$ states, $^3P_0$ will be having the lowest energy. Such an energy level diagram is shown in Fig. 1.15.

Similarly, we can arrive at the possible energy states of other atoms from their electronic configuration.

In the next section, you will be studying about the effect of magnetic field on the splitting of energy levels.

Note that $\frac{e\hbar}{2m}$ can be represented as Bohr magneton (β_e). You will read more about Bohr magneton in Unit 11 of Block 4.

1.10 THE ZEEMAN EFFECT

When an atom is subjected to a magnetic field, each line in its spectrum splits into a number of components. The splitting of the lines is proportional to the strength of the applied magnetic field. This effect was first observed by Zeeman in 1896 and is known as **Zeeman effect**.

Note that a charged particle having angular momentum (e.g. an electron or nucleus) acts like a tiny magnet and has a magnetic moment (μ) which is proportional to the angular momentum (J).

Thus, $\vec{\mu} \propto \vec{J}$

or $\vec{\mu} = \gamma \vec{J}$

where γ, the proportionality constant called gyromagnetic ratio, is given by $\frac{g_e e}{2m}$ or $\frac{g_e \beta_e}{\hbar}$.

Hence $|\vec{\mu}| = \frac{g_e \beta_e}{\hbar} \cdot \sqrt{J(J+1)}\,\hbar$

$= g_e \beta_e \sqrt{J(J+1)}$

Let us now understand why this effect is observed? You know that electrons have charge. The motion of charge (electrons around nucleus) produces a circulating electric current and this in turn generates a magnetic field. The magnetic dipole of the atom (μ) is related to the total angular momentum quantum number (J) by the following expression:

$$\mu = -\frac{g_e e}{2m}\sqrt{J(J+1)}\,\hbar\, J\, T^{-1} = -g_e \beta_e \sqrt{J(J+1)} \qquad \text{... (1.29)}$$

Here,

m is the mass of the electron

and e is the charge of the electron

g_e is called the Lande's splitting factor which can be calculated as

$$g_e = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad \text{... (1.30)}$$

In a magnetic field because of the interaction between the magnetic moment of the charged particle and the applied field, the charged particle experiences a torque which makes the angular momentum precess around the direction of the applied field. This is shown in Fig 10.3. The precessional frequency (called **Larmor frequency** is directly proportional to the applied field, i.e.

$\omega = \gamma B$

The component of this magnetic dipole in the z direction (μ_z) can be written as

$$\mu_z = -g_e \beta_e m_J \qquad \text{... (1.31)}$$

where m_J represents the components of **J** (the total angular momentum) in the z direction and m_J can have the following values:

$$m_J = J, J-1, \ldots, \frac{1}{2} \text{ or } 0, \ldots, -J \qquad \text{... (1.32)}$$

Since the component of the angular momentum in the direction of the field is also quantised and can take only discrete values of m_J therefore, only certain allowed orientations of angular momentum are possible. These allowed orientations have slightly different energies as is also shown in Fig. 1.16.

In other words, we can say that for a particular value of J we have $(2J + 1)$ components in the z direction. Also, note that m_J will be integral or half integral depending upon whether J is integral or half integral.

When we substitute different values of m_J in Eq. 1.31, we get different μ_z components.

The extent of interaction of different μ_z components with external magnetic field (B_z) will be different leading to different energy values and can be given as follows:

$$\text{interaction} = \Delta E = \mu_z B_z = -g_e \beta_e m_J . B_z \qquad \text{... (1.33)}$$

Thus we will have $(2J + 1)$ different values for ΔE in the above expression. In other words, this indicates the **lifting of degeneracy** by the application of external magnetic field. This means that in the presence of external magnetic field, the energy levels which were earlier degenerate, split into $2J + 1$ levels.

Let us reconsider the hydrogen (or sodium) spectrum.

Here, the lowest term is $^2S_{\frac{1}{2}}$. It has $L = 0, S = \frac{1}{2}$ and hence $J = L + S = \frac{1}{2}$.

So, $\quad m_J = +J \ldots -J = +\frac{1}{2}, -\frac{1}{2}$.

Therefore, this level will be split into two $(2J + 1 = 2 \times \frac{1}{2} + 1 = 2)$ levels in the presence of magnetic field.

You may also remember that the two doublet P states were characterised as $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$.

The first state, $^2P_{\frac{1}{2}}$ has $J = \frac{1}{2}$. Thus, it will lead to

$$m_J = \frac{1}{2} \text{ and } -\frac{1}{2} \text{ (using Eq. 1.32)}$$

Hence, when $\quad m_J = \frac{1}{2}, \ \mu_z = -g_e \beta_e \times \frac{1}{2} = -\frac{1}{2} g_e \beta_e \qquad$ (by Eq. 1.31)

And from Eq. 1.33

$$\Delta E = -\frac{1}{2} g_e \beta_e B_z \qquad \text{... (1.34)}$$

Similarly for $\quad m_J = -\frac{1}{2}, \mu_z = -g_e \beta_e \times -\frac{1}{2} = \frac{1}{2} g_e \beta_e \qquad$ ... (by Eq. 1.31)

and

$$\Delta E = \frac{1}{2} g_e \beta_e . B_z \qquad \text{... (1.35)}$$

Thus, according to the above equations, i.e., Eqs. 1.34 and 1.35 $^2P_{\frac{1}{2}}$ level is further split into two energy levels in the presence of magnetic field. These levels are separated by an energy difference of $g_e \beta_e B_z$. What about $^2P_{\frac{3}{2}}$ state? For this $J = \frac{3}{2}$ and it will be split into $2J + 1 = 2 \times \frac{3}{2} + 1 = 3 + 1 = 4$ levels.

The m_J values for these four levels will be as given below:

$$\begin{aligned} m_J &= J, J-1, \ldots, 0 \text{ or } \frac{1}{2}, \ldots, -J \\ &= \frac{3}{2}, \frac{3}{2} - 1, \ldots, -\frac{3}{2} \\ &= \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \end{aligned}$$

Eq. 1.31 can also be expressed in terms of γ as follows:

$$\mu_z = \gamma m_J \hbar$$

Gyromagnetic ratio (γ) is the ratio of magnetic moment to the angular momentum.

$\gamma = \frac{\mu}{J}$. Using μ from Eq. 1.29 and J from Eq. 1.28,

$$\text{we get } \gamma = \frac{-g_e \beta_e \sqrt{J(J+1)}}{\sqrt{J(J+1)}\,\hbar} = \frac{-g_e \beta_e}{\hbar}$$

Hence, Eq. 1.33 can be rewritten as $\Delta E = \gamma \hbar \ m_J B_z$.

We can also write $h\nu$ in place of ΔE in the above equation.

Thus,

$$h\nu = \gamma \hbar m_J B_Z$$

$$= \frac{\gamma h m_J B_Z}{2\pi}$$

or

$$\nu = \frac{\gamma m_J B_Z}{2\pi}$$

or $2\pi\nu = \gamma m_J B_Z$

When the two energy levels differ by $m_J = 1$, we get $2\pi\nu = \gamma B_Z$

The term $2\pi\nu$ is the angular frequency. It can be denoted by ω and is expressed in radians sec^{-1}.

As you will study later in Block 4 Unit 10, Sec 10.3, it is also known as Larmor frequency.

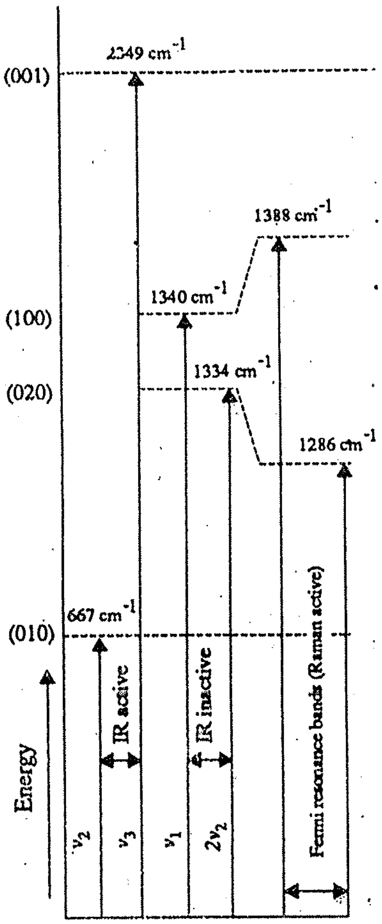
Wave number in cm is converted to m^{-1} unit during calculation. Thus 3652 cm^{-1} is written as 3.652×10^5 m^{-1}.
$1\ \text{cm}^{-1} = 10^2\ \text{m}^{-1}$

$$E(000) = hc\left(\left(\frac{1}{2} \times 3.652 \times 10^5\right) + \left(\frac{1}{2} \times 1.595 \times 10^5\right) + \left(\frac{1}{2} \times 3.756 \times 10^5\right)\right)\ \text{J}$$
$$= \frac{1}{2} \times 6.626 \times 10^{-34} \times 3 \times 10^8 \times 10^5\ (3.652 + 1.595 + 3.756)\ \text{J}$$
$$= 8.945 \times 10^{-20}\ \text{J}$$

So far, we discussed the IR spectrum of H_2O which is an angular triatomic molecule. Let us now discuss the IR spectra of CO_2 which is a linear triatomic molecule.

5.3.2 IR Spectrum of CO_2 Molecule

Among the four vibrations shown in Fig.5.1 for a triatomic linear molecule such as CO_2, the IR active vibrations are antisymmetric stretching (ν_3) and bending (ν_2) but not the symmetric stretching(ν_1) since it does not cause any change in the dipole moment. The two IR bands of CO_2 at 2349 cm^{-1} and 667 cm^{-1} correspond to ν_3 and ν_2, respectively. The band due to symmetric stretching (ν_1) at 1340 cm^{-1} is not observed in IR spectrum. However the stretching band is Raman active. In the case of CO_2, the first overtone of ν_2 i.e., $2\nu_2$ (2×667 cm^{-1} = 1334 cm^{-1}) has the same symmetry as the symmetric stretching mode and hence interacts with this fundamental vibration due to **Fermi resonance** giving rise to two bands. These two bands are not observable in IR spectrum but both are observable in Raman spectrum which will be discussed in the next unit. In fact, the Raman spectrum shows two bands at 1388 and 1286 cm^{-1}; the mean of these two values (1337 cm^{-1}) is close to ν_1 and $2\nu_2$. The overtone $2\nu_2$ which would normally be weak borrows intensity from the fundamental ν_1, and hence, two bands are observable in Raman spectrum.



Vibrational energy levels of CO_2 molecule

Earlier we stated the formula for the quantum mechanical vibrational energy of polyatomic molecules. We can calculate the quantum mechanical vibrational energy of a linear polyatomic molecule by carrying out summation over (3*N*–5)terms. But we leave it to you as an exercise in SAQ 2.

5.3.3 Complexity of the IR Spectra of Polyatomic Molecules

As we have discussed earlier, the infrared spectrum of a polyatomic molecule consists of an absorption band at each of the (3*N*–6) or (3*N*–5) fundamental frequencies for nonlinear and linear molecules, respectively. This is based on the assumption that each vibration is simple harmonic. But actually the vibrations are anharmonic, and therefore, we will have overtones of diminishing intensities at twice, thrice the fundamental frequency etc. In addition, we may have bands due to combination of two fundamentals (combination bands) or difference of two fundamentals (difference bands). These bands are weak. Also, a fundamental and an overtone may have frequencies very close to each other. The two close frequencies may resonate leading to higher and lower frequencies relative to the original. This is

Note that the bending mode of CO_2 has a perpendicular band symmetry whereas the overtone of the bending mode ($2\nu_2$) has parallel band symmetry like symmetric stretching mode.
Fig. 5.1 can be used for depicting the vibrational modes of CO_2. Note that the symmetric stretching mode is IR inactive whereas antisymmetric stretching and bending modes are IR active.

An overtone is an absorption band at twice, thrice, etc. the frequencies of the fundamental band.

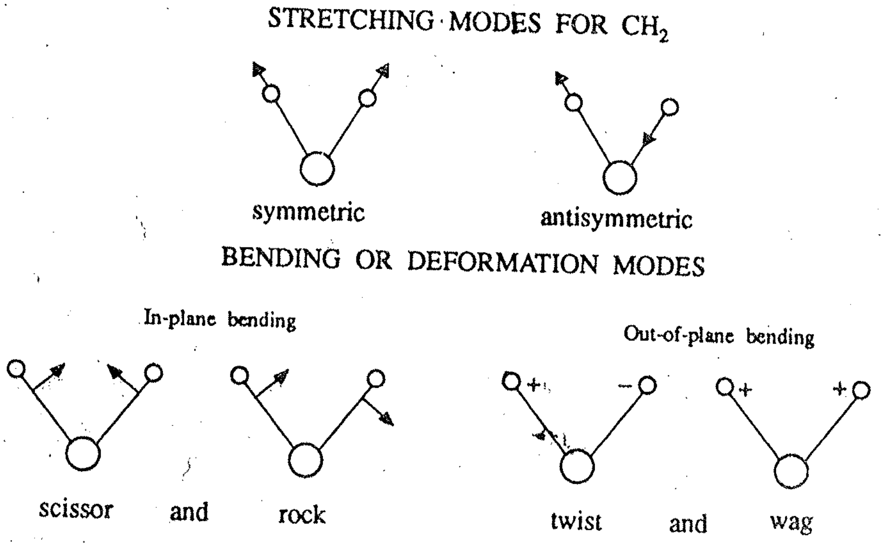


Fig. 5.5: Vibration modes in methylene group

called Fermi resonance and we have discussed it earlier. Thus an infrared spectrum of a compound will have strong fundamental absorptions and weak overtones, combination bands and Fermi resonance bands. As the number of atoms increase, the spectrum becomes complicated. In the case of polyatomic molecules, many out-of-plane bending vibrations also are responsible for the complexity of the IR spectra and a complete analysis of the IR spectrum becomes quite difficult. For instance, the stretching and bending modes of $>CH_2$ group are given in Fig.5.5.

The complexity of IR spectrum of even a simple molecule such as H_2O can be understood from the frequencies of the IR bands of water vapour given in Table 5.2.

Table 5.2 : Infrared Bands of H_2O Vapour

Wave number/cm^{-1}	Intensity*	Transition involved
1595	vs	(000) ⟶ (010)
3154	m	(000) ⟶ (020)
3652	s	(000) ⟶ (100)
3756	vs	(000) ⟶ (001)
5332	m	(000) ⟶ (011)
6874	w	(000) ⟶ (021)

* s = strong, m = medium, vs = very strong, w = weak.

In the next subsection, we shall examine the influence of rotational fine structure on the vibrational spectra of molecules. Generally, IR spectrum of a molecule is used for assigning the strongest bands and to identify the weaker ones as overtones or combination bands or difference bands. In fact, the detailed procedure involved in frequency assignment shall be illustrated in Sec. 6.7 of Unit 6 using the IR and Raman spectra of SO_2 molecule.

5.3.4 Vibration-Rotation Spectra of Polyatomic Molecules

In the last unit, we studied the effect of rotation on the vibration spectra of diatomic molecules. Now we briefly state some of the aspects of vibration-rotation spectra of polyatomic molecules having linear structure. Just for the purpose of having a simple treatment, we shall not be discussing nonlinear molecules.

It is interesting to note that the rotational fine structure of linear molecules depends on the way they undergo dipole change-parallel or perpendicular-with respect to principal axis of symmetry. We have illustrated these two types of vibrations for a linear triatomic molecule through Fig. 5.1. We shall state the selection rules for these two types separately.

Parallel vibrations of linear molecules

The selection rule for the parallel vibrations of linear molecules is stated below:

$\Delta J = \pm 1$, $\Delta v = \pm 1$ for simple harmonic motion

$\Delta J = \pm 1$, $\Delta v = \pm 1, \pm 2, \pm 3, ...$ for anharmonic motion

The spectra would be similar to diatomic molecules with P and R branches with equally spaced lines on either side of the band centre. There is no line corresponding to band centre. Fig.5.6 shows the P and R branches centering around 3310 cm^{-1} for HCN molecule which is linear.

Similarly, when the lines originate due to the transition of the electron from the M to K level, they are termed as K_β lines. Similar to K_α lines, they can also be subdivided as K_{β_1}, K_{β_2}, etc.

If an electron is ejected from the L shell and an electron from M shell takes its vacant place, then the lines corresponding to this emitted X–ray radiation in the spectrum will be called as L lines.

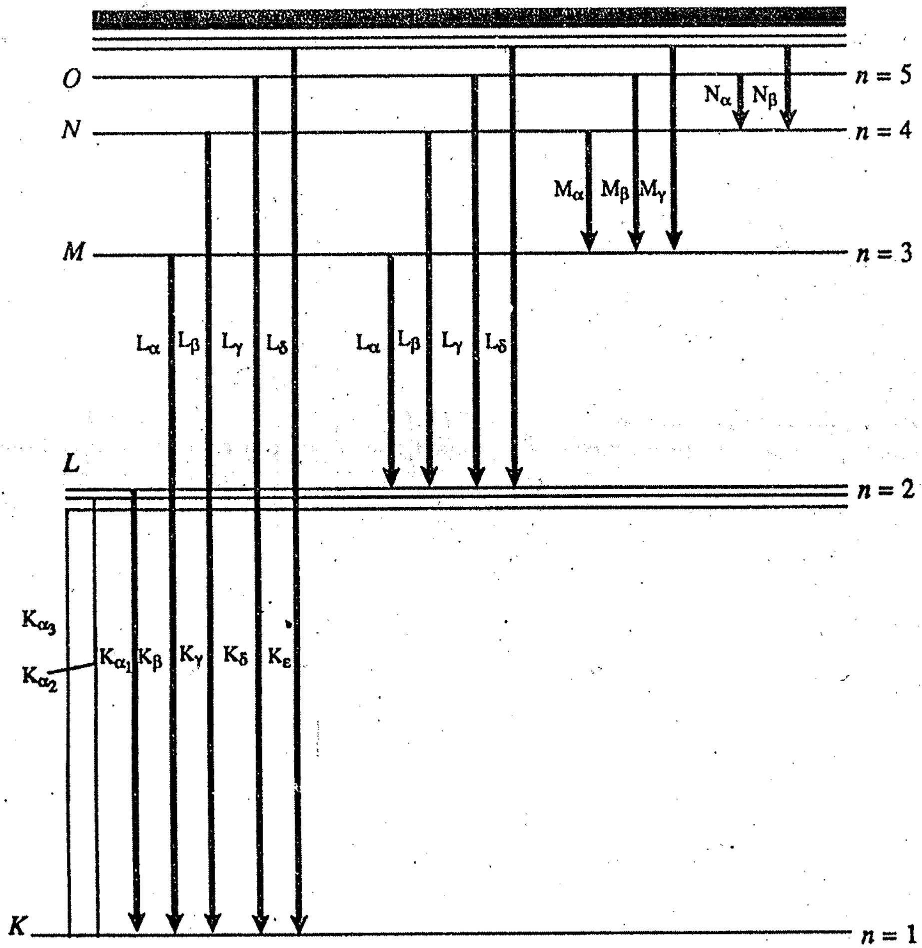


Fig. 1.18: Various transitions responsible for origin of lines in X–ray spectrum.

The X–ray emission spectrum so obtained is similar for all elements. But they differ from each other in the fact that the wavelengths at which various lines appear are different and depend upon the atomic number of the element. Such a relationship between wavelength and atomic number was discovered by Moseley and is known as **Moseley's Law**. This can be mathematically stated as

$$\lambda = \frac{c}{\nu} = a\,(Z-\sigma)^2 \qquad \text{... (1.36)}$$

Here, Z is the atomic number and σ is a constant which depends upon series of lines under consideration and a is another constant.

Since the X–ray fluorescence spectrum is characteristic of a particular atom, it can be used in its identification both qualitatively and quantitatively. The quantitative measurements involve the measurement of intensity of the lines.

Elements having atomic numbers between 12 and 92 can be analysed in air; but for elements having atomic numbers between 5 and 11, the experiment is to be carried out in vacuum because the fluorescence is absorbed by the air.

This method of detection of elements is non–destructive and does not require much sample preparation. Its applications are numerous and range from determination of trace elements in plants, analysis of ores, vulcanisation of rubber (detection of sulphur ensuring high quality of rubber) to the analysis of objects of art and antiques.

1.12 PHOTOELECTRON SPECTROSCOPY

You now know that various energy levels exist in an atom. In this section, you will study about a technique with the help of which electronic energy levels (of atoms and molecules) can be determined.

In this method, the sample is irradiated with monochromatic X–rays of known energy. This results in the ejection of an electron from the sample. The remaining excess energy of the X–rays is imparted to the electron as its kinetic energy. Thus, we can say that

$$\begin{array}{l}\text{Energy of the}\\ \text{incident}\\ \text{X–ray radiation}\end{array} = \text{Binding Energy} + \text{Kinetic energy} \qquad \dots (1.37)$$

An *X*–ray of wavelength 1 nm has an energy of 2×10^{-16} J. This amount of energy can cause ejection of electrons from the inner shells of many atoms.

Binding energy of an electron is the energy required to remove it from the atom. It is also called ionisation energy, which was referred earlier.

The kinetic energy of the electron is measured. The binding energy of the electron can then be obtained from the above relationship by knowing the energy of the incident X–rays and kinetic energy of the ejected electron. Experimentally, the number of electrons ejected as a function of their kinetic energy are detected. This leads to the measurement of binding energies of all the electrons present in the system. This information is also characteristic of a particular element and hence can be used to identify it.

Similar to X–ray photoelectron spectroscopy is the technique of ultraviolet photoelectron spectroscopy. In UV photoelectron spectroscopy, UV radiation is used as incident radiation. The energy of this radiation is sufficient to eject a valence electron whose kinetic energy is determined as done in case of X–ray photoelectron spectroscopy.

1.13 INTENSITY OF SPECTRAL LINES

We have based most of our discussion on the spectra of individual atoms. But what happens when there is a bulk of particles and a number of possible energy levels are available to them? Do all the particles occupy the lowest energy level? The answer to

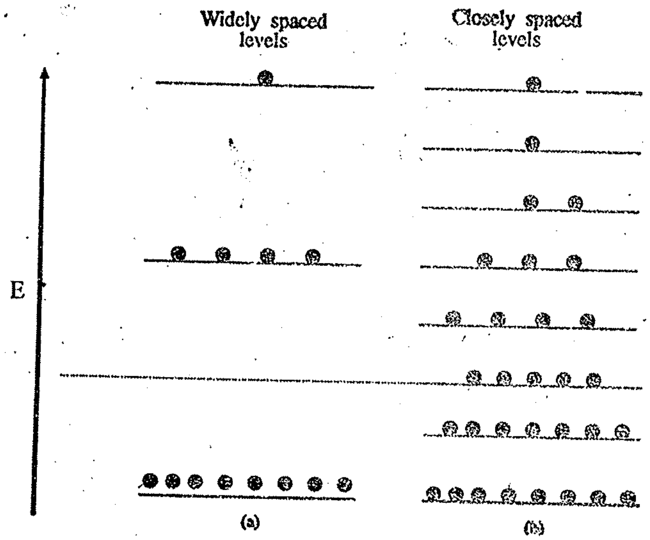


Fig. 1.19: The distribution of atoms or molecules in various energy levels.

this question is NO. Fig.1.19 shows the distribution of atoms or molecules in widely spaced and closely spaced energy levels.

The number of atoms or molecules N_j in a state with energy E_j relative to the number N_i with the lower energy E_i is given by Boltzmann distribution as follows:

$$\frac{N_j}{N_i} = e^{-\Delta E/kT} \quad \text{... (1.38)}$$

where N_J is the population (no. of particles) in the upper energy level (E_j),

N_i is the population of lower energy level (E_i),

ΔE is the energy difference between two levels,

T is the temperature in Kelvin.

and k is the Boltzmann constant having value 1.38×10^{-23} J K^{-1}.

Certainly, as the energy difference between the levels (ΔE) increases, the relative population of the upper level decreases.

Since the intensity of the spectral lines depends upon the initial population of the level. Other factors being equal, the transition arising from the most populated level will give rise to the most intense spectral line.

1.14 SUMMARY

In this unit, you learnt about the nature and characteristics of electromagnetic radiation. Various parameters such as frequency, wavelength etc. associated with electromagnetic radiation were defined and their interrelationship was discussed. Then, we discussed about the particle nature of electromagnetic radiation. The interaction of electromagnetic radiation with atoms was explained by taking the example of hydrogen atom spectrum. A detailed discussion of hydrogen atom spectrum was done including its fine structure. These concepts were extended to the spectra of hydrogen-like atoms. Then, spectra of multi-electron systems were taken and coupling schemes ($L - S$ and $J - J$) of angular momentum of these system were explained. In these systems, nomenclature of various energy states by using term symbols was also discussed. The spectra of helium and carbon were dealt as examples of multi–electron systems. Finally, the effect of magnetic field on atomic spectra was discussed under the title Zeeman effect. This was followed by sections on experimental techniques followed in detection of elements using atomic spectra which include techniques such as X–ray fluorescence spectroscopy and photoelectron spectroscopy. Lastly, the intensity of spectral lines was dealt.

1.15 TERMINAL QUESTIONS

1. Calculate the $\bar{\nu}$ for the first spectral line of Balmer series for hydrogen atom.

2. Which of the following elements would have singlet and triplet states in their atomic energy levels?
   Na, Mg, Cl, Ca, Cu, Ag, Ba

3. Derive the term symbol for the D state of a hydrogen atom.

1.16 ANSWERS

Self Assessment Questions

1. $E = \frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1}}{400\ \text{nm}}$$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1}}{400 \times 19^{-9}\ \text{m}}$$

$$= 4.966187 \times 10^{-19}\ \text{J} = 4.97 \times 10^{-19}\ \text{J}$$

2. **To obtain energy per mole, the above value of energy is to be multiplied by the Avogadro's Number. Thus**

$$E_{\text{per mole}} = 4.966187 \times 10^{-19}\ \text{J} \times 6.022 \times 10^{23}\ \text{mol}^{-1}$$

$$= 299063\ 78114\ \text{J mol}^{-1} = 299.06378114\ \text{kJ mol}^{-1}$$

$$= 2.99 \times 10^{5}\ \text{J mol}^{-1}$$

3. $\frac{m_e}{m_n} = 0.00027148$

$$R_D = R_\infty \frac{1}{1 + 0.00027148}$$

$$= 1.09737 \times 10^{7}\ \text{m}^{-1} \times \frac{1}{1.00027148} = 1.09707419 \times 10^{7}\text{m}^{-1}$$

$= 1.09707 \times 10^{7}\ \text{m}^{-1}$ (approximated using significant figures)

$$\bar{\nu}\ \text{Balmer} = R_D\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36}R_D = 15237\ \text{cm}^{-1}$$

4. $\Delta\bar{\nu} = 17.19\ \text{cm}^{-1}$

$$\Delta E = hc\bar{\nu}$$

$$= 6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1} \times 17.19\ \text{cm}^{-1}$$

$$= 4.4 \times 10^{-24}\ \text{J}$$

5. **Because Pauli's Exclusion principle is violated, as $S = 1$ means m_{s_1} and m_{s_2} should be $+\frac{1}{2}$.**

Terminal Questions

1. $\bar{\nu}_{\text{Balmer}} = R_H\left(\frac{1}{4} - \frac{1}{9}\right) = R_H\left(\frac{9-4}{36}\right) = \frac{5}{36}R_H\ \text{cm}^{-1}$

$$= \frac{5}{36} \times 1.09677 \times 10^{7}\ \text{m}^{-1} = 15233\ \text{cm}^{-1}$$

2. **Mg, Ca, Ba.**

3. **For a D state, $l = 2$ and $s = \frac{1}{2}$.**

Now, $j = l + s = 2 + \frac{1}{2} = \frac{5}{2}$

and $j = l - s = 2 - \frac{1}{2} = \frac{3}{2}$

Thus, $2S + 1 = 2 \times \frac{1}{2} + 1 = 2$; leading to term symbols $^2D_{\frac{5}{2}}$ and $^2D_{\frac{3}{2}}$.

UNIT 2 SYMMETRY OF MOLECULES

Structure

2.1 INTRODUCTION

The molecules with different structures show different reactivity pattern and molecular spectra. The question arises, "is there any way to relate structure, spectra and reactivity?". Such a relationship could help us both in understanding the nature of known substances and in predicting the properties of new ones. In this unit, we are going to discuss symmetry aspects of molecules and, we will indicate how symmetry could relate structure (or shape) to spectra (or to many of the physical properties).

In Unit 3 of CHE-01 (Atoms and Molecules) course, we have discussed

- the way of writing the Lewis structures of molecules (and ions) and
- predicting their shapes on the basis of valence shell electron pair repulsion theory.

As a continuation of the same, we shall relate shape of a molecule and symmetry aspects in this unit. We shall show how to classify molecules as point groups based on symmetry. We shall state the uses of point group classification in understanding the physical properties such as dipole moment, optical rotation and spectra. Some of the aspects of symmetry are covered under group theory in the Appendix part of this unit. We shall also indicate the uses of group theory in understanding the chemistry of molecules. In this unit, we shall attempt a qualitative treatment of molecular symmetry and group theory.

Objectives

After studying this unit, you should be able to:

- define symmetry elements and symmetry operations,
- state the list of symmetry elements in simple molecules,
- identify the point group of a molecule from the list of its symmetry elements, and
- state the implications of molecular symmetry.

2.2 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

It is worth recapitulating valence shell electron pair repulsion theory which has been **discussed in Unit 3 of CHE-01** course. The VSEPR theory helps us to explain the shapes and bond angles of molecules in relation to the number of shared and lone electron pairs around the central atoms.

We present in Table 2.1 the shapes of different molecules and ions according to VSEPR theory.

Table 2.1: Number of Electron Pairs in the Valence Shell of the Central Atom, and shape of Molecule or ion.

No. of Electron Pairs				
Total	**Bond pairs**	**Lone pairs**	**Shape**	**Examples**
2	2	0	linear	$HgCl_2$, $BeCl_2$
3	3	0	triangular planar	BF_3, BCl_3, CO_3^{2-}, NO_3^-
3	2	1	angular	$SnCl_2$(gas), NO_2^-, ClNO
4	4	0	tetrahedral	CH_4, BF_4^-, NH_4^+
4	3	1	trigonal pyramidal	NH_3, PF_3
4	2	2	angular	H_2O, ICl_2^+, NH_2^-
5	5	0	trigonal bipyramidal	PCl_5(gas), $SnCl_5^-$
5	4	1	see-saw	$TeCl_4$, IF_4^+, SF_4
5	3	2	T-shaped	ClF_3, BrF_3
5	2	3	linear	XeF_2, ICl_2^-
6	6	0	octahedral	SF_6, PF_6^-
6	5	1	square pyramidal	IF_5, SbF_5^{2-}
6	4	2	square planar	BrF_4^-, XeF_4

SAQ 1

Using VSEPR theory, predict the shape of PCl_3. Draw its structure.

....

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....

2.3 SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

In the last section, we saw how molecules can be classified on the basis of shape. It is better to classify the molecules based on their symmetry aspects. This could help us to understand the molecular properties such as dipole moment, optical activity and spectral characteristics. Before trying to classify molecules on the basis of symmetry, we must understand the terms, symmetry elements and symmetry operations.

Symmetry operation is the movement of an object such that it leaves the object looking the same. A symmetry operation brings the molecule into the equivalent or identical configuration. You can understand the words 'equivalent' and 'identical' configurations by using a cardboard which is shaped like an equilateral triangle (Fig. 2.1a). You label the three vertices of the triangle as 1, 2 and 3. Rotation of the triangular cardboard through 120° ($2\pi/3$) and 240° ($4\pi/3$) in the anticlockwise direction gives rise to equivalent configurations i.e., each configuration is indistinguishable from the original configuration (Figs. 2.1 b and c) whereas the rotation through 360° (2π) results in an identical configuration (Fig. 2.1 d). In equivalent configuration, the positions of the atoms in space *are similar* to those in the original configuration, i.e., before applying symmetry operation. In identical configuration, the positions of the atoms *are the same* as before applying symmetry operation. (Compare Figs. 2.1a and d).

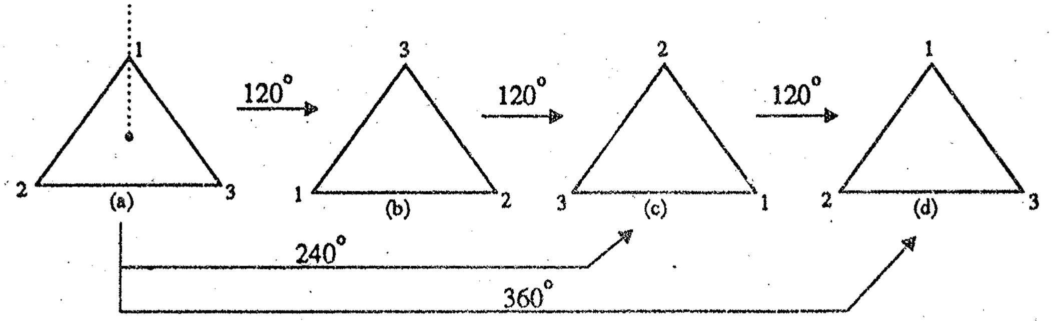

Fig. 2.1: (a) The configuration before rotation; the dotted line shows the axis of rotation in a direction perpendicular to the plane of the molecule.

(b) and (c) equivalent configurations (after anticlockwise rotation through 120° ($2\pi/3$) and 240° ($4\pi/3$).

(d) identical configuration (after rotation through 360° (2π)).

Similarly, reflection once across a plane passing through equilateral triangle type molecule can give rise to equivalent configuration, while another reflection through the same plane gives rise to identical configuration. For instance, imagine a perpendicular plane passing through vertex 1 of the equilateral triangle-shaped cardboard. This perpendicular plane is shown as a dotted line in Figs. 2.2 a and b. Reflection through this plane once results in equivalent configuration, Fig. 2.2b. Another reflection through this plane results in an identical configuration, Fig. 2.2c.

Rotation through 120° once, twice and thrice can be denoted by C_3^1, C_3^2 and C_3^3; C_3 also represents threefold axis of rotation. We shall discuss this in a detailed way in the next section.

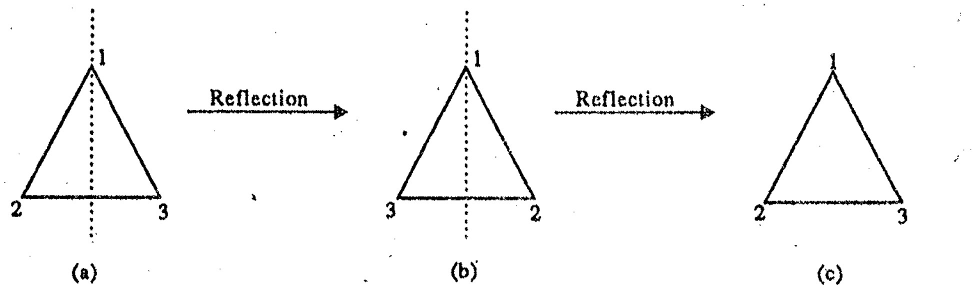

Fig. 2.2: a) The configuration before reflection.

b) The equivalent configuration resulting from reflection through a perpendicular plane (shown as dotted line passing through the vertex 1).

c) The identical configuration resulting from another reflection through the same plane.

The symmetry element is a line or a plane or a point whereas the symmetry operation is the operation performed to bring the object into an equivalent configuration.

So far we have seen rotation about an axis and reflection across a plane which are two of the five symmetry operations. All the symmetry operations are listed in Table 2.2. Corresponding to each symmetry operation, there is a symmetry element. **The symmetry element is a line or a plane or a point with respect to which the symmetry operation is performed.** The symmetry element is a geometrical property which is said to generate the operation. Table 2.2 lists the various symmetry elements and symmetry operations.

We will be using the same symbols for each pair of symmetry elements and symmetry operations. These symbols are indicated within brackets under the column 'Symmetry element' in Table 2.2.

Table 2.2: List of Symmetry Elements and Symmetry Operations

S. No.	Symmetry Element	Symmetry Operation
1.	n-fold axis of symmetry or proper axis of symmetry (C_n)	Rotation once or several times by an angle (equal to $360°/n$ or $2\pi/n$) about the axis; n must be an integer.
2.	Plane of symmetry (σ)	Reflection plane passing through the molecule
3.	Axis of improper rotation or alternating axis of symmetry or rotary-reflection axis (S_n)	Rotation about an axis by an angle $360°/n$ or $2\pi/n$ followed by reflection in a plane perpendicular to the axis of rotation
4.	Centre of symmetry (i)	Inversion of all atoms through the centre of symmetry
5.	Identity element (E)	Doing nothing to the object

The crystal symmetry includes translational symmetry whereas molecular symmetry does not include it.

At least one point in the molecule should be unaffected by all the symmetry operations. Also, all the symmetry operations possible for a molecule must intersect at this point. Thus, the symmetry operation should not lead to translational motion of the molecule in the space. This is the basic difference between the molecular symmetry and crystal symmetry.

This aspect will be made more clear in Sec. 2.9 where we shall distinguish between molecular point groups and crystallographic space groups. We shall explain the symmetry operations and symmetry elements in a detailed way in the sections to follow.

SAQ 2

Draw a square and label the corners 1, 2, 3 and 4. Also through diagrams indicate the equivalent configurations and the identical configuration arising out of rotation through 90° successively four times through an axis perpendicular to the square surface.

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2.4 ROTATION ABOUT AN AXIS OF SYMMETRY

The n-fold axis of symmetry (or the proper axis of symmetry) is a line about which a molecule is to be rotated through $360°/n$(or $2\pi/n$ or α) to obtain an equivalent configuration. The symbol for n-fold axis of symmetry is C_n. The subscript 'n' in C_n is called order of an axis which can be defined through Eq. 2.1.

$$\text{Order of axis} = n = \frac{360^\circ}{\text{Minimum angle of rotation } (\alpha) \text{ for obtaining equivalent configuration}} \quad \ldots(2.1)$$

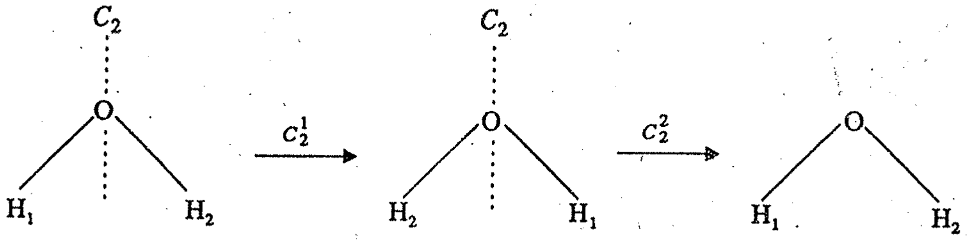
Note that

$$\alpha = \frac{2\pi}{n} = \frac{360^\circ}{n}$$

In the case of water molecule, rotation through 180° (= 360°/2) results in an equivalent configuration.

Hence, $$n = \frac{360^\circ}{180^\circ} = 2$$

i.e., H_2O molecule has a twofold axis of rotation (C_2 axis). C_2 axis of H_2O is illustrated in Fig. 2.3 along with the rotation through C_2 axis once (C_2^1) and twice (C_2^2); C_2^1 stands for 180° rotation once and C_2^2 stands for 180° rotation twice. The twofold axis of water is on the same plane as the oxygen and hydrogen atoms.



The subscripts 1 or 2 are used to indicate the interchanging of the hydrogen atoms.

Fig. 2.3: Twofold axis C_2 in water molecule; the effect of one C_2 rotation (C_2^1) is shown by interchange of H_1 and H_2 atoms. Application of C_2 twice (C_2^2) brings the molecule to identical configuration as indicated by the position of H_1 on the left side and H_2 on the right side.

In general a n-fold axis of symmetry (C_n) gives rise to $C_n^1, C_n^2, \ldots\ldots C_n^n$ operations, and,

$$C_n^n = E \quad \ldots(2.2)$$

For C_2 rotation,

$$\alpha = \frac{2\pi}{2} = 180^\circ$$

where E refers to identity operation. Identity operation means doing nothing to the molecule and after performing an identity operation, the molecule regains identical configuration. A rotation through 360° (C_n^n) is an instance of identity operation.

Note that C_n^n means n times rotation about C_n axis. We shall see shortly other ways of carrying out identity operation.

Note that as per Eq. 2.2 in H_2O molecule, rotation through C_2 axis twice leads to identical configuration.

i.e., $$C_2^1 C_2^1 = C_2^2 = E$$

The rotation operation by $2\pi/n$ (= α) is denoted as $C(\alpha)$.

The presence of C_3 axis in NH_3 can be understood on the basis of the fact that rotation through 120° about this axis results in an equivalent configuration. Using Eq. 2.1,

$$n = \frac{360^\circ}{120^\circ} = 3$$

The C_3 axis of NH_3 is shown in Fig. 2.4a.

The rotations through 120°, 240°, and 360° are denoted by the symbols C_3^1, C_3^2 and C_3^3, respectively. The operations C_3^1 and C_3^2 lead to equivalent configurations while C_3^3 leads to identical configuration. The equilateral triangle formed by joining the positions of three H atoms can be used to represent the effect of successive rotations by 120° three observed and the calculated values given below are those obtained experimentally and calculated (using the relationship between $\bar{\nu}$ and $\mu^{1/2}$).

Stretching vibration :	O–H	3620 cm^{-1}	(observed)
	O–D	2634 cm^{-1}	(calculated)
	O–D	2630 cm^{-1}	(observed)
Bending vibration :	C=C–H	815 cm^{-1}	(observed)
	C=C–D	598 cm^{-1}	(calculated)
	C=C–D	678 cm^{-1}	(observed)

5.5.2 Electronic Effects

Let us see the effect of electron withdrawing or donating groups on the IR absorption frequency of a particular group. Before we study this, it is advisable to recapitulate what you may have studied in Unit 5 of Organic Chemistry (CHE-05) course regarding electronic effects.

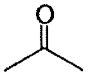
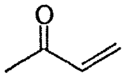
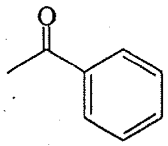
(i) Inductive effect

The inductive effect acts through the sigma (σ) electrons or bonds in a molecule. Inductive effect is felt only at short distances and it weakens as the length of the carbon chain increases. The groups which withdraw electron density from the neighbouring atoms in a saturated carbon chain are called *–I* groups and those which enhance electron density, the *+I* groups. A list of *–I* and *+I* groups are given in Table 5.2 in Unit 5 of CHE-05 course.

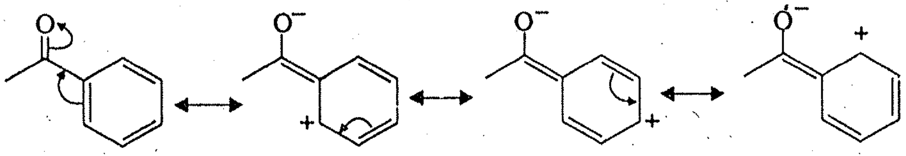
(ii) Resonance effect

In contrast to the inductive effect, the resonance effect acts through the *pi* bonds. The groups which withdraw electrons through *pi* bonds are *–R* groups while those which donate electrons are *+R* groups. A list of *+R* and *–R* groups are given in Table 5.6 of Unit 5 of CHE-05 course. While trying to see the influence of electronic effects on the IR frequency of a group, we have to bear in mind the following principles:

- Any substituent which enhances bond order (or shortens the bond length)in a group, causes an increase in IR frequency; if the substituent causes a decrease in bond order (or enhances the bond length), a decrease in IR frequency of the group results.
- If the inductive and resonance effects operate in opposite ways, then the one having predominant influence decides the IR frequency value.

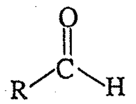
Carbonyl frequency	1720 cm^{-1}	1700 cm^{-1}	1700 cm^{-1}
	I	II	III

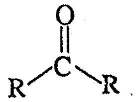


III IV V VI

Let us consider a few examples. The carbonyl frequencies of I, II and III can be rationalised by realising that *+R* nature of the vinyl ($-CH = CH_2$) and phenyl groups have a dominating influence over their *-I* nature. For instance, the resonance effect in III operates to decrease the bond order of the carbonyl group as per structures IV, V and VI. This could explain the lower carbonyl frequency in III as compared to I.

As an example for the change in absorption frequency caused by the inductive effect, we can see that the aldehydes have higher carbonyl absorption frequency than ketones have. The additional alkyl group in ketones which has $+I$ nature causes a decrease in C=O frequency.



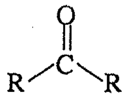


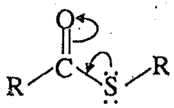
(R is alkyl group)

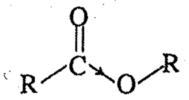
Carbonyl frequency Around 1735 cm^{-1} Around 1720 cm^{-1}

VII VIII

As another example, we can compare the carbonyl group frequencies of the ketone (VIII) with those of the thiol ester (IX) and the ester (X).







Carbonyl frequency Around 1720 cm^{-1} Around 1690 cm^{-1} Around 1740 cm^{-1}

VIII IX X

($+R > -I$ of S) ($+R < -I$ of O)

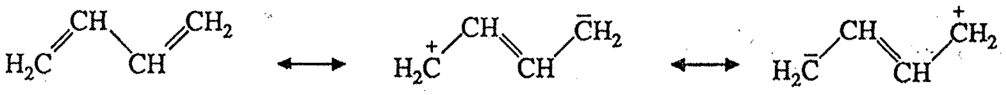
The $+R$ nature of sulphur atom is more than its $-I$ nature which leads to loss of double bond character of the carbonyl group in the thiol ester. This accounts for the lower frequency of the carbonyl group in the thiol ester IX as compared to VIII. On the other hand, in the case of ester X, the $-I$ effect of oxygen atom dominates over its $+R$ nature. This results in the shortening of the carbonyl bond in X and in the increase of carbonyl frequency as compared to VIII.

The role of conjugation in resonance effect can be illustrated using the IR frequency values of XI and XII.

C=C frequency 1650 cm^{-1} 1610 cm^{-1}

XI XII

The frequency of >C = C< group in XII decreases due to the following resonance structures (XIII and XIV) wherein the terminal bonds have bond order value between one and two.



XII XIII XIV

5.5.3 Effect of Hydrogen Bonding

Hydrogen bonding can occur in any system containing a proton donor group (X–H) and a proton acceptor (Y), if the *s* oribital of the proton can overlap effectively with the *p* orbital of the acceptor group. Atoms X and Y are electronegative and, Y possesses lone pair of electrons.

The common proton donor groups in organic molecules are carboxyl, hydroxyl, amino or amido groups. Common proton acceptor atoms are oxygen, nitrogen and the halogens. Unsaturated groups like the ethylenic linkage can also function as proton acceptors. Hydrogen bonding alters the force constant of both the groups and, stretching and bending frequencies are altered. Because of hydrogen bonding, the X–H stretching bands move to lower frequencies with increased intensity and band widening. The stretching frequency of the acceptor group, for example, of the >C=O group is also reduced but to a lesser degree than the proton donor group. The X–H bending vibration usually shifts to higher frequency, when hydrogen bonding occurs.

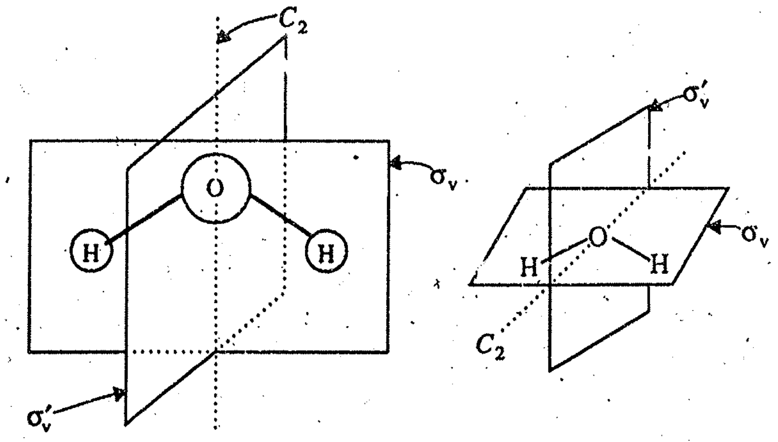
SAQ 4

State the symbols for the operations of six successive rotations through C_6 axis.

2.5 REFLECTION IN A PLANE OF SYMMETRY

A vertical plane passes through principal axis. Hence σ_v and σ'_v in H_2O are vertical planes. A horizontal plane (σ_h) is **perpendicular** to the principal axis.

A plane bisects the object under consideration so that one half of the object on one side of the plane is the mirror image of the half on the other side. If the plane contains the principal axis, it is called the vertical plane and is denoted by σ_v. H_2O has two vertical planes of symmetry (σ_v and σ'_v -Figs. 2.7. a and b) while NH_3 has three vertical planes of symmetry σ_v, σ'_v and σ''_v (Fig. 2.8).



(a) (b)

Fig. 2.7: a) Two vertical planes of symmetry (σ_v and σ'_v) in water.

b) σ_v plane is differently shown so that it is easier to visualise the two planes.

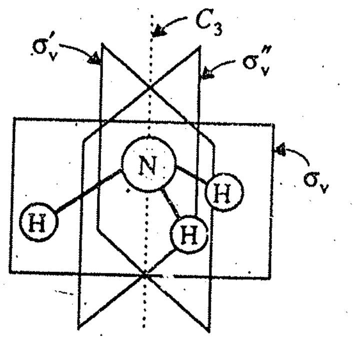


Fig. 2.8: The three vertical planes of symmetry in NH_3 (σ_v, σ'_v and σ''_v); each vertical plane of symmetry encloses one N—H bond also.

When the plane of symmetry is perpendicular to the principal axis, it is called the horizontal plane, and, is denoted by σ_h. For instance, the plane containing all the six carbon atoms and six hydrogen atoms in benzene is the horizontal plane, since it is perpendicular to the (C_6) principal axis.

Again let us examine the simple cases of NH_3 and BF_3. The fact that their shapes are different is shown up by the presence of different types of planes of symmetry. Thus, both these molecules have three vertical planes of symmetry. In addition to these, the planar molecule, BF_3, has a horizontal plane of symmetry but not NH_3 (which is pyramidal).

We shall also examine another type of plane of symmetry which is known as dihedral plane and is denoted by σ_d. A dihedral plane must be,

i) vertical (i.e., must contain the principal axis) and

ii) bisect the angle between two C_2 axes which are themselves perpendicular to the principal axis.

The terms 'conformation' and 'configuration' have to be properly understood. Various conformations of a molecule result due to rotation about C—C bond through different angles. For instance, ethane has two well known conformations, eclipsed and staggered. For a better understanding of the term, conformation, refer to Sec. 3.7 of Unit 3 of Block 1 of Organic Chemistry (CHE-05) course.

The term'configuration' refers to a particular spatial arrangement of atoms in a molecule. The optical isomers and geometrical isomers come under this category. In this context, you may refer to Sec. 2.2 of Unit 2 of Block 1 of Organic Chemistry course.

For instance, the staggered form of ethane (Fig. 2.9a) has three dihedral planes. Each dihedral plane contains the C_3 axis (which is the principal axis) and intersects two mutually perpendicular C_2 axis. One of the three dihedral planes is shown in Fig. 2.9b.

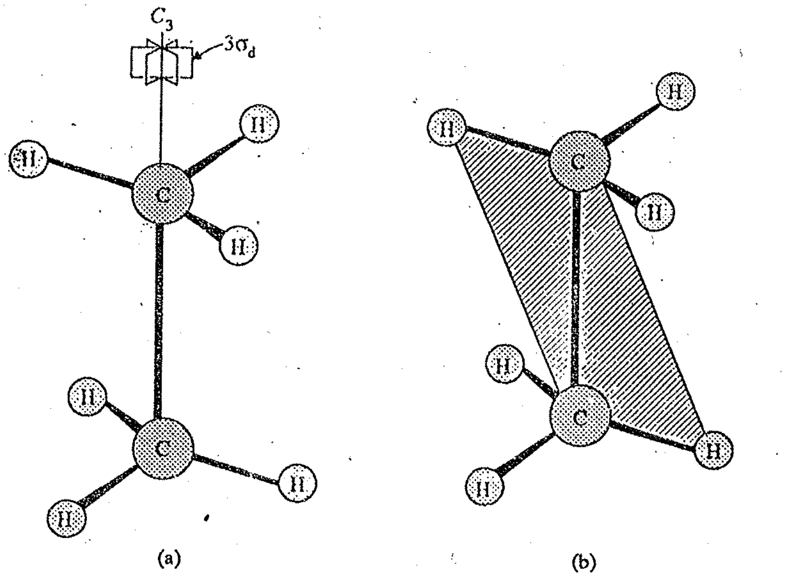


Fig. 2.9: (a) The staggered conformation of ethane. It has three σ_d planes and each σ_d plane contains C — C bond and a pair of C — H bonds.

b) One of the dihedral planes shown by the shaded portion.

The operation of reflection of same type (viz. vertical, horizontal or dihedral) conducted twice across a plane leads to identity operation:

i.e.,
$$\left.\begin{aligned} \sigma_v \sigma_v &= E \\ \sigma_h \sigma_h &= E \\ \sigma_d \sigma_d &= E \end{aligned}\right\} \quad \ldots(2.5)$$

Having studied the above, answer the following SAQs.

SAQ 5

Name the planes of symmetry in PCl_3. For its structure, refer to SAQ 1.

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....

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SAQ 6

$SOCl_2$ is pyramidal in shape. It has a plane of symmetry. Identify the atoms on this plane.

Hint: There is a simple restriction on the planes of symmetry. A plane must either pass through an atom or else that type of atom must occur in pairs being placed symmetrically on either side of the plane.

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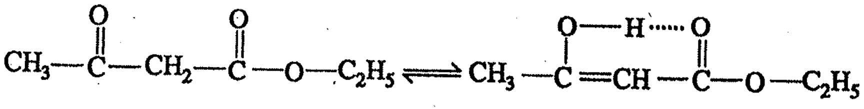
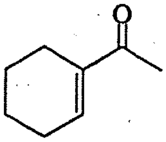
1724 cm^{-1}	keto carbonyl	keto form (XIX)
1748 cm^{-1}	ester carbonyl	
1650 cm^{-1}	ester carbonyl	enol form (XVI)

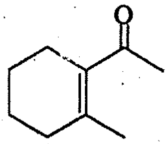


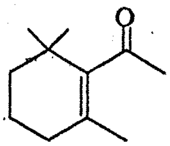
(XIX) (XVI)

5.5.4 Steric Effect

The steric effect arises due to spatial interactions between the groups. This has been discussed in detail in Subsec. 5.4.5 of Unit 5 of Block 1 of Organic Chemistry course. The most common instance of steric effect is that which arises when the bulky groups are present near a reactive group. Let us state an example. Generally, the resonance effect lowers the frequency of a carbonyl band as mentioned in the case of I, II and III in Subsec. 5.5.2 above. In order that the resonance forms may exist, there should be coplanarity between the $>C=C<$ and $>C=O$ groups. If the coplanarity is prevented due to steric effect, then the resonance structures (such as III to VI) may not be possible, which means interaction between $>C=C<$ and $>C=O$ groups is reduced. Consequently, the steric inhibition of resonance in XXI and (more so in) XXII causes the carbonyl frequency to be higher than that in XX.







Carbonyl frequency	1663 cm^{-1}	1686 cm^{-1}	1693 cm^{-1}
	XX	XXI	XXII

Thus we have seen in this section the perturbation of group frequencies due to structural features. Answer the following SAQ's.

SAQ 5

Arrange the following compounds in the increasing order of carbonyl frequency:

Acetophenone, *p*-methoxyacetophenone and *p*-nitroacetophenone.

....

....

....

SAQ 6

The infrared spectrum of 1-butanol (liquid film) has single broad band between 3500-3200 cm^{-1}; when it is diluted with CCl_4, it shows an additional band near 3650 cm^{-1}. Explain the reason.

Hint: 'Liquid film' means pure liquid is taken for spectral study without adding any solvent.

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5.6 APPLICATIONS OF IR SPECTRA IN STRUCTURE DETERMINATION

The infrared spectra find a wide range of applications. For instance, structure determination, quantitative analysis, hydrogen bonding studies and conformational studies are some of the fields where infrared spectra play a vital role. The method of determination of structure of simple inorganic compounds will be discussed in Unit 6 using IR and Raman spectral data. In this section, we shall discuss the role of IR spectra in arriving at the structure of organic compounds.

The matching of the IR spectrum of an unknown compound with those of known compounds provides the best means of structure identification of organic compounds. The finger print region could be particularly useful for this purpose. Infrared correlation charts such as Table 5.3 could be used to identify the hydrocarbon skeleton and the functional groups present in a molecule. To be sure of the structure of a compound, data from IR spectra should be supported by other evidences like its chemical, physical or other spectroscopic data (NMR,UV etc).

For instance in Unit 13 of this course, we shall come across many interesting problems of structure determination using a collection of spectral data. A preliminary assessment of structural details could be made using IR spectral data. For this you have to spend some time in finding the answers for the following questions.

I Hydrocarbon skeleton

Look for IR data indicating the presence of alkane, alkene, alkyne and aromatic residues. For doing this effectively, compare the IR spectral data of the compound with the entries under ' A. Hydrocarbon chromophore' of Table 5.3 and find the answers for the following questions:

(i) What is the type of hydrocarbon skeleton?

(ii) Is there any special features in the IR spectrum which throw light on substitution pattern?

You can arrive at the hydrocarbon skeleton using C–H stretching, C–H bending and C–C multiple bond stretching absorptions.

Look for specific indications regarding the type of aromatic substitution, *cis-trans* isomers, presence of *gem*-dimethyl groups etc.

II Functional groups

The nature of functional groups can be decided from the answers to the following questions.

(i) Does the compound have carbonyl group(s)?

Look for sharp IR band(s) in the region 1800-1600 cm^{-1}. If you find one such, answer the questions (a) to (e) given below.

(a) Does the spectrum have C–H stretching characteristic of an aldehyde?

(b) Does the spectrum have C–O stretching characteristic of an ester (or lactone)?

(c) Does the spectrum have O–H stretching characteristic of – COOH group?

(d) Does it show N–H stretching and bending vibrations characteristic of amides?

A molecular group is called a point group because one point in the molecule remains fixed under all the symmetry operations in the molecule. All the symmetry elements of a molecule intersect at this point. We may note that crystals have an additional element of symmetry known as translational symmetry, wherein symmetry arises from the translational motion of crystals through space. The crystals are classified into **space groups.** We are not going to discuss crystallographic symmetry in this unit.

The point group of a molecule can be denoted by a specific symbol. There are two kinds of notations, one devised by Schoenflies and, the other, by Hermann and Mauguin. The Schoenflies notation is more common for the discussion of molecular symmetry and the Hermann–Mauguin symbolism is exclusively used for the discussion of crystal symmetry. In Table 2.3, we shall give the Schoenflies notation for some of the point groups.

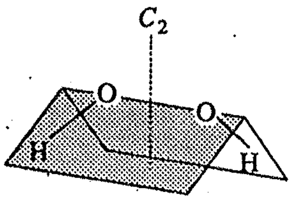


Fig. 2.15: H_2O_2 (partially opened book configuration)

Note that all dihedral groups have a C_n axis and nC_2 axes perpendicular to C_n axis. The dihedral groups mentioned in Table 2.3 are $D_3, D_{3h}, D_{6h}, D_{3d}$ and $D_{\infty h}$.

Table 2.3: Schoenflies Notation for Some Point Groups.

Schoenflies notation	Symmetry elements	Examples
C_1	E	CHFClBr
C_s	σ and E	Quinoline (Fig. 2.13)
$C_i\ (S_2)$	i and E	*meso*-tartaric acid (Fig. 2.14)
C_2	C_2 and E	H_2O_2 (partially opened book configuration (Fig. 2.15)).
C_{2v}	C_2, $2\sigma_v$ and E	H_2O and SO_2
C_{3v}	$2C_3$, $3\sigma_v$ and E	NH_3 and $CHCl_3$
$C_{\infty v}$	$2C_\infty$, $\infty\sigma_v$ and E	Linear molecules without centre of symmetry such as CO, OCS and HBr
C_{2h}	C_2, σ_h, i and E	*trans*-1,2-dichloroethylene
D_3	C_3, $3C_2$ and E	$[Co(en)_3]^{3+}$ (Fig. 2.16)
D_{3h}	$2C_3$, $3C_2$, σ_h, $3\sigma_v$, $2S_3$ and E	BF_3, PCl_5 (Fig.2.17) and eclipsed form of ethane
D_{6h}	$2C_6$, $2C_3$, $6C_2$, σ_h, $3\sigma_v$, $3\sigma_d$, $2S_3$, $2S_6$, i and E	C_6H_6
$D_{\infty h}$	$2C_\infty$, ∞C_2, $\infty\sigma_v$, σ_h, $2S_\infty$, i and E	All linear molecules with centre of symmetry such as H_2, Cl_2 and C_2H_2
D_{3d}	$2C_3$, $3C_2$, $3\sigma_d$, i, $2S_6$ and E	Staggered form of ethane
T_d	$8C_3$, $3C_2$, $6S_4$, $6\sigma_d$ and E	CCl_4 and CH_4 (Fig. 2.18)
O_h	$6C_4$, $8C_3$, $6C_2$, $3\sigma_h$, $6S_4$ $8S_6$, $6\sigma_d$, i and E	SF_6 (Fig. 2.19)

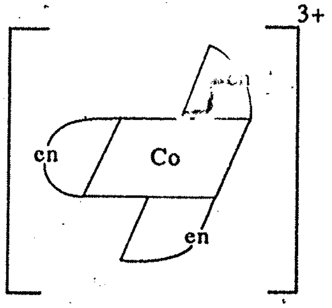


Fig. 2.16: $[Co(en)_3]^{3+}$ ion ; en stands for ethylene diamine

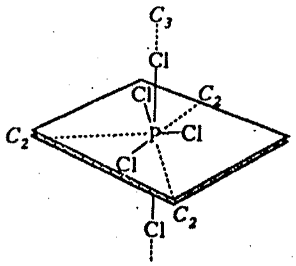
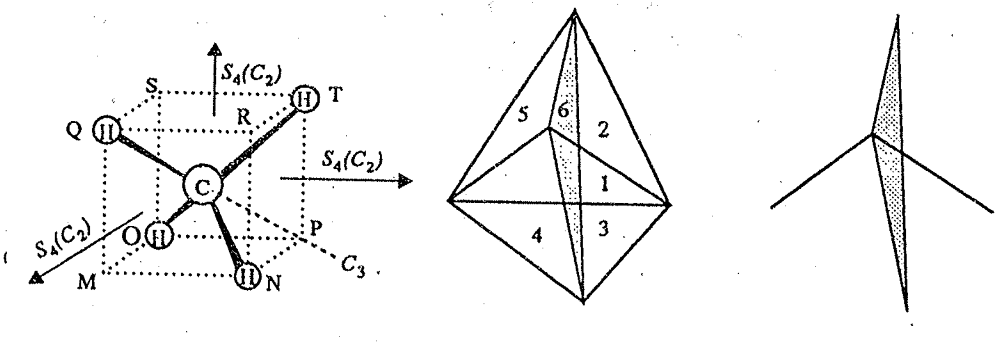


Fig. 2.17: PCl_5: note that the vertical Cl-P-Cl bonds constitute C_3 axis.

A group is called a cubic group, if it has many C_n axes of order greater than 2. The important cubic groups are T_d and O_h.

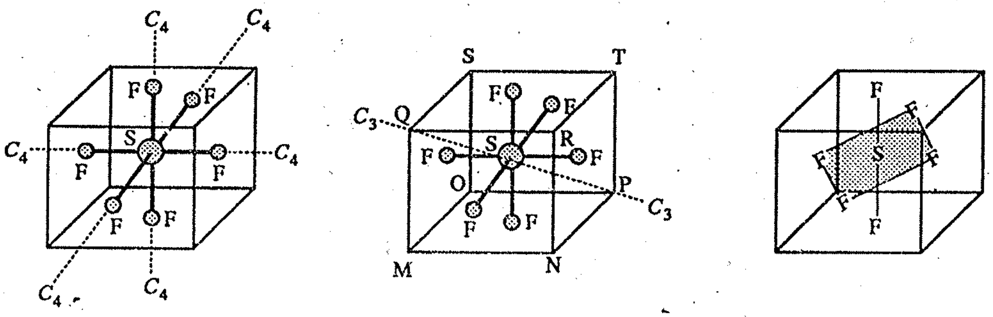


(a) (b) (c)

Fig. 2.18: a) Methane belonging to T_d group; the three cartesian axes serve as three C_2 (and also S_4) axes. The four C_3 axes are along the four C—H bonds (these C_3 axes are also the body diagonals—MT, NS, OR and QP); one of the C_3 axes (QP) is shown.

b) You can make six triangular planes in a tetrahedron by combining any two corners with the centre; do not confuse these six planes with four faces of the tetrahedron which are obtained by joining any three corners only. These six planes are $6\sigma_d$ for CH_4; each of the σ_d passes through the carbon and two hydrogen atoms and relates the other two hydrogen atoms as a mirror image of each other.

c) One of the six dihedral planes (σ_d).



(a) (b) (c)

Fig. 2.19: SF_6 with O_h point group symmetry; SF_6 is shown inside the cube.

(a) Each F—S—F linear arrangement is a C_4 axis; the three C_4 axes are at right angles to each other

(b) Four C_3 axes are located along the body diagonals (MT, NS, OR and QP) of the cube; one of the C_3 axes (QP) is shown.

(c) One of the three σ_h planes is shown by the shaded area; each σ_h plane comprises of two diagonal units of F—S—F; other symmetry elements are not shown.

Using the above materials, answer the following SAQ.

SAQ 9

Using your answers for SAQs 1,3 and 5, identify the point group of PCl_3.

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2.10 SOME IMPLICATIONS OF MOLECULAR SYMMETRY

The examination of molecules with respect to symmetry aspects could lead us to many useful conclusions. We shall examine a few of them.

2.10.1 Dipole Moment and Molecular Symmetry

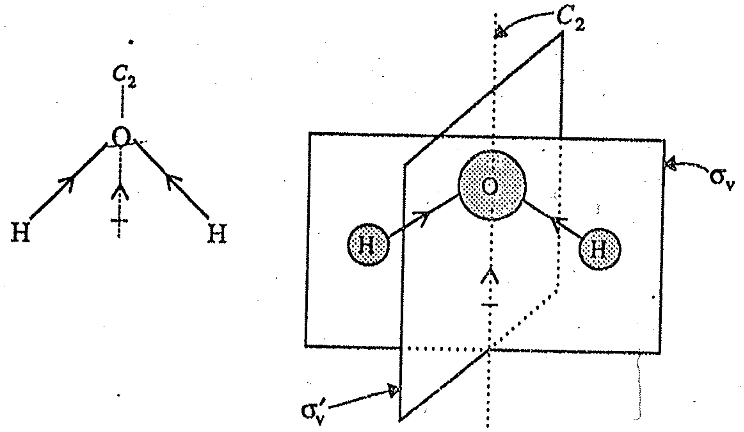
You are advised to study Secs. 6.4 to 6.6 and the Appendix portion of Unit 6 of CHE-01 (Atoms and Molecules) course to understand the dipole moment concept.

The statement that the dipole moment vector should be invariant (or totally symmetric) with respect to symmetry operations will be used in defining the allowed transitions in the Appendix of this unit.

Dipole moment is a vector quantity as defined in Sec. 6.4 of Unit 6 of CHE-01 (Atoms and Molecules) course. It has both direction and magnitude. The symmetry operation allowed for a molecule should not affect the direction or magnitude of the dipole moment vector. In other words, the dipole moment vector should be invariant and must be contained in each of the symmetry elements of the molecule. As a result of this, **only molecules belonging to the groups C_n, C_{nv} and C_s may have dipole moment.**

Let us illustrate this using H_2O molecule. As explained in the Appendix of Unit 6 of CHE-01 course, the direction of the resultant dipole moment vector in H_2O (indicated by ⇞ sign) is as shown in Fig. 2.20a.

You try C_2, σ_v or σ_v' operation (using Fig. 2.20b) through diagrams such as Fig. 2.3 and verify the fact that the dipole moment vector remains invariant after each symmetry operation.



(a) (b)

Fig. 2.20: Illustration of the fact that each of the symmetry elements of water contains the dipole moment vector. It is worth recollecting that H_2O has E, C_2 and $2\,\sigma_v$ as symmetry elements.

a) **H→—O stands for O—H bond moment and ⇞ stands for the direction of the resultant dipole moment vector. Note that the dipole moment vector lies along the C_2 axis.**

b) **Both σ_v and σ_v' planes contain the dipole moment vector. (b) is drawn to show that σ_v, σ_v' and C_2 contain the dipole moment vector.**

Note that molecular symmetry is a theoretical concept. Experimental quantities such as dipole moment or absorption frequencies (obtained from spectral measurements) help us in confirming the theoretical aspects such as symmetry of a molecule.

As shown in Fig. 2.20 a-b, the symmetry elements, C_2 axis and two σ_v planes, also contain the resultant dipole moment vector in H_2O molecule.

In molecules with the point groups such as C_{nh}, D_n, D_{nh}, etc., there are symmetry operations that correspond to turning the molecule upside down. This would reverse the direction of the dipole moment vector which is not allowed. Hence, the molecules belonging to the point groups such as C_{nh}, D_{nh} etc. cannot have dipole moment. Use Table 2.3 and see how many of the molecules possess dipole moment.

The presence or absence of dipole moment tells us about the symmetry of the molecule. We shall illustrate this taking two cases of triatomic molecules, H_2O and CO_2. H_2O has a dipole moment value of 6.14×10^{-30} C m. This confirms the bent structure of H_2O (as predicted by VSEPR theory in Sec. 2.2) and the fact that it could belong to the point group C_{2v} (a special case of C_{nv} which has permanent dipole moment).

CO_2 has zero dipole moment. This confirms the linear structure of CO_2 (as predicted by VSEPR theory) and the fact that it could belong to $D_{\infty h}$ point group.

It is worth recapitulating that the bent structure of H_2O and the linear structure of CO_2 have been explained in subsec. 6.6.3 of Unit 6 of CHE-01 (Atoms and Molecules) course based on O–H and C=O bond moments.

2.10.2 Symmetry and Optical Activity

In Sec. 6.10 of Unit 6 of CHE-01 course, we have explained the concept of optical activity. A molecule is optically active only if it could exist as **separate left-and right-handed forms** or mirror image isomers. Lactic acid (Fig. 2.21) is an example of an optically active molecule. From symmetry point of view, we can define optical acivity. **A molecule is optically active only if it cannot be superimposed on its mirror image through improper rotation.** Since a rotation about an axis followed by a **reflection** in a perpendicular plane (i.e., improper rotation) converts a right-handed object to a left-handed object, the presence of S_n axis indicates that a molecule **cannot exist in separate** left-and right-handed forms. This **implies that any optically active molecule will not have an axis of improper rotation, S_n.** It is important to check whether a molecule has S_n axis even in an implied way. For example, the molecules in the point group C_{nh} are not optically active, since these molecules have S_n axis as implied by the presence of both C_n axis and σ_h plane. All molecules with centre of symmetry are optically inactive. It is so since any molecule having the inversion centre possesses S_2 ; i is equivalent to C_2 followed by σ_h which is equivalent to S_2 as explained in Secs. 2.6 and 2.7.

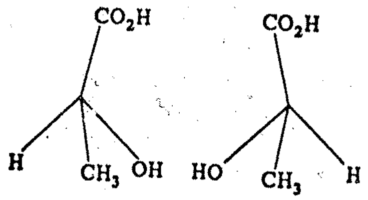


Fig. 2.21: Lactic acid: the left-and right-handed forms (mirror images).

Even if a molecule possesses only σ, then also it is optically inactive since σ is equal to S_1 [one full rotation of the molecule by 360° (C_1) through any axis, followed by reflection across a perpendicular plane]. Thus, fluorochloromethane (Fig. 2.22) which has σ is not optically active.

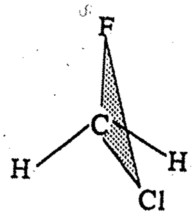


Fig. 2.22: σ plane in CH_2FCl encloses C, F and Cl.

To sum up, molecules having improper rotation axes will not be optically active. For example, lactic acid belongs to C_1 and is optically active. Molecules having σ (i.e., S_1), i (i.e., S_2) or any other S_n are optically inactive.

2.10.3 Spectra and Molecular Symmetry

We can examine the microwave and infrared spectral characteristics of a molecule to understand the molecular symmetry or vice versa.

We shall see in Unit 3 of this course that only molecules having permanent dipole moment can give rise to pure rotational (or microwave) spectra. Thus, only molecules belonging to the point groups C_{nv} and C_s which have permanent dipole moment can exhibit pure rotational spectra. For example, CO ($C_{\infty v}$) and CH_3Cl (C_{3v}) can exhibit pure rotational spectra but not CO_2 ($D_{\infty h}$) and CCl_4 (T_d). The former two possess permanent dipole moment but not the latter two. This again could help us in confirming the point group classification of a molecule.

In Units 4 and 5 of this course, we shall see that for a molecule to give rise to vibrational spectra, one or more vibrations of a molecule must give rise to a dipole moment change. The vibration spectra could be understood using the symmetry aspects of a particular vibration of a molecule. The assignment of infrared spectral frequencies to the specific vibrations causing the absorption can be made using group theory. We shall discuss some of the aspects of group theory in the Appendix of this unit and in Units 5 and 6.

Answer the following SAQs.

SAQ 10

CH_2Cl_2 has the following symmetry elements:

E, C_2 and $2\sigma_v$

a) Identify the point group.

b) Will the molecule show permanent dipole moment?

SAQ 11

Both CO_2 and CO are linear. Which of the two can exhibit pure rotational spectra? State the reason.

SAQ 12

1-Bromo-1-chloroethane belongs to C_1 point group. Is this molecules optically active? State the reason.

2.11 SUMMARY

In this unit, we have discussed symmetry aspects of molecules. We have explained the Shoenflies system of point group classification. We have given examples for the point groups of molecules. These ideas should enable you to relate the Lewis structure of a molecule to its point group. In some of the units of this course, we shall be using symmetry aspects of a molecule for understanding the molecular spectra.

2.12 TERMINAL QUESTIONS

1. (a) Using VSEPR theory, find the shape of $XeOF_4$.

Hints : Of the 8 electrons of Xe, 4 are involved in forming four Xe – F bonds; 2 electrons are involved in Xe→O bond which should be considered like a single covalent bond only. The other two electrons form a lone pair around Xe.

(b) Draw its shape.

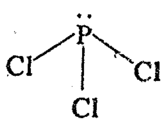
(c) Name the principal axis of $XeOF_4$.

2. (a) Although $CHCl_3$ has tetrahedral structure, it has symmetry elements similar to NH_3. The C–H bond in $CHCl_3$ is a C_3 axis. There are three σ_v planes, each plane enclosing C–H bond and one C–Cl bond. Identify the point group of $CHCl_3$.
   (b) Can it have permanent dipole moment?
   (c) Can it exhibit pure rotational spectra?
   (d) Can it be optically active?
3. (a) $[PtCl_4]^{2-}$ has a square planar structure. State the name of the two proper axes of symmetry.
   (b) Does it have centre of symmetry?
   (c) Can it have permanent dipole moment?
4. (a) HBr is a linear molecule. State the name of the principal axis of symmetry in it.
   (b) State its planes of symmetry.
   (c) Name its point group.
   (d) Can it have permanent dipole moment?
   (e) Can it exhibit pure rotational spectra?
5. H_2O belongs to C_{2v} group. Name the symmetry elements in it.
6. (a) For PF_5, predict the shape using VSEPR theory.
   (b) State any three symmetry elements in it.
   (c) Identify its point group.

2.13 ANSWERS

Self Assessment Questions

1. The central atom phosphorus has three bond pairs and one lone pair. Hence, it is trigonal pyramidal.



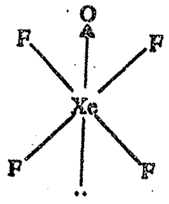
2. Through drawings it can be established that the equivalent configurations arise thrice one after the other, and finally the identical configuration.
3. PCl_3 has C_3 axis.
4. $C_6^1, C_6^2, C_6^3, C_6^4, C_6^5$, and C_6^6 $(=E)$.
5. There are 3 σ_v planes in PCl_3. Each σ_v plane encloses one P–Cl bond.
6. The plane of symmetry in $SOCl_2$ must pass through sulphur and oxygen atoms since one atom each is present. The two chlorine atoms must lie on front and back sides of this plane.
7. Presence of S_6 axis indicates that rotation through 60° followed by reflection in a perpendicular plane leads to equivalent configuration.
8. The dipole moment of C_6H_6 is zero, since it has a centre of symmetry.
9. Using Table 2.3, it can be shown that PCl_3 belongs to C_{3v} point group.
10. a) C_{2v}
    b) The molecule can have permanent dipole moment, since its point group (C_{2v}) is one among the C_{nv} groups.
11. CO_2 belongs to $D_{\infty h}$ point group and does not have permanent dipole moment. Hence, it cannot exhibit pure rotational spectra. CO belongs to $C_{\infty v}$ point group

and has permanent dipole moment. Hence, it can exhibit pure rotational spectra.

(12) 1-bromo-1-chloroethane is optically active, since it does not have S_n axis.

Terminal Questions

1. (a) $XeOF_4$ is square pyramidal in shape.

   (b) 

   (c) C_4

2. (a) C_{3v}

   (b) It can have permanent dipole moment.

   (c) It can exhibit pure rotational spectra.

   (d) It cannot be optically active.

3. (a) C_2 and C_4

   (b) It has centre of symmetry.

   (c) It cannot have permanent dipole moment.

4. (a) C_∞

   (b) $\infty\sigma_v$

   (c) $C_{\infty v}$

   (d) It can have permanent dipole moment.

   (e) It can exhibit pure rotational spectra.

5. E, C_2 and $2\sigma_v$.

6. (a) Trigonal bipyramidal

   (b) C_3, $3C_2$ (perpendicular to C_3) and σ_h

   (c) D_{3h}

2.14 APPENDIX

The Basic Aspects of Group Theory

The group theory is the mathematical method for dealing with the application of symmetry concepts to spectroscopy and molecular structure. We shall deal with the following aspects of group theory in this section:

i) The criteria of a group

ii) Character table of point groups

iii) Uses of character tables

The Criteria of Group

A group is a collection or a set of elements which should satisfy the five criteria mentioned below. The elements of a group are related to one another through a combination process. The elements of a group may be symmetry operations of a molecule or the real numbers ($-\infty$ to $+\infty$, inclusive of fractions). The combination process may be multiplication or addition. A group should satisfy the following five criteria:

1. The product of two elements of a group gives another element of the group.

Example

If A and B are two elements of a group, then the combination, AB, leads to C, which is also an element of the group. The combination AB means, B is carried out first and then A. The combination AB need not always be equal to BA (BA means A is carried out first and then B). That is the order of combination is quite important. Those groups for which AB = BA are said to be *commutative or Abelian* groups; i.e., in Abelian groups, each element commutes with other elements of the group.

2. An element combines with itself to form one of the elements of the group.

3. Every group has one element which commutes with all the elements of the group to leave them unchanged. This element is called the identity element and is indicated by the symbol *E*.

Examples

(a) $EA = AE = A$

(b) $EB = BE = B$

4. Every element has an inverse or reciprocal which also belongs to the group. The element and the inverse combine to give the identity element.

Examples

If A^{-1} is the inverse of A and, B^{-1} the inverse of B, we can write

$$AA^{-1} = A^{-1}A = E$$

$$BB^{-1} = B^{-1}B = E$$

5. Every element of the group obeys the associative law of combination. If A, B and C are three elements of a group and the process of combination is multiplication, then the associative law tells us that

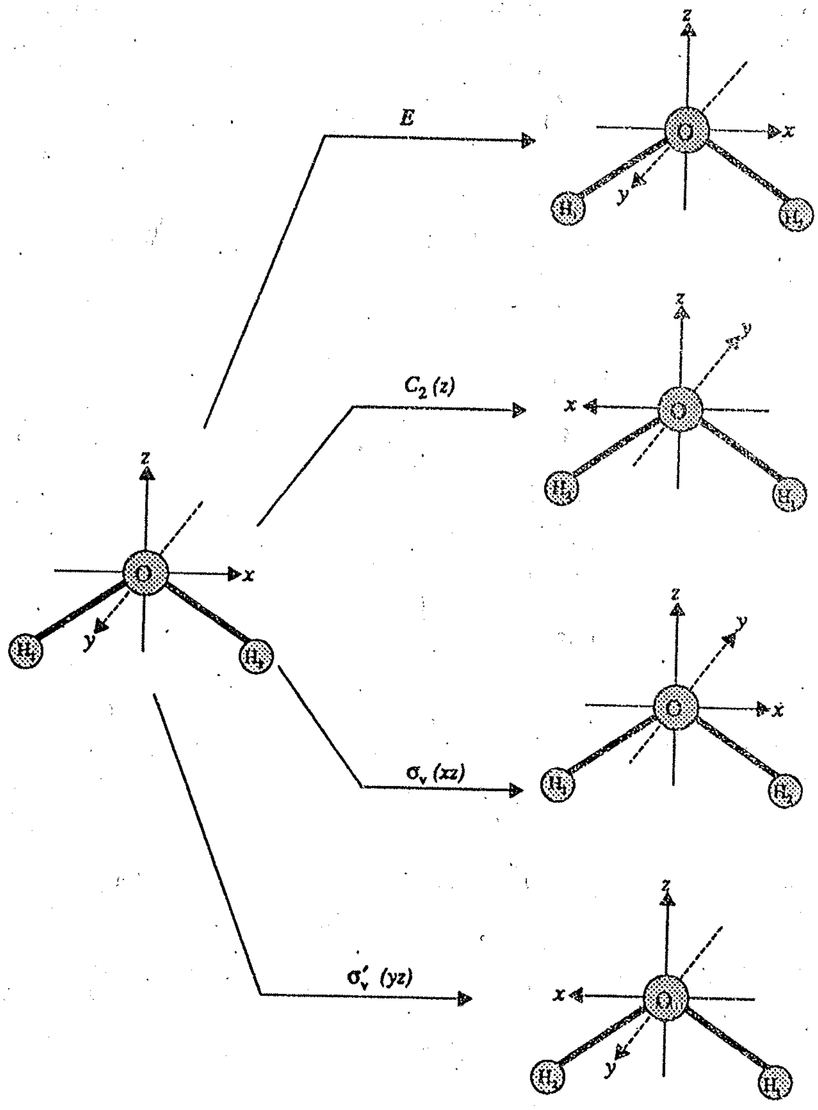
$$(AB)C = A(BC)$$

We can illustrate the criteria of groups using the symmetry operations of C_{2v} point group.

Example

The four symmetry operations of C_{2v} point group, E, $C_2(z)$, $\sigma_v(xz)$ and $\sigma_v'(yz)$ satisfy the criteria of group. Let us explain the significance of the operations, E, $C_2(z)$, $\sigma_v(xz)$ and $\sigma_v'(yz)$.

These operations can be understood using the following diagrams (Fig. A.1) where one has to observe how (i) the two hydrogen atoms 1 and 2 and (ii) the *x*, *y* and *z* coordinates of oxygen atom are affected by these operations.



$C_2(z)$ means rotation through 180° around z-axis.

Fig. A.1: E, $C_2(z)$, $\sigma_v(xz)$ and $\sigma_v'(yz)$ operations.

Note that C_2 operation is carried out around z-axis and it interchanges the positions of H_1 and H_2 atoms besides changing the x and y coordinates on oxygen atom. You can observe that the positions of the two hydrogen atoms and the coordinates of the oxygen atom remain the same as a result of E operation. But the $\sigma_v(xz)$ operation changes the y coordinate of oxygen atom while retaining the x and z coordinates of oxygen atom and the positions of two hydrogen atoms. The operation $\sigma_v'(yz)$ results in the change of positions of two hydrogen atoms and the x coordinate of the oxygen atom. Using the rules that define a group, we can construct the following multiplication table (Table A.1) for C_{2v} group.

The elements of a group are its constituents. The elements of the group discussed in this example are the symmetry operations such as reflection, rotation etc. These elements are not to be confused with symmetry elements such as plane of symmetry, axis of symmetry, etc.

Table A.1: Multiplication Table for C_{2v} group

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
E	E	$C_2(z)$	I $\sigma_v(xz)$	$\sigma_v'(yz)$
$C_2(z)$	$C_2(z)$	II E	$\sigma_v'(yz)$	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v'(yz)$	E	$C_2(z)$
$\sigma_v'(yz)$	$\sigma_v'(yz)$	$\sigma_v(xz)$	$C_2(z)$	E

Note that any particular symmetry operation appears only once in each column or each row. In order to verify the entries in Table A.1, you must remember the convention that the operation listed at the top of the table has to be carried out first followed by the operation listed at the left side. For example, the execution of operation $\sigma_v\,(xz)$ followed by the operation $C_2(z)$ gives rise to $\sigma_v'\,(yz)$. The sequence of carrying out the operations $\sigma_v\,(xz)$ and $C_2(z)$, and the resultant product, $\sigma_v'\,(yz)$ are represented by means of curved arrows I and II in Table A.1. The product of operations $\sigma_v\,(xz)$ and $C_2\,(z)$ can be represented by Eq. A.1.

$$C_2\,(z).\,\sigma_v\,(xz) = \sigma_v'\,(yz) \qquad \text{...(A.1)}$$

Eq. A.1 can be understood using Fig. A.2; this helps in verifying the first of the criteria of a group stated above.

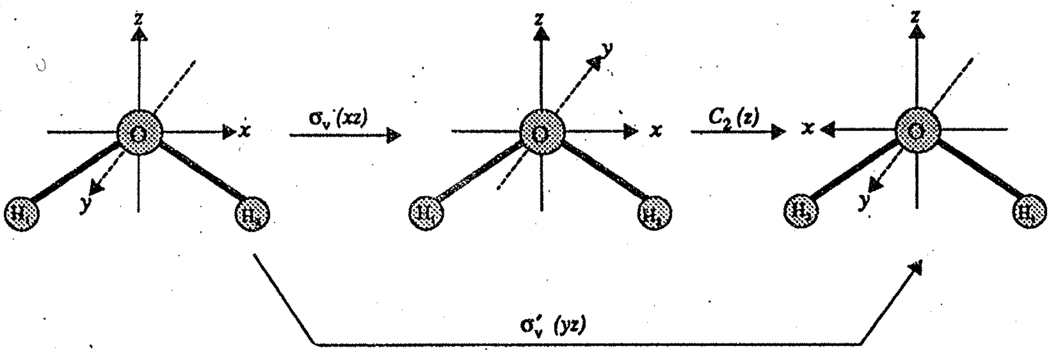


Fig. A.2: Illustration of Eq. A.1 [$C_2(z)\,\sigma_v(xz) = \sigma_v'\,(yz)$].

You can verify the other four criteria of group using the symmetry operations of C_{2v} group. Note that in C_{2v} group, the inverse of each element (i.e., symmetry operation) is the element itself.

Thus, $[C_2\,(z)]^{-1} = C_2\,(z)$

$$[\sigma_v\,(xz)]^{-1} = \sigma_v\,(xz)$$

$$[\sigma_v'\,(yz)]^{-1} = \sigma_v'\,(yz)$$

These are characteristic of C_{2v} group. These relationships along with the fact that $E^{-1} = E$ should help you in verifying the entries in Table A.1 and also the fact that $\sigma_v\,(xz)$, $\sigma_v'\,(yz)$, $C_2\,(z)$ and E form a group.

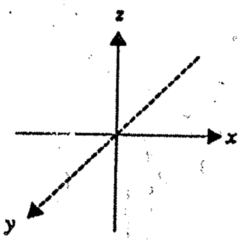
Next we shall devote our attention towards the formation of character table of C_{2v} point group. This could help us in studying some of the applications of group theory.

A matrix is a rectangular array of numbers or symbols for numbers, which may be combined with other such arrays according to certain rules. You go through Unit 13 of PMT Course or Unit 5 of MTE-04 Course for getting an elementary idea about matrices.

Character Table of Point Groups

The symmetry operations of a point group can be represented using a set of matrices. Each matrix is called a representative. The sum of the diagonal elements of a matrix is called its character. It is possible to reduce a matrix into smaller matrices known as irreducible matrices. A set of irreducible matrices corresponding to the symmetry operations of a point group is known as irreducible representation. Each irreducible representation describes the effect of symmetry operations on the directional properties such as translational coordinates (x, y, z) rotational coordinates (R_x, R_y, R_z) etc. It is possible to obtain useful information by listing the characters of all possible irreducible representations of a point group in a tablular form known as **character table**. The set of character values of each irreducible representation is denoted by the symbol τ.

We shall use a simple method to arrive at the character table of C_{2v} point group and then illustrate its uses. This can be done by seeing the effect of four symmetry operations of C_{2v} group on the signs of the lobes of p_x, p_y and p_z orbitals. If the signs of the lobes remain the same after performing a symmetry operation, the resulting change is represented by 1; on the other hand, if a symmetry operation changes the signs of the lobes, then it is represented by –1. In other words, the value of 1 signifies no change in signs of the lobes while a value of –1 signifies a change of sign.



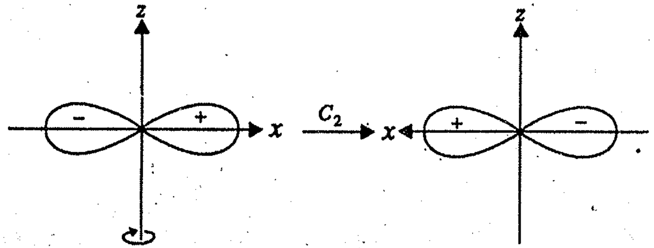
Effect of Symmetry Operations on p_x Orbital

The signs of the lobes of p_x orbital remain the same after identity operation (E); so E can be represented by 1.

$$Ep_x = 1\,p_x$$

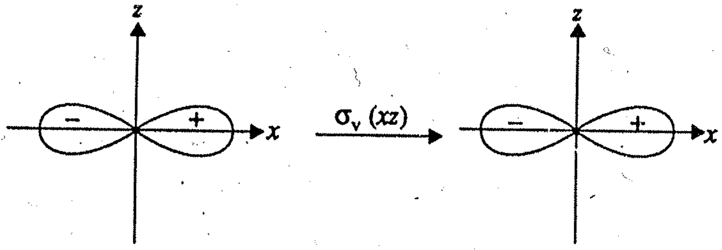
This can be understood since performance of identity operation means doing nothing.

The signs of the lobes of p_x orbital changes by C_2 operation (about the z axis) and hence, this operation can be represented by -1.



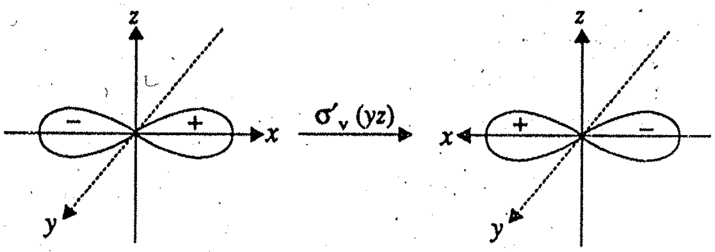
$$C_2 p_x = -1\,p_x$$

The signs of the lobes of p_x orbitals remain the same after reflection through $\sigma_v\,(xz)$ plane while there is a change after reflection through $\sigma_v'\,(yz)$ plane.



$$\sigma_v\,(xz)\,p_x = 1\,p_x$$

or $\sigma_v\,(xz)$ can be represented by 1.

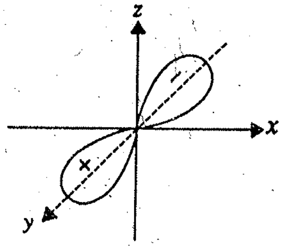


$$\sigma_v'\,(yz)p_x = -1\,p_x$$

or $\sigma_v'(yz)$ can be represented by -1.

The four numbers corresponding to the operations E, C_2, $\sigma_v(xz)$ and $\sigma_v'(yz)$ on p_x orbital constitute a representation which we shall call τ_1 and denote as follows:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
τ_1	1	-1	1	-1	x



p_y orbital

Effect of Symmetry Operations on p_y Orbital

If we proceed on similar lines, we can find out the four numbers corresponding to the four operations of C_{2v} group on p_y orbital and write τ_2 representation as shown below:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
τ_2	1	-1	-1	1	y

In other words, C_2 and $\sigma_v(xz)$ result in changes of signs of the p_y lobes whereas E and $\sigma_v'(yz)$ cause retention of signs.

Effect of Symmetry Operations on p_z Orbital

By similar arguments, we can arrive at the decision that E, C_2, $\sigma_v(xz)$ and $\sigma_v'(yz)$ do not change the signs of p_z orbital. Each of the operations can be denoted by 1 only in the representation τ_3.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
τ_3	1	1	1	1	z

Effect of Symmetry Operations on Quadratic Coordinates

From the columnwise products of τ_1, τ_2 and τ_3, we can get the τ values for xy, yz, and xz as follows:

	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$x\ (\tau_1)$	1	-1	1	-1
$y\ (\tau_2)$	1	-1	-1	1
$z\ (\tau_3)$	1	1	1	1
$xy\ (\tau_4)$	1	1	-1	-1
$yz\ (\tau_2)$	1	-1	-1	1
$xz\ (\tau_1)$	1	-1	1	-1

Note that
i) $\tau_4 = \tau_1\tau_2$
ii) $\tau_2 = \tau_2\tau_3$
iii) $\tau_1 = \tau_1\tau_3$

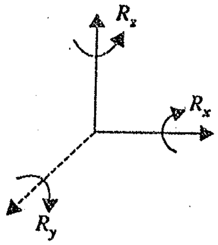
The representation (τ_4) for the operations on xy is different from the representations corresponding to the operations on x, y or z; but the representations for the operations on yz and xz are τ_2 and τ_1, respectively, which are same as for those on y and x.

You try columnwise products such as $\tau_1\tau_1$ or $\tau_2\tau_2$ or $\tau_3\tau_3$ for obtaining representations corresponding to the effect of the four operations on x^2, y^2 and z^2. If you work out correctly, you should be able to prove that all these representations are the same, viz, τ_3, which is the representation corresponding to the effect of the four operations on z.

	E	C_2	$\sigma_v\,(xz)$	$\sigma_v'\,(yz)$
x^2 or y^2 or z^2 (τ_3)	1	1	1	1

Effect of Symmetry Operations on R_x, R_y and R_z

The symbols, R_x, R_y and R_z, denote the rotations around the x-, y- and z-axes.



The molecule, H_2O, is in xz plane. The operation E on R_z leaves it unchanged. The operation C_2 around z-axis does not alter the direction of R_z rotation. Hence E and C_2 operations on R_z can be represented by 1. The operations, $\sigma_v\,(xz)$ and $\sigma_v'\,(yz)$, reverse the direction of R_z rotation, and hence, these two operations can be represented by –1.

$$ER_z = 1\,R_z$$

$$C_2R_z = 1\,R_z$$

$$\sigma_v\,(xz)R_z = -1\,R_z$$

$$\sigma_v'\,(yz)R_z = -1\,R_z$$

We can see that the representation corresponding to the effect of operations on R_z is same as τ_4.

	E	C_2	$\sigma_v\,(xz)$	$\sigma_v'\,(yz)$
R_z	1	1	–1	–1

Similarly the effect of the four symmetry operations on R_x and R_y can be stated through following representations:

	E	C_2	$\sigma_v\,(xz)$	$\sigma_v'\,(yz)$	
R_x	1	–1	–1	1	(τ_2)
R_y	1	–1	1	–1	(τ_1)

Thus we see that these are only four representations τ_1, τ_2, τ_3 and τ_4 for C_{2v} group. There are rules to give names to these representations which are known by the name, Mulliken notations. We shall not discuss these rules but use Mulliken notations of B_1, B_2, A_1 and A_2 for τ_1, τ_2, τ_3 and τ_4, respectively.

These four representations can be represented in a table called the character table of the C_{2v} group (Table A.2). Also, we would have arrived at the same table, had we started with the matrix representation of symmetry operations and proceeded to obtain the characters of irreducible representations.

The four rows of Table A.2 represent the sets of characters for the four irreducible representations of C_{2v} group.

Similarly, when $S = 1$ and multiplicity is 3, the state is called a **triplet state.** These states are illustrated in Fig. 1.14.

To decide transitions to which of these states are allowed, we have the selection rules for multi-electron systems as

Thus, all electronic configurations $1s^1 ns^1$, $1s^1 np^1$, $1s^1 nd^1$ where $n \geq 2$ give rise to both singlet and triplet levels.

$$\Delta S = 0,\ \Delta L = \pm 1,\ \Delta J = 0,\ \pm 1$$

Here, $\Delta S = 0$ implies that S should not change for an allowed transition. Thus, the transition will be allowed from

$$S = 1 \longrightarrow S = 1$$

or

$$S = 3 \longrightarrow S = 3$$

Remember that singlet to triplet or triplet to singlet transitions are not allowed.

Thus, transitions from **singlet to singlet** and **triplet to triplet** states will be allowed. Since the ground state of helium has $S = 1$ and is a **singlet** state, the allowed transitions are only to **higher singlet states.**

Let us next consider what $\Delta L = \pm 1$ implies? $\Delta L = \pm 1$ means that when L was 0 (zero) in the ground state, the excited state can have $L = 1$. This indicates that the excited state should be a P state.

Now what about its J value? J can be calculated as $L + S$. For this state $L = 1$ and $S = 0$, so $J = L + S = 1 + 0 = 1$.

The term symbol for the excited state will be

$$^{2S+1}L_J = {}^{2\times 0+1}L_J = {}^1P_1$$

(Remember that $L = 1$ state is denoted by P letter)

Note that for the singlet excited state of He having the atomic configuration $1s^1 2p^1$, the term symbol is $^1P_1$.

Thus, the allowed transition will be from

$$^1S_0 \longrightarrow {}^1P_1 \text{ state.}$$

(Remember that one electron still occupies $1s$ orbital and the configuration is $1s^1 2p^1$.

Note that this $^1P_1$ state could belong to any of the levels having $n \geq 2$. These transitions are depicted in Fig.1.14 (a).

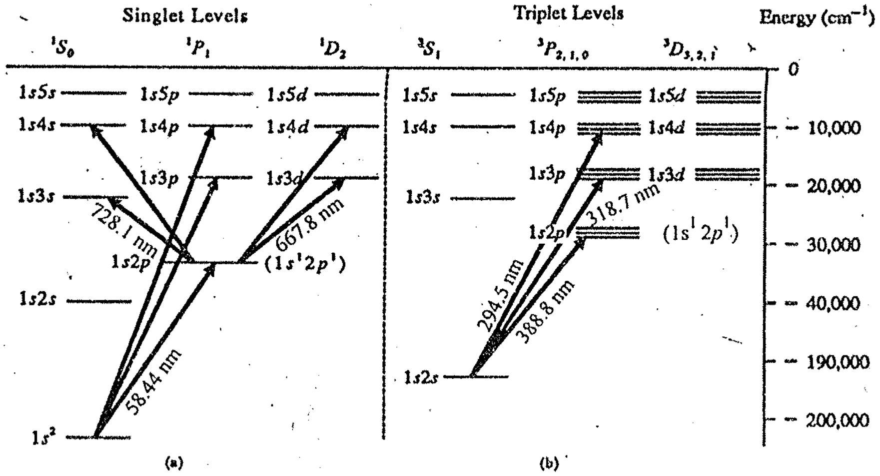


Fig. 1.14: Energy levels (for electrons) of Helium atom showing (a) singlet to singlet transitions and (b) triplet to triplet transitions.

The three $2P$ states where 2 is the value of n in the excited triplet state of helium (as shown in Fig. 1.14b) can be designated as follows:

$$2^3P_{2,1,0} \left\{ \begin{array}{l} \text{———— } 2^3P_0 \\ \text{———— } 2^3P_1 \\ \text{———— } 2^3P_2 \end{array} \right.$$

You should also note that these triplet levels correspond to atomic configuration $1s^1 2p^1$.

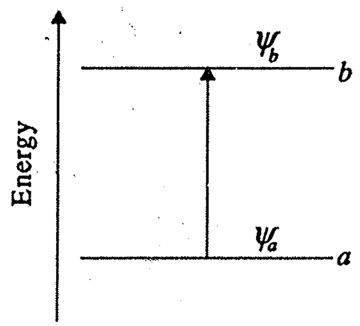
These levels arise as a result of spin-orbit coupling.

From this excited state, further transitions are possible in accordance to the selection rule $\Delta L = \pm 1$. When $\Delta L = +1$, transitions will occur to higher S or D states and when $\Delta L = -1$, the system will return to the ground state (with $L = 0$).

1. The Type of Initial and Final Energy States for Allowed Spectral Transitions

Let us first see how to decide whether a particular spectral transition is allowed or not. Let ψ_a and ψ_b be the wave functions of two energy states a and b, and **M**, the transition dipole moment operator for which the components are M_x, M_y and M_z. The transition **dipole moment** μ during the transitions between states a and b can be defined as

$$\mu = \int \psi_b \mathbf{M} \psi_a \, d\tau \qquad \text{...(A.2)}$$



where $d\tau$ is the volume element. The three components of transition dipole moment (μ_x, μ_y and μ_z) can be defined in terms of the components of dipole moment operator (M_x, M_y and M_z) along the three axes as follows:

$$\mu_x = \int \psi_b M_x \psi_a \, d\tau \qquad \text{...(A.3)}$$

$$\mu_y = \int \psi_b M_y \psi_a \, d\tau \qquad \text{...(A.4)}$$

$$\mu_z = \int \psi_b M_z \psi_a \, d\tau \qquad \text{...(A.5)}$$

But $\quad M_x = ex, M_y = ey$ and $M_z = ez \qquad$ ...(A.6)

where e is the electronic charge, and x, y and z are the cartesian coordinates.

M_x, M_y and M_z are the components of the transition dipole moment operator (M) whereas, μ_x, μ_y and μ_z are the components of transition dipole moment.

Combining Eqs. A.3 to A.6,

$$\mu_x = e \int \psi_b x \psi_a \, d\tau \qquad \text{...(A.7)}$$

$$\mu_y = e \int \psi_b y \psi_a \, d\tau \qquad \text{...(A.8)}$$

$$\mu_z = e \int \psi_b z \psi_a \, d\tau \qquad \text{...(A.9)}$$

The intensity of a transition is proportional to the square of the transition dipole moment. Dipole moment is a molecular property. Don't confuse the permanent dipole moment of a molecule with the term, transition dipole moment. Transition dipole moment comes into play when a molecule interacts with a radiation and is related to the probability of a transition taking place from one energy state to another.

For a spectral transition to occur from the state, a to b, atleast one of the components of μ (viz., μ_x, μ_y or μ_z) should be a finite quantity (i.e., should be nonzero). On the other hand, if all the components (μ_x, μ_y or μ_z) are zero, then the spectral transition is totally symmetry forbidden.

Further μ_x, μ_y or μ_z will be finite (i.e., nonzero), only if the product of the symmetry species of the functions, ψ_a and ψ_b, and the transition moment operator, M_x M_y or M_z (i.e., $\psi_b M_x \psi_a$, $\psi_b M_y \psi_a$ or $\psi_b M_z \psi_a$) is totally symmetric; for example, the product must belong to A_1 representation for the molecular point group C_{2v}. Since M_x, M_y and M_z transform like x, y and z coordinates, we can state that the transition moment integral will be nonzero, if the product of the symmetry species of the functions, ψ_b and ψ_a and the coordinates (x, y, z) is totally symmetric. Further, it can be shown that the symmetry species of the product, $\psi_b x \psi_a$, $\psi_b y \psi_a$ or $\psi_b z \psi_a$ will be totally symmetric, if the symmetry species of the product of the functions ψ_b and ψ_a is the same as that of x, y and z coordinates.

For example, let us examine whether the transition from the molecular state with symmetry of wave function (ψ_a) as A_1 to the state with symmetry of wave function (ψ_b) as B_1, is allowed for the molecules of C_{2v} group. From Table A.2, we know that x, y and z belong to B_1, B_2 and A_1 representations, respectively. Let us see whether any of the three products, $\psi_b x \psi_a$, $\psi_b y \psi_a$ or $\psi_b z \psi_a$ belongs to A_1 representation.

i) Representation of the product, $\psi_b x \psi_a$

Function	Symmetry species	Characters in four columns			
		E	C_2	$\sigma_v\,(xz)$	$\sigma_v'\,(yz)$
ψ_b	B_1	1	−1	1	−1
ψ_a	A_1	1	1	1	1
$\psi_b \psi_a$	B_1	1	−1	1	−1
x	B_1	1	−1	1	−1
$\psi_b \psi_a x$	A_1	1	1	1	1

You can see that the $\psi_b \psi_a$ product has the same representation as x. So $\psi_b \psi_a x$ (or $\psi_b x \psi_a$) is totally symmetric.

ii) Representation of the product, $\psi_b y \psi_a$

Function	Symmetry species	Characters in four columns			
		E	C_2	$\sigma_v\,(xz)$	$\sigma_v'\,(yz)$
ψ_b	B_1	1	–1	1	–1
ψ_a	A_1	1	1	1	1
$\psi_b \psi_a$	B_1	1	–1	1	–1
y	B_2	1	–1	–1	1
$\psi_b \psi_a y$	A_2	1	1	–1	–1

We can see that the symmetry species of the product, $\psi_b \psi_a$, is different from that of the y coordinate.

Hence, the product $\psi_b y \psi_a$ does not belong to A_1 representation.

iii) Representation of the product, $\psi_b z \psi_a$

Function	Symmetry species	Characters in four columns			
		E	C_2	$\sigma_v\,(xz)$	$\sigma_v'(yz)$
ψ_b	B_1	1	–1	1	–1
ψ_a	A_1	1	1	1	1
$\psi_b \psi_a$	B_1	1	–1	1	–1
z	A_1	1	1	1	1
$\psi_b \psi_a z$	B_1	1	–1	1	–1

Again $\psi_b \psi_a$ belongs to B_1 representation which is different from that of the z-coordinate. Hence, the product, $\psi_b \psi_a z$ also does not belong to totally symmetric representation.

Hence, we see that $\psi_b x \psi_a$ belongs to A_1 representation although $\psi_b y \psi_a$ and $\psi_b z \psi_a$ do not. Hence the x component of the transition dipole moment is non-zero. Therefore, we conclude that the transition $A_1 \longrightarrow B_1$ is allowed and is polarized in the x direction. By similar procedure, it can be shown that (i) the transitions $B_2 \longrightarrow A_2$ and $B_1 \longrightarrow A_2$ are allowed, the former being polarized in the x direction and the latter in the y direction and (ii) $A_1 \longrightarrow A_2$ and $B_1 \longrightarrow B_2$ transitions are not allowed.

Note that the transition moment has three components, μ_x, μ_y and μ_z. If only one, say, x component is different from zero, then the transition is said to be polarized in the x-direction. If two of the components, say, μ_x and μ_y are different from zero, then the transition is said to be polarized in the xy plane. If all the components (μ_x, μ_y and μ_z) are different from zero, then the transition is fully allowed. Similarly, if all the three components are zero, then transition is totally forbidden and its intensity is zero.

Specific Selection Rules

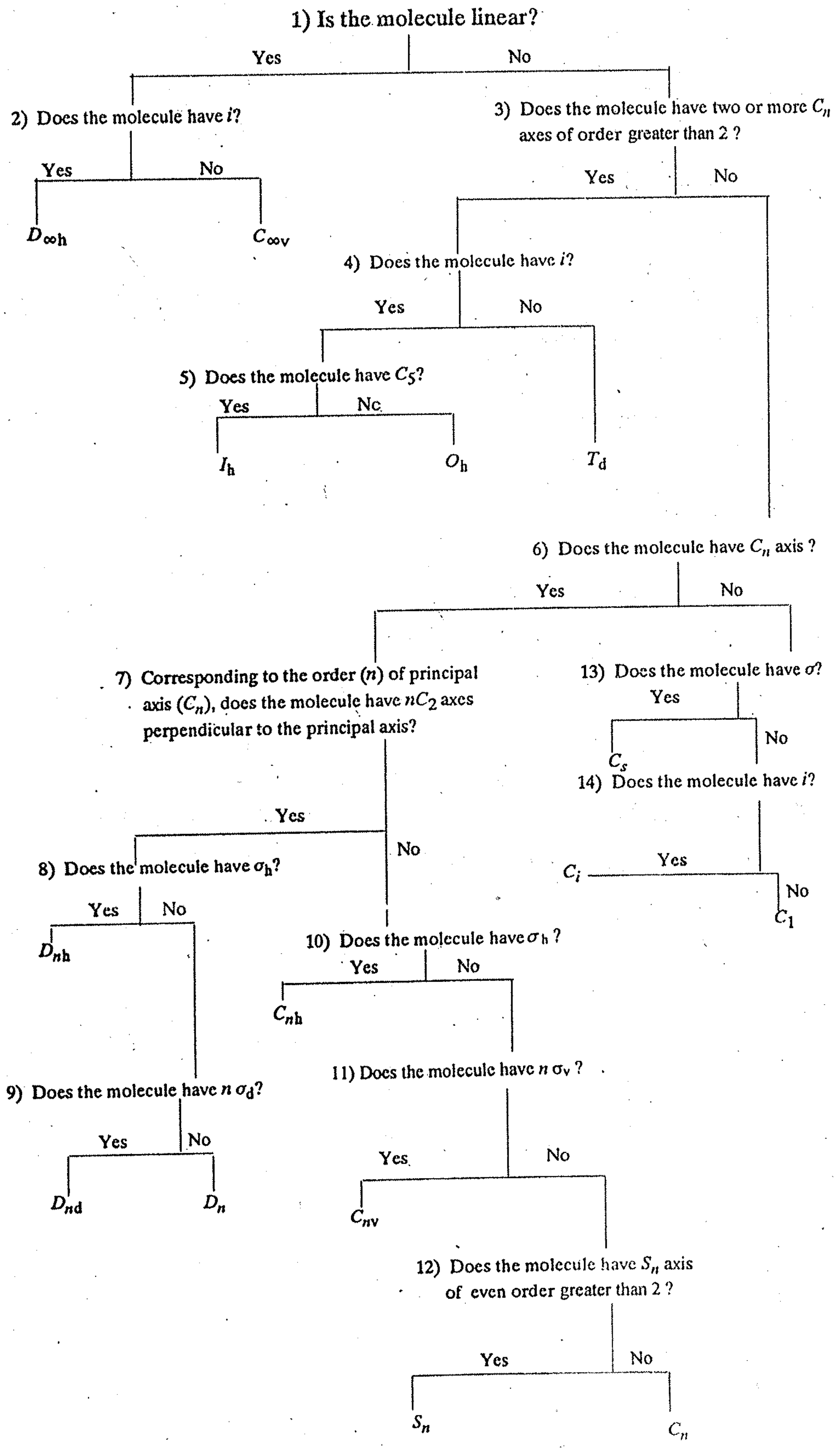
Further, a detailed study of the transition dipole moment leads to specific selection rules which state the conditions for the allowed transitions in terms of changes in quantum numbers. In Units 3 and 4, we shall study selection rules specific to rotation and vibration spectra.

Next, let us discuss the method of identifying point groups of molecules.

Identification of Point Groups

It is possible to find out the point group of a molecule by knowing its shape and symmetry elements and, by using Table A.4.

Table A.4: Flow Chart for Identifying Point Groups.



Note that the questions in the flow chart given above are numbered. This is done for referring to the questions which are relevant for identifying the point group of a particular molecule.

For identifying the point groups, the following steps would be quite useful:

Step i) Find out the shape of the molecule; this can be done using Sec. 2.2 of this unit.

Step ii) List the symmetry elements in the molecule.

Step iii) Mark those questions from Table A.4 which are relevant to the symmetry elements of the molecule under consideration. Write down the answers and the inference. The answer to the last question gives the point group of the molecule.

To predict the shape of the molecule, you may use Sec. 2.2 of this unit and Sec. 3.7 of Unit 3 of CHE-01 (Atoms and Molecules) course.

Let us examine a few examples in the light of the steps mentioned above:

I H_2

Step i) H_2 molecule has linear shape.

Step ii) H_2 has the following symmetry elements:

$E, 2C_\infty, \infty C_2$ (perpendicular to C_∞), σ_h, $\infty\sigma_v$, $2S_\infty$ and i

Step iii) The questions of Table A.4 relevant to this molecule are given below alongwith the answers:

1. **The molecule is linear** (Proceed to question 2).
2. H_2 **has** i. The answer to this question indicates that the point group of H_2 is $D_{\infty h}$.

In short, all linear molecules with i such as acetylene, and homonuclear diatomic molecules belong to $D_{\infty h}$ point group.

Note that in Step (ii), we have mentioned many symmetry elements for H_2 molecule. But in Step (iii), all these symmetry elements are not used for arriving at the point group of the molecule. Thus, the point group of a molecule can be found out by using a few symmetry elements only. While writing step (iii), follow Table A.4 carefully.

II HCl

Step i) HCl molecule has linear shape.

Step ii) HCl has the following symmetry elements:

$E, 2C_\infty$ and $\infty\ \sigma_v$.

Step iii) The questions of Table A.4 relevant to this molecule are given below along with the answers:

1. The molecule is **linear** (Proceed to question 2).
2. HCl does **not** have i. Hence, the point group of HCl is $C_{\infty v}$.

Similarly, all linear molecules without i such as heteronuclear diatomic molecules belong to $C_{\infty v}$ point group.

In each of the examples I to IV, we mention under step (iii) only relevant question numbers from Table A.4 along with answers. Thus, in Example III for H_2O, the relevant question numbers are 1, 3, 6, 7, 10 and 11. The "yes" or "no" part of the answer for each question can be inferred from the word in bold type. The answer to the last question gives the point group of the molecule.

III H_2O

Step i) H_2O molecule has angular shape.

Step ii) H_2O has the following symmetry elements:

$E, 2\sigma_v$ and C_2.

Step iii) The questions of Table A.4 relevant to this molecule are given below along with the answers:

1. The molecule is **not** linear (Proceed to question 3).

3. The molecule does **not** have two or more C_n axes of order greater than 2 (Proceed to question 6).

6. The molecule **has** C_2 axis. (Proceed to question 7).

7. The molecule does **not** have two C_2 axes perpendicular to the principal axis (C_2). (Proceed to question 10).

10. The molecule does **not** have σ_h (Proceed to question 11).

11. The molecule **has** $2\sigma_v$ The last answer indicates that the point group of H_2O is C_{2v}.

SO_2 is another example belonging to C_{2v} point group.

IV NH_3

Step i) NH_3 molecule has trigonal pyramidal shape.

Step ii) NH_3 has the following symmetry elements:

E, 2 C_3 and 3 σ_v.

Step iii) The questions of Table A.4 relevant to this molecule are given below along with the answers:

1. The molecule is **not** linear (Proceed to question 3).

3. The molecule does **not** have two or more C_n axes of order greater than 2 (Proceed to question 6).

6. The molecule **has** C_3 axis (Proceed to question 7).

7. The molecule does **not** have three C_2 axes perpendicular to C_3 axis (Proceed to question 10).

10. The molecule does **not** have σ_h (Proceed to question 11).

11. The molecule **has** 3 σ_v. Hence, the molecule belongs to C_{3v} point group.

As an exercise, you try to identify the point groups of BF_3 and C_6H_6.

UNIT 3 ROTATIONAL SPECTRA

Structure

3.1 INTRODUCTION

From this unit onwards we shall study the interaction of electromagnetic radiation with an assembly of molecules rather than atoms, as has been done in the first unit of this Block. This interaction will result in the so called molecular spectra of compounds. Just like we extracted information about the structure of atoms from the atomic spectra, we shall try to find out what information can be obtained from the molecular spectrum regarding the structure and the behaviour of a molecule.

It will be seen that absorption or emission of electromagnetic radiation in different regions, corresponding to different amounts of energy, would cause various types of changes in the molecule. Thus, the spectra in each region would give a definite and specific piece of information about the molecule. For instance, when the molecule is subjected to radiations in the microwave region, we get information about the rotational properties of the molecule which in turn gives the values of molecular parameters like bond length.

On the other hand, molecular spectrum in the infrared region is related to the vibrational properties of the molecule. About vibrational spectra, you will study in Units 4 and 5 of Block 2. Since each region of spectrum requires a separate source of characteristic radiation, sample preparation and recording technique, you will study about them separately in Unit 9 of Block 3.

In this unit, we will start our discussion with the concept of motion leading to the idea of moment of inertia associated with a rotating body. On the basis of the moment of inertia, molecules will be classified as linear, symmetric top, asymmetric top and spherical top molecules. We will then explain the rotational spectra of rigid linear molecules in detail. We will also see what happens when a molecule is not rigid? We will explain briefly the rotational spectra of simple polyatomic molecules and intensity of spectral lines.

Objectives

After studying this unit, you should be able to:

- define the moment of inertia,
- discuss the rotational spectra of rigid linear diatomic and triatomic molecules,
- give applications of study of rotational spectra,

- explain the effect of isotopic substitution and non–rigidity on the rotational spectra of a molecule,
- classify various molecules according to their values of moment of inertia,
- discuss the rotational spectra of simple polyatomic molecules, and
- relate the intensity of spectral lines with the population of a rotational level.

3.2 MOLECULAR MOTION AND ENERGY

The understanding of molecular motions help in the interpretation of molecular spectra. When we talk about molecular motions, there are various possibilities. When we want to specify the position of a body in space, we have to specify the **number of degrees of freedom** it possesses. The number of degrees of freedom is related to the number of independent coordinates required to specify the position of the body in space. For example, for a single particle we need **three** Cartesian coordinates x, y and z to specify its position. Hence, it is said to have **three** degrees of freedom. Thus, for a molecule having N atoms, the total number of degrees of freedom is $3N$.

For a single particle, only one type of motion is possible which is called **translational motion**. Hence, we can say that a single particle possesses three degrees of translational freedom.

But what about translational motion of molecules? A molecule contains two or more than two atoms. Since the atoms in a molecule are joined together, the molecule as a whole will show translatory motion and the atoms will not move independently. The translational motion of a molecule can be described in terms of the **centre of mass**. The centre of mass is the point where the whole mass can be considered to be concentrated. Thus, we can specify three coordinates for the centre of mass and say that it has three degrees of freedom, similar to a single particle. The translational motion of centre of mass of a molecule (non–linear) is shown in Fig. 3.1.

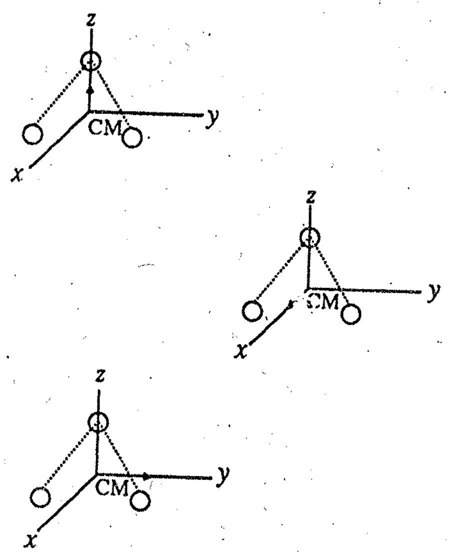


Fig. 3.1: Translational motion of centre of mass of a nonlinear molecule.

A molecule can store energy by way of molecular motions.

For a polyatomic molecule having N atoms, $(3N - 3)$ degrees of freedom still remain. These can be attributed to internal motions such as rotation and vibrations.

Let us now know more about rotational motion. The simplest case of rotation is that of a particle about a fixed point, as shown in Fig. 3.2.

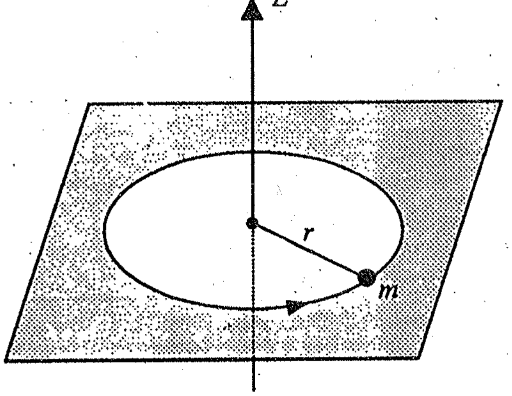


Fig. 3.2: Rotation of a particle about a fixed point.

The rotational kinetic energy of this particle having mass m and velocity v can be expressed as

$$E_k = \frac{1}{2}mv^2 = \frac{p2}{2m} \text{ where } p = mv \text{ is the momentum of the particle} \quad \text{... (3.1)}$$

The velocity of this particle could be expressed as the distance travelled by it divided by the time taken. For one revolution, we can say that

$$v = \frac{\text{distance}}{\text{time}} = \frac{2\pi r}{t} \quad \text{... (3.2)}$$

where t is the time taken for one revolution and is also known as *period.*

Also $$t = \frac{1}{\text{frequency}\,(f)} \quad \text{... (3.3)}$$

Substituting the value of t from Eq. 3.3 into Eq.3.2, we get

$$v = 2\pi r f \quad \text{... (3.4)}$$

Replacing v in Eq. 3.1 by its value from Eq.3.4, we can write

$$E_k = \frac{1}{2}m\,(2\pi r f)^2 \quad \text{... (3.5)}$$

The terms in the above equation can be rearranged as given below:

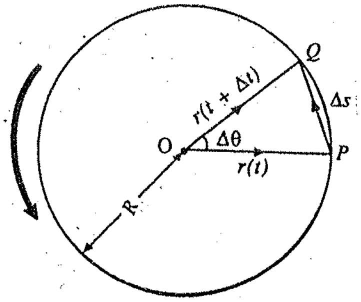
$$E_k = \frac{1}{2}mr^2\,(2\pi f)^2 \quad \text{... (3.6)}$$

The quantity mr^2 of the above equation is called the **moment of inertia** and is represented by I. The term $2\pi f$ is known as the **angular velocity** and is denoted by ω.

Thus, we can rewrite Eq.3.6 as

$$E_k = 1/2 I\,\omega^2 \quad \text{... (3.7)}$$

On comparing Eqs.3.1 and 3.7, we can say that in the equation for rotational motion (i.e., Eq. 3.7), moment of inertia is the equivalent of mass as used in **Eq.** 3.1. Also in Eq.3.7, angular velocity (ω) is used in place of linear velocity (v) used in Eq.3.1.



For circular motion if a particle P traverces an angle $\Delta\theta$ in time Δt, the arc PQ represented as Δs is given by the following relation:

$$r\,.\,\Delta\theta = \Delta s$$

Dividing by Δt on both the sides, we get

$$r\,.\,\frac{\Delta\theta}{\Delta t} = \frac{\Delta s}{\Delta t}$$

When $\Delta t \to 0$, we can write

$$r\,.\lim_{\Delta t \to 0}\frac{\Delta\theta}{\Delta t} = \lim_{\Delta t \to 0}\frac{\Delta s}{\Delta t}$$

$$r\cdot\frac{d\theta}{dt} = \frac{ds}{dt}$$

or $$r\,\omega = v$$

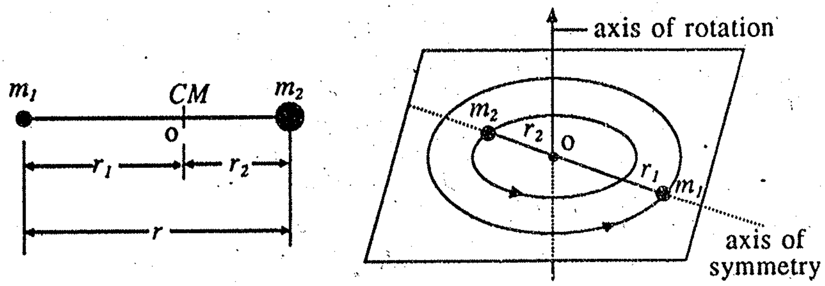
where ω is the angular velocity and v is the linear velocity. The, angular velocity, ω is defined as the number of radians of angle swept in unit time.

It is given by $\frac{d\theta}{dt}$, where $d\theta$ is the angle traversed in dt time. It is expressed in terms of radians $\sec^{-1}$.

3.3 ROTATIONAL SPECTRUM OF A RIGID DIATOMIC MOLECULE

Let us now apply the above ideas to the rotation of a diatomic molecule. We will first assume that this diatomic molecule is a **rigid body.** This means that the distance between the atoms, i.e. the bond length *does not* change during the **rotation.** In other words, vibrational movement is not taking place during rotation. We are also assuming that the centre of mass of the molecule is fixed. Hence, there is no translational motion of the molecule. No real molecule can be called an ideally rigid body. But many molecules may be considered as rigid because their vibrational motion is small. Let us now focus our attention on Fig. 3.3 which depicts the rotation of a rigid diatomic molecule.

Note that the axis about which the rotation takes place, is perpendicular to the axis of symmetry of the molecule.



(a) (b)

Fig. 3.3:(a) A rigid diatomic molecule.
(b) Rotation of a rigid diatomic molecule.

When such a molecule rotates, it rotates about an axis passing through its centre of mass(CM). The centre of mass is shown by the point O. For such a system, the centre of mass is such a point for which the following condition is satisfied:

$$m_1 r_1 = m_2 r_2 \qquad \text{... (3.8)}$$

We can rearrange Eq. 3.8 as follows

$$\frac{r_1}{r_2} = \frac{m_2}{m_1} \qquad \text{... (3.9)}$$

Using the characteristics of proportions, Eq.3.9 can be written as

$$\frac{r_1}{(r_1 + r_2)} = \frac{m_2}{(m_1 + m_2)} \qquad \text{... (3.10)}$$

or
$$r_1 = \frac{m_2 (r_1 + r_2)}{(m_1 + m_2)} \qquad \text{... (3.11)}$$

We also know that the bond length or the distance between two atoms, r, is equal to the sum of r_1 and r_2. Thus, we can write

$$r = r_1 + r_2 \qquad \text{... (3.12)}$$

Substituting $r = r_1 + r_2$ from Eq. 3.12 into Eq.3.11, we get

$$r_1 = \frac{m_2}{(m_1 + m_2)} \cdot r \qquad \text{... (3.13)}$$

On similar lines, we can get

$$r_2 = \frac{m_1}{(m_1 + m_2)} \cdot r \qquad \text{... (3.14)}$$

by starting from Eq.3.8 and rearranging it as

$$\frac{r_2}{r_1} = \frac{m_1}{m_2} \qquad \text{... (3.15)}$$

Why do not you try Terminal Question 1 and check it.

Let us now write the energy of this system using Eq.3.7.

$$E_k = 1/2\, I\, \omega^2 \qquad \text{... (3.7)}$$

You can imagine this molecule as a two particle system (Compare Figs. 3.2 and 3.3). Here, you can see that two particles (atoms having masses m_1 and m_2) are rotating about the point o. Thus, the rotational kinetic energy, E_k of this system will be the sum of the E_k values of both the particles. So, we can write

$$E_k = \frac{1}{2} m_1 r_1^2 \omega_1^2 + \frac{1}{2} m_2 r_2^2 \omega_2^2 \qquad \text{... (3.16)}$$

The angular velocities of the two masses m_1 and m_2 will be equal because of the rigidity of the molecule. Hence,

$$\omega_1 = \omega_2 \qquad \text{... (3.17)}$$

Note that the moment of inertia for the single particle was expressed as $I = mr^2$ and for a diatomic molecule (two particle system), it is expressed as $I = m_1 r_1^2 + m_2 r_2^2$. We can extend this argument and generalise it for polyatomic molecules as follows. For a polyatomic molecule, the moment of inertia about a particular axis is given by the sum of moments due to various nuclei about that axis, i.e., $I = \sum_i m_i r_i^2$ where r_i is the perpendicular distance of the nucleus of mass m_i from the axis.

Let this angular velocity be ω. So, we can rewrite Eq.3.16 as

$$E_k = \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2$$

$$= \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2)\, \omega^2 = \frac{1}{2} I \omega^2 \qquad \text{... (3.18)}$$

where I is the moment of inertia of the diatomic molecule.

The terms r_1 and r_2 can be eliminated from Eq. 3.18 by using the values of r_1 and r_2 from Eqs. 3.13 and 3.14, respectively, as given below:

$$E_k = \frac{1}{2} \left[m_1 \left(\frac{m_2 r}{m_1 + m_2} \right)^2 + m_2 \left(\frac{m_1 r}{m_1 + m_2} \right)^2 \right] \omega^2$$

$$= \frac{1}{2} \left[\frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r^2}{(m_1 + m_2)^2} \right] \omega^2$$

$$= \frac{1}{2} \frac{m_1 m_2 r^2}{(m_1 + m_2)^2} \left[m_2 + m_1 \right] \omega^2$$

$$= \frac{1}{2} \frac{m_1 m_2 r^2 \omega^2}{(m_1 + m_2)} \qquad \text{... (3.19)}$$

Remember that we have earlier defined I as mr^2.

Comparing Eq. 3.19 with Eq. 3.18, we can say that

$$E_k = \frac{1}{2} \frac{m_1 m_2 r^2 \omega^2}{(m_1 + m_2)} = \frac{1}{2} I \omega^2 \qquad \text{... (3.20)}$$

Thus, $$I = \frac{m_1 m_2}{(m_1 + m_2)} r^2 \qquad \text{... (3.21)}$$

Here, $\frac{m_1 m_2}{(m_1 + m_2)}$ can be denoted by μ which is known as the reduced mass.

Thus, we can write

$$I = \mu r^2 \qquad \text{... (3.22)}$$

Thus, the idea of using reduced mass is to mathematically simplify the rotation of a two-particle system into that of a one–particle problem. In other words, we have replaced the two masses m_1 and m_2 by a single mass μ. You must have also realised that similarly we have also replaced the two distances r_1 and r_2 by r.

At this stage, we have come to a point where we can deal with the rotation of a diatomic molecule having masses m_1 and m_2 in terms of the rotation of a single particle of mass μ having a distance r from the origin.

Let us now reconsider Eq.3.18 which says

$$E_k = \frac{1}{2} I \omega^2$$

This equation is alright as per the classical mechanics approach. But when we apply quantum mechanical approach to the molecule, certain restrictions appear on the rotational energy.

Do not confuse the L used in Eq. 3.24 with that used in unit 1. Here, L represents the angular momentum of the molecule undergoing end to end rotation about the centre of mass whereas in unit 1, it was used to denote the angular momentum of the electron in an atom.

Eq. 3.18 can be expressed in terms of angular momentum L which can be defined as

$$L = I\omega \qquad \text{... (3.23)}$$

Substituting L for $I\omega$ in Eq.3.18, we get

$$E_k = \frac{1}{2}\,\frac{L^2}{I} \qquad \text{... (3.24)}$$

Since the angular momentum is quantised, it can be expressed in terms of the rotational quantum number, J, as given below:

$$L = \sqrt{J(J+1)}\,.\frac{h}{2\pi} = \sqrt{J(J+1)}\,\hbar \qquad \text{... (3.25)}$$

The restriction on the value of J comes from quantum mechanics.

where J can take values 0, 1, 2, 3...

Substituting the above value of L in Eq.3.24, we get

$$E_k = \frac{1}{2}\cdot\frac{J(J+1)\hbar^2}{I} = \frac{J(J+1)\hbar^2}{2I} \qquad \text{... (3.26)}$$

The above equation gives the rotational energy of a molecule. The energy can also be expressed in terms of wave number, $\bar{\nu}$. The energies as expressed in terms of $\bar{\nu}$ are referred to as **term values** and are denoted by $F(J)$. The SI unit of a term value is m^{-1} but they are usually expressed in cm^{-1}.

We have used $\hbar = \frac{h}{2\pi}$ in Eq.3.27.

Thus,
$$\bar{\nu} = F(J) = \frac{E_k}{hc} = \frac{J(J+1)h^2}{8\pi^2 I\,.\,hc} = \frac{J(J+1)\,h}{8\pi^2 Ic} \qquad \text{... (3.27)}$$

The term $\frac{h}{8\pi^2 Ic}$ can be represented by a constant B which is known as **rotational constant**. Hence, Eq.3.27 can be written as

$$\bar{\nu} = BJ(J+1)$$

Thus, when $J = 1$, $\bar{\nu} = 2B\ \text{cm}^{-1}$

$J = 2$, $\bar{\nu} = 6B\ \text{cm}^{-1}$

$J = 3$, $\bar{\nu} = 12B\ \text{cm}^{-1}$

and so on.

The corresponding energy levels are depicted in Fig. 3.4

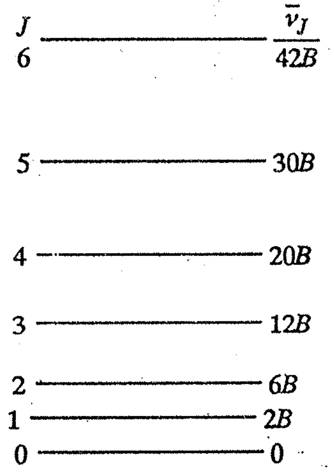


Fig. 3.4: Rotational levels of a rigid diatomic molecule.

10 A

But we are more interested in knowing the difference between these energy levels so that we can know the radiation of what frequency or wavenumber is absorbed or emitted when a molecule changes from one rotational level to the other. Thus, we can write the difference between two rotational levels as follows.

$$\Delta E = E_{k_{J'}} - E_{k_J}$$ where J' is the final rotational level and J is the initial rotational level.

$$= \frac{J'(J'+1)h^2}{2I} - \frac{J(J+1)h^2}{2I}$$

$$= \frac{h^2}{2I}[J'(J'+1) - J(J+1)] \qquad \text{... (3.28)}$$

The $\bar{\nu}$ for the above energy change can be given as follows:

$$\nu_{J'-J} = B[J'(J'+1) - J(J+1)] \qquad \text{... (3.29)}$$

From Fig. 3.4, we can see that the *energy difference* between the successive energy levels is 2*B*, 4*B*, 6*B*, 8*B*, 10*B* and so on. The spectral lines originating from these transitions will appear as shown in Fig. 3.5.

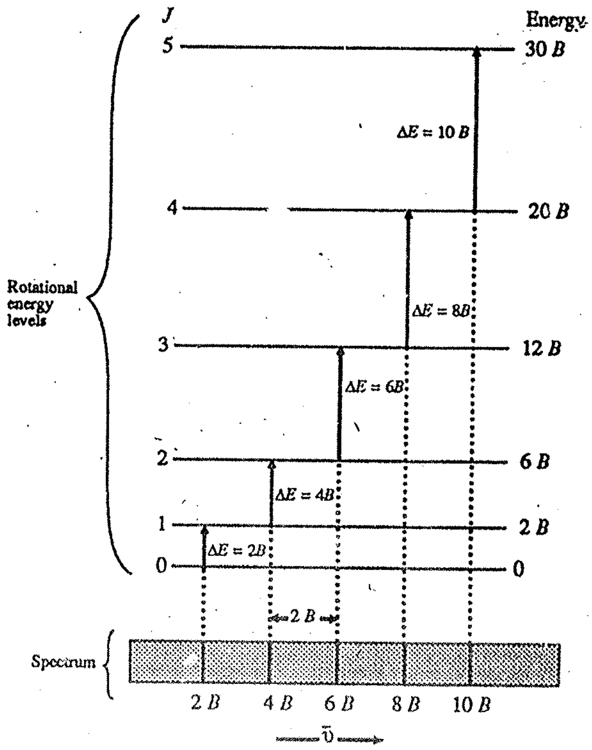


Fig. 3.5: The transitions between the various rotational levels and spectral lines arising from these transitions.

If you carefully see Fig. 3.5, we will notice that these spectral lines are equally spaced and there is a constant difference of $2B$ between the successive lines.

For a molecule to show rotational spectrum, the following requirements should be met.

i) The first condition which a molecule should satisfy for showing rotational spectra is that it should possess a permanent dipole moment. This is because a rotating dipole produces an oscillating electric field which interacts with the oscillating field of the radiation.

ii) There is a further restriction on rotational transitions for molecules having permanent dipole moment. The selection rule for linear molecule is $\Delta J = \pm 1$. So transitions could be from rotational levels having $J = 0 \rightarrow J = 1$; $J = 1 \rightarrow J = 2$; $J = 2 \rightarrow J = 3$; $J = 3 \rightarrow J = 4$ and so on and in the reverse order also.

Another factor which governs the intensity of rotational lines is the population of the initial or ground state. You will study about this in Sec. 3.7.

The Condition for the Occurrence of Pure Rotation Spectra

In the Appendix of Unit 2, we have mentioned the applications of character tables. One of the applications lies in determining whether a spectral transition could occur from an energy state a to the energy state b. For such a transition to occur,.at least one of the components of the transition dipole moment, $\boldsymbol{\mu}$, which is equal to $\int \psi_b \mathbf{M} \psi_a$, must have a non–zero value. You may be aware that ψ_b and ψ_a refer to the wave functions of the energy states, b and a, whereas M is the dipole moment operator. In case of pure rotation spectra, it means that at least one of the three components of transition dipole moment, μ_x, μ_y or μ_z in x, y and z directions must have a non zero value in order that the molecule absorbs in the microwave region. μ_x, μ_y and μ_z are related to M_x, M_y and M_z which are the components of the dipole moment operator M as given below:

$$\mu_x = \int \psi_b M_x \psi_a \, d\tau \qquad \text{... (A.1)}$$

$$\mu_y = \int \psi_b M_y \psi_a \, d\tau \qquad \text{... (A.2)}$$

$$\mu_z = \int \psi_b M_z \psi_a \, d\tau \qquad \text{... (A.3)}$$

Note that μ (bold type) stands for transition dipole moment whereas μ (Roman type) refers to the permanent dipole moment. Also μ_x, μ_y and μ_z are the components of transition dipole moment in x, y and z directions.

Also M_x, M_y and M_z are related to the permanent dipole moment, μ, of a rotor and the polar coordinates, θ and ϕ, as per Eqs. A.4 to A.6. For understanding the resolution of the dipole moment operator M in terms of M_x, M_y and M_z as per Eqs. A.4 to A.6 and Fig. A.1, you are advised to go through Eq. 2.54 of Unit 2 of CHE–01 ('Atoms and Molecules' Course) where the relationship between the spherical polar coordinates and the cartesian coordinates is given.

$$M_x = \mu \sin\theta \cos\phi \qquad \text{... (A.4)}$$

$$M_y = \mu \sin\theta \sin\phi \qquad \text{... (A.5)}$$

$$M_z = \mu \cos\theta \qquad \text{... (A.6)}$$

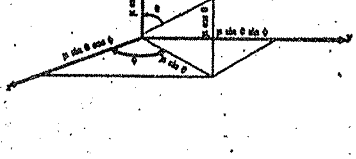


Fig. A.1: Transformation of cartesian to spherical polar coordinates.

If a molecule lacks permanent dipole moment (i.e., $\mu = 0$), then M_x, M_y and M_z and hence, μ_x, μ_y and μ_z are zero as per Eqs. A.1 to A.6. For a molecule having zero dipole moment, all the three components of transition dipole moment are thus equal to zero. As a result of this, a molecule with zero dipole moment cannot give rise to pure rotation spectra. In other words, for a molecule to absorb in the microwave region, it must have permanent dipole moment. In sub-Sec. 2.10, of the last unit, we have mentioned that only molecules belonging to the groups C_n (C_1 and C_2) and C_{nv} (C_{2v}, C_{3v}, ...$C_{\infty v}$) and C_s may have permanent dipole moment. Now you can understand as to why HBr, CO and OCS (all of $C_{\infty v}$ point group) can exhibit pure rotation spectra but H_2 and CO_2 of $D_{\infty h}$ point group) cannot.

SAQ 1

What is the effect of decrease in the moment of inertia on the energy of the rotational level?

....

....

....

SAQ 2

What is the necessary condition for a molecule to show rotational spectrum?

....

....

....

3.4 APPLICATIONS OF STUDY OF ROTATIONAL SPECTRA

(i) Determination of moment of inertia and bond length

From the last section, you know about the relationship between the energy (or wavenumber) of radiation absorbed or emitted, required for the change of rotational level and the moment of inertia. You can now think of the reverse process of what we have learnt above. If we determine the frequency of radiation absorbed or emitted required for the change of a particular rotational level, we can relate it to the value of B, the rotational constant. Once B is determined, we can calculate the moment of inertia using the expression $B = \frac{h}{8\pi^2 Ic}$. The value of moment of inertia so obtained can be used to give the value of r, the bond length if we know the reduced mass of the system. One such example is illustrated below:

The value of rotational constant, B of some molecules as obtained from their rotational spectrum is given below:

Molecule	B/cm^{-1}
CO	1.93128
HF	20.90
HBr	8.4648
HCl	10.59
HI	6.426
KCl	0.1286
NaCl	0.2180
NO	1.70

The transition from $J = 0$ to $J' = 1$ for HCl takes place at $\bar{\nu} = 21.18\ \text{cm}^{-1}$. What is the bond length of $^1\text{H}^{35}\text{Cl}$?

Let us follow the steps we have listed above.

$$\bar{\nu}_{J=0 \rightarrow J'=1} = 21.18\ \text{cm}^{-1}$$

Thus, $\bar{\nu} = 2B\ \text{cm}^{-1}$ (from Eq. 3.29)

So, $$B = \frac{\bar{\nu}}{2} = \frac{21.18}{2} = 10.59\ \text{cm}^{-1}$$
$$= 10.59 \times 10^2\ \text{m}^{-1}$$

Also, $$I = \frac{h}{8\pi^2 Bc}$$

So, $$I = \frac{6.626 \times 10^{-34}\ \text{Js}}{8 \times (3.14)^2 \times 10.59 \times 10^2\ \text{m}^{-1} \times 2.998 \times 10^8\ \text{m s}^{-1}}$$
$$= 0.2646 \times 10^{-46}\ \text{kg m}^2$$

Now $I = \mu r^2$

To know r, from the above equation, we have to first calculate μ as shown below:

$$\mu = \frac{m_{Cl} \cdot m_H}{m_{Cl} + m_H}$$

$$= \frac{(35.45)\,(1.008)}{(35.45 + 1.008)} \times \frac{10^{-3}}{6.022 \times 10^{23}}$$

$$= 1.627 \times 10^{-27}\ \text{kg}$$

Thus,

$$r^2 = \frac{I}{\mu}$$

$$r^2 = \frac{0.2646 \times 10^{-46}\ \text{kg m}^2}{1.627 \times 10^{-27}\ \text{kg}}$$

$$r = \sqrt{\frac{0.2646 \times 10^{-46}\ \text{m}^2}{1.627 \times 10^{-27}}}$$

$$= 1.275 \times 10^{-10}\ \text{m}$$

$$r = 127.5\ \text{pm}$$

(ii) Another application of the study of rotational spectra is in the determination of the mass of a particular isotope or isotopic abundance of a particular isotope.

You know that isotopes differ from each other in atomic mass. If we consider a particular molecule and another substituted molecule having an isotope of a particular atom substituted, there will be a difference in the masses of these two molecules. For example, if we consider $^{12}C^{16}O$ and $^{13}C^{16}O$, there is an increase in the mass of $^{13}C^{16}O$ as compared to $^{12}C^{16}O$. Then, the reduced mass of the molecule having higher mass isotope, i.e. $^{13}C^{16}O$ in this case, is more than the $^{12}C^{16}O$. This would lead to a higher value of I for $^{13}C^{16}O$ which in turn indicates a lower value for rotational constant, B for this molecule. The experimental values of rotational constants of $^{12}C^{16}O$ and $^{13}C^{16}O$ are as given below:

Rotational constant for $^{12}C^{16}O = B = 1.92118\ \text{cm}^{-1}$

Rotational constant for $^{13}C^{16}O = B' = 1.83669\ \text{cm}^{-1}$

If we carefully examine the expression $B = \dfrac{h}{8\pi^2 Ic}$, we conclude that the terms h, π, c are all constant and B is inversely proportional to I. Thus, we can write

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic} \cdot \frac{8\pi^2 I'c}{h}$$ (here I and I' represent the moment of inertia for $^{12}C^{16}O$ and $^{13}C^{16}O$, respectively.

$$= \frac{I'}{I}$$

And $I' = \mu' r^2$ and $I = \mu r^2$

Thus, $$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046 \qquad \text{... (3.30)}$$

(the bond length r of the molecule does not change on isotopic substitution)

From the above equation, we know the ratio of μ' to μ. Thus, if we know μ, we can calculate μ'.

Hence $$\mu' = 1.046\ \mu \qquad \text{... (3.31)}$$

We know that atomic mass of $^{16}O = 15.9994$ and that of $^{12}C = 12.00$

So,
$$\mu' = \frac{15.9994\, m_{^{13}C}}{15.9994 + m_{^{13}C}} \qquad \text{... (3.32)}$$

and
$$\mu = \frac{12 \times 15.9994}{12 + 15.9994} \qquad \text{... (3.33)}$$

Expressing the Eq. 3.31 in terms of atomic masses as expressed in Eq. 3.32 and 3.33, we get

$$\frac{15.9994\, m_{^{13}C}}{15.9994 + m_{^{13}C}} = 1.046 \times \frac{12 \times 15.9994}{12 + 15.9994}$$

On solving the above equation, we obtain the value of $m_{^{13}C} = 13.0007$ which is the precise value of mass of ^{13}C isotope and is in agreement with the value obtained by other methods. Before we close our discussion on the determination of atomic mass of an isotope, we would also like to focus your attention on the appearance of the rotational spectra after isotopic substitution. You have studied above in case of $^{13}C^{16}O$ that substitution of a heavier isotope leads to a decrease in the value of rotational constant. Since the value of B is related to the spacing of spectral lines in the rotational spectrum, a lower value of B' indicates smaller separation between the rotational levels and also in spectral lines. This is shown in Fig. 3.6.

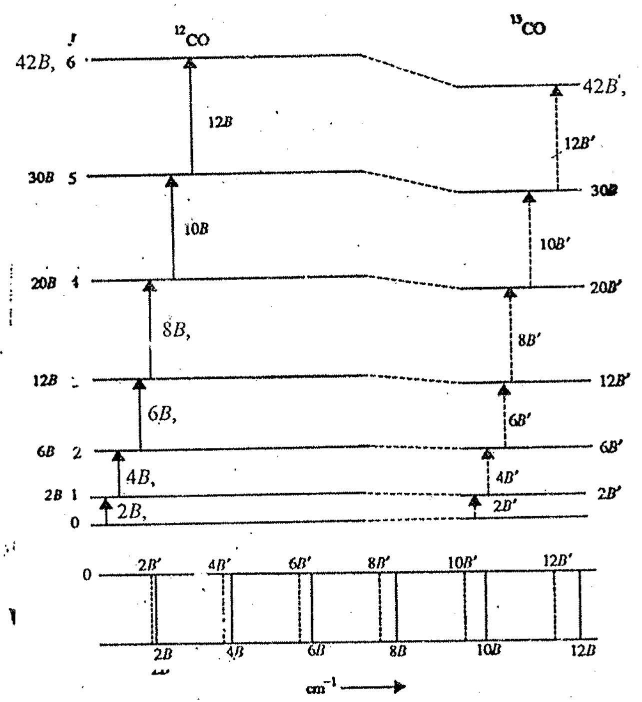


Fig. 3.6: Decrease in spacing between rotational levels and spectral lines due to isotopic substitution.

Till now we based our discussions on the rigid diatomic molecules. In the next section, you will study what happens when we are dealing with a non–rigid molecule. Before going to the next section, answer SAQ 3 given below to check your understanding about the above section.

SAQ 3

From the rotational spectra of ^{14}NO and ^{15}NO,it was found that $\frac{B}{B'} = 1.0361$ where B and B' are rotational constants for ^{14}NO and ^{15}NO, respectively. Calculate the atomic mass of ^{15}N if the masses of ^{14}N and O are 14.004 and 15.9994, respectively.

3.5 NON-RIGID ROTORS

The rigid rotors we considered before present an ideal case and actually when a molecule rotates, its atoms experience a centrifugal force. Since the bonds are elastic to some extent, when a non-rigid molecule rotates, the centrifugal force leads to the stretching of the bonds. This stretching leads to an increase in the bond length and hence an increase in the moment of inertia. As a result of this, there is a decrease in the separation between the rotational energy levels and also in the spectral lines. see Figs. 3.7 and 3.8.

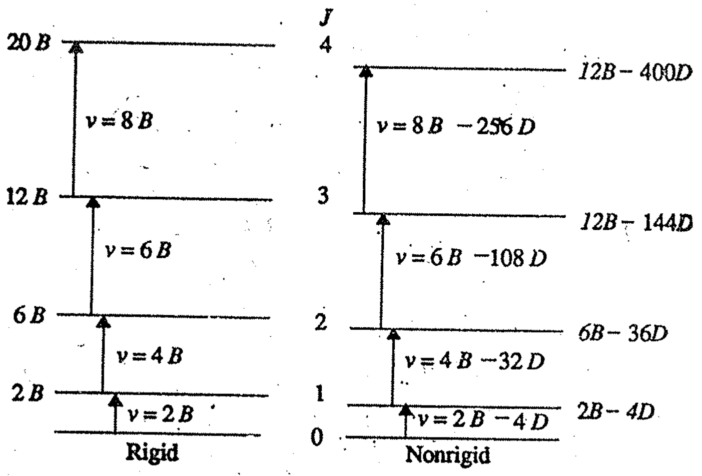


Fig. 3.7: Effect of centrifugal distortion on the energy levels of a diatomic rotor.

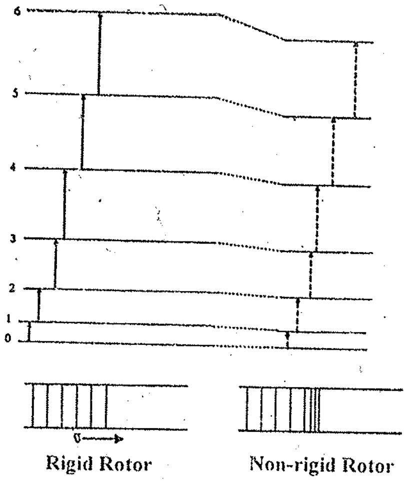


Fig. 3.8: Energy level diagram for the rigid and non-rigid rotators. The spectral lines arising from the transitions are indicated below the energy level diagrams.

This effect is taken care of if we write the ν as given below:

$$\bar{\nu} = BJ(J+1) - DJ^2(J+1)^2 \quad \text{... (3.34)}$$

where D is the **centrifugal distortion constant** and is given by the following equation.

$$D = \frac{4B^3}{\omega^2} \quad \text{... (3.35)}$$

The value of D is obtained from the spectral results and is always very much less than B. The spectra of non-rigid molecules will show a decrease in the spacing between rotational levels and in spectral lines similar to the one shown in Fig. 3.6 but here the decrease will be comparatively much smaller.

In the next section, you will study about the rotational spectra of polyatomic molecules.

3.6 ROTATIONAL SPECTRA OF POLYATOMIC MOLECULES

Till now, we focussed our attention on the simple case of linear diatomic molecules. The rotation of a polyatomic molecule is quite complex as compared to the diatomic molecules considered above. The rotation of a polyatomic molecule could be simplified and understood in a better way if we consider components of the rotation about the three principal axes. Thus, a three dimensional molecule will have three moments of inertia about the three axes (x, y, z). You may remember that in the previous case of a diatomic molecule, we considered the rotation about an axis perpendicular to the axis of symmetry of the molecule. But actually, the rotation of the diatomic molecule could be about all the three axes $(x, y$ and $z)$ as shown below:

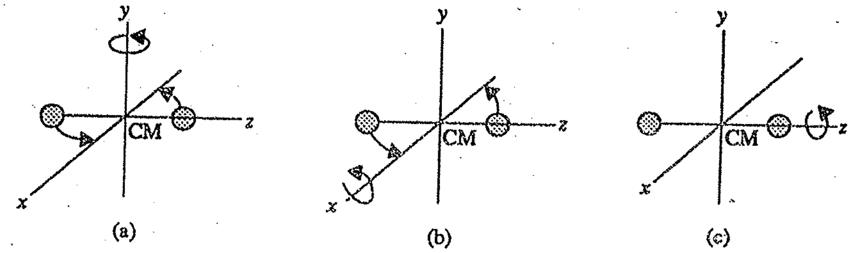


Fig. 3.9 : Rotation of a diatomic molecule about centre of mass:
(a) about x axis (b) about y axis (c) about z axis.

Note that the moment of inertia about the molecular axis is zero and the moment of inertia about the other two axes perpendicular to the molecular axis are identical.
Hence, only one numerical value of I occurs for a linear molecule and the energy is defined by only one quantum number, J.

Let the moments of inertia for the above rotations be represented by I_B, I_C and I_A, respectively. Since the rotations as shown in part (a) and (b) are equivalent, we can say $I_B = I_A$. In part (c), the moment of inertia about the bond axis (y-axis) has a very small value as compared to I_B and I_C and we can use an approximation that $I_A = 0$. The small value of I_A could be attributed due to the differences in the masses and the radii **of the nucleus and the electrons.**

You know that most of the mass of the molecule is concentrated in the nuclei of its atoms in a very small space. But the electrons having very less mass occupy relatively large space. Therefore, the electrons contribute a major share to the moment of inertia along the axis of symmetry because only they will be contributing to the motion. The total moment of inertia (both due to electrons and nucleus) is very small. Since the energy of the rotational levels is proportional to $\frac{1}{I}$, the energy of the rotational levels corresponding to rotation about the symmetry axis (Fig. 3.9(c)) will be **very-very high as compared to that of the rotational levels for rotations shown in Figs.** 3.9**(a) and (b). Thus, these rotational levels will not contribute to the rotational spectra and the value of moment of inertia used in Eq. 3.26 could be either** of I_B or I_C because **both of them are equal.**

With this background in our mind, let us shift our attention to polyatomic molecules. Polyatomic molecules can be classified into various groups according to their values of moments of inertia along the three principal axes. Such a classification is given below in Table 3.1.

In case of polyatomic molecules when the rotation in three dimensions is possible, kinetic energy of rotation (E_k) can be given as

$$E_k = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2 \quad \text{... (3.36)}$$

Similar to Eq. 3.24, we can write

$$E_k = \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C} \quad \text{... (3.37)}$$

where $L_A = I_A \omega_A$

$L_B = I_B \omega_B$

$L_C = I_C \omega_C$

Here, the magnitude of total angular momentum is given as follows:

$$L^2 = L_A^2 + L_B^2 + L_C^2$$

Thus for linear molecules where $I_A = 0$, Eq. 3.37 becomes as follows:

$$E_k = \frac{(L_A^2 + L_B^2)}{2I_A} = \frac{L^2}{2I_A}$$

Table 3.1 : Various Classes of Polyatomic Molecules.

Moments of Inertia		Type of Rotor	Examples	Rotational Constant
$I_B = I_C$, $I_A = 0$		Linear	CO, HCl, OCS	$A = \alpha$, $B = C$
$I_B = I_C = I_A$		Spherical top	CH_6, SF_6	$A = B = C$
$I_A < I_B = I_C$	Prolate		CH_3F, CH_3Cl	$A > B = C$
		Symmetrical top		
$I_A > I_B = I_C$	Oblate		BCl_3, C_6H_6	$A = B > C$
$I_A \neq I_B \neq I_C$		Asymmetric top	CH_2Cl_2, H_2O	$A \neq B \neq C$

About the linear systems, you have already studied in detail for diatomic molecules. Similarly, we can treat linear triatomic and other linear polyatomic molecules.

Let us study the case of a triatomic molecule OCS. Here also we will assume that it is a rigid molecule. If you see the structure of OCS shown in Fig. 3.10, you can find that there are two bond lengths, C–O and C–S. But we have one value for the moment of inertia which cannot give two values of bond distances. This problem can be solved by using isotopic substitution as follows.

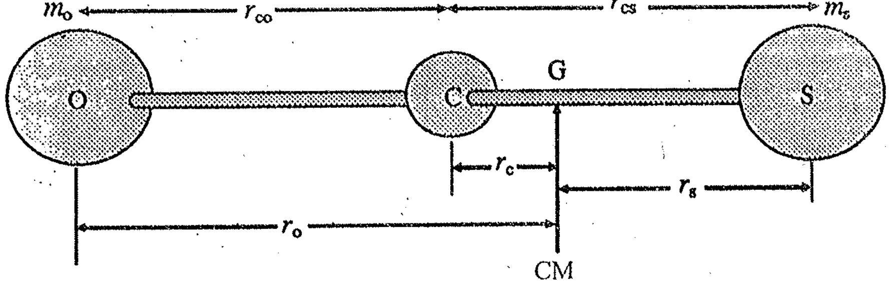


Fig. 3.10: OCS molecule.

Let the masses of O, C and S be represented by m_o, m_c and m_s, respectively. Also let the distances of the atoms O, C and S from the centre of mass (G) be represented as r_o, r_c and r_s, respectively. The centre of mass (G) will be such that

$$m_o r_o + m_c r_c = m_s r_s \qquad \text{... (3.38)}$$

The moment of inertia of this system (I) is given by the following equation.

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \qquad \text{... (3.39)}$$

We can express r_o and r_s by the following expressions (see Fig. 3.10).

$$r_o = r_{co} + r_c \qquad \text{... (3.40)}$$

and $$r_s = r_{cs} - r_c \qquad \text{... (3.41)}$$

We can substitute the above values of r_o and r_s from Eqs. 3.40 and 3.41 into Eq. 3.38 to yield the following expression.

$$\mathrm{m}_o (r_{co} + r_c) + m_c r_c = m_s (r_{cs} - r_c)$$

or $$\mathrm{m}_o r_{co} + m_o r_c + m_c r_c = m_s r_{cs} - m_s r_c$$

Bringing all the terms containing r_c on one side, we can write

$$\mathrm{m}_o r_c + m_c r_c + m_s r_c = m_s r_{cs} - m_o r_{co}$$

$$r_c (m_o + m_c + m_s) = m_s r_{cs} - m_o r_{co}$$

If we represent $m_o + m_c + m_s$, the total mass by M, the above equation becomes as given below

$$r_c M = m_s r_{cs} - m_o r_{co} \qquad \text{... (3.42)}$$

Similarly, we can express Eq. 3.39 for I in terms of r_o and r_s as given below:

$$I = m_o (r_{co} + r_c)^2 + m_c r_c^2 + m_s (r_{cs} - r_c)^2$$

$$= m_o r_{co}^2 + m_o r_c^2 + 2m_o r_{co} r_c + m_c r_c^2 + m_s r_{cs}^2 + m_s r_c^2 - 2m_s r_{cs} r_c -$$

Rearranging, we get

$$I = m_o r_c^2 + m_c r_c^2 + m_s r_c^2 + 2r_c (m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2 \qquad \text{... (3.43)}$$

$$= M r_c^2 + 2r_c (m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2 \qquad \text{... (3.44)}$$

Substituting value of r_c from Eq. 3.42 ino the above equation, we get

$$I = M\left(\frac{m_s r_{cs} - m_o r_{co}}{\mathrm{M}}\right)^2 + 2\left(\frac{m_s r_{cs} - m_o r_{co}}{M}\right) \cdot (m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2$$

$$= M\left(\frac{m_s r_{cs} - m_o r_{co}}{M}\right)^2 - \frac{2\,(m_o r_{co} - m_s r_{cs})^2}{M} + m_o r_{co}^2 + m_s r_{cs}^2$$

$$= m_o r_{co}^2 + m_s r_{cs}^2 - \frac{(m_o r_{co} - m_s r_{cs})^2}{M} \qquad \dots (3.45)$$

Eq. 3.45 can be simplified to the following expression.

$$I = \frac{1}{M}\left[m_o m_c r_{co}^2 + m_c m_s r_{cs}^2 + m_o m_s (r_{co} + r_{cs})^2\right]$$

Eq. 3.45 is the one on which we will further focus our discussion. It contains the two unknown distances r_{co} and r_{cs}. Suppose we carry out an isotopic substitution in the molecule. i.e., we substitute ^{18}O in place of ^{16}O and then record the rotational spectra. The equation for moment of inertia (I') of this new molecule thus becomes as given below:

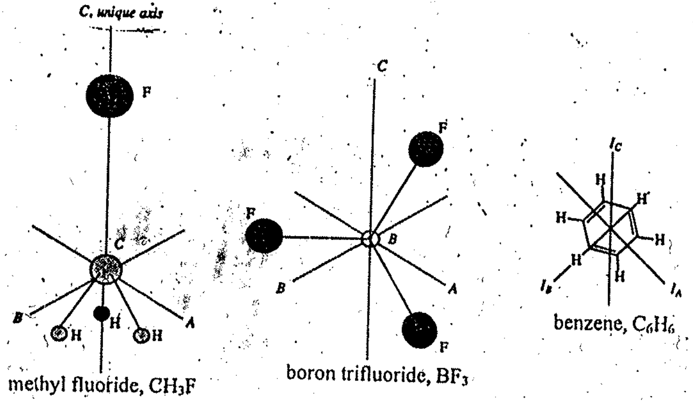
You may remember that bond distances do not change when isotopic substitution is carried out.

$$I' = m'_o r_{co}^2 + m_s r_{cs}^2 - \frac{(m_o' r_{co} - m_s r_{cs})^2}{M'} \qquad \dots (3.46)$$

where m_o' represents the mass of the isotope of oxygen. Now, we have two equations [Eqs. 3.45 and 3.46] and we can evaluate two unknowns r_{co} and r_{cs} provided we know the other parameters in these equations.

Next category of molecules is that of **spherical top**. These molecules have all the three moments of inertia as identical. As far as the value of rotational energy is concerned, it can be obtained by using any one of the above values of moment of inertia. These molecules behave similar to linear molecules as far as their rotation is concerned. The same equation as obtained for linear molecules can be applied to give the value of E_k or B. But because these molecules, being symmetric in nature, do not possess any dipole moment; Thus, these molecules do not show pure rotational spectra.

We will next consider **symmetric top** molecules. You are aware that in these molecules, two moments of inertia are equal but the third one is different. When this third moment of inertia is less than the other two equal moments of inertia, the molecules are known as **prolate molecules**. On the other hand, when the third moment of inertia is greater than the other two moments of inertia, then the molecules are known to be of oblate type. Both these type of molecules are shown below in **Fig. 3. 11**.



methyl fluoride, CH_3F boron trifluoride, BF_3 benzene, C_6H_6

Fig. 3.11: Prolate and oblate symmetric molecules.

Again, in these molecules first we consider that the molecules are rigid and derive the energy expression by solving the Schrödinger equation. The following equation is obtained by using the above method.

$$\bar{\nu}_{J,K} = \frac{E_{J,K}}{hc} = BJ\,(J+1) + (A-B)\,K^2\ \text{cm}^{-1} \qquad \text{... (3.47)}$$

We will not go into the details of arriving at Eq. 3.47. It is valid for prolate molecules.

where, $$B = \frac{h}{8\pi^2 I_B c}$$

$$A = \frac{h}{8\pi^2 I_C c}$$

For oblate molecules,

$\bar{\nu} = B\,J(J+1) - (B-C)K^2\ \text{cm}^{-1}$

Here, J is the total angular momentum and K is the component of angular momentum about the *unique axis*. The unique axis along the C–X bond of CH_3X molecule is shown in Fig.3.11.Obviously the values of K will be smaller than or equal to J. Thus, K can take the following values.

Unique axis is also known as Top axis.

$$K = J,\ J-1,\ J-2,\ \ldots,0,\ \ldots,\ (J-1),\ -J \qquad \text{... (3.48)}$$

So, K can take $2J + 1$ values.

From the above equation, you can see that K can have negative values as well. The +ve and –ve values are associated with the clockwise and anticlockwise rotation about the symmetry axis. When $K = 0$, it means that there is no rotation about the symmetry axis or unique axis.

Eq. 3.50 permits determination of only one rotational constant. Hence the complete geometry of a symmetric top molecule cannot be determined by using this single value of B obtained from spectra. In such a case, isotopic substitution is used in structure determination.

Eq. 3.47 shows that the rotational energy depends upon the K^2 terms. So the anticlock wise or clockwise rotation (i.e., the +ve and –ve values of K) will have same value for K^2 or energy. Thus, the levels corresponding to $+K$ and $-K$ will be degenerate.

Thus, centrifugal distortion leads to a slight separation of the components of J.

The selection rules for the rotation of such molecules are

$$\Delta J = \pm 1 \text{ and } \Delta K = 0 \qquad \text{... (3.49)}$$

The selection rule of ΔK comes from the fact that there is no dipole moment about the symmetry axis (rotation about which is represented by K), hence electromagnetic radiation cannot interact with the rotation about this axis. Hence, it is expressed as $\Delta K = 0$.

If we apply the above selection rules to Eq. 3.47, we get

$$\begin{aligned}\bar{\nu}_{(J+1,K)} - \bar{\nu}_{(J,K)} &= [B\,(J+1)\,(J+2) + (A-B)K^2] - [(BJ\,(J+1) + (A-B)K^2] \\ &= 2B\,(J+1)\ \text{cm}^{-1} \qquad \text{... (3.50)}\end{aligned}$$

where $J = 0, 1, 2$..............

You can see that K is not reflected in the final equation for rotation and Eq. 3.50 is similar to expression for $\bar{\nu}$ obtained for the rotation of linear molecules.

Similar to the case of linear molecules, the centrifugal distortions due to non–rigid nature of real molecules are taken care of by incorporating an additional term in the energy expression as given below in Eq. 3.51:

$$\bar{\nu}_{(J,K)} = B\,J(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{J,K} J\,(J+1)K^2 - D_K K^4\ \text{cm}^{-1}$$

$$\bar{\nu}_{(J+1,K)} - \bar{\nu}_{(J,K)} = 2B\,(J+1) - 4D_J\,(J+1)^3 - 2D_{JK}\,(J+1)K^2\ \text{cm}^{-1} \qquad \text{... (3.51)}$$

Thus, we could take the case of symmetric top molecules to be similar to that of linear molecules. The same procedure can be used for calculating B and I and bond lengths for symmetric top–molecules as done earlier for linear molecules. But here, there will be a difference in the observed spectrum for symmetric top molecules as far as the splitting of rotational lines is concerned. Since each value of J is associated with $2J + 1$ values of K and the levels corresponding to $+K$ and $-K$ being degenerate. This leads to the fact that the spectral line associated with a particular level will be split into $J + 1$ components. Thus, the following splitting pattern will be observed.

when,	J	K	$\bar{\nu}$ (from Eq. 3.51)
	1	0	$4B - 32D_J$
		± 1	$4B - 32D_J - 4D_{J,K}$
		0	$6B - 108\,D_J$
	2	± 1	$6B - 108D_J - 6D_{J,K}$
		± 2	$6B - 108D_J - 24D_{J,K}$

Thus, the spectrum obtained will look like as shown below in Fig. 3.12.

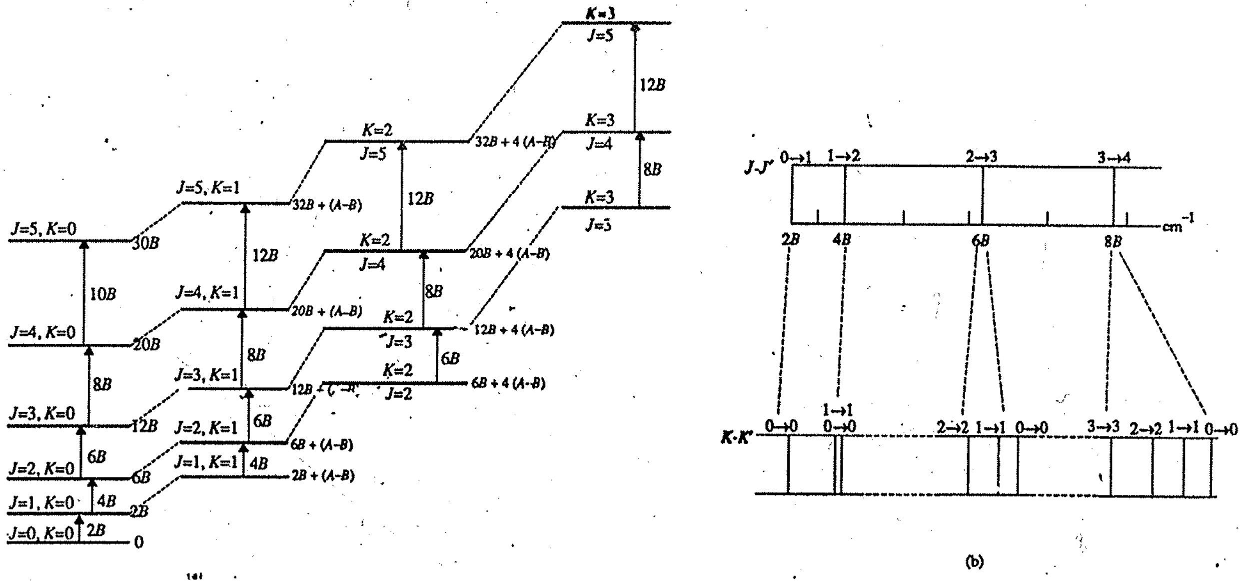


Fig. 3.12: (a) Rotational energy levels of prolate symmetric top molecules. (b) Splitting of rotational spectral lines for symmetric top molecules.

Remember that no such splitting was observed for linear molecules. In other words, by studying the spectra, you can know whether a certain molecule is of linear type or of symmetrical top type.

The analysis of rotational spectra of last class of molecules, i.e., **Asymmetric top** molecules is quite complex and a general expression for energy cannot be written for them. Each molecule of this class requires individual treatment. In this course, we will not go into the details of analysis of rotational spectra for this kind of molecules.

Note that in case of symmetric top molecules, each lines is really a superposition of $(J + 1)$ lines.

In the next section, you will study about the intensity of spectral lines.

3.7 POPULATION OF ROTATIONAL ENERGY LEVELS AND THE INTENSITIES OF SPECTRAL LINES

According to the selection rule, all those transitions where $\Delta J = \pm 1$ are possible. It has been shown by calculations that the probability of all such transitions is the same. However, this does not mean that all the transitions will have the same intensity. Although the chances of a molecule going from $J = 0$ to $J = 1$ is the same as $J = 2$ to $J = 3$, yet the intensity of the two lines may differ. This is so because the total number of molecules initially present in $J = 0$ will be different from the molecules present in $J = 2$. The larger the number of molecules present in a particular state, the larger will be the chances of transitions to the next state and hence greater will be the intensity.

The population of the energy state depends on (1) Boltzmann distribution and (2) the degeneracy of the state.

Boltzmann distribution can be expressed as,

$$\frac{N_J}{N_0} = e^{-\Delta E_J/kT} \qquad \text{... (3.52)}$$

where, N_J = number of molecules in any state

N_0 = number of molecules in the lowest level, i.e., $J = 0$

E_J = energy difference between the two states

k = Boltzmann constant

T = temperature in Kelvin

Eq. 3.52 can be rewritten as,

$$\frac{N_J}{N_0} = e^{-BhcJ(J+1)/kT} \qquad \text{... (3.53)}$$

One thing is clear from Eqs. 3.52 and 3.53 that the population of different states keeps on decreasing in an exponential manner as we keep on increasing the J value.

However, there is another factor–the degeneracy of the state which will affect the population. We shall not discuss the origin and number of such degenerate states, except to emphasise that degeneracy of a state increases the population of a particular energy state.

The net result of the two factors is that the population rises to a maximum and then decreases as J value increases. The band with maximum intensity is given by,

$$J_{\max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \qquad \text{... (3.54)}$$

SAQ 4

Calculate the relative population of first two rotational energy levels for HCl at 300K. Use $B = 10.49\ \text{cm}^{-1}$

....

....

3.8 SUMMARY

In this unit, you learnt about various types of energies associated with different kind of molecular motions. Rotational motion was the one in which were interested in. In this context, the terms moment of inertia and angular velocity were explained. Then, the rotation of a rigid diatomic molecule was discussed in detail. The energy levels associated with such molecules were considered which in turn were related to the observed rotational spectra.

The applications of rotational spectra study were highlighted. The case of non–rigid molecules was also explained. This was followed by the discussion of rotational spectra of polyatomic molecules. In this class, linear, spherical and symmetric top molecules were discussed.

Lastly, the relationship between the intensity of rotational spectral lines with population of rotational levels was described.

3.9 TERMINAL QUESTIONS

1. Using $m_1 r_1 = m_2 r_2$, derive $r_2 = \frac{m_1 r}{(m_1 + m_2)}$.
2. Calculate the energy in terms of $\bar{\nu}$ of the energy level corresponding to $J = 7$.
3. What is the selection rule for a rigid diatomic molecule to show rotational spectrum?
4. Which of the following molecules will show rotational spectra?

   $O=C=O$, HF, N_2

5. If the rotational constant for $H\,^{35}Cl$ is $10.59\ cm^{-1}$, what is the value of rotational constant for $^2D\ ^{35}Cl$?

Use mass of $^{35}Cl = 58.06 \times 10^{-27}$ kg

mass of $^2D = 3.344 \times 10^{-27}$ kg

mass of $^1H = 1.673 \times 10^{-27}$ kg

3.10 ANSWERS

1. From Eq. 3.26, a decrease in moment of inertia will lead to an increase in the energy of the rotational level.
2. It should possess a permanent dipole moment.
3. $$\frac{B}{B'} = \frac{\mu'}{\mu} = 1.0361$$

$$\mu' = 1.0361 \times \mu$$

$$\frac{^{15}N \times 15.9994}{^{15}N + 15.9994} = \frac{1.0361\,(14.004 \times 15.9994)}{14.004 + 15.9994}$$

$$^{15}N = 14.98257$$

4. $$\frac{hcB}{kT} = \frac{(6.626 \times 10^{-34}\ J\,s)(2.998 \times 10^{8}\ m\,s^{-1})(10.4\ cm^{-1})(10^{2}\ m^{-1})}{(1.3806 \times 10^{-23}\ J\,K^{-1})(300\ K)}$$

$$= 5.007 \times 10^{-2}$$

For $J = 0$, $\frac{N_J}{N_O} = 1$

For $J = 1$, $\frac{N_J}{N_O} = e^{-2(5.007 \times 10^{-2})}$

Terminal Questions

1. $$m_1 r_1 = m_2 r_2$$

$$\frac{r_2}{r_1} = \frac{m_1}{m_2}$$

From the characteristics of proportions,

$$\frac{r_2}{r_1 + r_2} = \frac{m_1}{m_1 + m_2}$$

$$r_2 = \frac{m_1 (r_1 + r_2)}{(m_1 + m_2)}$$

$$= \frac{m_1 r}{(m_1 + m_2)}$$

2. $$= BJ(J+1)$$

$$= B \times 7\,(7+1)$$

$$= B \times 7 \times 8$$

$$= 56B$$

3. $\Delta J = \pm 1$

4. **HF**

5. **5.446 cm^{-1}**

Further Reading

1. J.R.Dyer, Application of Absorption Spectroscopy of Organic Compounds, Eastern Economy Edition, Prentice-Hall of India Pvt.Ltd.
2. D.H.Williams and Ian Fleming, Spectroscopic Methods in Organic Chemistry. Tata Mc Graw Hill Publishing Co. Ltd. 4thEd.
3. C.N Banwell, Fundamentals of Molecular Spectroscopy, 3rd Ed, Tata McGraw Hill Publishing Co. Ltd.

NOTES

Uttar Pradesh
Rajarshi Tandon Open University,

UGCHE -10
Spectroscopy

Block

2

IR AND RAMAN SPECTRA

INFRA RED AND RAMAN SPECTROSCOPY

In the first block of this course, you studied about some fundamental aspects of atomic spectra, symmetry, Group Theory and Rotational Spectra. In this block, you will come across the Infra Red Spectra of diatomic and polyatomic molecules and Raman Spectroscopy.

This block is divided into three units. Unit 4 deals with vibrational spectra of diatomic molecules, while the infrared spectra of polyatomic molecules is dealt with in Unit 5. Unit 6, which is the last unit of this block, is devoted to Raman Spectroscopy.

In Unit 4, you will first study about the vibration of a single particle supported by a spring. Then vibration of a diatomic molecule is discussed on similar lines. The harmonic oscillator model of diatomic molecules is consdered and their vibrational spectra is explained. Then, the effect of anharmonicity on the vibrational spectra is considered. Finally the rotational-vibrational spectra of diatomic molecules is discussed.

Unit 5 aims at highlighting the important aspects of infrared spectra of polyatomic molecules. This unit begins with the explanation of different kinds of degrees of freedom. Then the infrared spectra of some simple molecules such as H_2O and CO_2 are discussed. This is followed by an account of the vibration-rotation spectra of polyatomic molecules. The group frequencies of various classes of organic compounds have been discussed alongwith factors affecting them. Finally the application of infrared spectra is structure determination is explained.

In the Appendix to Unit 5, the use of group theory in finding out the symmetry species of the normal modes of vibration and in determining the number of infrared active vibrations in H_2O and NH_3 has been discussed.

Unit 6 deals with Raman Spectroscopy. It starts with a discussion on the origin of Raman Spectrum in terms of classical and quantum-mechanical concepts. After that rotational Raman and vibrational Raman spectra are explained followed by Vibration-Rotation Raman Spectra. Then Polarised Raman spectra is briefly included. Finally the applications of IR and Raman Spectroscopy are illustrated using some simple examples. The Appendix to Unit 6 explains the application of group theory in identifying Raman active vibrations and in understanding the mutual exclusion principle.

Objectives

After studying this block, you should be able to:

- explain Hooke's law and motion of a harmonic oscillator,
- discuss the infrared spectrum of a diatomic molecule,
- predict the effect of anharmonicity on the vibrational spectrum of a diatomic molecule,
- state the selection rules for vibrational transitions in a diatomic molecule,
- explain zero point energy,
- discuss the energy levels and selection rules for a vibrating rotator,
- calculate the number of vibrational modes in a polyatomic molecule,
- explain the energy level scheme of water,
- illustrate the use of group frequencies in structure determination of a molecule,
- list various factors affecting the group frequencies,
- elaborate the steps involved in the analysis of IR spectra of simple molecules,
- give classical and quantum mechanical explanations of the origin of Raman spectrum,
- differentiate between infrared and Raman spectroscopy,
- describe the rotational, vibrational and vibration-rotation Raman Spectra,
- explain Mutual Exclusion Principle,
- give applications of IR and Raman Spectroscopy.

UNIT 4 VIBRATIONAL SPECTRA OF DIAMOTIC MOLECULES

Structure

4.1 INTRODUCTION

While going through Unit 7 of the course "Atoms and molecules" (CHE-01), you might have appreciated the use of vibrational spectroscopy as an analytical technique for the determination of molecular structure. In the last block of this course, two units viz. Units 1 and 3 have been devoted to atomic spectra and rotational spectra, respectively. In this unit and Unit 5, we will discuss vibrational spectroscopy which is another kind of spectroscopy dealing with molecules.

In this unit, the theory and applications of vibrational spectra of diatomic molecules will be described. The vibrational spectra of polyatomic molecules is discussed in Unit 5.

In this unit, we will start our discussion with the classical example of the vibration of a single particle supported by a spring. The similarity of the vibration in a diatomic molecule with the vibration of a single particle is then brought about and possible transitions for the harmonic oscillator model of diatomic molecules are discussed. This is followed by the explanation of observed vibrational spectra of diatomic molecules, the introduction of anharmonicity and the rotational- vibrational spectra of diatomic molecules.

Objectives

After studying this unit, you should be able to:

- discuss Hooke's law and motion of a harmonic oscillator,
- explain observed infrared spectra of diatomic molecules,
- evaluate harmonic frequency of diatomic oscillator, force constant and anharmonicity constant from the observed infrared spectra,
- predict vibrational frequencies of isotopically substituted molecules if the vibrational frequencies of unsubstituted molecules are known,
- evaluate zero point energies, and
- explain rotational-vibrational spectra of diatomic molecules.

4.2 HARMONIC OSCILLATOR

Consider a particle of mass m held by a rigid support through a spring as shown in Fig. 4.1(a). When this particle is displaced from its equilibrium position a [see Fig. 4.1(b) or (c)] using some external force (like pushing or pulling by hand), it is observed that the particle tends to go back to its equilibrium position after the force is withdrawn. As it will be explained in sub-Sec 4.2.2, the particle not only goes back to its equilibrium position but goes still further on the opposite side till the distance is equal to the initial displacement and if there is no frictional loss or gravitational pull, the particle keeps moving between the two extremes in a periodic motion. Such oscillations are referred to as **Simple Harmonic Motion (SHM)** and the particle is referred as a **Harmonic Oscillator.**

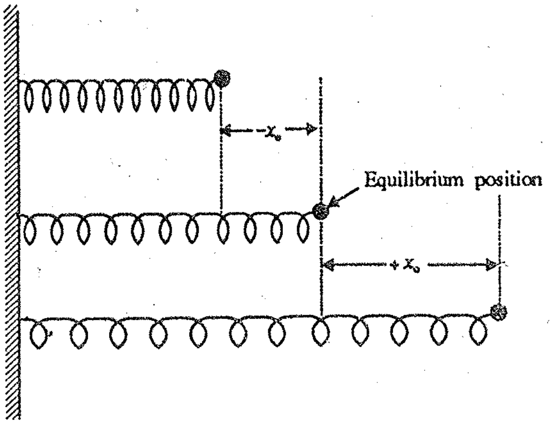


Fig. 4.1: Contraction (c) and expansion (b) of the spring showing displacement of the particle from its equilibrium position (a). The restoring froce F acts in a direction opposite to the direction of displacement.

4.2.1 Hooke's Law

The motion of the particle referred above towards its equilibrium position after the external force is withdrawn can be explained as follows. On giving a displacement (x) to the particle, a force called **restoring force** (F) arises in the spring in the direction opposite to that of the displacement and acts to bring it back to its equilibrium position. A spring which behaves in this manner is said to obey *Hooke's law.* Hooke's law states that *the restoring force (F) is proportional to the displacement (x) and acts in a direction opposite to the direction of the displacement.* This can be represented mathematically as:

Note that the negative sign in Eq. 4.1 indicates that if the displacement is positive, the restoring force is negative and vice-versa.

$$F \alpha -x$$

or $$F = -kx \qquad ...(4.1)$$

The proportionality constant, k is called the force constant of the spring. The force constant k is a measure of the strength of the spring. Hence, a large value of k means a stronger and less flexible spring. From Eq. 4.1 it may be further noticed that for a given value of x, a larger value of k will result into a larger restoring force.

4.2.2 Equation of Motion

It is experimentally observed that if the particle is displaced from its equilibrium position by a distance $+x_0$ (Fig. 4.1b) and the external force is withdrawn, the particle returns to the equilibrium position (Fig. 4.1a) and then continues to move to a position, $-x_0$, away from the equilibrium position (Fig. 4.1c). The state of the spring in Fig. 4.1b and 4.1c corresponds to the stretched and the compressed states, respectively. And as mentioned above, if there is no frictional loss or gravitational pull the particle continues to move between these two extremes passing through the equilibrium position. If the value of the maximum displacements (also called **amplitude**) on the two extremes is denoted by $-x_0$ and $+x_0$, then the value of the displacement (or amplitude) x after time t sec is given by a cosine function (Fig. 4.2) as shown below:

$$x = x_0 \cos 2\pi \nu_{\text{osc}} t \qquad \text{...(4.2)}$$

where ν_{osc} is the oscillation frequency in sec^{-1}. Equation 4.2 represents the equation of motion of the particle.

Similar to Eq. 4.2, x can also be given as

$$x = x_0 \sin 2\pi \nu_{\text{osc}} t$$

You must also remember that the sin function is 90° out of phase with respect to the cos function.

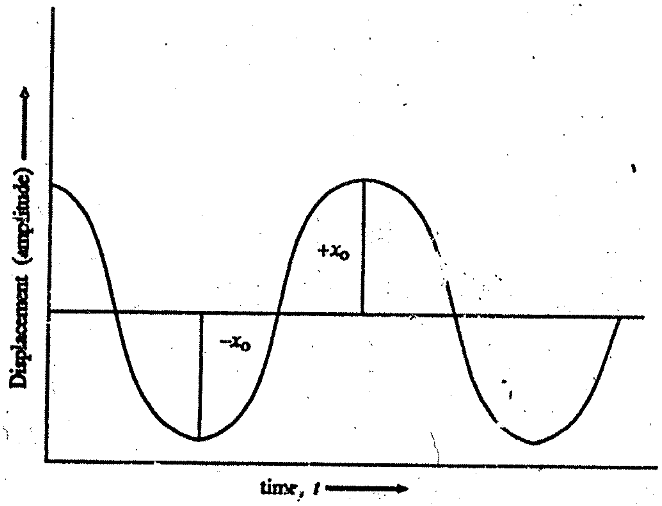


Fig. 4.2: A cosine function represents the equation of motion of the harmonic oscillator.

4.2.3 Expressions for Force Constant and Characteristic Frequency

Now, the restoring force F in Eq. 4.1 can be represented in terms of Newton's second law of motion as:

$$F = ma \qquad \text{...(4.3)}$$

where a is the acceleration of motion which is denoted by second differential of x with respect to time, i.e. $a = \frac{d^2x}{dt^2}$. This on combination with Eq. 4.1 gives

$$m\frac{d^2x}{dt^2} = -kx \qquad \text{...(4.4)}$$

Using Eq. 4.2 for x, we find

$$\frac{d^2x}{dt^2} = -4\pi^2\nu_{osc}^2 x_0 \cos 2\pi\nu_{osc} t = -4\pi^2\nu_{osc} x \qquad ...(4.5)$$

$\because \; x = x_0 \cos 2\pi\nu_{osc} t$

$$\frac{dx}{dt} = -x_0 2\pi\nu_{osc} \sin 2\pi\nu_{osc} t$$

$$\frac{d^2x}{dt^2} = -x_0 (2\pi\nu_{osc})^2 \cos 2\pi\nu_{osc} t$$

$$= -4\pi^2\nu_{osc}^2 x_0 \cos 2\pi\nu_{osc} t$$

The results of Eqs. 4.4 and 4.5 on combination give

$$-kx = -4\pi^2\nu_{osc}^2 xm$$

From the above equation, we can get the expression for the force constant, k as

$$k = 4\pi^2\nu_{osc}^2 m \qquad ...(4.6)$$

and that for the oscillation frequency, ν_{osc} as

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad ...(4.7)$$

Thus, for a given spring with force constant, k and a particle of mass, m there is only one oscillation frequency possible, ν_{osc}, which is independent of the maximum displacement of the particle. This is called **characteristic frequency** of the harmonic oscillator.

4.2.4 Potential Energy Curve

If F_{ext} is the external force applied to displace the particle by a distance dx, the work done in doing so is stored as potential energy (P.E.), dV. Thus

$$dV = F_{ext}\, dx \qquad ...(4.8)$$

Note that work is given as follows:
work = force × distance

Since the external force is equal and opposite of the restoring force ($-F$) exerted by the spring, we can write

$$dV = -F\, dx \qquad ...(4.9)$$

or

$$\frac{dV}{dx} = -F = kx \quad \text{or} \quad dV = kx\, dx \qquad ...(4.10)$$

If equilibrium position is taken as that of zero potential enrgy, integration of above equation gives

$$V = \frac{1}{2}kx^2 \qquad ...(4.11)$$

Since potential energy varies linearly with the square of the displacement, a plot of V vs. x gives a parabola as shown in Fig. 4.3.

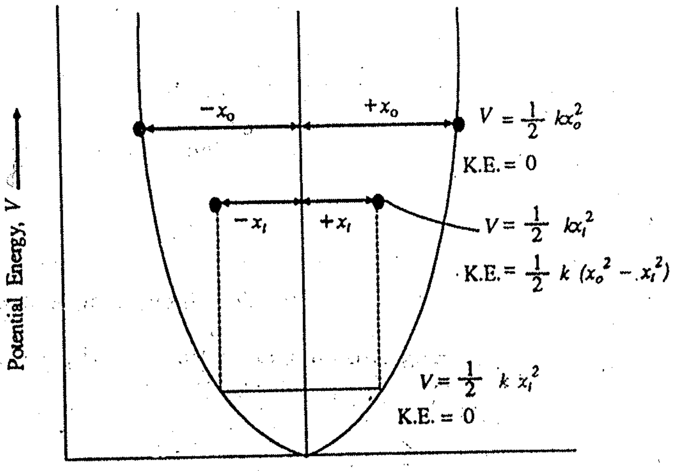


Fig. 4.3: Potential energy curve of the harmonic oscillator.

Now let us imagine that the particle has been displaced by a distance x_0 and released. When it is displaced by a distance x_0, at that point it has gained a potential energy of $\frac{1}{2}kx_0^2$. After its release, say at a time t if the displacement is x_t, then its potential energy be $\frac{1}{2}kx_t^2$. The difference, $\frac{1}{2}kx_0^2 - \frac{1}{2}kx_t^2$ represents the kinetic energy of the particle which is given by $\frac{1}{2}mv^2$ where v is the velocity of the particle at a displacement x_t. Thus one can determine the velocity of the particle at a displacement x_t if one knows the values of m, k, x_0 and x_t.

Thus,

$$\text{K.E.} = \frac{1}{2}k\,(x_0^2 - x_t^2) = \frac{1}{2}mv^2 \qquad \text{...(4.12)}$$

Using $v = \frac{dx}{dt}$, we can write

$$\text{K.E.} = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = 2\,m\pi^2\nu_{\text{osc}}^2 x_0^2 \sin^2(2\pi\nu_{\text{osc}}t) \qquad \text{...(4.13)}$$

$$\text{P.E.} = \frac{1}{2}kx_t^2 = 2\,m\pi^2\nu_{\text{osc}}^2 \cos^2(2\pi\nu_{\text{osc}}t) \qquad \text{...(4.14)}$$

$$\text{Total energy} = \frac{1}{2}kx_0^2 = 2\,m\pi^2\nu_{\text{osc}}^2 x_0^2 \qquad \text{...(4.15)}$$

$\because\ x = x_0 \cos 2\pi\nu_{\text{osc}}t$

$\frac{dx}{dt} = -x_0\, 2\pi\nu_{\text{osc}} \sin 2\pi\nu_{\text{osc}}t$

$\left(\frac{dx}{dt}\right) = x_0^2\, 4\pi^2\nu_{\text{osc}}^2 \sin^2 2\pi\nu_{\text{osc}}t$

4.2.5 Quantisation and Energy Levels

As you have been introduced in Unit 2 of the "Atoms and Molecules" Course (CHE-01), the motion of a microscopic particle can be described in quantum machanics by Schrödinger's wave equation. Similarly, the motion of a harmonic oscillator, if the particle involved is microscopic in nature, can be discussed by solving Schrödinger wave equation. We shall not go into the details of the solution, however, we shall use the results obtained which are very interesting.

The wave equation of this system is given as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0 \qquad \text{...(4.16)}$$

where ψ is the wave function of the oscillator, h is Planck's constant and E is the total energy of the oscillator. The solution of this equation gives the energy, E as given below:

$$E = \frac{h}{2\pi}\sqrt{\frac{k}{m}}\left(\text{v} + \frac{1}{2}\right) \qquad \text{...(4.17)}$$

where v is an integer and can take values 0, 1, 2, ...etc. and is known as **vibrational quantum number.**

You may remember from Unit 2 of 'Atoms and Molecules' (CHE-01) course that Schrödinger Equation for a particle in one - dimension can be given as follows:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

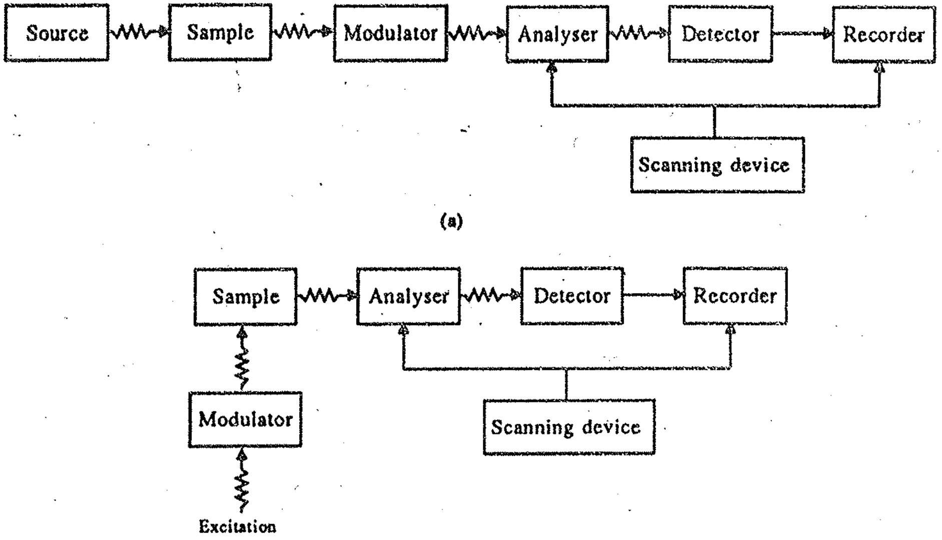
Thus, for $V = \frac{1}{2}kx^2$, we get

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0$$

Using Eq. 4.7, we can write Eq. 4.17 as given below:

$$E = h\,\nu_0\left(\text{v} + \frac{1}{2}\right) \qquad \text{...(4.18)}$$

The expression for E given in Eq. 4.18 deserves some further analysis. It shows that E has different values for different values of v. Increasing v by one integer increases the



(a)

(b)

Fig.1.5: Schematic representation of (a) an absorption spectrophotometer and (b) an emission spectrophotometer.

can expect dark lines for each of these absorptions. This is shown in Fig. 1.6 (a). Fig 1.6 (b) shows an emission spectrum which shows discrete set of lines, each corresponding to the emission of radiation (energy) when the system changes from the higher energy state to the lower energy state. In this transition, the electronic configuration of the atom changes and it gives a signal in the spectrum of the sample.

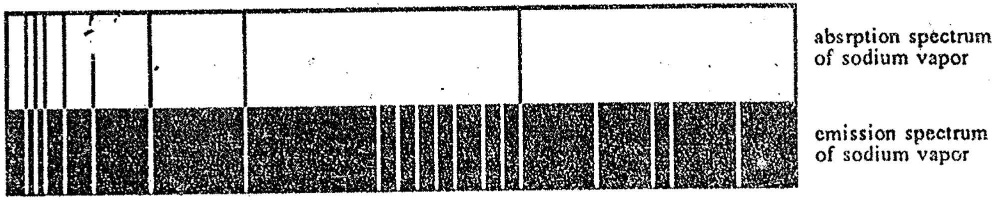


Fig.1.6: (a) A typical absorption spectrum; (b) An emission spectrum.

Since in this unit, we will be restricting our discussion to the spectra of atoms, we will be mainly concerned with the transition of electrons from one atomic energy level to the other. Let us start our study of atoms with the simplest atom, i.e., hydrogen.

Keep in mind that the value of E_n given by Eq. 1.7 is correct when the mass of the nuclei is infinite. Strictly speaking, when the motion of the nuclei is also taken into account, the value of E_n is given as follows:

$$E_n = \frac{-Z^2 e^4 \mu}{8 \varepsilon_0^2 h^2 n^2}$$

where μ is the reduced mass of hydrogen atom.

1.4 THE ATOMIC SPECTRUM OF HYDROGEN

The hydrogen atom has a single electron. You can recall from Sec. 1.10, Unit 1, Block 1 of 'Atoms and Molecules' course (CHE-01) that the energy of an electron in nth orbit of the hydrogen atom, E_n, can be given by the following expression.

$$E_n = \frac{-Z^2 e^4 m}{8 \varepsilon_0^2 h^2 n^2} \qquad \dots (1.7)$$

where Z is the atomic number,

e is the charge of the electron,

m is the mass of the electron,

ε_0 is the permittivity in vacuum and has the value
$8.854 \times 10^{-12}\ \mathrm{C^2\,N^{-1}\,m^{-2}}$,

h is Planck's constant,

and n is the number of the orbit.

Let us consider the energy difference between the first and the second energy state. This can be given as

$$\Delta E = E_2 - E_1 = \frac{-Z^2e^4m}{8\varepsilon_0^2h^2n_2^2} - \frac{-Z^2e^4m}{8\varepsilon_0^2h^2n_1^2}$$

$$= \frac{Z^2e^4m}{8\varepsilon_0^2h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{... (1.8)}$$

Using Eq.1.5, we can say that the wave number of the radiation associated with the above energy difference can be expressed as given in Eq.1.9.

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{Z^2e^4m}{8\varepsilon_0^2h^3c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{... (1.9)}$$

The term $\dfrac{Z^2e^4m}{8\varepsilon_0^2h^3c}$ is called the **Rydberg constant** and is denoted by symbol R_{H} for hydrogen. Thus, we can rewrite Eq.1.9 as given below:

$$\bar{\nu} = R_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{... (1.10)}$$

The experimental value of Rydberg constant as obtained from spectral data is $1.09677 \times 10^7\ \mathrm{m^{-1}}$.

The theoretical value of Rydberg constant can be calculated by substituting the values of various terms as given below:

$$R_{\mathrm{H}} = \frac{Z^2e^4m}{8\varepsilon_0^2h^3c}$$

$$= \frac{(1)^2 \times (1.602 \times 10^{-19}\ \mathrm{C})^4 \times 9.109 \times 10^{-31}\ \mathrm{kg}}{8 \times (8.854 \times 10^{-12}\ \mathrm{C^2\,N^{-1}\,m^{-2}})^2 \times (6.626 \times 10^{-34}\ \mathrm{J\,s})^3 \times 2.998 \times 10^8\ \mathrm{m\,s^{-1}}}$$

$$= 1.09737 \times 10^7\ \mathrm{m^{-1}}$$

The theoretical value of Rydberg constant is denoted by R_∞.

This difference between the experimental value of Rydberg constant (R_{H}) and theoretical value of Rydberg constant (R_∞) is about 60 $\mathrm{cm^{-1}}$. This is because the calculation was made on the basis of an infinitely massive nucleus. If we take into account the finite mass of the nucleus then we have to consider the hydrogen atom as a two particle system having masses m_1 and m_2.

$$\nu_{\text{osc}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{... (4.28)}$$

$$V = \frac{1}{2}k(r - r_e)^2 \qquad \text{... (4.29)}$$

$$\text{K.E.} = \frac{1}{2}\mu v^2 \qquad \text{... (4.30)}$$

where ν_{osc} is the characteristic oscillational frequency of the system under consideration, and $v = \mathrm{d}(\Delta r)/\mathrm{d}t$.

The vibrations in diatomic molecule can be treated in a similar way. Instead of the spring with force constant k, we have in the case of diatomic molecules binding of the two nuclei through a bond with a force constant k and these nuclei oscillate with a characteristic oscillational frequency, ν_{osc}.

Extending the similarity further the wave equation for oscillation in diatomic molecule can be given similar to Eq 4.16 viz.

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}(\Delta r)^2} + \frac{8\pi^2\mu}{h^2}\left[E - \frac{1}{2}(\Delta r)^2\right]\psi = 0 \qquad \text{... (4.31)}$$

and the expression for energy similar to Eq. 4.17 can be given as

$$E = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(\mathrm{v} + \frac{1}{2}\right) \qquad \text{... (4.32)}$$

4.3.1 Zero Point Energy

Let us study the above equation more carefully. You will realise that even for v = 0, the energy E is not zero and the molecule oscillates with a definite value of frequency. The energy at v = 0 is given by $E_0 = \frac{1}{2}h\,\nu_{\text{osc}}$ and is referred to as **zero point energy.** The zero point energy corresponds to the energy of the molecule in the vibrational ground state.

4.3.2 Infrared Spectra and Selection Rules

If infrared radiations are passed through a sample of diatomic molecules in the gas phase and the transmitted radiations are analysed through the monochromator and detector of a spectrometer (for details of working see - Unit 9) an infrared spectrum is obtained. The infrared spectrum results from the absorption of radiation causing transition from one energy level to another. The observed line position in the spectrum gives information about the difference between the energy levels. However, the intensity of the spectral lines gives information about the population of levels involved in the transition. The spectrum so obtained is characteristic of the diatomic molecule under investigation. The spectrum is employed to get information about the vibrations of the molecule and interactions between the vibrational and rotational motions.

The infrared spectral bands observed for HCl are shown schematically in Fig. 4.6. Notice a signal with a strong intensity followed by two more of weak intensity (Fig. 4.6 a). The positions of the signals are given in terms of frequency of radiation absorbed, $\bar{\nu}$ (cm^{-1}).

The frequency, ν (sec^{-1}) $= c\,\bar{\nu}$ (cm^{-1}), where c is the velocity of light.

Because of various broadening mechanisms as well as rotational fine structure, these signals do not appear as single lines but appear as bands. Depending on the resolution of the equipment used, the bands show different type of features and fine structure as shown in Fig. 4.6 (c). We shall try to understand salient points of this spectrum in the following sections.

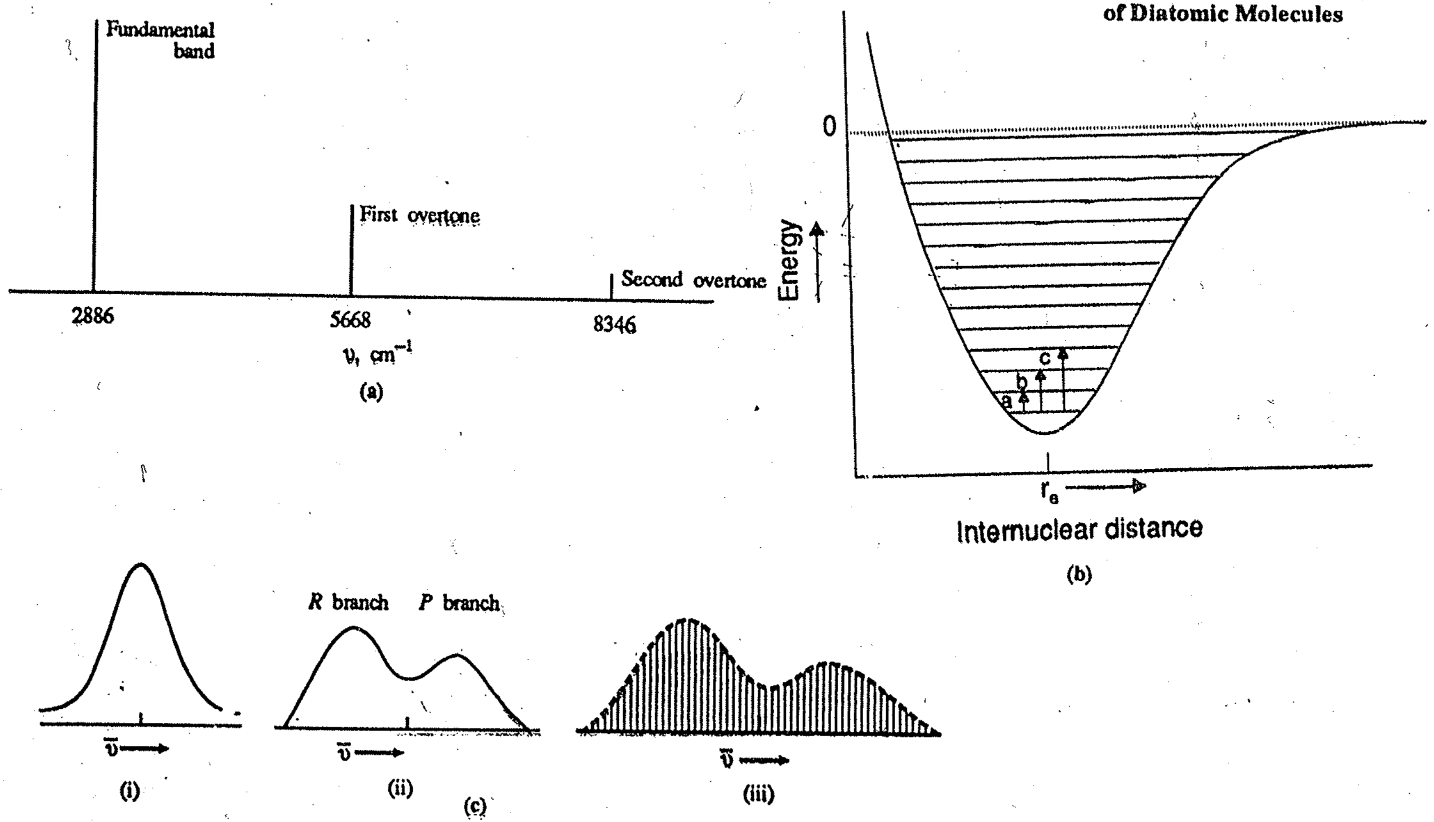


Fig. 4.6 (a): Schematic representation of the positions and intensities of first three bands of HCl. The number in notation $0 \rightarrow 1$, $0 \rightarrow 2$ and $0 \rightarrow 3$ indicate the initial and final levels of each transition.

(b) A typical potential energy curve for a diatomic molecule. The minimum in the curve r_e corresponds to the equilibrium distance between the atoms. Horizontal lines represent vibrational levels. Transitions shown by a, b and c are the fundamental, first overtone and second overtone, respectively. The deviation from equal spacing between energy levels is due to anharmonicity, as you will study in Sec 4.4.

(c) Fundamental band of HCl under (i) low, (ii) moderate and (iii) high resolutions.

As given in Fig. 4,4, the energy levels for diatomic molecules, when considered similar to those of harmonic oscillator, are equidistant with an energy gap equal to $h\,\nu_{osc}$ where ν_{osc} is the vibrational frequency of the diatomic molecule in sec^{-1} and h is Planck's constant. A promotion of the diatomic oscillator from a lower level to an upper level can take place if an external energy, equal to the energy gap between the two levels, is supplied. If the energy supplied is in the form of an electromagnetic radiation with frequency ν sec^{-1}, a transition will occur if $E = E_2 - E_1 = h\,\nu$ where E_2 and E_1 denote energies of the final and the initial levels. Note the difference between ν and ν_{osc}; the former denotes the frequency of electromagnetic radiation whereas the latter denotes the oscillational frequency of the diatomic molecule. If the quantum numbers, v for final and initial levels are given by v_f and v_i respectively, then

$$h\nu = h\,\nu_{osc}\,(v_f - v_i) \qquad \text{... (4.33)}$$

An absorption of radiation takes place and the oscillator flips from energy level with quantum number v_i to that with v_f as shown in Fig. 4.7. The transitions for which Δ v = 1 are called **fundamental transitions** and those with Δv = 2,3,4 etc. are called **first, second, third etc. overtones** respectively.

Eq. 4.33 shows that *a fundamental transition takes place if the frequency of electromagnetic radiation is equal to the oscillation frequency of the diatomic molecule. The overtone transitions take place if the frequency of electromagnetic radiation is an integral multiple of the oscillational frequency.*

$$\bar{\nu} = R_H \left(\frac{1}{(1)^2} - \frac{1}{n_2^2} \right) \qquad \text{... (1.13)}$$

When we substitute the above values of n_2 in Eq.1.13, we can get the values for $\bar{\nu}$. For example,

when $$n_2 = 2, \bar{\nu} = R_H \left(\frac{1}{1} - \frac{1}{(2)^2} \right) = R_H \left(1 - \frac{1}{4}\right) = R_H \times \frac{3}{4} = \frac{3}{4} R_H$$

Thus, we can get

$$\bar{\nu} = \frac{3}{4} R_H, \frac{8}{9} R_H, \frac{15}{16} R_H, \frac{24}{25} R_H \,\text{.......}\, \text{cm}^{-1}$$

for $n_2 = 2, 3, 4, 5,$ ... respectively.

Such a series of lines with above wave numbers was observed in the atomic spectrum of hydrogen by Lyman and is called **Lyman series** after him. Experimentally, this series was observed in the **ultraviolet region** of the electromagnetic spectrum. You can see the lines corresponding to this series in Fig. 1.9 and also in detail in Fig. 1.8.

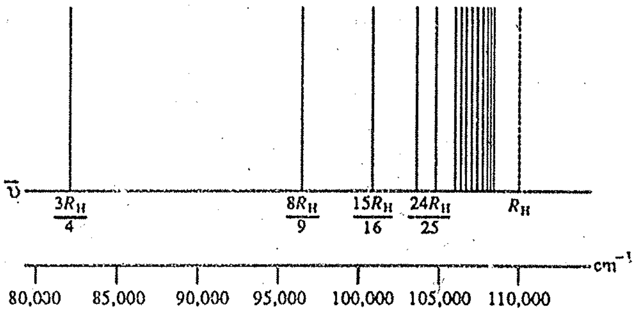


Fig.1.8: Lyman series showing convergence at $\bar{\nu} = R_H$.

You can see in Fig. 1.8 that when $\bar{\nu} = R_H$, there is a **continuum** after this point in the spectrum. From Eq. 1.13, you can see that $\bar{\nu} = R_H$ only when $n_2 = \infty$. In other words, this represents the removal of the electron from the atom which means ionisation of the atom. **Thus, we can measure the ionisation energy of the electron by knowing R_H or $\bar{\nu}$.**

The value of $\bar{\nu}_H$ as determined from the observed spectrum of hydrogen also led to the calculation of precise value of R_H which is equal to 109677.581 cm^{-1}.

Wave number is related to energy as

$$1\,\text{cm}^{-1} = 1.987 \times 10^{-23}\,\text{J}.$$

Ionisation energy can be obtained with the help of photoelectron spectrosocpy which you will study in detail in Sec. 1.12 of this unit.

Similar series of spectral lines called **Balmer, Paschen, Brackett** and **Pfund** series were also observed for $n_1 = 2, 3, 4, 5$ respectively and $n_2 = (n_1 + 1), (n_1 + 2), (n_1 + 3)$.... etc. The energy levels, electronic transitions and spectral lines corresponding to these series are shown in Fig.1.9.

Decreasing spacing between spectral lines for Balmer series of hydrogen spectrum.

n_2	Observed $\bar{\nu}$(cm^{-1})	Calculated $\bar{\nu}$(cm^{-1})	Spacing $\bar{\nu}$(cm^{-1})
3	15230	15233	5340
4	20570	20565	2460
5	23030	23032	1340
6	24370	24373	810
7	25180	25181	530
8	25710	25706	

Fig. 1.9 also shows that in each series as the value of n_2 **increases**, the separation between the energy levels **decreases**. In other words, separation between the spectral **lines decreases** with **increasing** value of n_2 till it reaches a convergence limit at $n_2 = \infty$. As you know this convergence limit represents the ionisation of the electron, any energy greater than this limit, if supplied to the system, will only increase the kinetic energy of the ejected electron and will result in the **increase** in the velocity of the ejected electron. Since the kinetic energy is not quantised, it can be increased any **amount** by supplying energy to the electron and that is why the spectrum in this region shows a **continuum.**

Till this point, we have been successful in explaining the origin of different lines in the atomic spectrum of hydrogen. However, when closely observed, hydrogen spectrum reveals a fine structure. For example, in the Lyman series, every line was observed to be consisting of two lines (doublet) very close to each other. Thus, unless these lines were properly resolved, these two lines appeared as a single line. The spectrum becomes more complicated for other series where every line shows a multiplet structure.

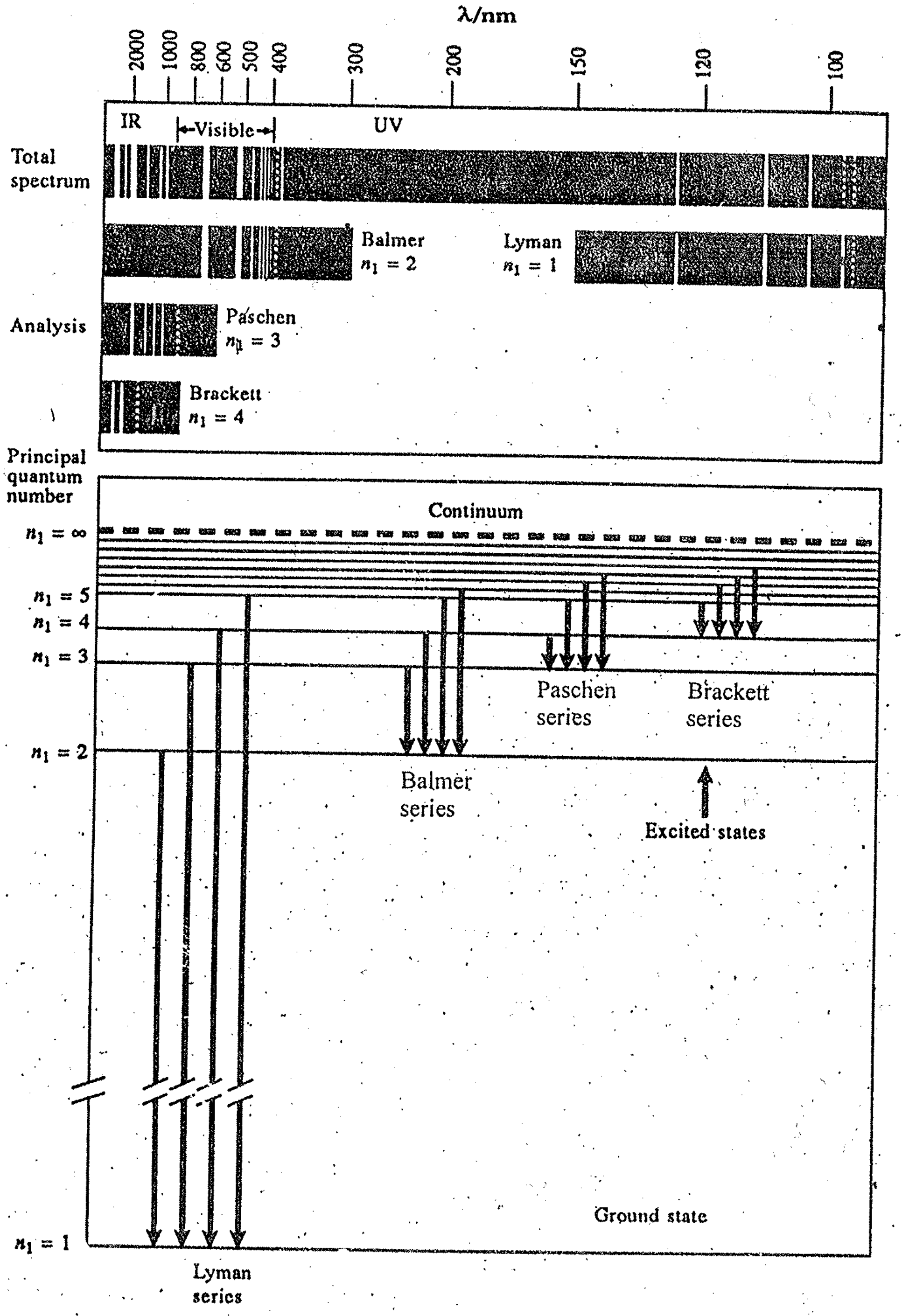


Fig. 1.9: A sketch of energy levels for various series of spectral lines observed in the atomic spectrum of hydrogen.

Let us study the next section to find out the reason for the fine structure of hydrogen atom spectrum.

But before that you can check your understanding of the above section by answering the following SAQ.

And since the fundamental transition takes place with electromagnetic radiation of frequency equal to oscillational frequency, we can write that

$$\frac{\nu_{HCl}}{\nu_{DCl}} = \frac{\bar{\nu}_{HCl}}{\bar{\nu}_{DCl}} = \sqrt{2} \qquad \ldots (4.40)$$

Thus when HCl is changed to DCl, the fundamental transition in infrared spectrum is observed at a lower frequency of electromagnetic radiation than that for HCl and the ratio between these frequencies is given by Eq. 4.40.

In general, we can say that

$$\frac{\nu^{l}}{\nu} = \sqrt{\frac{\mu}{\mu^{l}}}$$

where ν^{l} and μ^{l} denote the frequency and the reduced mass for the isotopically substituted molecule.

SAQ 2

If the fundamental transition for O–H species is observed at 3735 cm^{-1}, find out the position of the corresponding transition for O–D species.

……………………………………………………………………………………………………

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SAQ 3

Calculate the ratio between the zero point energies of HCl and DCl.

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……………………………………………………………………………………………………

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4.3.5 Vibrational Term Value

Eqs. 4.28 and 4.32 give expression for energy of diatomic oscillator as follows:

$$E = h\nu_{osc}(\mathrm{v} + \frac{1}{2}) \qquad \ldots (4.41)$$

If we divide both sides of Eq 4.41 by hc, we get

$$\frac{E}{hc} = \frac{\nu_{osc}}{c}(\mathrm{v} + \frac{1}{2}) \qquad \ldots (4.42)$$

The term E/hc is referred to as the **term value** $G(\mathrm{v})$ and the term ν_{osc}/c, the **harmonic frequency** $\bar{\nu}_{osc}$. Both $G(\mathrm{v})$ and $\bar{\nu}_{osc}$ have the units of wave number i.e. cm^{-1}, thus giving the new expression for energy of the vibrational levels in term values as follows.

$$G(\mathrm{v}) = \bar{\nu}_{osc}(\mathrm{v} + \frac{1}{2}) \quad (\text{in } cm^{-1}) \qquad \ldots (4.43)$$

This is a convenient expression for equating the frequency of the oscillator, $\bar{\nu}_{osc}$ with the frequency of the electromagnetic radiation absorbed for fundamental transition of the harmonic oscillator, $\bar{\nu}$ as given below:

For $\mathrm{v} = 0,\ G(0) = \frac{1}{2}\bar{\nu}_{osc}$ ... (4.44)

and for $\mathrm{v} = 1,\ G(1) = \frac{3}{2}\bar{\nu}_{osc}$ ... (4.45)

Thus, $G(1) - G(0) = \bar{\nu}_{0\rightarrow 1} = \bar{\nu}_{osc}$ ... (4.46)

It may be further noted that Eq. 4.44 represents the zero point energy in cm^{-1}

4.4 ANHARMONICITY

As was shown in Fig. 4.3, the potential energy curve of a harmonic oscillator is a parabola. Increase of displacement x_0 continuously shows an increase in the energy. In a diatomic molecule where change in the internuclear distance, Δr_0 is equated to the displacement, x_0 of harmonic oscillator, it is not realistically possible to expect higher and higher potential energy with increasing value of Δr_0 since after a certain increase in bond distance, dissociation takes place and the molecule breaks into the constituent atoms. The true variation of the potential energy with internuclear distance and the potential energy function for harmonic oscillator model of diatomic molecule are shown in Fig. 4.8.

Also note that in an anharmonic oscillator the energy levels are not equally spaced in contrast to the case of a harmonic oscillator shown in Fig. 4.4.

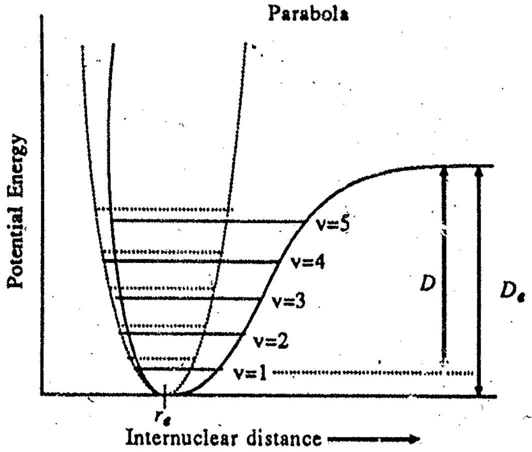


Figure 4.8 : The variation of potential energy with internuclear distance for a diatomic molecule is shown by solid line. The potential energy function for a harmonic oscillator is shown by broken line.

The deviation from harmonic oscillator behaviour is termed as **anharmonicity.** Note that the minimum in the curve occurs at r_e, the equilibrium internuclear distance. You can also see that in the vicinity of r_e, the curve very closely approximates the harmonic oscillator. However, at larger internuclear separation, the anharmonic curve shows significant deviation from the harmonic curve.

You will now study about the Morse Potential function which gives a better agreement with the real curve.

4.4.1 Morse Potential

A mathematical equation for expressing the potential energy of diatomic molecule was given by P.M. Morse and is called Morse potential. This can be written as follows.

$$V(\Delta r) = D_e\left[1 - e^{-\beta\Delta r}\right]^2 \qquad \text{... (4.47)}$$

where $\Delta r = r - r_e$, D_e is dissociation energy of the molecule measured from the minimum of the curve and β a constant is given by

$$\beta = \nu_{osc}\sqrt{\frac{2\pi^2 c\mu}{D_e h}} \qquad \text{... (4.48)}$$

where π, c, h have their usual meaning and μ, D_e and ν_{osc} are respectively the reduced mass, dissociation energy and oscillational frequency.

Unlike a parabola, Morse curve allows for dissociation at high energy.

The dissociation energy, D_e measured at the minimum of the P.E. curve is called the *equilibrium dissociation energy.* However, the *spectroscopic dissociation energy,* D_0 is energy of the lowest vibrational level (v = 0). Thus,

$$D_0 = D_e - \frac{1}{2}h\nu_{osc}$$

4.4.2 Energy Levels of Anharmonic Oscillator and Selection Rules

Since in our analysis of IR transitions, we are mainly concerned with bond distance

Now what will be the value of m_l for $l = 0$? It will be zero as per Eq.1.19 and the angular momentum will also be zero according to Eq 1.15.

Similarly, for $l = 1$, $m_l = +1, 0, -1$ from Eq.1.19. When we substitute these integral values of m_l in Eq.1.18, we get z components of angular momentum (m_l) as given below:

When $m_l = +1, \quad \mathbf{l}_z = 1.\ \hbar \ = \hbar$ ...(1.20a)

$m_l = 0, \quad \mathbf{l}_z = 0\,\hbar$ ...(1.20b)

$m_l = -1, \quad \mathbf{l}_z = -1.\ \hbar \ = -\hbar$ ...(1.20c)

Also note in Fig. 1.10(c) that the values of $\mathbf{l}_z$ for $l = 1$ are $-\hbar$, 0 and $+\hbar$.

The angular momentum **l** and its $\mathbf{l}_z$ components for $l = 1(m_l = +1, 0, -1)$ are shown in Fig.1.10(c).

Remember that the magnitude of angular momentum (**l**) whose z components are given by the above Eqs.1.20a, 1.20b, 1.20c, is given by Eq.1.15 as

$$
\begin{aligned}
|\mathbf{l}| &= \sqrt{l\,(l+1)}\,\hbar \\
&= \sqrt{1\,(1+1)}\,\hbar \\
&= \sqrt{2}\,\hbar
\end{aligned}
\qquad \text{...(1.21)}
$$

Thus, **the magnitude of angular momentum vector** for $l = 1$ is $\sqrt{2}\ \hbar$. This is shown in Fig.1.10(b).

Going back to Eq. 1.20, we can say that the z component of the angular momentum has precise values. If we apply **Heisenberg uncertainty principle** it says that the angle of orientation of the angular mementum vector around the z-axis is **completely indefinite.** Thus, there is an equal probability of locating the angular momentum vector in all the directions around z axis. Thus, this vector takes the conical shape as shown in Fig.1.10(c). Note that vector $m_l = 0$, has no z component ($\mathbf{l}_z = 0$) lies in the xy–plane.

You will study in Sec. 1.10 that this degeneracy can be lifted in the presence of the magnetic field.

It is also worth mentioning here that the energy of electron depends on the **magnitude of the angular momentum and not on its direction.** This leads us to conclude that all the values of m_l (corresponding to a particular l) have same value of **l** and have equal energy and are, therefore, **degenerate.**

Note that in case of hydrogen atom, the energy depends upon the principal quantum number (n) only but for multi-electron systems it depends both on n and l.

Vector Nature of Spin Angular Momentum

You should not confuse between s and m_s. The spin quantum number s of an electron (which is generally referred as spin) has the value $\frac{1}{2}$. But m_s, which is the magnetic spin quantum number for the z component of spin angular momentum can take the values $+\frac{1}{2}$ and $-\frac{1}{2}$.

You are aware that the spin quantum number s is equal to 1/2. The quantum laws again specify that spin angular momentum, s, can take only those directions for which its components in the reference direction (s_z) are **half integral** multiples of $\hbar$. Thus,

$$\mathrm{s}_z = m_s\,\hbar$$

where m_s is equal to +1/2 or –1/2 and is known as *spin magnetic quantum number.*

The allowed directions for the spin angular momentum vectors are shown in Fig. 1.11.

At this juncture, you have enough knowledge of orbital and spin angular momenta. Therefore, we can now proceed to the concept *of total angular momentum* as given by Eq. 1.17.

$$\cos\theta = \frac{\mathrm{s}_z}{|\mathrm{s}|} = \frac{m_s\hbar}{\sqrt{s\,(s+1)}\,\hbar}$$

When $m_s = +\frac{1}{2}$

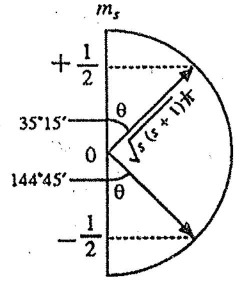


Fig. 1.11: The allowed directions of spin angular momentum for an electron.

Similar to Eqs. 1.15 and 1.16, we can represent **j** in terms of **total angular momentum quantum number,** j such that the magnitude of **j** can take the following values:

$$|\mathbf{j}| = \sqrt{j(j+1)}\,\hbar = \sqrt{j(j+1)} \text{ in units of } \hbar \qquad ...(1.22)$$

where j can take values $|(l+s)|,\ |(l+s-1)|,\ ...,\ |(l-s)|$

Let us find out j for an s electron.

Here $l = 0$ and $s = \frac{1}{2}$.

Thus $j = |(l+s)|,\ |(l+s-1)|,\ ...,\ |(l-s)|$

$$= |(0+\tfrac{1}{2})|,\ |(0+\tfrac{1}{2}-1)|, ...,\ |(0-\tfrac{1}{2})|$$

$$= |\tfrac{1}{2}|,\ |(-\tfrac{1}{2})|$$

$$= \frac{1}{2}$$

Hence, $\mathbf{j} = \sqrt{j(j+1)j}\,\hbar$

$$= \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar$$

$$= \sqrt{\frac{1}{2}\cdot\frac{3}{2}}\,\hbar = \frac{\sqrt{3}}{2}\hbar$$

Next we will do similar steps for a p electron. For a p electron, $l = 1$ and $s = \frac{1}{2}$. Substituting these values of l and s in the following expression,

$$|j| - |(l+s)|,\ |(l+s-l)|, ..., |(l-s)|$$

we get, $j = \left(1+\frac{1}{2}\right),\ \left(1-\frac{1}{2}\right)$

$$= \frac{3}{2},\ \frac{1}{2}$$

These two values of j yield $\mathbf{j} = \sqrt{\frac{15}{2}}\,\hbar$ and $\sqrt{\frac{3}{2}}\,\hbar$ using Eq. 1.22.

The two values of **j** represent two values of energy; thus, indicating the existence of two energy levels of a p electron corresponding to $l = 1$. It may also be emphasised here that all p-levels will be split into two energy levels corresponding to $j = 1/2$ and $j = 3/2$, irrespective of whether they are $2p$, $3p$, $4p$ ..... states.

Similarly, for a d level when $l = 2$ and $s = \frac{1}{2}$, we can say that

$$\cos\theta = \frac{\frac{1}{2}\hbar}{\sqrt{s(s+1)}\,\hbar}$$

$$= \frac{\frac{1}{2}}{\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}}$$

$$= \frac{\frac{1}{2}}{\sqrt{\frac{3}{4}}} = \frac{1}{\sqrt{3}}$$

$\therefore\ \theta = 35°\,15'$

When $m_s = -\frac{1}{2}$

$$\cos\theta = \frac{-\frac{1}{2}\hbar}{\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\hbar} = -\frac{1}{\sqrt{3}}.$$

Therefore, $\theta = 144°\,45'$

For s electron

$l = 0, s = \frac{1}{2}$

$j = |(l+s)|,\ |(l+s-1)|,\ ...\ |(l-s)|$

$j = \left|\left(0+\frac{1}{2}\right)\right|, \left|\left(0+\frac{1}{2}-1\right)\right|, ...\ |(0-\frac{1}{2})|$

$= \frac{1}{2}$

For p electron

$l = 1, s = \frac{1}{2}$

$j = |(1+\frac{1}{2})|,\ |(0+\frac{1}{2}-1)|, ...\ |(1-\frac{1}{2})|$

$= \frac{3}{2}, \frac{1}{2}$

For d electron

$l = 2, s = \frac{1}{2}$

$j = |(2+\frac{1}{2})|,\ |(2+\frac{1}{2}-1)|,\ ...(2-\frac{1}{2})$

$= 5/2, 3/2$

Note that $l + s$ gives the maximum value of j and $l - s$ (or $s - l$ if $s > l$) gives the minimum value of j. The j can take all positive values from maximum to minimum, the succesive values deffering by one unit only.

For an s electron only the spin angular momentum is responsible for the total angular momentum.

number corresponds to the rotational quantum number (J). The transitions described above are shown in Fig. 4.9.

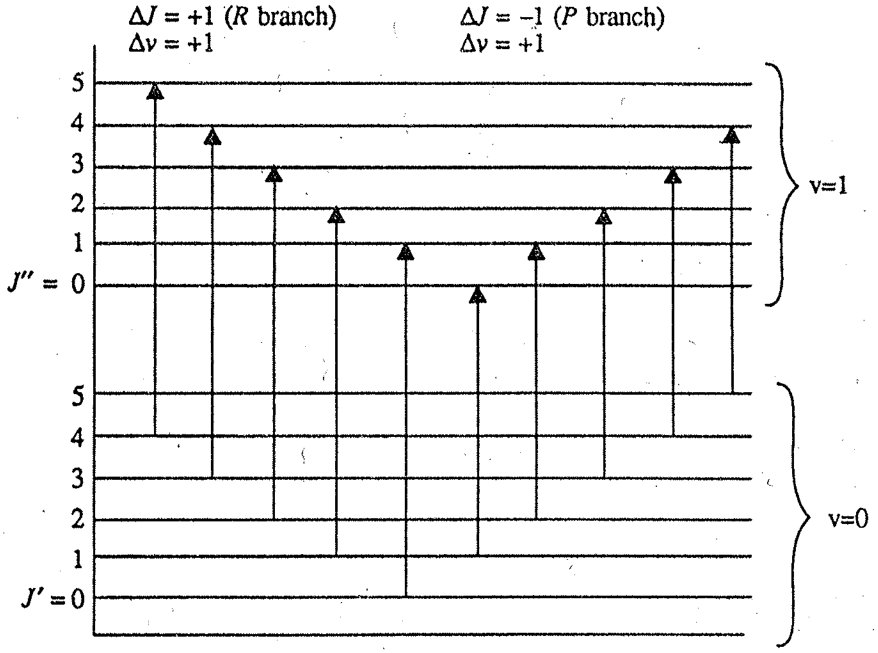


Fig. 4.9: The series of transitions with $\Delta v = +1$ and $\Delta J = \pm 1$.

For the vibrational transition $\Delta \nu = +1$, the series of transitions with $\Delta J = -1$ is called ***P* branch** and the series of transitions with $\Delta J = +1$ is called ***R* branch.** For harmonic oscillator and rigid rotator model

$$\begin{aligned}\Delta E_{v,J} &= E_{v',J'} - E_{v''J''} \\ &= h\nu_{osc}(v' - v'') + Bhc\,[J'(J'+1) - J''(J''+1)] \qquad \text{... (4.61)}\end{aligned}$$

For $v' = 1$ and $v'' = 0$, the R branch is represented by $J' = J'' + 1$ and P branch is represented by $J' = J'' - 1$. The energy expressions for the two branches are given below and they are shown schematically in Fig. 4.10.

$$\Delta E_{v,J} = h\nu_{osc} + 2Bhc\,(J''+1)\,,\ R \text{ branch} \qquad \text{... (4.62)}$$

where $J'' = 0, 1, 2...$

and $$\Delta E_{v,J} = h\nu_{osc} - 2BhcJ''\,,\ P \text{ branch} \qquad \text{... (4.63)}$$

where $J'' = 1, 2, 3...$

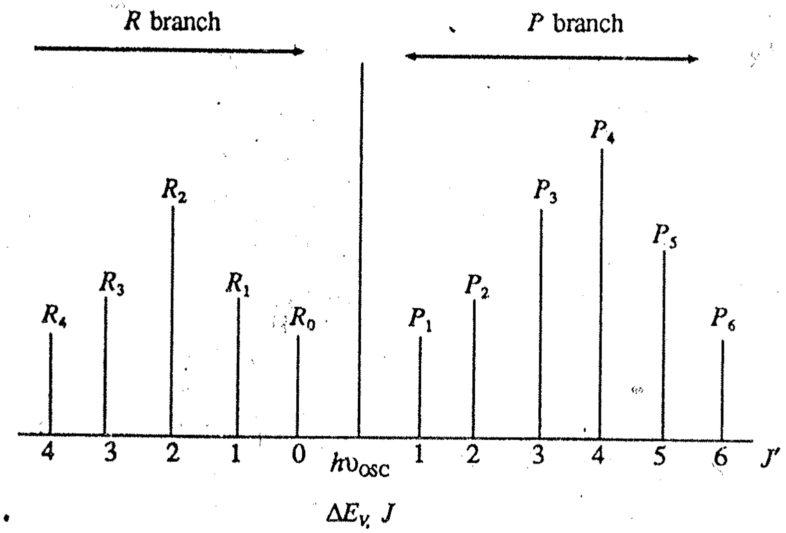
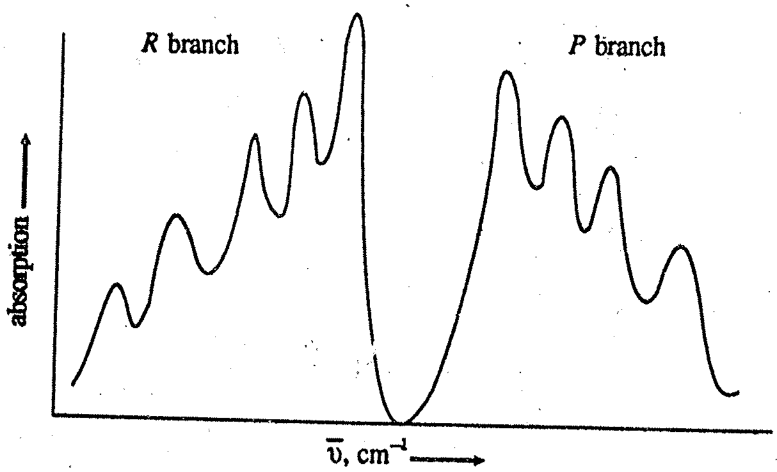


Fig. 4.10: P and R branches showing energies of transitions with varying J'' values.

Since $\Delta J = 0$ is not allowed, the transitions with $\Delta E_{v,J} = h\nu_{osc}$ is not observed under these conditions. This is referred to as **Q branch.** The infrared spectrum of a diatomic molecule with this model will have two rotational vibrational bands with a dip in the centre corresponding to $\Delta J = 0$ as shown in Fig. 4.11. In working out the expressions for $\Delta E_{v,J}$ given by Eqs. 4.62 and 4.63, it is assumed that the diatomic molecule behaves like a rigid rotator and harmonic oscillator and also that the rotational constant B does not vary with the vibrational quantum number. In practice, however, these assumptions are not true and the expressions get slightly modified when these assumptions are taken into consideration.



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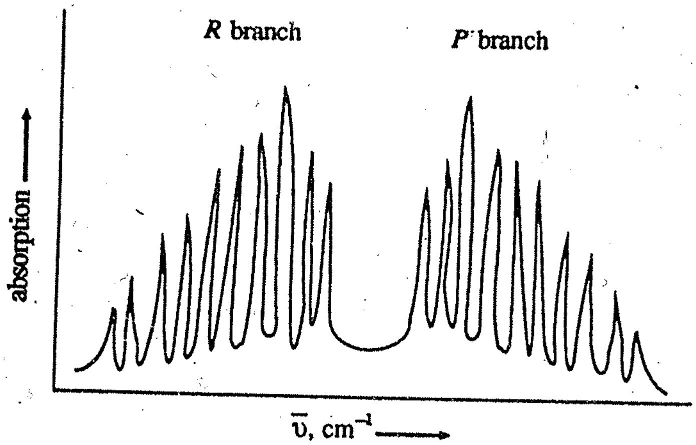

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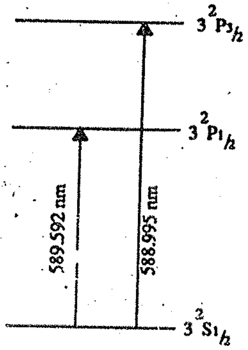
Fig. 4.11: The vibrational rotational infrared spectrum of a diatomic molecule with rigid rotator and harmonic oscillator model.

4.5.3 Symmetric Top Vibrating Rotator Model

As mentioned in Unit 3, a diatomic molecule can be considered as linear rotator if mass of electrons is ignored. The moment of inertia in the direction of the internuclear axis is zero and the moments of inertia in the other two directions (x, y) perpendicular to this axis are equal and nonzero. In case the mass of the electrons is also considered the moment of inertia in the z-direction is small but finite and therefore, $I_x = I_y >> I_z$. This is referred to a symmetric top model. The selection rules under these conditions for vibrational-rotational transitions get modified as $\Delta v = \pm 1$ and $\Delta J = 0, \pm 1$. The molecules belonging to this category thus will have all the three (P, Q, R) branches allowed and the infrared spectrum has a central branch (Q) surrounded by two branches P and R on the low and high energy side of the Q branch. It is found that for HCl molecule only P and R branches are observed in the vibrational rotational infrared spectrum whereas for NO molecule all the three branches observed.

momentum. Thus, these elements can be considered similar to hydrogen atom as far as their spectrum is concerned. The energy level diagram of sodium is shown in Fig. 1.13.



Energy level diagram for transitions corresponding to D-lines of sodium.

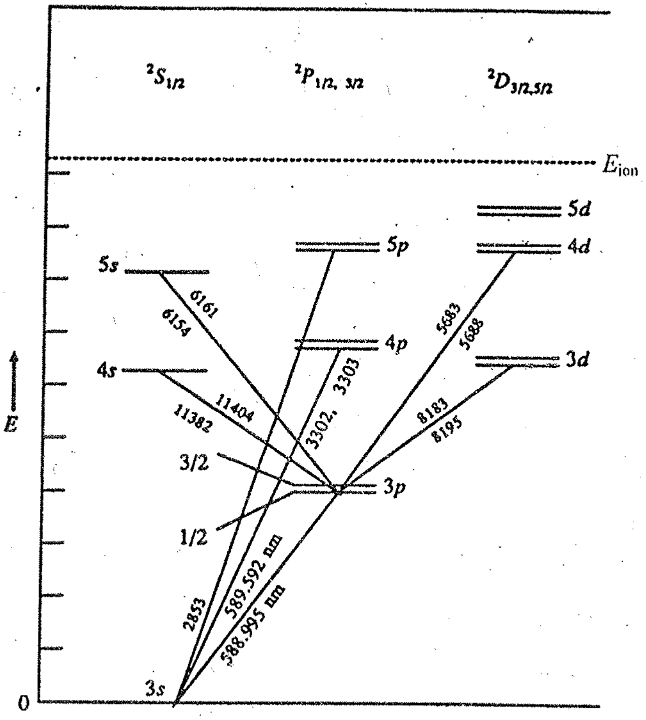


Fig. 1.13: The energy level diagram of sodium atom.

Here, the 3*s* electron will require least energy to get excited as compared to the inner electron of first and second shell. Similar to the hydrogen atom, there are two energy levels available (corresponding to $j = \frac{3}{2}$ and $j = \frac{1}{2}$) at the 3*p*, 4*p*, ... etc. levels. The 3*s* electron can be excited to any of these two 3*p* levels and the energy required for these excitations corresponds to 588.995 nm and 589.592 nm. These two lines of atomic spectrum of sodium are commonly known as *D*-lines (Fig. 1.13). Also note that on further absorption of energy this electron from 3*p* levels can be promoted to higher *s* and *d* states ($\Delta l = +1$). But we will not go into details of these transitions and stop our discussion of spectrum of sodium here. Other species such as He^+, Be^+ and B^{2+} which have one electron in their outermost shelll show a spectrum similar to hydrogen.

For 3*s* to 3*p* (or 4*p*, 5*p*,... transitions, $\Delta l = +1$.

SAQ 4

Calculate the difference in the energy of the energy levels in J units corresponding to two *D* lines in the atomic spectrum of sodium if $\Delta \bar{\nu} = 17.19\ \text{cm}^{-1}$.

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1.7 MULTI–ELECTRON SYSTEMS

So far, you have studied about the spectra of atoms containing a single electron in their outermost orbit. In this section, we will discuss the spectrum of multi-electron atoms which have more than one electron in their outermost orbit.

In these kinds of atoms, interelectronic interactions also affect the energy states. There are two ways in which the orbital and spin angular momenta of many electron systems can combine. The first method is called the *L–S* coupling (or the Russel–Saunders coupling) and the second method is called the *j – j* coupling. Let us now study about these two schemes. We will discuss *L–S* coupling in detail because it is more relevant to our discussion regarding lighter elements.

L–S Coupling

This scheme of coupling explains the atomic spectra of elements having atomic number upto 30. In this method, we assume that the orbital angular momenta of all the electrons combine to give the **total orbital angular momentum, L**. Similarly, the spin angular momenta of various electrons can be combined to give **total spin angular momontum, S**. Finally, the total orbital angular momentum and total spin angular momentum could be added to get the **total angular momentum, J**.

Total orbital angular momentum $|\mathbf{L}| = \sqrt{L(L+1)}$ in units of $\hbar$ ...(1.23)

where L is the **total orbital angular momentum quantum number** and can be obtained according to the following equation for the electrons 1 and 2.

$$L = |(l_1 + l_2)|,\ |(l_1 + l_2 - 1)|, \ldots, |(l_1 - l_2)| \qquad \ldots (1.24)$$

Eq. 1.24 is also known as Clebsch– Gordan series.

Note that

$$\vec{L} = \sum \vec{l_i}$$

where l_i is the angular momentum of individual electron.

Also, $M_L = \sum m_{l_i}$

where m_{l_i} is the z component of angular momentum of individual electron and M_L gives the component of total angular momentum in the z – direction.

Similarly we can write **total spin angular momentum, S** of individual electrons 1, 2, ... etc. as

$$|\mathbf{S}| = \sqrt{S(S+1)} \text{ in units of } \hbar \qquad \ldots (1.25)$$

where S is the **total spin quantum number** of individual electrons. It can be obtained by summation of the individual quantum numbers $s_1, s_2, \ldots$ etc. of electrons 1, 2, ... etc. and can take the values as

$$S = |(s_1 + s_2)|,\ |(s_1 + s_2 - 1)|, \ldots, |(s_1 - s_2)| \qquad \ldots (1.26)$$

Similarly

$$\vec{S} = \sum s_i$$

where s_i is the spin angular momentum of the individual electron.

Also,

$$M_S = \sum m_{s_i}$$

where m_{s_i} is the z – component of spin angular momentum of individual electron and M_S is the component of total spin angular momentum in the z – direction.

Now, we have **L** and **S** as given by Eqs.1.23 and 1.25 and can calculate **J**. For this the L and S can be obtained from Eqs. 1.24 and 1.26 and combined to give J such that

$$J = |(L + S)|,\ |(L + S - 1)|, \ldots, |(L - S)| \qquad \ldots (1.27)$$

This total angular momentum quantum number, J is related to total angular momentum, **J**, as

$$|\mathbf{J}| = \sqrt{J(J+1)} \text{ in units of } \hbar \qquad \ldots (1.28)$$

Thus, from the above equation, we can calculate **J** values corresponding to various values of J, which correspond to various energy levels for a given atom.

With this we finish our discussion of *L–S* coupling. Before going to the next section which deals with the Atomic Spectrum of Helium, let us briefly go through what is known as *j–j* coupling. For larger atoms, the orbital angular momentum and the spin angular momentum of each individual electron is combined to yield total angular momentum j as given below:

$$l_1 + s_1 = j_1$$

Then, $j_1, j_2, \ldots$ for all electrons are combined to finally yield **J** as

$$\mathbf{J} = j_1 + j_2 + \ldots$$

Let us now study about the atomic spectrum of helium.

(iii) At high resolution rotational fine structure shows *P* and *R* branches and a dip is observed in the place of *Q* branch since transitions with $\Delta J = 0$ are not allowed.

Terminal Questions

1. $h\nu_{osc}$

2. The energy of the molecule at v = 0, i.e. at vibrational ground level is called zero point energy.

3. $\Delta v = \pm 1$ for harmonic oscillator

   $\Delta v = \pm 1, \pm 2, \pm 3$ etc. for an anharmonic oscillator.

4. ~ 22,540 cm^{-1}.

UNIT 5 INFRARED SPECTRA OF POLYATOMIC MOLECULES

Structure

5.1 INTRODUCTION

In the previous unit, we learnt the principles of vibrational spectra of diatomic molecules. We have explained the aspects like spacings between vibrational levels and also the concept of zero point energy. The vibration-rotation spectra of diatomic molecules have also been discussed.

In this unit, we will study the IR spectra of molecules containing more than two atoms, i.e., polyatomic molecules. First, we shall discuss the number of vibrational degrees of freedom for linear and nonlinear molecules. We will proceed to explain the energy level scheme for water molecule. Then we will learn to identify the presence of functional groups in organic compounds with the help of chart of group frequencies. We will also discuss how the isotopic substitution, inductive effect, resonance effect, hydrogen bonding and steric effect affect the group frequencies in IR spectra. Finally in the Appendix part, we shall outline the steps involved in the analysis of IR spectra of molecules.

Objectives

After studying this unit you should be able to:

- calculate the number of vibrational modes in polyatomic molecules,
- discuss the energy level scheme for water,

But if the helium atom is already present in the excited triplet state, its configuration in the lowest level will be $1s^1 2s^1$. From this level one electron can be excited to higher **triplet** levels. ($\Delta S = 0$). These transitions are shown in Fig. 1.14 (b). Let us study the transition from $1s2s$ to $1s2p$ level.

For the $1s2s$ triplet level.

$$\begin{aligned} M_s &= m_{s_1} + m_{s_2} \\ &= \frac{1}{2} + \frac{1}{2} \\ &= 1;\ \text{hence } S = 1. \end{aligned}$$

$$L = l_1 + l_2 = 0 + 0 = 0$$

$$J = L + S = 0 + 1 = 1$$

Term symbol of this atomic state ${}^{2S+1}L_J$ will be ${}^3S_1$.

Thus, the configuration $1s^1 2p^1$ gives size to ${}^1P_1$ (singlet) as well as ${}^3P_{2,1,0}$ (triplet) states.

For a $1s2p$ level (which is an excited state).

$$M_s = m_{s_1} + m_{s_2} = \frac{1}{2} + \frac{1}{2} = 1.\ \text{Thus } S = 1.$$

So,

$$2S + 1 = 2 \times 1 + 2 = 3$$

$$\begin{aligned} L &= \left|\left(l_1 + l_2\right)\right|, \left|\left(l_1 + l_2 - 1\right)\right|, \ldots, \left|\left(l_1 + l_2\right)\right| \\ &= (0+1), (0+1-1)), \ldots, |(0-1)| = 1, 0 \\ J &= |(L+S)|, |(L+S-1)|, \ldots, |(L-S)| \\ &= |(L+S)|, |(L+S-1)|, \ldots, |(L-S)| \\ &= (1+1), (1+1-1), (1-1) \\ &= 2, 1, 0 \end{aligned}$$

Thus, the term symbols for this level will be

$${}^{2S+1}L_J = {}^{2\times 1+1}P_{2,1,0} = {}^3P_{2,1,0}$$

Thus, this level has three states corresponding to ${}^3P_2$, ${}^3P_1$, ${}^3P_0$. Its triplet nature is indicated by the $2S + 1 (= 3)$ value as a superscript in the atomic term symbol. You should also keep in mind that the subscript gives the value of J, the total angular momentum quantum number associated with a particular state.

Let us now come to the transitions from ${}^3S_1$ to ${}^3P_2$, ${}^3P_1$ and ${}^3P_0$ states.

To check whether these are allowed or not, let us calculate J for them.

$$\text{For } {}^3S_1 \longrightarrow {}^3P_2;\ \Delta J = 2 - 1 = 1$$

$$\text{For } {}^3S_1 \longrightarrow {}^3P_1;\ \Delta J = 1 - 1 = 0$$

$$\text{and}\quad \text{For } {}^3S_1 \longrightarrow {}^3P_0;\ \Delta J = 0 - 1 = -1$$

Thus, $\Delta J = +1, 0$ and -1.

This is in accordance with the selection rule $\Delta J = \pm 1, 0$. So these transitions are allowed. Thus, these transitions will appear as triplets in the atomic spectrum.

Further transitions from ${}^3P$ states to ${}^3D$ or ${}^3S$ states are possible and give complex patterns. But we will not go into details of these transitions and that is the reason why these transitions are not shown in Fig. 1.14 (b).

At this stage, it is enough for you to know that the spectrum of helium shows two types of transitions, viz., from singlet to singlet and from triplet to triplet states. Since $\Delta S = 0$, transitions from singlet to triplet or triplet to singlet states are not allowed and are called spin forbidden transitions.

The alkaline earth metals such as beryllium, magnesium, calcium etc. and other species having two electrons in their valence shell show spectrum similar to that of helium.

Helium atoms in singlet states constitute *parahelium* and those in triplet states constitute *orthohelium*. Ordinary helium is a mixture of parahelium and orthohelium. Parahelium and orthohelium are inter convertible by exchange of energy.

SAQ 5

Why for the ground state of He atom having configuration $1s^2$, triplet state ($S = 1$) is not possible?

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1.9 SPECTROSCOPIC STATES OF CARBON

The electronic configuration of carbon is $1s^2\,2s^2\,2p^2$. We can term the two electrons in $2p^2$ orbital as equivalent as they have same values of n and l. The $1s$ and $2s$ orbitals being completely filled, do not contribute to the angular momentum. Therefore, only $2p^2$ electrons will be responsible for the angular momentum. For these two electrons, $l_1 = 1$ and $l_2 = 1$;

so
$$L = \left|\left(l_1 + l_2\right)\right|, \left|\left(l_1 + l_2 - 1\right)\right|, \left|\left(l_1 + l_2 - 1\right)\right| \ldots \left|\left(l_1 - l_2\right)\right|$$
$$= \left|(1+1)\right|, \left|(1+1-1)\right|, \left|(1+1-2)\right|$$
$$= 2, 1, 0$$

Hence, the corresponding states will be denoted by D, P and S. Similarly, S can also take values 0 and 1, depending upon whether the spins are paired or not. So, we have singlet and triplet levels for each of D, P and S states. Thus, the possible states are ^3D, ^3P, ^3S, ^1D, ^1P and ^1S.

By applying Pauli's exclusion principle, we can derive the allowed energy states which are ^1D, ^1S and ^3P states. To determine which one of the three states is a ground state, Hund's rule is used. According to this rule,

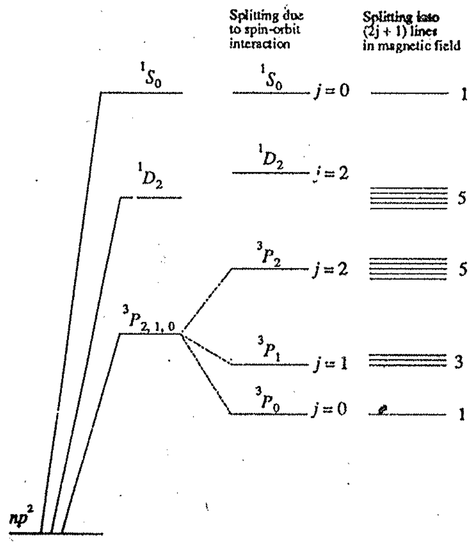

Fig. 1.15: Energy level diagram for carbon.

and d) while a nonlinear triatomic molecule has only one bending vibration (5.2 c). Thus for a linear triatomic molecule (e.g., CO_2), we could expect four vibrational modes, two stretching and two bending. Both these bending vibrations are identical in all respects except the direction. Such vibrations have same frequency (and energy) and, are said to be degenerate. For instance, the two bending vibrations of CO_2 are degenerate. As a result of this, only three absorption bands are found for CO_2 - two corresponding to the stretching vibrations and one to the bending vibration. A nonlinear angular triatomic molecule (e.g., H_2O) also has three vibrational modes, two being due to the stretching modes and one due to the bending mode. The difference between the linear and nonlinear triatomic molecules lies in the degeneracy of the bending mode of the former.

Degeneracy of a vibrational mode is the number of normal modes which have same energy. For instance, the degeneracy of ν_2 mode of CO_2 is two since the two bending modes (in-plane and out-of-plane) have same energy.

Using the materials in this section, answer the following SAQ.

SAQ 1

State the number of stretching and bending modes of C_2H_2.

5.3 IR SPECTRA OF SOME POLYATOMIC MOLECULES

First we shall discuss the IR spectrum of simple molecules like H_2O and CO_2.

5.3.1 IR Spectrum of H2O Molecule

As mentioned in the last section, water, a nonlinear molecule, has three normal modes of vibrations. Fig.5.3 shows the IR spectrum of water in an inert solvent.

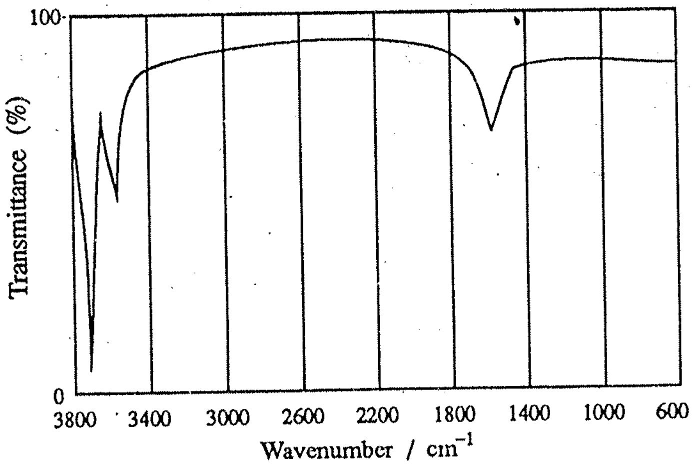

Fig.5.3 : Infrared spectrum (schematic) of H2O in an inert solvent showing three dominant absorptions.

We can notice two sharp bands at higher frequency region (at 3756 cm^{-1} and 3652 cm^{-1}) and one sharp band at lower frequency region (at 1595 cm^{-1}). Group theory can be used in assigning vibrational modes to the observed IR absorption frequencies. Two examples (H_2O and NH_3) are discussed in the Appendix part of this unit. The frequencies at 3652 cm^{-1}, 1595 cm^{-1} and 3756 cm^{-1} are associated with symmetric stretching, symmetric bending and antisymmetric stretching modes, respectively. All the three vibrations are associated with a change in dipole moment, which is a necessary condition for a vibration to be infrared active. It is also possible to draw vibrational energy level diagram corresponding to these three bands as in Fig. 5.4. The quantum numbers for each of the vibrational levels are shown below ν_1, ν_2 and ν_3. The quantum number notation is useful in identifying each of the energy sublevels. For instance, '000' means $\nu_1 = \nu_2 = \nu_3 = 0$; '010' means $\nu_1 = 0, \nu_2 = 1$ and $\nu_3 = 0$; '020' means $\nu_1 = 0, \nu_2 = 2$ and $\nu_3 = 0$ and so on. You can see that the wave number corresponding to the energy difference between $E(100)$ and $E(000)$ is $3652\,\text{cm}^{-1}$; the wave number corresponding to the energy difference between $E(010)$ and $E(000)$ is $1595\ \text{cm}^{-1}$ and the wave number corresponding to the energy difference between $E(001)$ and $E(000)$ is $3756\ \text{cm}^{-1}$. The three vibrational modes which are associated with the three IR bands are similar to those shown in Fig.5.2.

The notation '000' means that the molecule is in the vibrational energy level given by the quantum numbers, $(\nu_1 \nu_2 \nu_3) = (000)$.

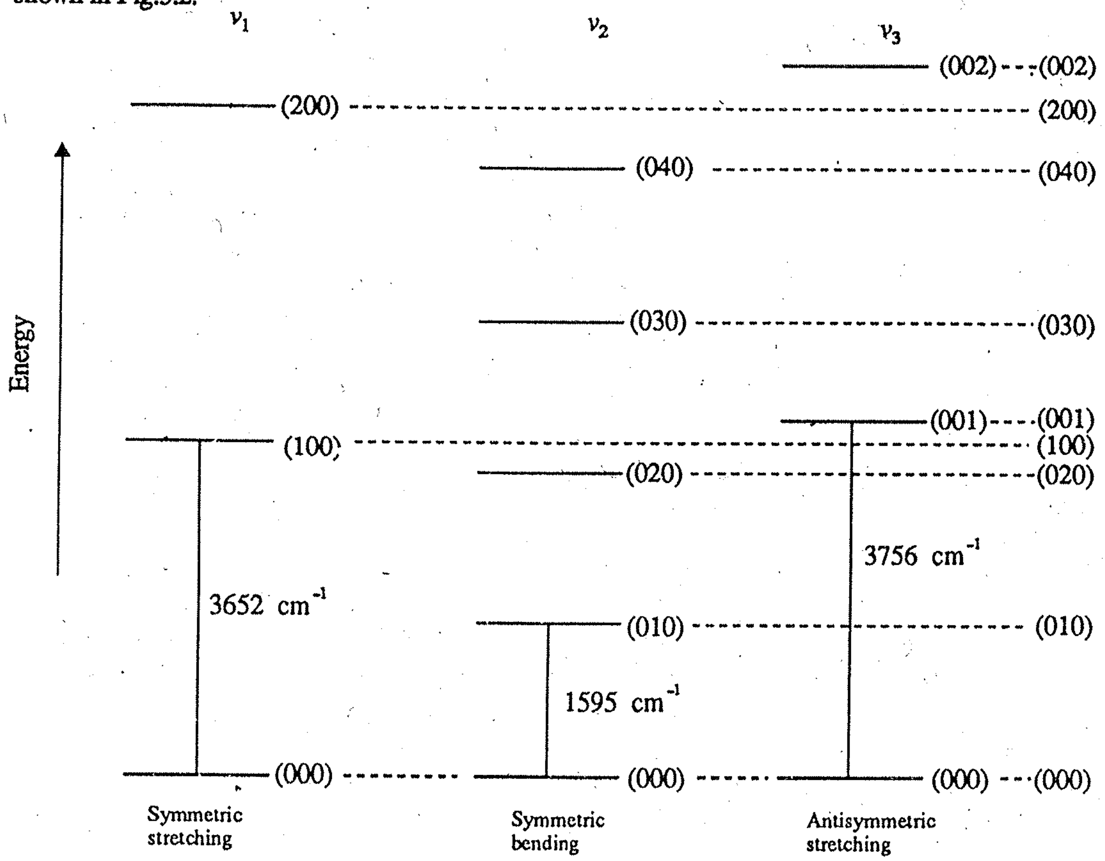

Fig. 5.4 : The three vibrational energy levels for water molecule.

The quantum mechanical vibrational energy of a polyatomic molecule containing N atoms is given by,

$$E\,(\nu_1\,\nu_2\,.....) = hc\ \sum\ (\nu_i + d_i/2)\,\bar{\nu}_i \quad \text{(summation over all } \nu_i)$$

where ν_i, d_i and $\bar{\nu}_i$ are the quantum number, degeneracy and fundamental frequency for a particular vibrational mode, ν_i. In case of H_2O, this equation can be written as

$$E(\nu_1\nu_2\nu_3) = hc\,[((\nu_1 + 1/2)\,3.652 \times 10^5)$$
$$+ ((\nu_2 + 1/2)\,1.595 \times 10^5) + ((\nu_3 + 1/2)\,3.756 \times 10^5)\,]\ \text{J}$$

Unit of E = units of $hc\bar{\nu}$
$= \text{J s m s}^{-1}\,\text{m}^{-1}$
$= \text{J}$

since degeneracy is 1 for each of the modes in H_2O molecule.

Using this equation, we can calculate the total zero point energy for H_2O molecule as shown below:

This is diagramatically represented in Fig. 1.16 below.

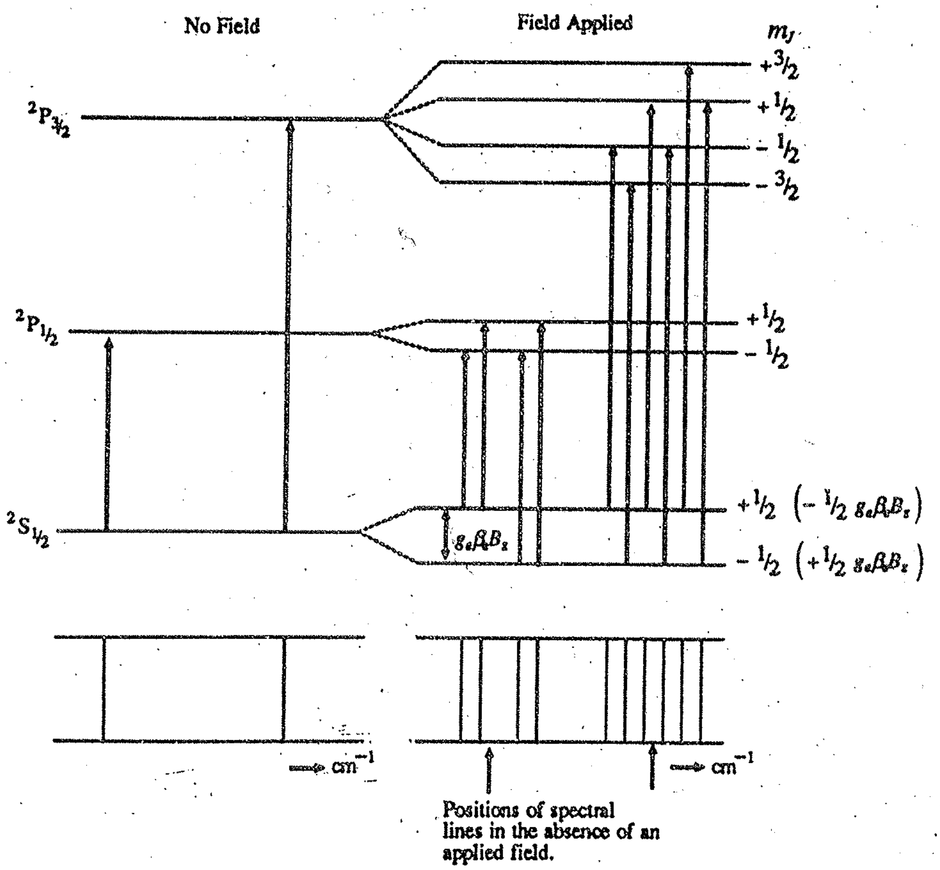

Fig.1.16: Splitting of various energy levels in the presence of magnetic field.

Thus, a transition from the lower $^2S_{\frac{1}{2}}$ level to $^2P_{\frac{1}{2}}$ level (which was a single line in the absence of magnetic field) will show **four lines** according to the four transitions possible in the presence of magetic field. In other words, we can say that the original single line in the absence of magnnetic field is split into **four** lines in the presence of magnetic field. Here, the additional selection rule is $\Delta m_J = 0, \pm 1$. Similarly, a transition from $^2S_{\frac{1}{2}}$ to $^2P_{\frac{3}{2}}$ yields **6 lines** in the presence of magnetic field.

Let us now understand the magnitude of splitting of these lines. If we calculate g_e for $^2S_{\frac{1}{2}}$, $^2P_{\frac{1}{2}}$, $^2P_{\frac{3}{2}}$ levels using Eq.1.30, we get, $g_e = 1, \frac{1}{3}$ and $\frac{2}{3}$, respectively for these levels. These values are in the ratio 3:1:2. Since splitting is proportional to g, these levels are split in the above ratio. In other words, we can say that **splitting is not uniform or equal for all the levels.** This is known as **anomalous Zeeman effect.** Now, you may be curious to know what is **normal Zeeman effect?** When the splitting of levels is **identical** in the presence of magnetic field, then the effect is known as **normal Zeeman effect**. For example, in helium atom consider the singlet states. For these states $2S + 1 = 1$. It yields, $S = 0$. Then, $L = J$. Therefore, from Eq. 1.30.

$$g_e = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$= 1 + \frac{J(J+1) + 0 - L(L+1)}{2J(J+1)}$$

$$= 1 + \frac{J(J+1) - J(J+1)}{2J(J+1)} = 1 + 0 = 1$$

[since $L = J$
$L(L+1) = J(J+1)$]

Therefore, from Eq.1.33, when $g_e = 1$ splitting will be identical and proportional to the applied magnetic field only and will have a constant value for a particular value of the applied magnetic field, B_z.

Thus, the Zeeman effect gives very useful information which can be used to deduce the term symbols in the following way:

i) Number of lines obtained in presence of magnetic field is related to the J value of the initial and final states involved in that particular transition.

ii) g_e values obtained from the splitting tell about the L and S values of the electron undergoing the transition.

In the next two sections, you will study about two techniques which help us in the experimental determination of energy levels of atoms.

1.8 X-RAY FLUORESCENCE SPECTROSCOPY

When an X–ray or a fast moving electron collides with an atom, its energy may be absorbed by the atom. In case the energy is sufficient to knock one of the electrons from the inner shell (K, L, M, etc.) of the atom, it removes the electron creating there a vacant position. Then, the outer electron falls into this vacant position and the X–ray photons are emitted in this process. The X–rays so emitted are characteristic of the element bombarded.

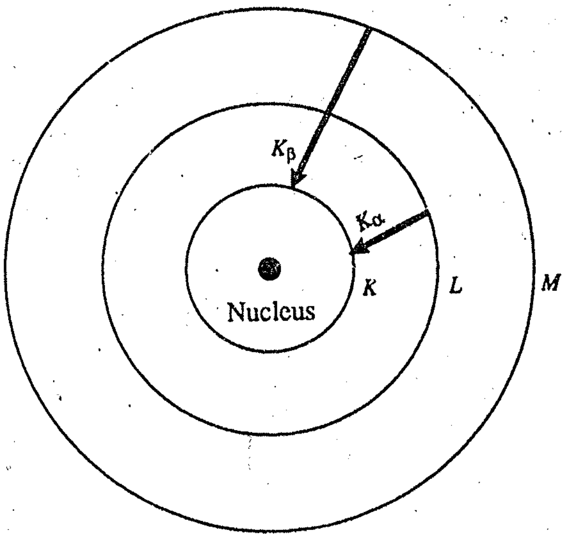

Fig. 1.17: Various shells of an atom.

Here, you should note that within a shell, there are many energy levels. The electron can be knocked off from any one of these levels (transitions between these may also take place) giving rise to a range of radiation. This is shown in Fig. 1.17.

In case the initial excitation is brought about by X–rays, the phenomenon is known as **flourescence.** In this case, the spectrum so obtained is termed as **X–ray fluorescence spectrum.** In such a spectrum, the emitted radiation is always lower in energy than the exciting X–rays.

The innermost shell is K shell and the maximum amount of energy is required to remove an electron from this shell.

When the transition of the electron (to fill the gap) takes place from the L to the K shell, the lines appearing in the spectrum are called K_α X–rays. These can be further subdivided as K_{α_1}, K_{α_2} ... etc. corresponding to the electrons originating from the various sublevels of the L shell. This is shown in Fig. 1.18.

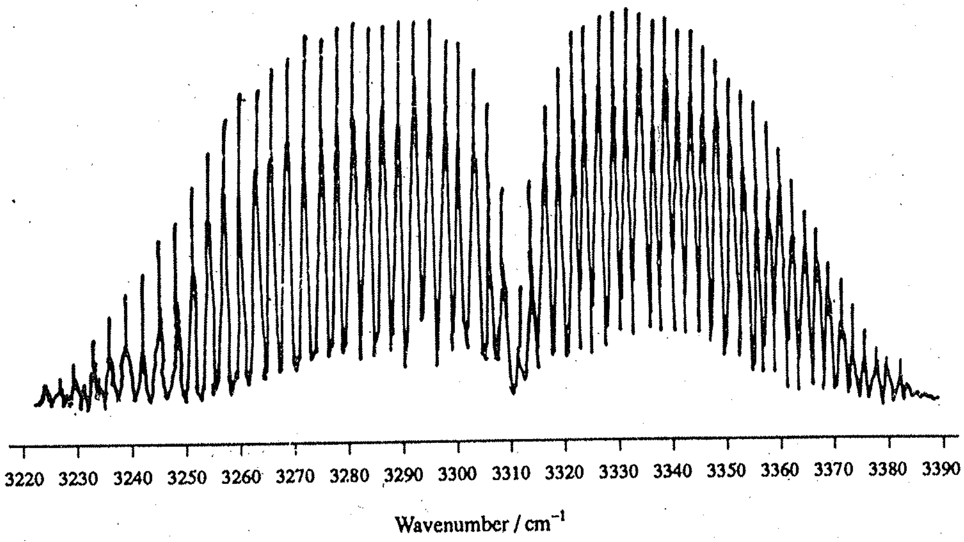

Fig.5.6 : Spectrum of symmetric stretching vibration of HCN molecule showing P and R branch lines.

For larger molecules, the value of B may be so small that separate lines can no longer be resolved in the P and R branches. In this case, rotational fine structure is lost and a typical PR contour is seen (Fig.5.7).

A nonlinear molecule cannot give rise to such a simple PR band and so, observation of PR band somewhere within a spectrum is a sufficient proof that the molecule is linear or nearly linear.

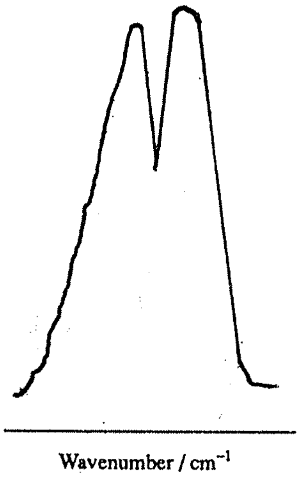

Fig.5.7 : Typical PR contour arising due to low resolution.

Perpendicular vibrations of linear molecules

The selection rule for these vibrations is given below:

$\Delta v = \pm 1, \quad \Delta J = 0, \pm 1$ for simple harmonic vibration

This means, a vibrational change could take place with no simultaneous rotational transition. You may remember that $\Delta J = 0$ corresponds to Q branch. The nature of the spectrum then depends on the difference between B values in the upper and lower levels. Normally these two values are not much different with the result that Q branch appears as a broad absorption band. If the rotational fine structure is unresolved, this band has the distinctive contour as shown in Fig. 5.8.

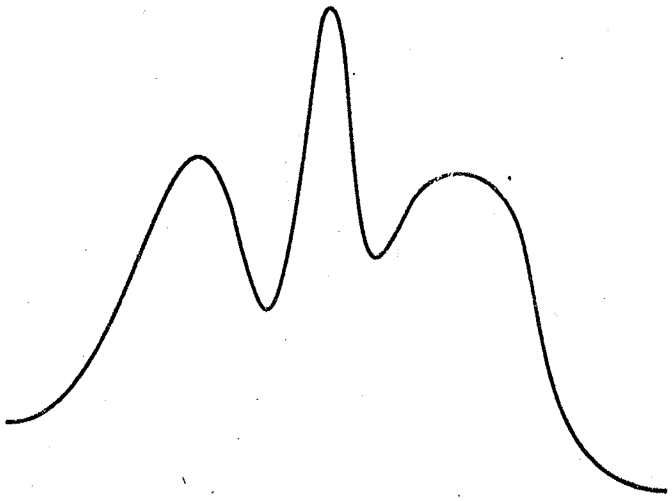

Fig. 5.8 : The contour of *PQR* band under low resolution.

The utility of studying vibration-rotation spectra is more for nonpolar molecules like CO_2, C_2H_2, CH_4 etc. for which dipole moment is zero. These molecules do not give rise to pure rotation spectra. These molecules however show infrared or Raman spectra. If these spectra exhibit resolved fine structure, the moment of inertia of the molecule can be obtained.

Although nuclear spin also has a significant effect on the rotational fine structure of vibration spectra, we do not intend studying the same.

Answer the following SAQ's.

SAQ 2

Assuming that $\bar{\nu}_1$, $\bar{\nu}_2$ and $\bar{\nu}_3$ of CO_2 are 1340 cm^{-1}, 667 cm^{-1} and 2349 cm^{-1}, calculate its zero point energy.
(**Hint :** Degeneracy (d_i) is 1 for ν_1 and ν_3 but 2 for ν_2).

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SAQ 3

Calculate the wavenumbers of the first and second overtones of ν_2 of CO_2. Use $\bar{\nu}_2$ from SAQ 2.

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5.4 GROUP FREQUENCY CONCEPT AND CHART OF GROUP FREQUENCIES

The normal modes of vibration can be divided into two types, namely, skeletal vibrations and the characteristic group vibrations. The skeletal vibrations involve displacements of all atoms to the same extent. The skeletal vibrations usually fall in the range 1400 – 700 cm^{-1}. The ether linkage, saturated hydrocarbon chain, aromatic rings etc. give rise to skeletal vibration bands. A complex pattern of bands may occur in the IR spectrum of a compound which could be identified as due to a particular skeletal structure. We shall discuss this later in this section.

The second type of normal modes known as the characteristic group vibrations involve the displacement of only a small portion of the molecule independent of the rest of the molecule. The absorption bands which arise due to the characteristic group vibrations are called **group frequencies.** The group frequencies are in general independent of the structure of the molecule as a whole. A few instances of the perturbation of group frequencies are discussed in the next section.

Many commonly occurring functional groups such as $-CH_3$, $>C=O$, $-NH_2$ etc. have characteristic group frequencies when they are present in a molecule. For example, all compounds containing a $-CH_3$ group possess absorption bands in the region of 2950 cm^{-1} (stretching) and 1400 cm^{-1} (bending). Similarly all compounds having the $>C=O$ group have a strong band at about 1700 cm^{-1}. Such group frequencies are listed in Table 5.3 which is also known as chart of group frequencies.

Table 5.3 : Group Frequencies

		Group	Intensity	Range/cm^{-1}	
A.	**Hydrocarbon chromophore**				
1.	**C – H STRETCHING**				
	a.	Alkane	(m-s)	2962-2853	
	b.	Alkene	(m)	3100-3000	
	c.	Alkyne	(s)	3300	
	d.	Aromatic	(v)	3030	
2.	**C – H BENDING**				
	a.	Alkane, C–H	(w)	1340	
		Alkane, CH_2	(m)	1485-1445	
		Alkane, CH_3	(m) (s)	1470-1430 1380-1370	and
		Alkane, *gem*-dimethyl (doublet)	(s) (s)	1385-1380 1370-1365	and
		Alkane, *tert*-butyl (doublet)	(m) (s)	1395-1385 ~ 1365	and
	b.	Alkene, monosubstituted (vinyl)	(s) (s) (s)	995-985 915-905 1420-1410	and
		Alkene, disubstituted, *cis*	(s)	690	
		Alkene, disubstituted, *trans*	(s) (m)	970-960 1310-1295	and

	Group	Intensity	Range/cm^{-1}	
	Alkene, disubstituted, *gem*	(s) (s)	895-885 1420-1410	and
	Alkene, trisubstituted	(s)	840-790	
c.	Alkyne	(s)	630	
d.	Aromatic substitution type:			
	Five adjacent hydrogen atoms	(v,s) (v,s)	750 700	and
	four adjacent hydrogen atoms	(v,s)	750	
	three adjacent hydrogen atoms	(v,m)	780	
	two adjacent hydrogen atoms	(v,m)	830	
	one hydrogen atom	(v,w)	880	
3.	**C–C MULTIPLE BOND STRETCHING**			
a.	Alkene, nonconjugated	(v)	1680-1620	
	Alkene, monosubstituted (vinyl)	(m)	1645	
	Alkene, disubstituted, *cis*	(m)	1656	
	Alkene, disubstituted, *trans*	(m)	1675	
	Alkene, disubstituted, *gem*	(m)	1653	
	Alkene trisubstituted	(m)	1669	
	Alkene tetrasubstituted	(w)	1669	
b.	Alkyne, monosubstituted	(m)	2140-2100	
	Alkyne, disubstituted	(v,w)	2260-2190	
c.	Aromatic	(v)	1600	
		(v)	1580	
		(m) (m)	1500 1450	and
B.	**Carbonyl chromophore**			
1.	**KETONES**			
a.	Saturated	(s)	1725-1705	
b	α,β–Unsaturated	(s)	1685-1665	
c.	Aryl	(s)	1700-1680	
2.	**ALDEHYDES**			
a.	Carbonyl stretching			
	Saturated, aliphatic,	(s)	1740-1720	
	α,β-Unsaturated, aliphatic	(s)	1705-1680	
	Aryl	(s)	1715-1695	
b.	C–H stretching (two bands)	(w) (w)	2900-2820 2775-2700	and

Group	Intensity	Range/cm^{-1}
3. ESTERS		
a. Carbonyl stretching		
Saturated, acyclic	(s)	1750-1735
Saturated, cyclic:		
δ-lactones (and larger rings)	(s)	1750-1735
γ- lactones	(s)	1780-1760
β-lactones	(s)	1820
Unsaturated:		
Vinyl ester type	(s)	1800-1770
α,β-unsaturated and aryl	(s)	1730-1717
α-ketoesters	(s)	1755-1740
β-ketoesters (enolic)	(s)	1650
b. C–O stretching		
All types of esters stated above; one or two bands	(s)	1300-1050
4. CARBOXYLIC ACIDS		
a. Carbonyl stretching:		
Saturated aliphatic	(s)	1725-1700
α,β –unsaturated aliphatic	(s)	1715-1690
Aryl	(s)	1700-1680
b. Hydroxyl stretching (bonded), several bands	(w)	2700-2500
c. Carboxylate anion stretching	(s) (s)	1610-1550 and 1400-1300
5. AMIDES		
a. Carbonyl stretching		
Primary, solid and concentrated solution	(s)	1650
Primary, dilute solution	(s)	1690
Secondary, solid and concentrated solution	(s)	1680-1630
Secondary, dilute solution	(s)	1700-1670
Tertiary, solid and all solutions	(s)	1670-1630
b. N–H stretching		
Primary, free: two bands	(m) (m)	3500 and 3400
Primary, bonded: two bands	(m) (m)	3350 and 3180
Secondary, free: one band	(m)	3430
Secondary,bonded: one band	(m)	3320-3140

Group	Intensity	Range/cm^{-1}
c. N–H bending		
Primary amides, dilute solution	(s)	1620-1590
Secondary amides, dilute solution	(s)	1550-1510
C. Miscellaneous chromophoric groups		
1. ALCOHOLS AND PHENOLS		
a. O–H stretching		
Free O–H	(v, sh)	3700-3600
Intermolecularly hydrogen bonded (changes on dilution)		
single bridge compounds	(v, sh)	3550-3450
Polymeric association	(s, b)	3400-3300
Intramolecularly hydrogen bonded (no change on dilution)		
Single bridge compounds	(v, sh)	3570-3450
Chelate compounds	(w,b)	3200-2500
b. O–H bending and C–O stretching		
Primary alcohols	(s) (s)	1050 and 1350-1260
Secondary alcohols	(s) (s)	1100 and 1350-1260
Tertiary alcohols	(s) (s)	1150 and 1410-1310
Phenols	(s) (s)	1200 and 1410-1310
2. Ethers		
C–O stretching		
Dialkyl ethers	(s)	1150-1070
Alkyl vinyl ethers or alkyl phenyl ethers	(s) (s)	1275-1200 and 1075-1020
3. AMINES		
a. N–H stretching		
Primary, free; two bands	(m) (m)	3500 and 3400
Secondary, free; one band	(m)	3500-3310
Imines (=N–H); one band	(m)	3400-3300
b. N–H bending		
Primary	(s-m)	1650-1590
Secondary	(w)	1650-1550

Group	Intensity	Range/cm^{-1}
c. C–N stretching		
Aromatic, primary	(s)	1340-1250
Aromatic, secondary	(s)	1350-1280
Aromatic, tertiary	(s)	1360-1310
Aliphatic	(w) (w)	1220-1020 and 1410
4. UNSATURATED NITROGEN COMPOUNDS		
a. C≡N stretching Alkyl nitriles	(m)	2260-2240
α,β – Unsaturated alkyl nitriles	(m)	2235-2215
Aryl nitriles	(m)	2240-2220
b. C=N stretching (imines, oximes)		
Alkyl compounds	(v)	1690-1640
α,β – Unsaturated compounds	(v)	1660-1630
c. C–NO_2, Nitro compounds		
aromatic	(s) (s)	1570-1500 and 1370-1300
aliphatic	(s) (s)	1570-1550 and 1380-1370
5. HALOGEN COMPOUNDS		
C–X stretching		
a. C–F	(s)	1400-1000
b. C–Cl	(s)	800-600
c. C–Br	(s)	600-500
d. C–I	(s)	500
6. SULFUR COMPOUNDS		
a. S–H stretching	(w)	2600-2550
b. C=S stretching	(s)	1200-1050
c. S=O stretching		
Sulfonamides	(s) (s)	1180-1140 and 1350-1300
Sulfonic acids	(s) (s) (s)	1210-1150 1060-1030 and 650

Abbreviations: s = strong, m = medium, w = weak, v = variable
b = broad, sh = sharp.

Now we will investigate in a detailed way the characteristic regions of IR absorption using which it is possible to identify the functional groups. We know that IR region falls between wavenumbers 4000 cm^{-1} and 600 cm^{-1}. The whole region can be divided into **four distinct regions** to facilitate easy identification of functional groups in a polyatomic organic molecule. The four distinct regions of absorption are given below:

4000 – 2500 cm^{-1}
2500 – 2000 cm^{-1}
2000 – 1500 cm^{-1}
1500 – 600 cm^{-1}

4000 – 2500 cm^{-1} region

The absorption occurring due to stretching of X–H bond (X = O, N and C) falls in this region. For organic compounds, the stretching vibrations noticed in this region invariably point out the presence of O–H, N–H or C–H. This region extends upto 2500 cm^{-1}

The **O–H stretching** band occurs at 3700 – 3600 cm^{-1} when not involved in hydrogen bonding. It is a relatively broad band. The O–H group of alcohols and phenols gives absorption in this region. Regarding the O–H stretching frequency of carboxylic acids, we shall discuss shortly under hydrogen bonding effect in Subsec. 5.5.3. The **N–H stretching** can be noticed between 3500 and 3100 cm^{-1}. The amines and amides give absorption in this region. The primary amines (having $-NH_2$ group) show a doublet structure (two sharp bands), while secondary amines, (having > N–H group) give only one sharp band. The tertiary amines understandably do not show absorption as these do not have N–H bond.

The **C–H stretching** from aliphatic compounds also occur in the range of 3300-2850 cm^{-1}. They are moderately broad. A little care has to be exercised while identifying C–H stretching, because C–H stretching of aromatic compounds occur as shoulder above 3000 cm^{-1}. To be precise, the shoulder of aromatic hydrogen atoms can be noticed around 3030 cm^{-1}. The antisymmetric and symmetric stretchings of methylene ($> CH_2$) and methyl ($-CH_3$) groups can be seen between 2965 and 2880 cm^{-1}. The C–H stretching vibrations of alkenes occur between 3100 and 3000 cm^{-1} while those of alkynes occur around 3300 cm^{-1}.

2500 – 2000 cm^{-1} region

The compounds containing triple bond absorb in this region. The triple bond corresponds to bond order three. The strength of the bond and hence the force constant is high. Since the vibrational frequency is directly proportional to the square root of force constant, the triple bonds absorb at higher frequency as compared to double and single bonds.

The **carbon-carbon triple bond** ($-C\equiv C-$) absorbs between 2300 and 2100 cm^{-1}. The band is normally of weak intensity. The nitrile group absorbs between 2300 – 2200 cm^{-1}. Further the band due to nitrile group is of medium intensity. Only by the intensities of the bands, these two groups can be distinguished. The change involved in dipole moment is greater for $-C\equiv N$ group than for $-C\equiv C-$ group. This is the reason for greater intensity of band for $-C\equiv N$ than for $-C\equiv C-$ group.

2000 – 1500 cm^{-1} region

All compounds having double bond show absorption in this region. The groups which exhibit significant absorption in this region are $>C=C<$ and $>C=O$. Among these two, the $C=O$ stretching is easy to recognise in the IR spectra. It is an intense band observed between 1830 and 1650 cm^{-1}. This absorption helps in identifying carbonyl group in organic compounds. The $C=C$ stretch is much weaker in character and can be noticed around 1650 cm^{-1}

1500 –600 cm^{-1} region

We have so far dealt with the groups which absorb above 1500 cm^{-1}. It is also easy to assign the bands above 1500 cm^{-1} to a particular group. But below 1500 cm^{-1}, it will not be easy to assign the bands. Especially in the region 1450-900 cm^{-1}, even structurally similar molecules give different absorption patterns. This is the reason for referring to this region as **fingerprint region.**

In this region, many of the single bonds such as C-C, C-N, C-O absorb, apart from absorptions due to **skeletal vibrations** mentioned at the beginning of this section. Further, there will also be coupling of vibrational bands. For example, $C-C$ stretching frequencies can couple with $C-H$ bending vibrations. Much useful information can be derived from the finger print region. We shall now see briefly the characteristic absorption in this region.

i) The $C-H$ stretching is between 1400-1000 cm^{-1} and it is an intense band.

ii) The aromatic rings and alkenes in general give rise to out-of-plane $C-H$ bending vibrations and can be seen between 1000-700 cm^{-1}.

iii) In substituted benzenes, the spectral pattern in this region give information whether it is monosubstituted or 1,2-,1,3- or 1,4- disubstituted. This is because C-H bonds adjacent to these substituted positions appear distinctively in 850-690 cm^{-1} region. The position of absorption band varies with respect to substitution pattern as shown below:

Monosubstituted	750 cm^{-1} and 700 cm^{-1}
o-disubstituted	750 cm^{-1}
m-disubstituted	780 cm^{-1}
p-disubstituted	830 cm^{-1}

iv) The compound containing *gem*-dimethyl groups ($>C(CH_3)_2$) has a doublet band at about 1375 cm^{-1}.

v) The compound containing a chain of at least four methylene groups shows band at 720 cm^{-1}.

We shall discuss the applications of IR spectra in structure determination in Sec 5.6.

SAQ 4

The infrared spectrum of 2-methyl propan-1-ol has the following absorption bands:

3400 cm^{-1}	(broad)
2960 cm^{-1}	(medium)

1450 cm^{-1}	(medium)
1380 cm^{-1} 1370 cm^{-1}	(sharp doublet)
1050 cm^{-1}	(sharp)

Indicate the groups responsible for these bands.

....

....

....

5.5 PERTURBATION OF GROUP FREQUENCIES

The frequency of a particular IR band can be altered due to isotopic substitution, electronic effects, hydrogen bonding or steric effect. These aspects are to be understood carefully in order to derive useful information from the infrared spectra of compounds.

5.5.1 Mass Effect

The isotopic substitution causes a change in the reduced mass of a functional group. Since the vibrational wavenumber is related to the masses of atoms, the change in reduced mass causes a change in the wavenumber of absorption. Let us illustrate this by seeing the effect of deuterium substitution on the wavenumber of absorption of C–H bond.

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = \left(\frac{\mu_{C-H}}{\mu_{C-D}}\right)^{1/2} = \left(\frac{m_C \cdot m_H}{N_A\,(m_C + m_H)} \cdot \frac{(m_C + m_D)\,N_A}{m_C \cdot m_D}\right)^{1/2}$$

$$= \left(\frac{m_H}{(m_C + m_H)} \cdot \frac{(m_C + m_D)}{m_D}\right)^{1/2}$$

$\bar{\nu}$ is proportional to $\mu^{1/2}$ since,

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where m_C, m_H and m_D are the atomic masses of carbon, hydrogen and deuterium and N_A is the Avogadro constant.

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = \left(\frac{1 \times (12 + 2)}{(12 + 1) \times 2}\right)^{1/2}$$

$$= \left(\frac{14}{13 \times 2}\right)^{1/2} = 0.7338$$

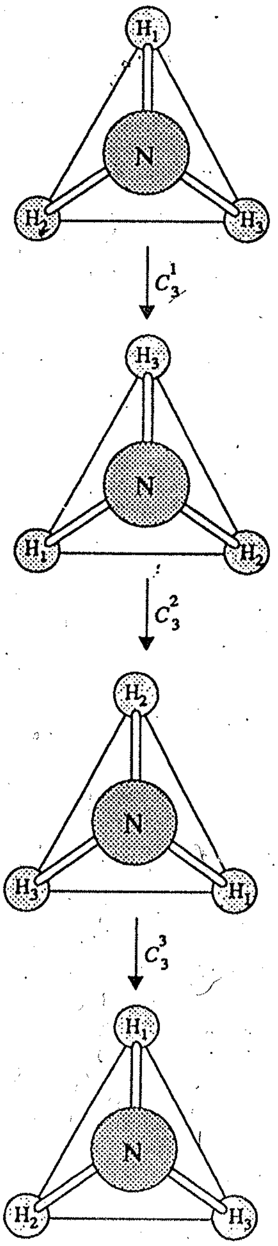
Hence, $\bar{\nu}_{C-D} = 0.7338\ \bar{\nu}_{C-H}$

$$= (0.7338 \times 2900)\ cm^{-1} \qquad (\text{since } \bar{\nu}_{C-H} = 2900\ cm^{-1})$$

$$= 2128\ cm^{-1}$$

Thus, we see that the substitution of heavier isotope reduces the vibrational frequency of a bond. This aspect is of much value in the IR spectral analysis of compounds and in the assignment of IR frequencies to a particular mode of vibration. Two more examples of the effect of isotopic substitution on IR frequency are given below. The

The rotations, C_3^1, C_3^2 and C_3^3 in NH_3 and BF_3 can be explained using the figures given below. As far as NH_3 molecule is concerned, it must be realised that the three vertices of the equilateral triangle represent the three hydrogen atoms of NH_3 while nitrogen atom is above the plane of equilateral triangle so that the shape of the molecule is trigonal pyramidal. In case of BF_3, the three vertices of the equilateral triangle represent the three flourine atoms and the boron atom is also in the plane of this triangle in keeping with the triangular planar shape of BF_3 molecule.



times. For this, use Figs. 2.1 a-d; Figs. 2.1 b, c and d are the results of C_3^1, C_3^2 and C_3^3 operations. You can understand these operations using the figures given in the margin.

In other words, a threefold axis of symmetry gives rise to three operations, C_3^1, C_3^2 and C_3^3.

Also $$C_3^1 C_3^1 = C_3^2 \qquad ...(2.3)$$

i.e., rotation through 240° is equivalent to rotation through 120° twice.

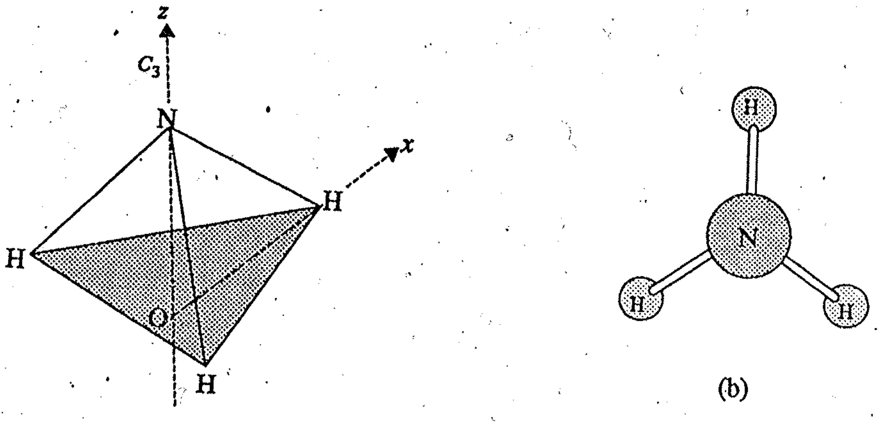
Further, $$C_3^2 C_3^1 = C_3^3 = E \qquad ...(2.4)$$

i.e., a rotation by 240° after a rotation through 120° is equal to rotation by 120° three times (C_3^3) or rotation by 360°. The operation C_3^3 is equivalent to identity operation, E.

The difference between the trigonal pyramidal molecule NH_3 and planar molecule BF_3 can be seen from the fact that these two molecules have different numbers of axes of symmetry. For example, NH_3 has only a threefold axis of symmetry but BF_3 has one threefold axis of symmetry (perpendicular to the plane of the molecule and passing through atom B) and three twofold axes of symmetry. Each C_2 axis in BF_3 is along one of the B – F bonds (Figs. 2.5 a-b). Thus, the three C_2 axes are perpendicular to C_3 axis in BF_3.

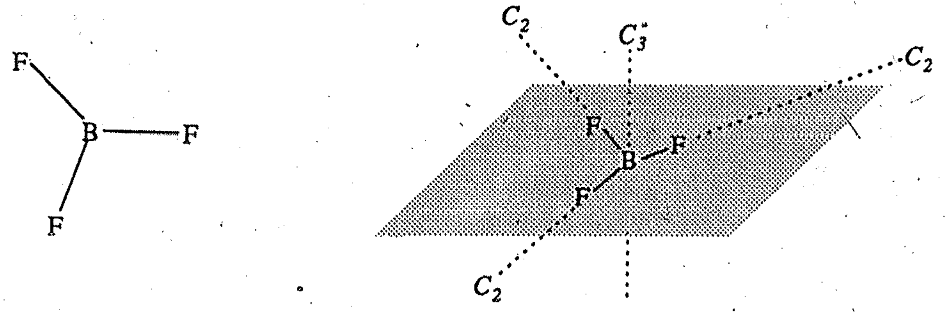
Let us examine benzene molecule. Benzene has one C_6 axis (perpendicular to the molecular plane) and six C_2 axes (Figs. 2.6 a-b). Three of the C_2 axes pass through the mid points of the opposite and parallel sides of the hexagon (i.e., in between C – C bonds) while three others pass through the opposite corners of the hexagon (i.e., along C – H bonds). Hence in benzene, the six C_2 axes are perpendicular to C_6 axis.

If a molecule has many C_n axes of different orders, then the axis with the highest order is called the principal axis of the molecule. Thus, the C_3 axis in BF_3 is its principal axis. Benzene has C_6 axis as its principal axis.



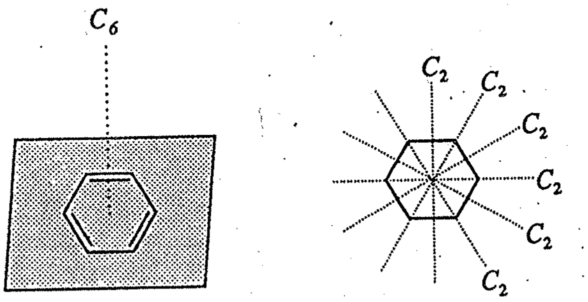
(a) (b)

Fig.2.4: (a) The shape of NH_3 molecule—trigonal pyramidal; point O lies in the xy plane (shown as shaded area) and on the z axis which is C_3 axis passing through nitrogen atom. The three hydrogen atoms form an equilateral triangle in the xy plane. (b) The top view of NH_3 molecule which is used in drawing the figures given at the margin to denote C_3^1, C_3^2 and C_3^3 operations.



(a) (b)

Fig. 2.5: (a) The shape of BF_3 molecule — triangular planar (b) Threefold axis of symmetry in BF_3; it is perpendicular to the molecular plane. The molecular plane is shown by the shaded area. Each B — F bond is also a twofold axis of symmetry. All the three C_2 axes are in the molecular plane.



(a) (b)

Fig 2.6: (a) C_6 in benzene; it is perpendicular to the molecular plane (shown as shaded area)
(b) The three C_2 axes along opposite C—H bonds and three C_2 axes in between parallel C — C bonds.

Since $n = 2\pi/\alpha$, n tends to infinity as α tends to zero. Also note that α is a continuous angle variable.

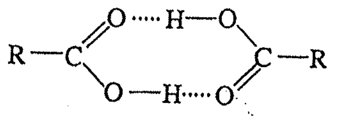
Linear molecules such as H_2, HCl, CO_2, COS, etc. have C_∞ axis along their molecular axes since rotation through even any small angle gives rise to an equivalent configuration. In other words, the angle of rotation for obtaining equivalent configuration is infinitesimally small (i.e., $\alpha \to 0$) for linear molecules such that application of Eq. 2.1 leads to the conclusion that $n = \infty$.

Using the above ideas, answer the following SAQs.

SAQ 3

You have predicted the shape of PCl_3 in SAQ 1. Name the axis of symmetry in PCl_3.

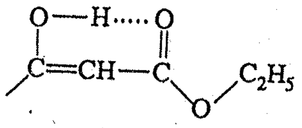
This shift is less pronounced compared to the stretching frequency shift.



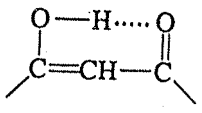
XV

There can be intermolecular or intramolecular hydrogen bonding. Intermolecular hydrogen bonding (or association)may result in dimer molecules or in polymers. For example, carboxylic acids form dimers (XV).

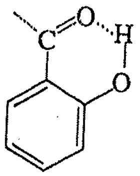
Intramolecular hydrogen bonding is possible in systems where 5 or 6 membered ring formation is possible as in XVI, XVII and XVIII.



XVI



XVII



XVIII

Intermolecular hydrogen bonding (or association)is affected by concentration change and temperature change, whereas these factors do not influence intramolecular hydrogen bonding. As a result of this, dilution or temperature change can alter the IR spectral pattern of associated molecules. For instance, dilution reduces the possibility of dimer or polymer formation. So at low concentrations, intermolecular hydrogen bonding possibility becomes less and the intensity of the corresponding absorption band also becomes less. This can be illustrated as follows:

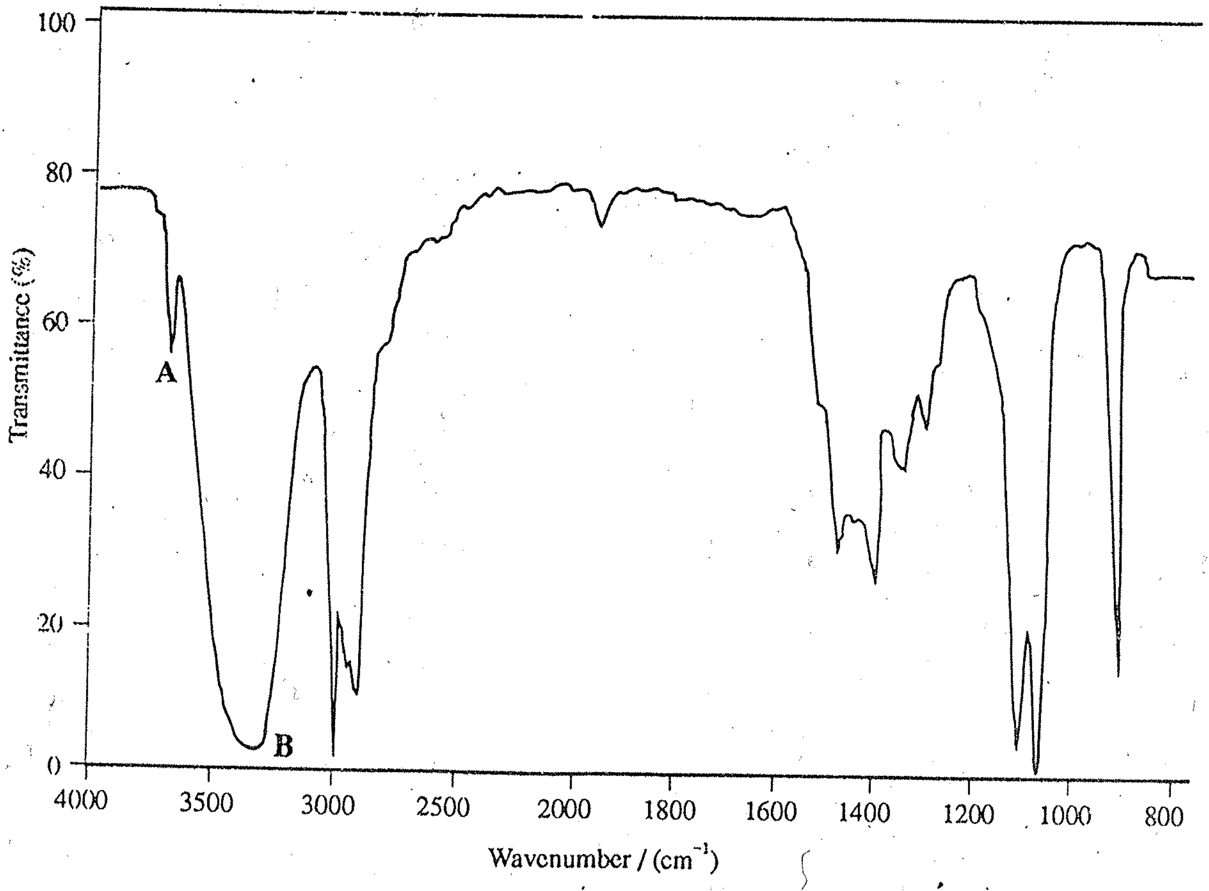


Fig.5.9 : Infrared spectrum of ethanol (10% *V/V* in CCl_4).

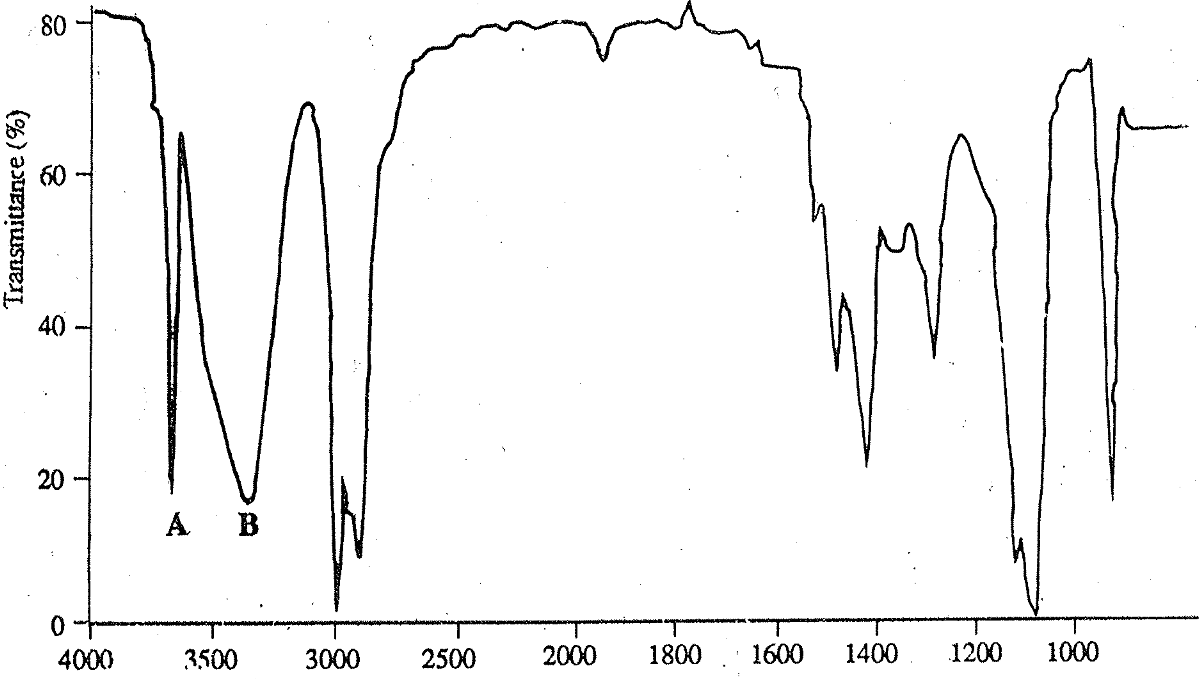


Fig.5.10: Infrared spectrum of ethanol (1%V/V in CCl_4).

The IR spectra of both 10% and 1% ethanol in CCl_4 show the effect of concentration on intermolecular H-bonding. Figs.5.9 and 5.10 show these spectra. In Fig.5.9, the 10% ethanol solution has one sharp absorption at 3640 cm^{-1} (A) and a strong broad absorption at 3340 cm^{-1} (B). Two such peaks are also noticed in Fig.5.10 for 1% ethanol. However in 1% ethanol, the sharp band at 3640 cm^{-1} (A) has increased intensity and, to balance this, the intensity of the broad band at 3340 cm^{-1} is less. From these considerations, the sharp band has been taken to be due to monomeric form of ethanol (O–H bond unassociated) and broad band due to the polymeric form (O–H bond associated). The amount of monomer or unassociated alcohol has increased on dilution resulting in the gain of intensity of sharp band (at 3640 cm^{-1}) relative to the broad band (at 3340 cm^{-1}).

The effect of temperature on intermolecular H-bonding is similar to the one noticed in the case of concentration. The association of molecules is prevented at higher temperatures and so the increase in the intensity of sharp band at 3640 cm^{-1} is noticed. It is desirable to determine the spectra of a sample under different conditions of physical state or concentration. In very dilute solution or in the vapour phase, molecular association effects are minimised, whereas in solid state or in concentrated solution, molecular association effects are considerable. For example in the IR spectrum of pure liquid acetic acid, $C=O$ stretching is seen at 1718 cm^{-1}; in the vapour phase, two carbonyl bands are seen at 1733 cm^{-1} and 1786 cm^{-1}. The $C=O$ absorption in the liquid state is attributed to the dimer only, whereas, the two bands at 1733 cm^{-1} and 1786 cm^{-1} in the vapour state are due to the dimer and monomer, respectively. The absorption caused by free O-H stretching of a carboxylic acid is observed near 3550 cm^{-1} whereas the bonded $O-H$ in the dimeric form absorbs in the region 2700-2500 cm^{-1}. Also when a carbonyl group is involved in intramolecular hydrogen bonding, it has lower stretching frequency. For instance, acetophenone (III) has carbonyl absorption at 1700 cm^{-1} whereas 2-hydroxyacetophenone (XVIII) which has intramolecular hydrogen bonding has carbonyl absorption band at 1635 cm^{-1}, showing a decrease of 65 cm^{-1}.

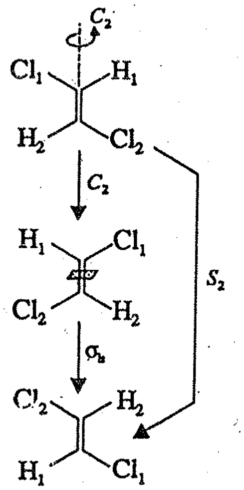
The existence of keto and enol forms can be understood in terms of the effect of hydrogen bonding on IR spectral frequencies. For instance, ethyl acetoacetate which has both keto and enol forms shows absorption characteristic of both the forms.

2.6 IMPROPER ROTATION ABOUT AN AXIS OF IMPROPER ROTATION

An n-fold improper rotation consists of n-fold rotation followed by a horizontal reflection. Improper rotation about an axis is also known as rotary-reflection operation. Such an axis is called rotary-reflection axis or alternating axis of symmetry or improper axis of symmetry (S_n).

In the Appendix part, we shall discuss the importance of combining operations such as in Eq. 2.6.

In *trans*-dichloroethylene, S_2 being equivalent to C_2 operation followed by σ_h can be shown as follows:



To cite an example, the staggered conformation of ethane has improper axis of order 6(S_6). To illustrate this fact, the rotation of the staggered conformation of ethane by 60° (C_6) followed by reflection through the horizontal plane (σ_h) has been shown in Fig. 2.10. You can see from this figure that C_6 followed by σ_h which is equivalent to S_6 leads to an equivalent configuration.

i.e.,

$$\sigma_h C_6 = S_6 \qquad ...(2.6)$$

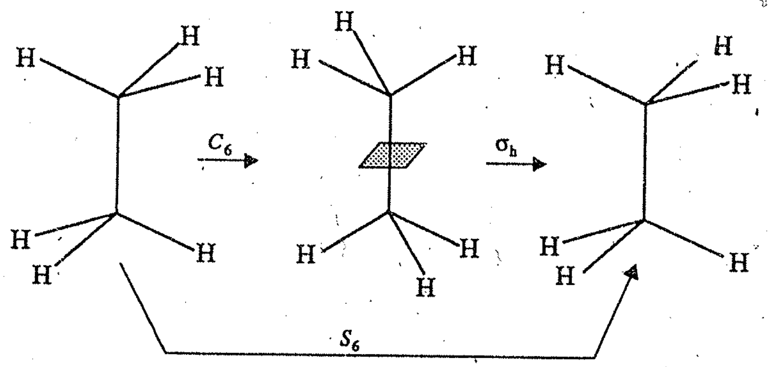


Fig. 2.10: S_6 in staggered conformation of ethane shown in terms of C_6 and σ_h.

To understand the displacement of particular hydrogen or chlorine atoms, the subscripts 1 and 2 are used. Also note that S_2 is equivalent to i, the inversion operation, which we shall discuss in the next section.

The presence of improper axis of symmetry in a molecule may seem difficult to identify. But it is useful for deciding whether a molecule is optically active or not. This aspect will be made clear in Subsec. 2.10.2 of this unit. Your understanding of this section can be verified by answering the following SAQ.

SAQ 7

The staggered conformation of ethane has S_6 axis. What do you mean by this?

....

....

....

2.7 INVERSION THROUGH CENTRE OF SYMMETRY

Inversion is the process of drawing a line from any point through the centre of the molecule to an equal distance on the other side from the centre to arrive at an equivalent point. The centre of the molecule which generates inversion is called the centre of symmetry or the inversion centre (i).

All homonuclear diatomic molecules (e.g., H_2, N_2, etc.) possess the centre of symmetry. Also CO_2, C_2H_4 (Fig. 2.11), C_6H_6, SF_6 and the staggered conformation of ethane possess centre of symmetry.

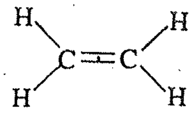


Fig. 2.11: The dot represents the centre of symmetry in ethylene.

H_2O, NH_3, BF_3 and CH_4 do not possess centre of symmetry. In Sec. 6.6.3 of Unit 6 of Atoms and Molecules course, we have indicated that the presence of centre of symmetry in a molecule leads to zero dipole moment for the molecule. We will recall this idea in Sec. 2.10.1 of this Unit. Similar to reflection, the operation of inversion conducted twice through the centre of symmetry leads to identity operation.

$$i . i = E \qquad \ldots(2.7)$$

Answer the following SAQ.

Note that i is a special case of improper rotation, when the angle of rotation is 180° ($\alpha = 2\pi/2 = \pi$).

Also $\sigma_h C_2 = S_2 = i$

This relationship has been illustrated using *trans*-dichloroethylene in the previous section.

SAQ 8

What do you think could be the dipole moment of benzene?
State the reason.

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2.8 IDENTITY

The operation of identity (E) consists of doing nothing. The corresponding element is the entire object. All molecules possess identity element. One reason for its inclusion is that some molecules (e.g., CHFClBr, Fig. 2.12) have only this symmetry element; another reason is connected with one of the fundamental aspects of group theory (which we shall mention in the Appendix of this unit). We have already mentioned the relationships of rotation, reflection and inversion with identity operation through Eqs. 2.2, 2.5 and 2.7.

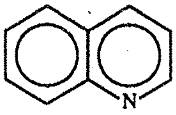


Fig. 2.13: Quinoline

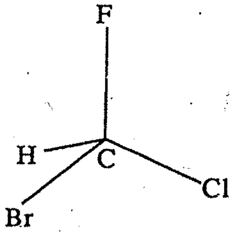


Fig. 2.12: CHFClBr which has only identity as the element of symmetry.

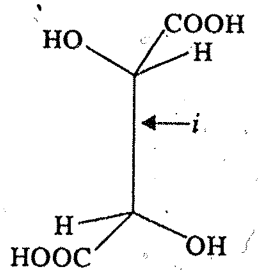


Fig. 2.14: *meso*-tartaric acid

So far, we discussed in detail the symmetry elements and symmetry operations. In the next section, let us see how the molecules can be classified according to symmetry.

2.9 POINT GROUPS OF MOLECULES

Point groups of molecules are classes of molecules which have same list of symmetry elements. Thus, CH_4 and CCl_4, have same list of symmetry elements and, belong to the same point group, and, are different from the point group to which H_2O belongs. The classification of molecules into point groups is of help in understanding the spectral characteristics, dipole moment values etc. of molecules.

The method of identifying point groups of molecules has been discussed in the Appendix.

(e) Could it be a ketone only?

Remember that the compound could have two carbonyl groups even. Note down the inferences and find the answers for the following questions also.

(ii) Does it show O–H stretching, O–H bending and C–O stretching bands characteristic of alcohols or phenols?

(iii) Does it show only C–O absorption without O–H stretching band (which is characteristic of ethers)?

(iv) Does it show N–H stretching, N–H bending and C–N vibrations characteristic of amines?

(v) Does it have vibrations characteristic of $-C\equiv N$, $>C=N-$ or $-NO_2$ groups?

(vi) Does it have S–H, C = S or S = O vibrations characteristic of thiols, thioacids, sulphonyl derivatives etc.?

III Some special features regarding structure

The answer to the following question can throw light on some structural aspects:

Does the spectrum show any special features which bring out the presence of tautomers, intramolecular hydrogen bonding, intermolecular hydrogen bonding etc.?

The answers to the above questions provide us information regarding hydrocarbon skeleton and the functional groups present in the compound. Let us work out three problems using the above approach.

Example 1

A compound of molecular formula C_7H_8 has IR bands at the following frequencies:

3050 cm^{-1}

2900 cm^{-1}

1600 cm^{-1}

1500 cm^{-1}

1430 cm^{-1}

1380 cm^{-1}

750 cm^{-1}

700 cm^{-1}

Suggest a possible structure for the compound.

We have to look for the answers for only the questions relating to the hydrocarbon skeleton, since the molecular formula suggests that it is a hydrocarbon and it cannot have any specific functional group.

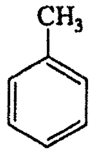
Hydrocarbon skeleton

The presence of aromatic ring is indicated by the presence of bands at 3050 cm^{-1} (aromatic C–H stretching) and at 1600 cm^{-1} and 1500 cm^{-1} (C–C multiple bond stretching of the aromatic ring). The presence of $-CH_3$ and or $>CH_2$ groups is hinted by the absorptions at 2900 cm^{-1} (aliphatic C–H stretching) and at 1430 cm^{-1} and 1380 cm^{-1} (aliphatic C–H bending).

Substitution type

The absorptions at 750 cm^{-1} and 700 cm^{-1} show the presence of monosubstituted benzene ring (C_6H_5-).

Since the molecular formula is C_7H_8, we can infer that it has a $-C_6H_5$ group and a $-CH_3$ group ($C_7H_8 - C_6H_5 = CH_3$). Hence, the possible structure of the compound is



This needs confirmation through NMR data.

Example 2

A compound has molecular formula C_4H_8O. The NMR spectrum shows the presence of two methyl groups and one methylene group. Further NMR spectrum excludes the possibility of aldehyde group. The IR spectrum shows the following prominent bands:

2941-2850 cm^{-1}	(medium)
1716 cm^{-1}	(sharp)
1459 cm^{-1}	(medium)

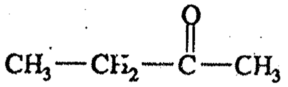
Arrive at the structure of the compound.

Hydrocarbon skeleton

The hydrocarbon skeleton is of alkane type since the C–H stretching (2941-2850 cm^{-1}) and bending vibrations (1459 cm^{-1}) indicate the presence of one or more $-CH_3$ and $>CH_2$ groups.

Functional group

The absorption at 1716 cm^{-1} shows the presence of $>C=O$ group. The molecular formula indicates the presence of only one oxygen atom and this, in conjunction with IR band at 1716 cm^{-1} indicates that the compound should be an aldehyde or a ketone. Since NMR spectrum excludes the presence of aldehyde group, the structure of the compound is



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

This structure is in line with NMR spectral data which show the presence of two $-CH_3$ groups and one $>CH_2$ group. This example will be discussed again with detailed NMR data in Unit 13 (as problem 1).

Example 3

A compound of molecular formula $C_9H_{10}O_2$ yields the following IR data:

3022 cm^{-1} (weak)

2940 cm^{-1} (weak)

1730 cm^{-1} (sharp)

1605 cm^{-1} and 1504 cm^{-1} (weak)

1060 cm^{-1} (sharp)

835 cm^{-1} (sharp)

NMR data provides information regarding the presence of two $-CH_3$ groups and one $>C_6H_4$ group. Suggest possible structures.

The structures can be arrived at as follows.

Hydrocarbon skeleton

The absorptions at 3022 cm^{-1}, 1605 cm^{-1} and 1504 cm^{-1} bring out the presence of aromatic ring. Further the absorption at 2940 cm^{-1} is suggestive of the presence of one or more $-CH_3$ and or $>CH_2$ groups.

Substitution type

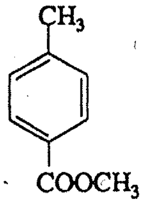
The band at 835 cm^{-1} is indicative of *p*- disubstitution.

Functional group

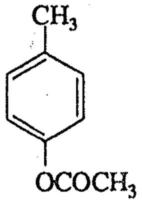
The absorptions at 1730 cm^{-1} and 1060 cm^{-1} indicate the presence of ester group.

On the basis of available IR and NMR data, we can conclude that the compound has (i) *p* $- C_6H_4$ group (ii) two methyl groups and (iii) one ester group.

Possibly one of the methyl groups is attached directly to the benzene ring and another methyl group forms part of the ester group, i.e., either as $-COOCH_3$ or CH_3COO- As it is, the two possible structures are:



or



More evidences are required to take a clear decision regarding structure.

From the above examples, you can understand that IR data could give vital clues regarding the hydrocarbon skeleton and the functional groups. For arriving at the exact structure, more spectral data are required.

Answer the following SAQ.

SAQ 7

A compound has the molecular formula C_7H_5N. It has the following absorption bands:

$3050\ cm^{-1}$

$2240\ cm^{-1}$

$1600\ cm^{-1}$

$1500\ cm^{-1}$

$750\ cm^{-1}$

$700\ cm^{-1}$

Arrive at the structure of the compound.

....

....

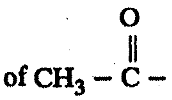
....

5.7 SUMMARY

In this unit we discussed the method of calculation of vibrational degrees of freedom of linear and nonlinear polyatomic molecules. We explained the IR spectra of H_2O and CO_2. The use of the chart of group frequencies has been stated. The perturbation of group frequencies arising out of mass effect, electronic effects, hydrogen bonding and steric effect has been discussed. Finally the method of using IR spectra for determination of structure of organic compounds has been illustrated. In the Appendix portion, we have explained the steps involved in ascertaining the IR active vibrations. For this purpose, group theory is being made use of.

5.8 TERMINAL QUESTIONS

1. Calculate the number of stretching and bending modes of PF_3 and CH_4.
2. SiF_2 vapour is angular in shape and it belongs to C_{2v} group. The frequencies for its symmetric stretching, symmetric bending and antisymmetric stretching modes are $855\ cm^{-1}$, $345\ cm^{-1}$ and $872\ cm^{-1}$, respectively. Calculate its total zero point energy.
3. The infrared spectrum of nonane has the following three prominent bands: $2960\ cm^{-1}$, $1450\ cm^{-1}$ and $1370\ cm^{-1}$. Identify the groups responsible for these absorptions.



4. The infrared spectrum of $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-SH$ has the following prominent bands:

$2960\ cm^{-1}$
$2500\ cm^{-1}$

1700 cm^{-1}

1450 cm^{-1}

1380 cm^{-1}

Indicate the groups responsible for these bands.

5. Explain the following:

   a) The C=O frequency in acyl chlorides is higher than that in alkyl esters.

   b) The C=O frequency in methyl acetate is less than that in phenyl acetate.

6. 2,4-Pentanedione shows a broad band stretching from 3400 cm^{-1} to 2400 cm^{-1} which is unchanged on dilution. Try to identify this band.

7. A compound has the molecular formula $C_4H_{10}O$. It has no prominent absorption bands above 3000 cm^{-1}, in the region 2900-1500 cm^{-1} or below 1000 cm^{-1}. The main absorption bands are given below:

   2970 cm^{-1}
   1450 cm^{-1}
   1370 cm^{-1} Separate bands - no doublet
   1100 cm^{-1}

   Suggest possible structures for the compound.

5.9 ANSWERS

Self Assessment Questions

1. A linear molecule has $(N-1)$ stretching and $(2N-4)$ bending vibrations. Since N is four for C_2H_2, there are three stretching and four bending vibrations.

2. $$E(000) = hc[(0 + 1/2)\bar{\nu}_1 + (0 + 1)\bar{\nu}_2 + (0 + 1/2)\bar{\nu}_3]\ \mathrm{J}$$

   $$= 6.626 \times 10^{-34} \times 3 \times 10^8 \times 10^2 [(1340 \times 1/2) + 667 + (2349 \times 1/2)]\ \mathrm{J}$$

   $$= 4.992 \times 10^{-20}\ \mathrm{J}$$

   The factor 10^2 is used to convert cm^{-1} into m^{-1}.

3. The first and the second overtones of ν_2 appear at 1334 cm^{-1} and 2001 cm^{-1}.

4.

3400 cm^{-1}		O – H stretching
2960 cm^{-1}		C – H stretching of $-CH_3$ and $>CH_2$ groups
1450 cm^{-1}		C – H bending of $>CH_2$ group
1380 cm^{-1} 1370 cm^{-1}	and	C – H bending of *gem*-dimethyl groups
1050 cm^{-1}		O – H bending and C – O stretching

5. *p*-methoxyacetophenone < acetophenone < *p*-nitroacetophenone.

   The $+R$ nature of $-OCH_3$ group and $-R$ nature of *p*-nitro group which interact with the carbonyl group result in the change in the carbonyl frequency as mentioned above.

6. The single broad band of the pure alcohol is due to associated –O–H group. On dilution, the free –O–H group stretching also appears.

7. **Hydrocarbon skeleton**

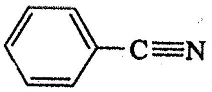
The presence of aromatic ring is brought out by the presence of bands at 3050 cm^{-1} (aromatic C – H stretching). The absorptions at 1600 cm^{-1} and 1500 cm^{-1} are due to C – C multiple bond stretching of the aromatic ring.

Substitution type

The bands at 750 cm^{-1} and 700 cm^{-1} (C – H bending) are characteristic of monosubstituted benzene ring.

Functional group

The absorption at 2240 cm^{-1} brings out the presence of $-\text{C}\equiv\text{N}$ group. Keeping in mind the molecular formula (C_7H_5N), the structure assigned is



Terminal Questions

		Stretching	Bending
1.	PF_3	3	3
	CH_4	4	5

2. The degeneracy is 1 for each of the three modes.

$$\begin{aligned}E(000) &= hc[(\bar{\nu}_1 \times 1/2) + (\bar{\nu}_2 \times 1/2) + (\bar{\nu}_3 \times 1/2)]\ \text{J}\\ &= 6.626 \times 10^{-34} \times 3 \times 10^{8} \times 10^{2}[(855 \times 1/2) + (345 \times 1/2) + (872 \times 1/2)]\ \text{J}\\ &= 2.059 \times 10^{-20}\ \text{J}\end{aligned}$$

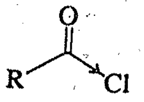
3.

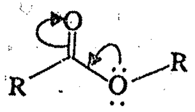
2960 cm^{-1}	(C–H stretching of $-CH_3$ and $>CH_2$ groups)
1450 cm^{-1} 1370 cm^{-1}	(C–H bending of $-CH_3$ and $>CH_2$ groups)

4.

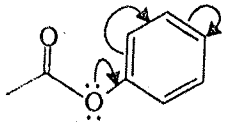
2960 cm^{-1}	C – H stretching of $-CH_3$ group
2500 cm^{-1}	S – H stretching
1700 cm^{-1}	C = O stretching
1450 cm^{-1} 1380 cm^{-1}	and C – H bending of $-CH_3$ group

5. a) The dominance of –*I* nature over +*R* is more prominent in the case of chloro group than for –OR group. This may possibly be responsible for the higher carbonyl frequency in the case of acyl chlorides.





b) In phenyl acetate, the nonbonding pair on aryl oxygen is partly drawn into the ring and its conjugation with carbonyl group is diminished. When this happens in phenyl acetate, –*I* effect of oxygen becomes dominant and carbonyl group moves to higher frequency as compared to that in methyl acetate.



6. 2,4-Pentanedione exists in keto and enol forms. The broad band mentioned is due to the enolic O – H stretching which is involved in intramolecular hydrogen bonding.

7. **The carbon skeleton**

The C – H stretching absorption at 2970 cm^{-1}, and C – H bending absorptions at 1450 cm^{-1} and 1370 cm^{-1} indicate the presence of $-CH_3$ and $>CH_2$ groups. Absence of doublets around 1370 cm^{-1} rule out the possibility of *gem*-dimethyl or *t*-butyl branching.

Functional group

The absorption at 1100 cm^{-1} indicates ether linkage.

The two possible structures are given below:

$$CH_3 - CH_2 - O - CH_2 - CH_3$$

$$CH_3 - O - CH_2 - CH_2 - CH_3$$

5.10 APPENDIX

We can use group theory for finding the symmetry species of the normal modes of vibration of a molecule and also for determining the number of infrared active vibrations in a molecule. We can also associate the experimentally observed IR absorption bands with the vibrational modes. Using H_2O and NH_3 molecules as examples, we shall explain the steps involved in identifying the number of IR active vibrations of a molecule. In the Appendix of Unit 6, we shall explain how the assignment of frequencies to the vibrational modes is done by using IR and Raman spectra.

Analysis of IR spectra of molecules

You must recapitulate the group theory discussed in the Appendix of Unit 2 in order to understand the materials discussed here. Let us first state the steps involved in identifying the number of IR active vibrations of a molecule.

Step 1 : Find the reducible representation for all the symmetry operations of the molecule.

Step 2 : Obtaining the reducible representation of all the vibrations.

Step 3 : Obtain the symmetry species of the vibrational modes.

Step 4 : Identify the symmetry species of each vibrational mode.

Step 5 : Identify the infrared active vibrational modes.

Let us apply these steps to identify the IR active vibrations of H_2O molecule. You are aware that H_2O has the following symmetry operations :

$$E, C_2, \sigma_v(xz) \text{ and } \sigma'_v(yz).$$

Step 1 : Finding the reducible representation for all the symmetry operations of the molecule

We shall discuss a simple method to build the characters of a reducible representation

(R) of a molecule and then apply this to H_2O first and later to NH_3. The character $\chi_R^t(p)$ for a particular symmetry operation (p) in a reducible representation R is given by the product of

(i) The number of atoms (n_a) which are not shifted by the symmetry operation and

(ii) The contribution $\chi_R(p)$ that each unshifted atom makes to the character for a particular symmetry operation p in a reducible representation, R.

i.e., $$\chi_R^t(p) = n_a \cdot \chi_R(p) \qquad \ldots(A.1)$$

n_a values

In case of water, n_a values for the symmetry operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ are given below:

(i) E does not shift any of the three atoms in H_2O and, $n_a = 3$.

(ii) C_2 rotation does not shift oxygen but interchanges two hydrogen atoms (see Fig.2.3 of Unit 2), i.e. $n_a = 1$.

(iii) $\sigma_v(xz)$ reflection does not shift any of the three atoms since this reflection is in the molecular plane (see Fig.2.7 of Unit 2), i.e., $n_a = 3$.

(iv) $\sigma'_v(yz)$ reflection does not shift oxygen atom whereas it shifts the two hydrogen atoms (see Fig. 2.7 of Unit 2), i.e., $n_a = 1$.

$\chi_R(p)$ values

The contribution $\chi_R(p)$ that each unshifted atom makes to the character for a particular symmetry operation p in a reducible representation can be obtained using Table A.1.

Table A.1 : $\chi_R(p)$ values

	Proper rotation		Improper rotation		
p	E	$C(\alpha)$	σ	$S(\alpha)$	i
$\chi_R(p)$	3	$1 + 2\cos\alpha$	1	$-1 + 2\cos\alpha$	-3

The proper rotation by $\alpha = 2\pi/n$ is denoted as $C(\alpha)$ while improper rotation by α is denoted as $S(\alpha)$. Note α is the minimum angle of rotation.

One must note that the identity operation E is equivalent to proper rotation through 2π and that the character $\chi_R(E)$ is a special case for proper rotation with $\alpha = 2\pi$. Similarly $\sigma = S(2\pi)$ with character $\chi_R(\sigma) = -1 + 2\cos 2\pi = 1$, and, $i = S(\pi)$ with character $\chi_R(i) = -1 + 2\cos\pi = -3$ are special cases of the general result for improper rotation, $S(\alpha)$. It is therefore only necessary to consider two kinds of symmetry operations, proper rotation $C(\alpha)$ and improper rotation, $S(\alpha)$. Further, the character, $\chi_R(C_2) = 1 + 2\cos\pi = -1$, since C_2 is proper rotation with $\alpha = \pi$.

The calculation of $\chi_R^t(p)$ for each symmetry operation can be done using Eq. A.1 as follows:

p	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$\chi_R(p)$	3	-1	1	1	
n_a	3	1	3	1	
$\chi_R^t(p)$ (using Eq. A.1)	9	-1	3	1	...(A.2)

Step 2: Obtaining the reducible representation of all the vibrations

In order to obtain the reducible representation of all the vibrational modes of H_2O molecule, we must subtract the characters of the symmetry operations in the irreducible representations of translations and rotations from the characters of symmetry operations given by Eq. A.2. The translations belong to B_1, B_2 and A_1 as per C_{2v} character table because they are influenced by the symmetry operations in the same way as x, y and z directions. Similarly the rotations belong to B_2, B_1 and A_2, since R_x, R_y and R_z belong to these three symmetry species as per C_{2v} character table.

Character Table of C_{2v} Group

Four classes of operations

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$			
A_1	1	1	1	1	z	x^2, y^2, z^2	
A_2	1	1	–1	–1		xy	R_z
B_1	1	–1	1	–1	x	xz	R_y
B_2	1	–1	–1	1	y	yz	R_x

Irreducible representations of C_{2v} group

From C_{2v} character table, the sum of the characters of the symmetry operations in the irreducible representations of translations is given by $B_1 + B_2 + A_1$.

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$B_1 + B_2 + A_1$	3	–1	1	1	...(A.3)

Similarly, the sum of the characters of the symmetry operations in the irreducible representations of rotations is given by $B_2 + B_1 + A_2$.

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$B_2 + B_1 + A_2$	3	–1	–1	–1	...(A.4)

Hence the characters of the symmetry operations in the reducible representation of vibrations (τ) is given by subtracting Eqs. A.3 and A.4 from Eq. A.2 as follows:

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$\chi_R^t(p)$	9	–1	3	1	
$-[(B_1 + B_2 + A_1)$	3	–1	1	1]	
$-[(B_2 + B_1 + A_2)$	3	–1	–1	–1]	
τ	3	1	3	1	...(A.5)

Eq. A.5 represents the characters of the symmetry operations ($\chi(p)$) in the reducible representation, τ.

Again τ represents the reducible representation of all the vibrational modes of H_2O molecule.

Step 3: Obtaining the symmetry species of the vibrational modes

In order to obtain the symmetry species of the vibrational modes, we have to split the reducible representation τ into various irreducible representations by using the reduction formula (Eq. A.6). Before stating the reduction formula, we should know the following:

Note that N is the number of operations in a class while h is the number of operations in a group.

(i) $\chi_I(p)$, the character for each symmetry operation in an irreducible representation I.

(ii) $\chi(p)$, the character for each symmetry operation in the reducible representation, τ.

(iii) N, the number of symmetry operations in a class (which is equal to the number of equivalent operations in the class).

(iv) h, the order of the group (which is equal to the total number of operations in the group).

The word 'class' will be explained shortly.

Obtaining the character $\chi_I(p)$ for each symmetry operation in an irreducible representation, I.

The entries below the operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ in the first row of the character table of C_{2v} group give the characters for these operations in the irreducible representation, A_1.

$$\chi_{A_1}(E) = 1$$

$$\chi_{A_1}(C_2) = 1$$

$$\chi_{A_1}(\sigma_v(xz)) = 1$$

$$\chi_{A_1}(\sigma'_v(yz)) = 1$$

Similarly the entries in the second row of the C_{2v} character table give the characters of the symmetry operations of C_{2v} group in the irreducible representation, A_2.

You may revise the characteristics of the character tables A.2 and A.3 discussed in the Appendix part of Unit 2. Table A.2 of Unit 2 contains the sets of characters for the four symmetry operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ in the four irreducible representations, A_1, A_2, B_1 and B_2 of C_{2v} group. Table A.3 of Unit 2 contains the sets of characters for the three classes of symmetry operations in the three irreducible representations, A_1, A_2 and E of C_{3v} group.

$$\chi_{A_2}(E) = 1$$

$$\chi_{A_2}(C_2) = 1$$

$$\chi_{A_2}(\sigma_v(xz)) = -1$$

$$\chi_{A_2}(\sigma'_v(yz)) = -1$$

The entries in the third and fourth rows of C_{2v} character table give the characters of the symmetry operations of C_{2v} group in the irreducible representations, B_1 and B_2, respectively.

Obtaining the character $\chi(p)$ for each symmetry operation in the reducible representation τ.

In the reducible representation τ of C_{2v} group, the character for each symmetry operation is as indicated in Eq. A.5.

$$\left.\begin{aligned} \chi(E) &= 3 \\ \chi(C_2) &= 1 \\ \chi(\sigma_v(xz)) &= 3 \\ \chi(\sigma'_v(yz)) &= 1 \end{aligned}\right\} \qquad \text{...(A.5)}$$

Obtaining the number of symmetry operations (*N*) in a Class

We denote the number of symmetry operations in a class as *N*. The term 'class' is better explained using the symmetry operations of C_{3v} group. We shall be presently using the materials of Secs. 2.4 and 2.5 of Unit 2. A set of operations are in the same class if they are equivalent operations. The word "equivalent operations" means that such operations lead to equivalent configurations of the molecule. For instance, C_3^1 and C_3^2 operations (mentioned in Sec. 2.4 of Unit 2) lead to equivalent configurations. Hence C_3^1 and C_3^2 are equivalent operations and these two operations belong to the same class. As mentioned in Sec. 2.5 of Unit 2, σ_v, σ'_v and σ''_v operations in NH_3 molecule are equivalent operations and each of these planes passes through nitrogen atom and a hydrogen atom and relates the other two hydrogen atoms as a mirror image of each other. Hence σ_v, σ'_v and σ''_v belong to the same class and $N = 3$ for this class. Also *E* is an operation which does not have any equivalent operation and hence *E* is a class in itself for which $N = 1$. Hence C_{3v} point group has three classes, *E*, $2C_3$ and $3\sigma_v$ with *N* values of 1, 2 and 3, respectively.

The characters of all elements in a class are same. Hence, only the characters of the classes are given in the character table. In C_{2v} character table, each element (i.e., symmetry operation) is a class. **The four symmetry operations in C_{2v} group are four classes.**

In C_{3v} group, *E* is a class in itself; the two C_3 operations, C_3^1 and C_3^2 constitute a class and are denoted as $2C_3$ in C_{3v} character table (given in Table A.3 in Unit 2 and also towards the end of this Appendix). Also the three operations, σ_v, σ'_v and σ''_v constitute another class and are denoted as $3\sigma_v$. Hence there are three classes in C_{3v} group.

In the case of H_2O (C_{2v} group), each of the four operations *E*, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ belongs to different class. Note that $\sigma_v(xz)$ in H_2O is in the molecular plane which contains both the hydrogen atoms and the oxygen atom while $\sigma'_v(yz)$ is perpendicular to $\sigma_v(xz)$ plane and it passes through only oxygen atom and relates the two hydrogen atoms as a mirror image of each other (Fig.2.7 of Unit 2). Hence there are four classes of operations in C_{2v} group each having $N = 1$.

Obtaining the order of the group (*h*)

Order of the group (*h*) is the total number of operations in a group. In C_{2v} group, there are four symmetry operations and hence, $h = 4$.

Having understood the terms required, we shall state the reduction formula which is useful in obtaining the symmetry species of the vibrational modes.

Reduction formula

$$\left.\begin{array}{l}\text{Number of times } (n_I) \text{ an} \\ \text{irreducible representation } I \\ \text{occurs in the reducible} \\ \text{representation } (\tau)\end{array}\right\} = \frac{1}{h} \sum_{\substack{\text{over all} \\ \text{classes}}} \chi_I(p) \cdot \chi(p) \cdot N \qquad \text{...(A.6)}$$

'$\sum\limits_{\substack{\text{over all}\\\text{classes}}}$' means summation of the terms $\chi_I(p) \cdot \chi(p) \cdot N$ for all the classes of a point group.

Let us reduce the reducible representation τ of C_{2v} group into the irreducible representations, A_1, A_2, B_1 and B_2. Using the $\chi_I(p)$ values of A_1, A_2, B_1 and B_2 representations of C_{2v} group and knowing that (i) $h = 4$ for C_{2v} group and (ii) $N = 1$ for each of the four classes of operations in C_{2v} group, we can find out n_I for each of the four irreducible representations, *I*.

$$\left.\begin{array}{l}\text{Number of times } A_1 \text{ symmetry} \\ \text{species occurs in} \\ \text{representation } \tau\end{array}\right\} = n_{A_1}$$

$$=\frac{1}{4}\left[\underset{\leftarrow E\rightarrow}{(\overset{\overset{\chi_{A_1}(E)}{\downarrow}}{1}\times\overset{\overset{\chi(E)}{\downarrow}}{3}\times\overset{\overset{N}{\downarrow}}{1})}+\underset{\leftarrow C_2\rightarrow}{(1\times 1\times 1)}+\underset{\leftarrow\sigma_v(xz)\rightarrow}{(1\times 3\times 1)}+\underset{\leftarrow\sigma'_v(yz)\rightarrow}{(1\times 1\times 1)}\right]$$

$$=\frac{1}{4}[3+1+3+1]=2$$

Hence, $n_{A_1}=2$ or A_1 occurs twice in the reducible representation, τ.

Note that there are four classes of operations in C_{2v} group. Hence there are four terms in the summation corresponding to four classes.

In the calculation of n_{A_1}, using Eq. A.6, there are four terms corresponding to E, C_2, $\sigma_v(xy)$ and $\sigma'_v(yz)$.

The first term marked,

$$\underset{\leftarrow E\rightarrow}{(\overset{\overset{\chi_{A_1}(E)}{\downarrow}}{1}\times\overset{\overset{\chi(E)}{\downarrow}}{3}\times\overset{\overset{N}{\downarrow}}{1})}$$

stands for the application of the formula for the class of operation, E. This term is obtained using the relationships,

$\chi_{A_1}(E)=1$,

$\chi(E)=3$ and

$N=1$

Similarly the second term stands for the application of formula for the class of operation, C_2. The third and fourth terms stand for the classes of operations, $\sigma_v(xz)$ and $\sigma'_v(yz)$, respectively.

Similarly,

$$n_{A_2}=\frac{1}{4}\left[\underset{\leftarrow E\rightarrow}{(1\times 3\times 1)}+\underset{\leftarrow C_2\rightarrow}{(1\times 1\times 1)}+\underset{\leftarrow\sigma_v(xz)\rightarrow}{((-1)\times 3\times 1)}+\underset{\leftarrow\sigma'_v(yz)\rightarrow}{((-1)\times 1\times 1)}\right]$$

$$=\frac{1}{4}[3+1-3-1]=0$$

i.e., A_2 does not occur in the reducible representation τ.

$$n_{B_1}=\frac{1}{4}\left[(1\times 3\times 1)+((-1)\times 1\times 1)+(1\times 3\times 1)+((-1)\times 1\times 1)\right]$$

$$=\frac{1}{4}[3-1+3-1]=1$$

Hence, B_1 occurs once in the reducible representation, τ.

$$n_{B_2}=\frac{1}{4}\left[(1\times 3\times 1)+((-1)\times 1\times 1)+((-1)\times 3\times 1)+(1\times 1\times 1)\right]$$

$$=\frac{1}{4}[3-1-3+1]=0$$

So, B_2 does not occur in the reducible representation, τ. In short τ can be split into $2A_1+B_1$. In other words, symmetry species of vibrations $=2A_1+B_1$.

In Sec. 5.2, we have mentioned that H_2O which is an angular triatomic molecule must have three vibrational modes, namely, symmetric stretching (ν_1) symmetric bending (ν_2) and antisymmetric stretching (ν_3). We now understand that two of these vibrations must belong to A_1 symmetry while the third one must belong to B_1 symmetry. In the next step, we shall identify the symmetry species of each mode of vibration.

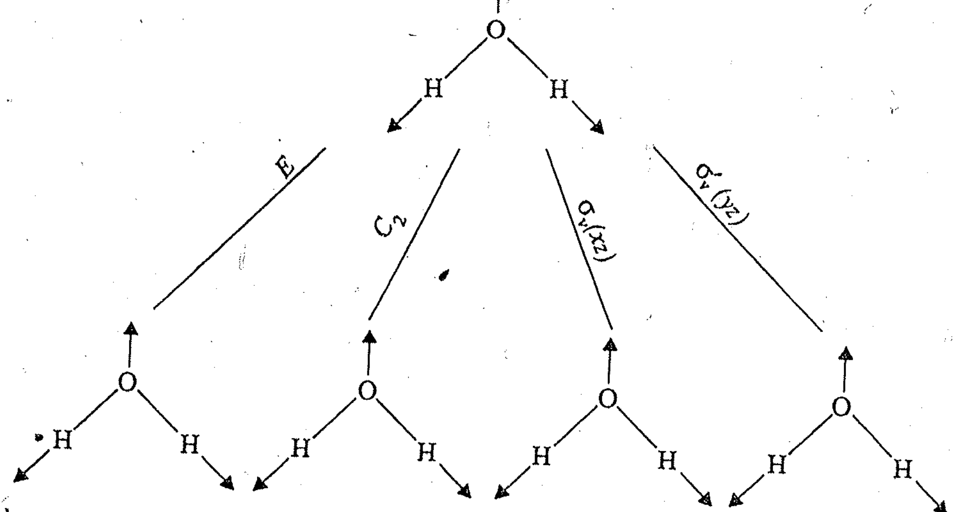
Step 4 : Identifying the symmetry species of each vibrational mode

We arrive at the irreducible representations of symmetric stretching, symmetric bending and antisymmetric stretching modes by performance of the symmetry operations on the molecule.

Irreducible representation of symmetric stretching mode

We can identify the set of character values for each of the four operations E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$ over the symmetric stretching mode. If the performance of an operation does not change the direction of arrows in a stretching mode, 1 is given as the character value; but if the direction of arrows changes by the performance of an operation, –1 is given as the character value.

As mentioned in Sec. 5.2, the arrows attached to each atom show the direction of its motion during half of the vibration. During the other half of the vibration, the movement will be in the opposite direction.



Directions of the arrows	No change	No change	No change	No change
Character value	1	1	1	1

Symmetry species of symmetric stretching = A_1

You may remember that C_2 rotation is around z axis and because of C_2 rotation, the two H atoms change their positions; but again the directions of two arrows around these H atoms are similar to those of the initial configuration suggesting no change in the direction of the stretching mode. $\sigma_v(xz)$ does not bring about a change in the direction of the stretching mode since xz reflection takes place in the molecular plane. $\sigma'_v(yz)$ reflection takes place in a direction perpendicular to the molecular plane and it brings about the reflection of two H atoms; but again, there are two arrows with the direction similar to those of the original configuration which indicates that there is no change in the stretching mode. Hence the character value of 1 is obtained in each of the four operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$, indicating that the symmetric stretching vibration belongs to A_1 representation.

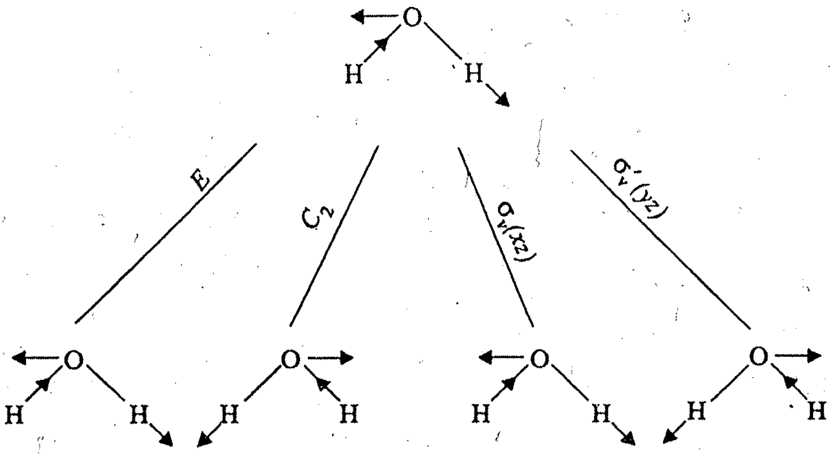
Irreducible representation of the symmetric bending mode

It can be shown using the diagrams that after performing each of the four symmetry operations, E, C_2, $\sigma_v(xz)$ and $\sigma'_v(yz)$, the arrows are in the same directions showing no change in the direction of the bending mode. You may try this as an exercise. So, the character values corresponding to these four operations are 1, 1, 1, 1 which indicates that the symmetric bending mode also belongs to A_1 representation.

Irreducible representation of the antisymmetric stretching mode

The effect of the four symmetry operations on the arrows drawn for the antisymmetric stretching is explained through the diagram as follows:

"Totally symmetric A_1 representation" means that a particular vibration does not show any change in direction due to any of the symmetry operations. The result of each operation on the vibration is + 1".



Directions of the arrows	No change	Change	No change	Change
Character value	1	−1	1	−1

Symmetry species of antisymmetric stretching = B_1

Hence, antisymmetric stretching vibration belongs to B_1 representation.

It is worth pointing out that symmetric stretching and symmetric bending modes derive their name from the fact that these two stretching modes belong to the **totally symmetric** A_1 representation. On the other hand, antisymmetric stretching mode owes its name to the fact that it is antisymmetric to at least two of the operations, C_2 and $\sigma'_v(yz)$.

Thus we have seen that two of the normal modes belong to A_1 representation while the third belongs to B_1 representation as mentioned earlier in Step 3.

Step 5: Identifying the infrared active vibrational modes

In the Appendix portion of Unit 2 and under the title, "uses of character tables", we have shown that for a spectral transition to occur from the state a to b, at least one of the components of the transition dipole moment (μ_x, μ_y, or μ_z) should be nonzero. We have explained that for an allowed spectral transition, the symmetry species of the product, $\psi_b \psi_a$ must be same as that of x, y or z coordinate. Such a spectral transition is symmetry allowed, since the product of the symmetry species of the functions ψ_b and ψ_a and that of one of the coordinates x, y or z becomes totally symmetric i.e., $\psi_b x \psi_a$ or $\psi_b y \psi_a$ or $\psi_b z \psi_a$, belongs to A_1 representation.

Using the procedure followed in Appendix of Unit 2 for obtaining the representation of the products $\psi_b x \psi_a$, $\psi_b y \psi_a$ or $\psi_b z \psi_a$ you can try to prove that

(i) the symmetric stretching and bending modes are IR active and are polarized in the z-direction and

(ii) the antisymmetric stretching mode is also IR active and is polarized in the x-direction.

To prove the above statements, the following hints also will be useful :

(i) For the symmetric stretching and bending modes, $\psi_b = A_1$, $\psi_a = A_1$ and $\psi_b \psi_a = A_1$; since, $z = A_1$, $(\psi_b \psi_a) z = A_1 A_1 = A_1$ and the z-component of the transition dipole moment (μ_z) is nonzero.

(ii) For the antisymmetric stretching mode, $\psi_b = B_1$, $\psi_a = A_1$ and $\psi_b \psi_a = B_1 A_1 = B_1$; since $x = B_1$, $(\psi_b \psi_a) x = B_1 B_1 = A_1$ and the x-component of the transition dipole moment (μ_x) is nonzero.

Note that the results (i) $\psi_b = A_1$ for symmetric stretching and bending modes, and (ii) $\psi_b = B_1$ for the antisymmetric stretching mode follow from our discussion on the irreducible representations of the vibrational modes in Step 4. Also the ground state belongs to A_1 i.e., $\psi_a = A_1$ for all these three modes.

Hence, all the three vibrational modes of H_2O are IR active.

Here it is worth making the generalisation:

A vibration will be IR active, if it belongs to the same symmetry species as a component of transition dipole moment, i.e., to the same symmetry species as x, y, or z.

We shall shortly apply this rule to NH_3 molecule which belongs to C_{3v} group.

In Sec. 6.7 of Unit 6, the assignment of vibrational modes to the experimentally observed IR absorption bands will be explained using IR and Raman spectra.

You are aware that NH_3 has the following symmetry operations :

$E, C_3^1, C_3^2, \sigma_v, \sigma'_v$ and σ''_v (See Secs. 2.4 and 2.5 of Unit 2).

Also C_3^1 and C_3^2 belong to one class, σ_v, σ'_v, σ''_v belong to another class while E is a class in itself. Hence the operations are grouped under three classes:

$$E,\ 2C_3 \text{ and } 3\sigma_v$$

The character table for C_{3v} is given below:

Character Table of C_{3v}

	Three classes in C_{3v}					
C_{3v}	E	$2C_3$	$3\sigma_v$			
A_1	1	1	1	z	z^2, x^2+y^2	
A_2	1	1	–1			R_z
E	2	–1	0	(x, y)	(xy, x^2-y^2) (xz, yz)	(R_x, R_y)

Irreducible representations of C_{3v} group

Step 1: Reducible representation for all the symmetry operations of NH_3

To find the characters of the reducible representation using Eq. A.1, we must know n_a and $\chi_R(p)$ for each of the symmetry operations. While arriving at n_a and $\chi_R(p)$ values, it is enough to consider only one member of each class. Hence, n_a, $\chi_R(p)$ and $\chi_R^t(p)$ of E, C_3 and σ_v are to be calculated for finding the reducible representation of the molecule.

You may be aware that operation E does not shift any of the four atoms in NH_3; hence $n_a = 4$ for E. During C_3 (C_3^1 or C_3^2) operation, nitrogen atom alone is not shifted; hence $n_a = 1$ for C_3. During any of the three σ_v operations, nitrogen atom and one of the H atoms are not shifted. Hence $n_a = 2$ for σ_v.

We can obtain $\chi_R(p)$ values of E, C_3 and σ_v using Table A.1 as follows:

	E	$C(120°)$	σ_v
$\chi_R(p)$	3	$1 + 2\cos 120° = 0$	1

For C_3 axis, the order of axis (n) = 3. Using Eq. 2.1 of Unit 2, minimum angle of rotation

$(\alpha) = 360°/3 = 120°$

Also $C(120°) = 1 + 2\cos 120°$
$= 1 - (2 \times 1/2)$
$= 0$

because $\cos 120° = -\sin 30°$
$= -1/2$

The calculation of $\chi_R^t(p)$ for each symmetry operation can be shown as follows:

r	E	$2C_3$	$3\sigma_v$	
$\chi_R(p)$	3	0	1	
n_a	4	1	2	
$\chi_R^t(p)$ (calculated as per Eq. A.1)	12	0	2	...(A.7)

Step 2 : Obtaining the reducible representation of all the vibrations

As done in the case of H_2O molecule, we shall subtract the characters of symmetry operations in the irreducible representations of translations and rotations from the characters of symmetry operations given by Eq. A.7 so that we could obtain the reducible representation of all the vibrational modes of NH_3 molecule.

As per C_{3v} character table, the translations belong to E and A_1, because these are influenced by the symmetry operations in the same way as x, y and z directions. Similarly the rotations belong to E and A_2 since R_x, R_y and R_z belong to these symmetry species.

Hence the sum of the characters of the symmetry operations in the irreducible representations of translations is given by E + A_1 (Eq. A.8); and the sum of the characters of the symmetry operations in the irreducible representations of rotations is given by E + A_2 (Eq. A.9).

Using C_{3v} character table, E + A_1 and E + A_2 can be calculated. The characters of the symmetry operations in the reducible representation of vibrations (τ) is given by subtracting Eqs. A.8 and A.9 from Eq. A.7.

	E	$2C_3$	$3\sigma_v$	
$\chi'_R(p)$	12	0	2	...(A.7)
$-[(E + A_1)$	3	0	1	...(A.8)]
$-[(E + A_2)$	3	0	-1	...(A.9)]
	6	0	2	...(A.10)

Eq. A.10 represents the characters of the symmetry operations ($\chi(p)$) in τ, the reducible representation of all vibrational modes of NH_3 molecule.

Step 3: Obtaining the symmetry species of the vibrational modes

We shall use Eq. A.6 to obtain the symmetry species of the vibrational modes of NH_3 molecule. We know that for C_{3v} group, $h = 6$, since there are six operations:

$$E, C_3^1, C_3^2, \sigma_v, \sigma'_v \text{ and } \sigma''_v$$

Also $N = 1$ for the class of operation, E; $N = 2$ for the class of operations C_3^1 and C_3^2 and $N = 3$ for the class of operations, σ_v, σ'_v and σ''_v

To get $\chi(p)$, we have to use Eq. A.10 and, to get $\chi_I(p)$, we have to use character table of C_{3v}.

$$\left.\begin{array}{l}\text{Number of times}\\ A_1 \text{ symmetry species}\\ \text{occurs in } \tau \text{ representation}\end{array}\right\} = n_{A_1}$$

$$= 1/6\,[(1 \times 6 \times 1) + (1 \times 0 \times 2) + (1 \times 2 \times 3)]$$

$$= 1/6\,[12] = 2$$

Similarly, $n_{A_2} = 1/6\,[(1 \times 6 \times 1) + (1 \times 0 \times 2) + ((-1) \times 2 \times 3)]$

$$= 1/6\,[6 - 6] = 0$$

$$n_E = 1/6\,[(2 \times 6 \times 1) + ((-1) \times 0 \times 2) + (0 \times 2 \times 3)]$$

$$= 2$$

Hence symmetry species of vibrations = $2A_1 + 2E$.

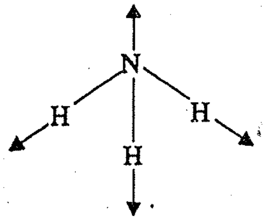
The two vibrations which belong to the symmetry species A_1 must be totally symmetric with respect to all symmetry operations, while two others belonging to E are antisymmetric and are doubly degenerate.

Step 4 : Identifying the symmetry species of each vibrational mode

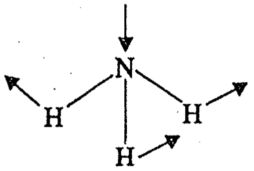
The four fundamental modes of NH_3 given below can be examined with respect to the symmetry operations E, C_3 and σ_v. The vibrational modes for which the directions of the arrows remain the same after performing each one of these three operations belong to the totally symmetric species, A_1. Those vibrational modes for which there is a change in the direction of arrows could be considered to belong to the symmetry species E through a process of elimination.

If you proceed correctly, you will find that one stretching vibration and one bending vibration belong to the totally symmetric species (A_1). Evidently the other two belong to the antisymmetric species (which are assumed to belong to E, the doubly degenerate mode).

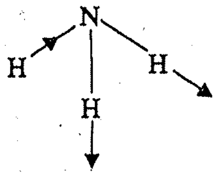
The four fundamental vibrational modes of NH_3 are given below:



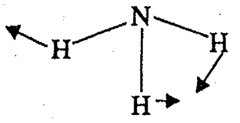
Symmetric stretching
A_1



Out-of-plane symmetric bending
A_1



Antisymmetric stretching
E



Antisymmetric bending
E

Step 5 : Identifying the infrared active vibrational modes

Using the method indicated for H_2O molecule, you may try to see whether the two vibrational modes with A_1 and the other two with E symmetry are IR active. By using the generalisation stated earlier regarding the infrared activity of vibration, we can conclude that all these are expected to be IR active since (i) two of the vibrational modes (symmetric stretching and out-of-plane symmetric bending) belong to A_1 to which z also belongs and (ii) the other two vibrational modes, (antisymmetric stretching and antisymmetric bending), belong to E to which x and y also belong. Hence all the four fundamental modes are expected to be IR active.

UNIT 6 : RAMAN SPECTROSCOPY

Structure

6.1 INTRODUCTION

The origin of Raman spectrum lies in the scattering of radiation by molecules. During the scattering of radiation, there is a change in the direction of the photon on interaction with matter. For example, the blue colour of the sky is the result of scattering of light by air molecules. The interaction of monochromatic radiation with matter may result in an (i) elastic collision or (ii) inelastic collision. The resultant radiation after an elastic collision will have the same frequency as that of the incident radiation and is known as **Rayleigh scattering.** Thus in Rayleigh scattering, the frequency of the resultant radiation is the same as that of the incident radiation but the direction of the radiation is changed. On the other hand, if there is an inelastic collision, then the direction as well as the frequency of the resultant radiation would be different from that of the incident radiation. Thus due to inelastic collision, there is a transfer of energy between the electromagnetic radiation and the molecules of the medium. Although the energy thus available for exchange may be stored in the molecule in electronic, vibrational or rotational modes, it is the exchange with the vibrational modes that is of the greatest interest to chemists. The transfer of energy consequent to inelastic collision is of the order of 3-3000 cm^{-1} which lies in the far infrared to infrared region of the electromagnetic spectrum. These inelastic collisions can, therefore, give us information about the rotations and vibrations of the molecules. The study of such radiation arising out of inelastic collisions is called Raman spectroscopy. In this unit, we shall study the basic concepts related to Raman spectroscopy and its applications.

Objectives

After studying this unit you should be able to:

- explain the origin of Raman spectrum in terms of classical and quantum mechanical concepts,
- differentiate between infrared and Raman sp

- describe the rule of mutual exclusion and explain its use in the determination of structure of molecules, and
- illustrate the applications of Raman spectra.

6.2 ORIGIN OF RAMAN SPECTRUM

In 1923, Smekal predicted that on irradiation of a substance with a monochromatic light, scattering of radiation will take place and some of the scattered radiation should have different frequencies from that of the incident radiation. In 1928, Raman experimentally established the existence of such frequencies above and below that of the incident beam. However, molecules gain or lose energy according to quantum laws. When the molecules gain energy, the scattered photons will be of lower energy or frequency and appear in the spectrum as Stokes lines. On the other hand, if the molecules lose their energy to the photons, the scattered radiation will appear with higher frequency than the incident radiation, and the resultant lines are called anti-Stokes lines. The main bulk of the scattered radiations will appear unaltered in energy and is termed as Rayleigh scattering.

6.2.1 Classical Theory of Raman Spectrum

We can consider the molecules of a substance as a sea of electrons in which the positively charged nuclei are **embedded.** If such a system is subjected to a static electric field, the electrons will be attracted to the positive pole and the positively charged nuclei will be attracted towards the negative pole. The separation of charges gives rise to induced dipole moment in the molecules. The molecules are then said to be polarized. The magnitude of the induced dipole moment depends on the strength of the applied field (E) and the polarizability (α) of the molecule.

$$\mu = \alpha E \qquad ...(6.1)$$

Polarizability has the dimension of volume and it is considered to be proportional to the volume of the molecule.

The polarizability of a molecule is a measure of the ease with which a molecule can be distorted. Some molecules may get distorted or deformed much more easily than the others. Polarizability has already been explained in Unit 6 of Block 1 of Atoms and Molecules course. Polarizability of any molecule need not be the same in all directions. For example, even for a simple homonuclear diatomic molecule, the electrons forming the bond can easily be displaced by an electric field applied along the bond axis as compared to the case when the field applied is at right angles to bond axis. In other words, polarizability of molecules is an anisotropic property. The anisotropic nature of molecular polarizability facilitates activity in Raman spectra.

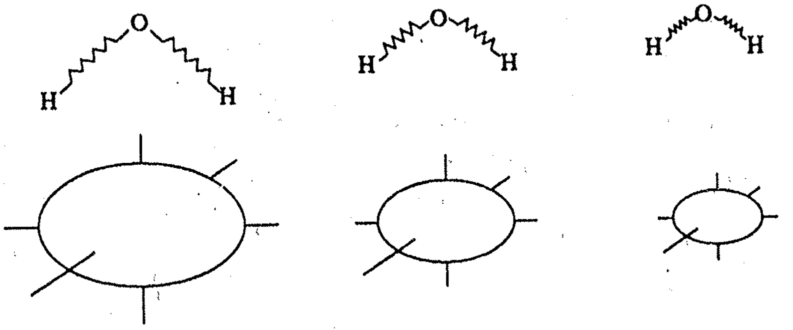
Isotropic property has the same value in all the directions. Density of a substance is an example for isotropic property, since it is same for any portion of a substance, irrespective of the directions.

An anisotropic property has different values along different directions of applications of a force field. X-ray diffraction by crystals is an instance of anisotropic property. The anisotropic nature of polarizability is the main factor deciding the activity in Raman spectra.

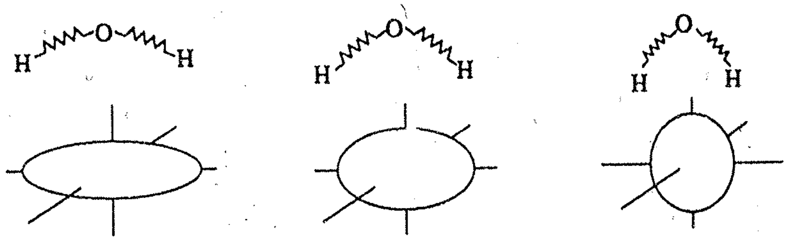
Polarizability of a spherical species is an isotropic property. For instance, the polarizability of atoms is isotropic. Polarizability of spherical top molecules (like CH_4, SF_6) is also isotropic.

Using classical theory it is possible to prove that in order to obtain Raman spectrum, the molecular vibration (or rotation) must cause some change in the polarizability of the molecule. We shall just take this result without trying to prove the same. It is possible to depict polarizability changes in terms of polarizability ellipsoids where we represent the polarizability in various directions. The ellipsoid is a three dimensional surface for which the distance from the electrical centre of the molecule is inversely proportional to the square root of the polarizability (i.e., $1/\sqrt{\alpha}$). Thus where the polarizability is the greatest, the distance from the axis of the ellipsoid is the least and vice versa. During each of the three modes of vibrations of H_2O, symmetric stretching mode (ν_1), bending mode (ν_2) and antisymmetric stretching mode (ν_3), the polarizability changes and hence all the three are Raman active (Fig.6.1).

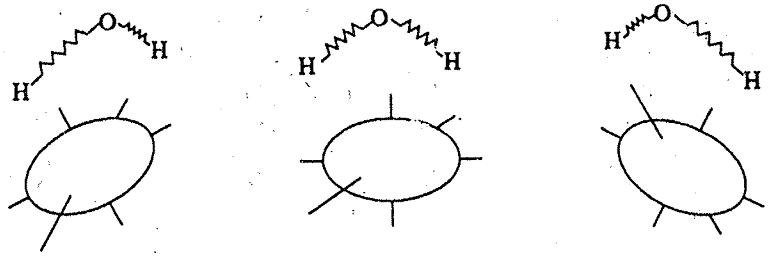
A periodically changing polarizability is the requirement for a Raman band.



(a) Symmetric stretching, (A_1)



(b) Symmetric bending (A_1)

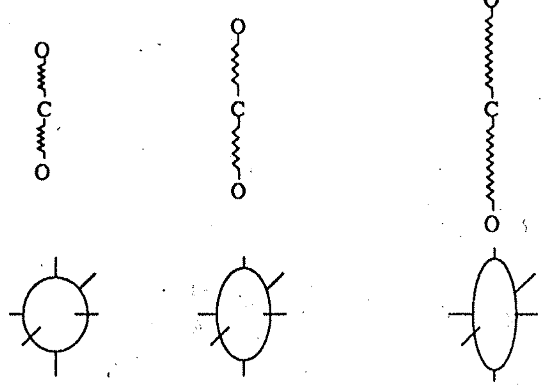


(c) Antisymmetric stretching, (B_1)

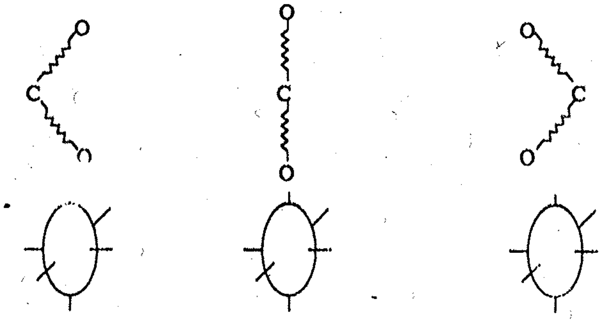
Fig.6.1 : **The shapes of the polarizability ellipsoids of H_2O molecule during three vibrational modes; the centre column shows the equilibrium position of the molecule while those in the right and left are extremes of vibration. (a), (b) and (c) stand for symmetric stretching mode (ν_1), the bending mode (ν_2) and the antisymmetric stretching mode (ν_3), respectively. All the three vibrations of H_2O involve a change at least in one of the three aspects of polarizability ellipsoids, namely, size, shape or direction.**

In Figs. 6.1 and 6.2, the symmetry species of vibrations (such as A_1, B_1, $\sum_g^+$, $\sum_u^+$ and Π_u) are mentioned in terms of group theory symbols. In this connection, go through Table 6.2 in Sec 6.7, the marginal matter given along with it and the character tables at the end of the Appendix of this unit.

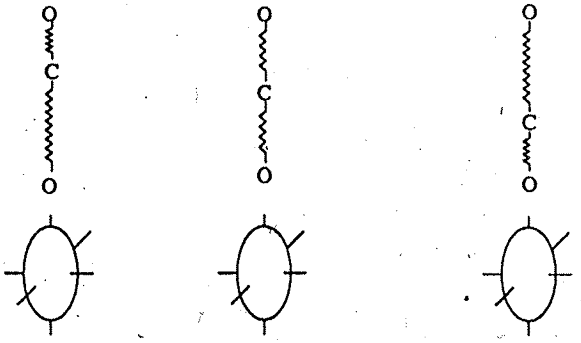
In the case of CO_2 molecule, it is seen that during symmetric stretching (ν_1), polarizability changes because of the change in ellipsoid size and this mode is Raman active. For the bending (ν_2) and antisymmetric stretching modes (ν_3), there is no overall change in polarizability ellipsoid (Fig.6.2). Hence the bending and antisymmetric stretching modes of CO_2 are Raman inactive. This aspect can be explained as follows. The molecular polarizability of a molecule can be thought of in terms of bond polarizabilities. We can assume that a net periodic polarizability change facilitates activity in Raman spectra. The symmetric stretching mode of CO_2 is Raman active since the polarizability changes in each bond during stretching or compression add up to give a net periodic polarizability change. For the antisymmetric stretching mode of CO_2, the polarizability change in one bond cancels that for the other bond and this mode is Raman inactive. Similarly during the bending vibrations of CO_2, the net polarizability change is zero, since the two C–O bonds are bent in opposite directions during each of the bending vibrations of bond angle expansion or compression and hence, the bending mode is also Raman inactive.



(a) Symmetric stretching, (Σ_g^+)



(b) Bending, (Π_u)



(c) Antisymmetric stretching, (Σ_u^+)

Fig.6.2. : The shapes of polarizability ellipsoids of CO_2 molecule during (a) symmetric stretching (ν_1) (b) bending (ν_2) and (c) antisymmetric stretching (ν_3) modes. Of these three, only symmetric stretching accounts for overall change in the ellipsoid and only this is Raman active.

In Units 3 and 4, we have studied that in the infrared (or microwave) region, a vibration (or rotation) is active only when it brings about a change in the dipole moment of the molecule . We can generalise that any vibration(or rotation) which causes a change in the polarizability of the molecule will be Raman active whereas any vibration (or rotation) which brings about a change in the electric dipole moment of the molecule will be infrared (or microwave)active. Some vibrations may be both Raman and infrared active. Group theory can be elegantly used to find out whether a vibration will be Raman active or not. A brief discussion along these lines is given in the Appendix of this unit.

6.2.2 Quantum Theory of Raman Spectrum

Let us discuss the quantum mechanical treatment of Raman spectrum. Consider the interaction of a photon of frequency ν with an isolated molecule. The oscillating electric field associated with the photon of energy $h\nu$ interacts with the molecule and deforms the electronic configuration of the molecule. For some infinitesimally small period of time, the photon and the molecule may be considered to constitute a new state, which may be called a virtual state. The molecule has reached this new state through interaction with the photon; this state is higher in energy to the extent of the energy of the incident beam, $h\nu$. The virtual state is an unstable state and a photon is immediately emitted as scattered radiation, while the molecule returns to one of the states associated with the molecule. Let E_a and E_b be the initial and final energy states of the molecule. If ν and ν' are frequencies of the incident and the scattered radiations, we can write using the law of conservation of energy,

$$h\nu + E_a = h\nu' + E_b \qquad \ldots(6.2)$$

$$E_a - E_b = h(\nu' - \nu) \qquad \ldots(6.3)$$

If $E_a = E_b$, then the scattered radiation will have the same frequency as the incident radiation ($\nu' = \nu$) as evident from the above equation. Thus the collision between the photons and the molecules is an elastic one and the scattering is of Rayleigh type.

If $E_a < E_b$, then the frequency of the scattered radiation ν' will be less than the frequency of the incident radiation ν (or the wavelength of the scattered radiation (λ')) will be more than that of the incident radiation (λ) i.e. in Stokes lines, $\nu' < \nu$ or $\lambda' > \lambda$. In other words, some portion of the energy is transferred from the incident radiation to the molecules and thus scattered radiation appears at a lower frequency (or at longer wavelength) in the spectrum. The scattered radiation appears as Stokes lines in the Raman spectrum.

Finally if $E_a > E_b$, the scattered radiation will appear at higher frequency (or at shorter wavelength) than the incident radiation and it is known as anti-Stokes lines, i.e., in anti-Stokes lines, $\nu' > \nu$ and $\lambda' < \lambda$. The origin of Stokes lines, Rayleigh lines and the anti-Stokes lines are shown in Fig. 6.3a. The schematic diagram of Raman spectra of a diatomic gas is shown in Fig. 6.3b.

While working problems using Eq. 6.4, you have to remember the following:

(i) $\bar{\nu}$ is the wavenumber ($1/\lambda$) of the incident radiation.

(ii) $\bar{\nu}'$ is the wavenumber ($1/\lambda'$) of the scattered radiation; $\bar{\nu}'$ is also called the absolute wavenumber at which a band will be observed in the Raman spectrum or the position of the Raman line.

(iii) $\Delta\bar{\nu}$ corresponds to the wavenumber of the vibration band in the vibrational Raman spectrum or the spacing between a particular set of lines in the rotational Raman spectrum.

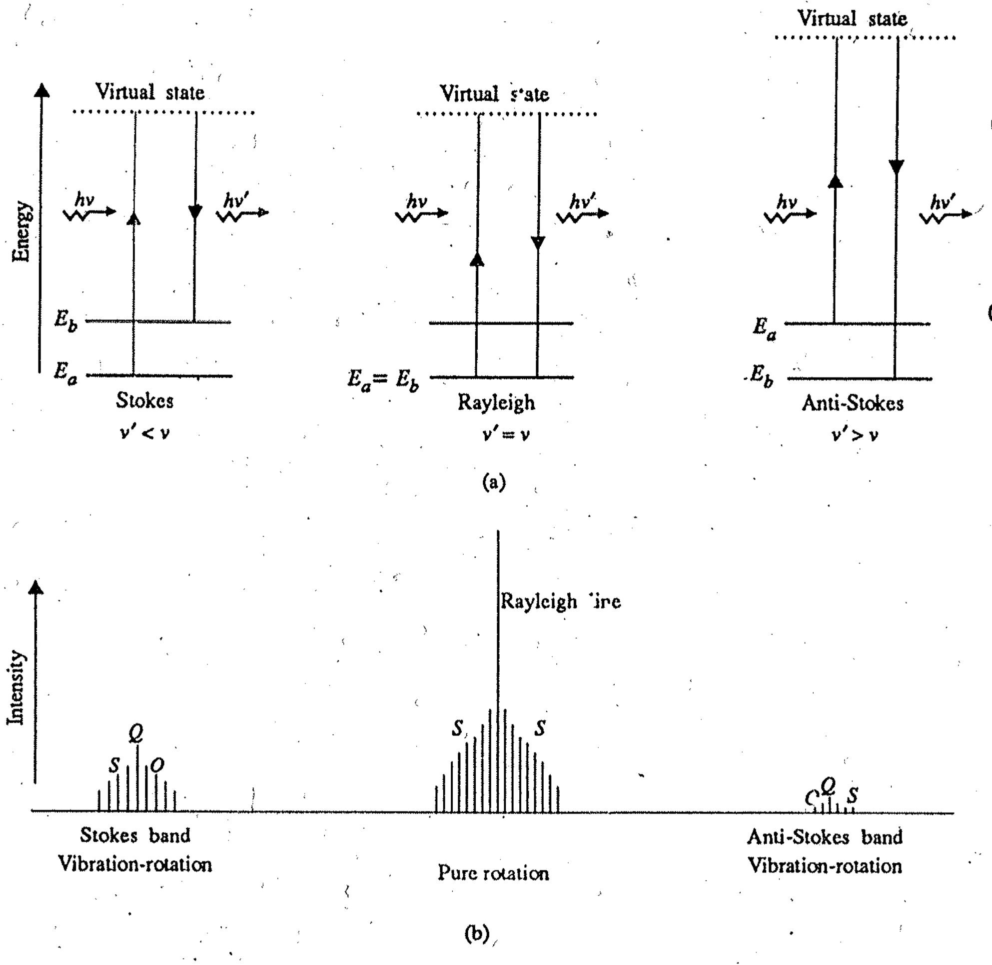


Fig. 6.3: (a) The interactions that give rise to the Stokes, anti-Stokes and Rayleigh lines.
(b) The schematic diagram of Raman spectrum of a diatomic gas.

Since the transfer of energy to and from the molecules follow the same quantum laws, both Stokes and anti-Stokes lines appear at equal spacing from the Rayleigh line. In order to give a common expression for Stokes and anti-Stokes lines, we can write in terms of wavenumbers,

$$\bar{\nu}' - \bar{\nu} = \pm \Delta \bar{\nu} \quad \text{....(6.4)}$$

where $\bar{\nu}'$ and $\bar{\nu}$ are wavenumbers of the scattered and incident radiation, respectively and, $\Delta \bar{\nu}$, is the rotational or vibrational or rotation-vibration wavenumber of the molecule. $\Delta \bar{\nu}$ is known as the Raman shift. The plus sign in Eq. 6.4 refers to anti-Stokes lines while the minus sign refers to Stokes lines.

Raman spectrum is a plot of intensity of scattered radiation as a function of wavenumber. The band corresponding to $\bar{\nu}$ constitutes the Rayleigh line. The bands to the left of $\bar{\nu}$ are Stokes lines since $(\bar{\nu}' - \bar{\nu})$ for these are negative. The bands to the right of $\bar{\nu}$ have positive $(\bar{\nu}' - \bar{\nu})$ values and these are anti-Stokes lines. The intensity of the lines depends on the population at different energy levels (Fig. 6.3b). The relative heights of lines are indicative of relative intensities.

There are more molecules in the ground state than in the excited state and, the former class gives rise to the Stokes lines while the latter gives rise to the anti-Stokes lines; hence, Stokes lines are more intense than the anti-Stokes lines (Fig. 6.3b).

The intensity of Raman scattering in general is very low. Only about 10^{-5} of the incident radiation is Rayleigh-scattered and the total amount of Raman-scattered radiation is about 10^{-2} that of the Rayleigh-scattered radiation. It is customary to observe only Stokes emission, since anti-Stokes emission for vibrational energy transfer is usually too weak to be detected.

The experimental details of obtaining Raman spectra will be discussed in Unit 9 of this course.

From the above discussion you can understand that the ideal source for Raman spectroscopy must be both very intense and highly monochromatic. The development of laser as a source has greatly facilitated the usage of Raman spectroscopy.

It is found that the Raman shift $(\Delta \bar{\nu})$ is generally of the order of 3-3000 cm^{-1}. The Raman shift can be observed from far infrared to infrared region but Raman spectroscopy should not be taken as a kind of infrared or microwave spectroscopy . It is important to remember that a "Raman frequency" of $2 \times 10^5\ \text{m}^{-1}$ is not measured in the infrared region but corresponds to an emission at a wavelength of 540.8 nm for excitation by an Ar laser. You go through the following examples.

Example 1

The Raman spectrum of $C_2H_2(g)$ observed using 435.80 nm Hg incident radiation shows one of the lines at 511.00 nm. Determine the wavenumber of the vibration band $(\Delta \bar{\nu})$.

Since $\lambda' > \lambda$, the observed band is a Stokes line.

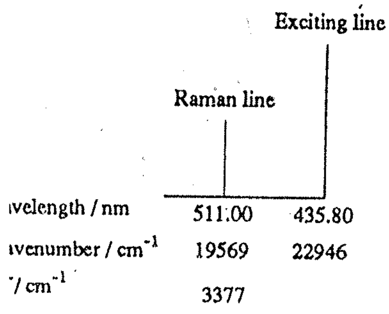
Applying Eq. 6.4 for a Stokes line,

$$-\Delta \bar{\nu} = \bar{\nu}' - \bar{\nu}$$

or

$$\Delta \bar{\nu} = \bar{\nu} - \bar{\nu}' = 1/\lambda - 1/\lambda'$$

$$= 3.377 \times 10^5\ \text{m}^{-1} = 3377\ \text{cm}^{-1}$$



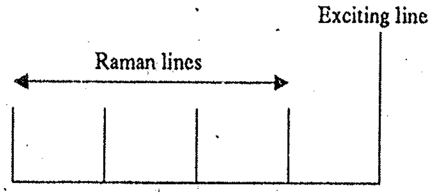
Example 2

The Raman spectra of CF_4(g) was observed using the 435.80 nm Hg exciting energy. Four bands corresponding to the four fundamental vibrations were observed at 444.25 nm, 448.16 nm, 453.80 nm and 461.64 nm. Determine the wavenumbers $(\Delta \bar{\nu})$ of these fundamental vibrations.

Since $\lambda' > \lambda$ for all the lines, these are Stokes lines. Applying Eq. 6.4 for Stokes lines,

$$\bar{\nu}' - \bar{\nu} = -\Delta \bar{\nu}$$

we can calculate the wavenumbers of these vibrations as shown below:



Wavelength / nm	461.64	453.80	448.16	444.25	435.80
Wavenumber / cm^{-1}	21662	22036	22313	22510	22946
$\Delta\bar{\nu}$ / cm^{-1}	1284	910	633	436	

In the next three sections, we shall discuss the rotational, vibrational and vibration-rotation Raman spectra of molecules in detail. However, before proceeding to the next section, you may answer the following SAQ.

SAQ 1

Would all the rotational and vibrational transitions of a molecule be Raman active ?

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6.3 ROTATIONAL RAMAN SPECTRA

In Unit 3 of this course while discussing the pure rotational spectra, we classified the molecules under the categories of linear, spherical top, symmetric top and asymmetric top. We also stated mathematical expressions for the calculation of energies of different rotational levels as well as for the energy involved in the transition from one level to another for molecules belonging to these categories. For our discussion on the rotational Raman spectra, we shall follow the same classification.

Linear molecules

As derived in Unit 3 of this course, the rotational energy levels for a linear molecule are given by Eq. 6.5.

$$\varepsilon_J = BJ(J+1)\ \text{cm}^{-1} \qquad \text{...(6.5)}$$

where $J = 0, 1, 2$, etc, B is the rotational constant for the molecule and ε_J is the rotational energy expressed in wavenumbers.

In Eq. 6.5. we have neglected the higher order terms since in Raman spectra, such high precision is generally not obtained. The selection rule for rotational Raman spectra is

$$\Delta v = 0 \ \text{and}$$
$$\Delta J = 0, \pm 2 \ \text{(in the same vibrational level)}$$

The transition $\Delta J = 0$ means that the scattered radiation has the same frequency as the incident radiation and it appears as Rayleigh scattering only.

When $\Delta J = +2$, we can write for a transition $J \rightarrow J+2$,

It is worth recollecting that the selection rule for microwave spectra is $\Delta J = \pm 1$. But in rotational Raman spectra, the selection rule is

$$\Delta J = 0, \pm 2$$

We know that the rotational changes in the Raman spectrum depend on the polarizability of the molecule. The polarizability in turn is associated with two dipole transitions – one for the incoming, and one for the outgoing photon. Hence, there will be two quantum rotational jumps as given by

$$\Delta J = \pm 2$$

$$\Delta\varepsilon_{rot} = B\,[(J+2)(J+3) - J(J+1)]\ \text{cm}^{-1}$$

$$= B(4J+6)\ \text{cm}^{-1} \qquad \text{....(6.6)}$$

where $J = 0, 1, 2, 3, ...$ and it is the rotational quantum number in the lower state.

$\Delta\,\varepsilon_{rot}$ stands for the rotational energy change in cm^{-1} unit during the transition. We shall use the term $\Delta\,\bar{\nu}_{rot}$ instead of $\Delta\varepsilon_{rot}$ and write,

$$\Delta\,\bar{\nu}_{rot} = B(4J+6)\ \text{cm}^{-1} \qquad \text{....(6.7)}$$

Eq. 6.4 can be rewritten for rotational spectra as follows:

$$\bar{\nu}' - \bar{\nu} = \pm\,\Delta\,\bar{\nu}_{rot} \qquad \text{....(6.8)}$$

$\Delta\,\bar{\nu}_{rot}$ is the Raman shift for the rotational Raman spectra or the rotational Raman shift.

Using Eq. 6.7 we can write,

$$\bar{\nu}' - \bar{\nu} = \pm B\,(4J+6)\ \text{cm}^{-1} \qquad \text{....(6.9)}$$

We can understand that $+\Delta\,\bar{\nu}_{rot}$ stands for anti-Stokes lines while $-\,\Delta\,\bar{\nu}_{rot}$ stands for Stokes lines.

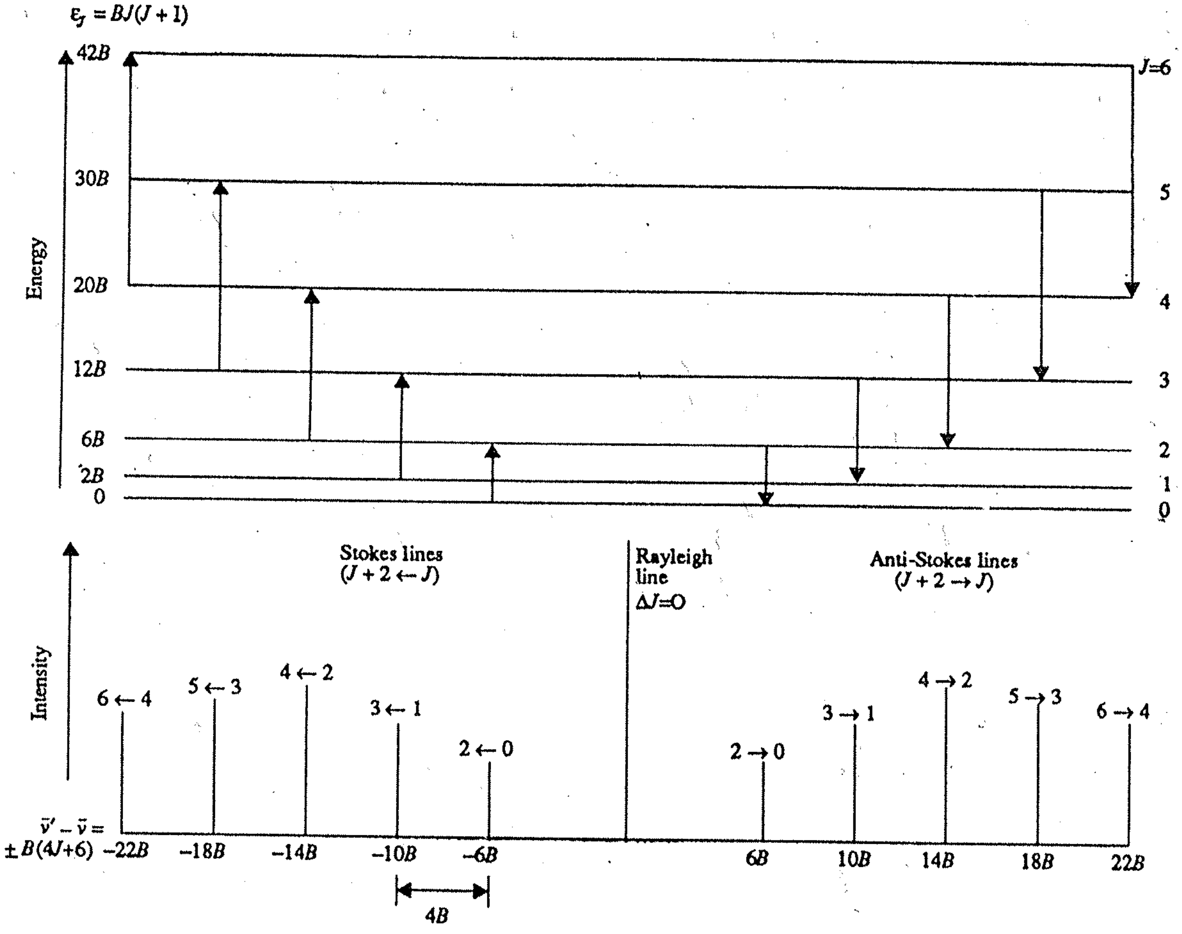

Fig. 6.4: Pure rotational Raman spectrum of a diatomic molecule—schematic diagram.

The schematic Raman rotational spectrum of a diatomic molecule is given in Fig. 6.4. Each transition is labelled according to the transitions. The relative heights of lines are indicative of relative intensities of lines which again depend on the population at various energy levels.

There is a general rule for labelling any series of lines in the spectrum which states that when $\Delta J = +2, +1, 0, -1, -2$, the corresponding group of frequencies are called *S, R, Q, P* and *O* branches of the spectrum, respectively. Thus in the above case, when $\Delta J = +2$, we shall observe *S*-branch of the spectrum. Notice that when $J = 0$ is substituted in Eq. 6.9, the separation of the first line from the exciting line is found to be $6B$. Once the value of rotational constant B is known, we can evaluate the moment of inertia of the molecule since,

$$B = \frac{h}{8\pi^2 Ic}$$

Since $\Delta \bar{\nu}_{rot} = B(4J + 6)$, substituting different values of $J = 0, 1, 2, 3$, etc., we get the corresponding lines at $6B$, $10B$, $14B$, $18B$ etc. (less than or greater than) from the exciting radiation ($\bar{\nu}$) for the Stokes and the anti-Stokes lines, respectively as shown in Fig. 6.4.

Thus the spacing between the lines would be $4B$.

Rotational Raman spectra for molecules like H_2, O_2, HCN, CO_2, C_3O_2 etc. have yielded useful information about their molecular structure. This information is especially useful for homonuclear diatomic molecules which give no infrared or microwave spectra. Raman spectrum with rotational fine structure is generally not obtained for linear molecules having more than three atoms.

It should be mentioned that if the molecule has a centre of symmetry (as in the case of H_2, N_2, O_2, CO_2) the nuclear spin exerts its effect in the Raman and IR spectra. The intensity pattern can be explained using nuclear spin effect. We shall not go into the theoretical background of this aspect but state a few examples. The significant conclusion is that the intensity pattern of rotational Raman spectra has a vital role to play while providing data regarding molecular structure.

In order to show the nuclear spin effect on the intensity pattern, let us consider two types of molecules, one having zero nuclear spin and another having nonzero nuclear spin.

(i) In the rotational Raman spectra of molecules like O_2 (with ^{16}O atoms) and CO_2 (with ^{12}C and ^{16}O atoms, both having zero nuclear spin), every alternate rotational level is absent. One can see an interesting variation between the rotational Raman spectra of CO_2 and O_2. In CO_2, every level with odd J value is missing and thus transitions from $J = 1, 3, 5, \ldots$ levels are completely absent (as shown by dotted lines in Fig. 6.5), while lines of even J values are observed.

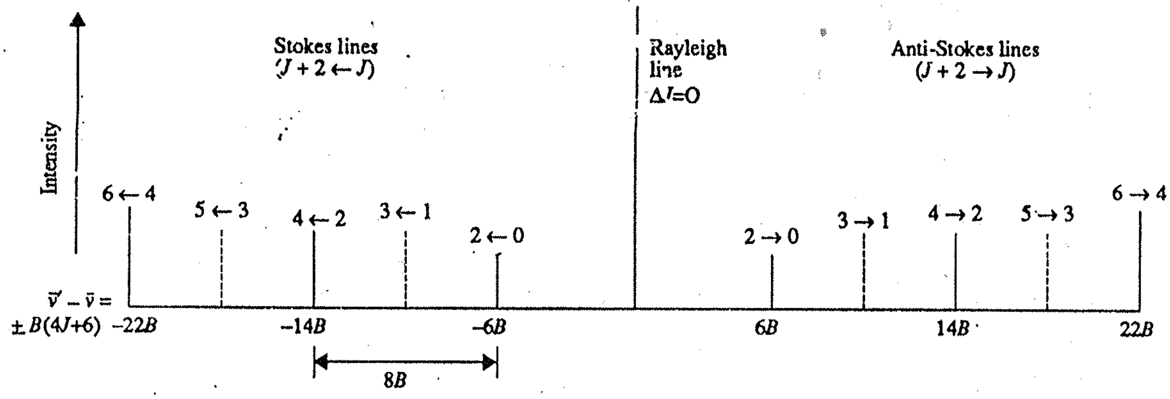

Fig. 6.5 : Schematic diagram of pure rotational Raman spectra of CO_2. Note that all the odd J lines of CO_2 are absent (as shown by the dotted lines). All the allowed transitions (i.e., those of even J values) are shown by solid lines.

The average line separation then is equal to $8B$ (i.e., $\Delta \bar{\nu} = 8B$) while the difference between the first Stokes line and the first anti-Stokes line is $12B$. Similarly in the Raman spectrum of $^{16}O_2$, the spectral transitions correspond to energy levels with odd J values and those from even J values are missing. The average line separation is equal to $8B$ while the separation between the first stokes line, and the first anti-Stokes line is $20B$. Let us try to work out the following problem.

Example 3

The rotational Raman spectra of $CO_2(g)$ showed a series of absorption peaks separated by 3.16 cm^{-1} in the S branch. What is the value of the rotational constant (B) for CO_2 molecule ?

In the case of CO_2, $\Delta \bar{\nu}_{rot} = 8B$

$$B = \frac{3.16}{8}\ cm^{-1}$$

$$= 0.395\ cm^{-1}$$

$$= 39.5\ m^{-1}$$

(i) In the case of molecules like $^1H_2$, $^{14}N_2$ etc. (which have nonzero nuclear spin), the intensity of every alternate line decreases. The intensity ratio of 2:1 in favour of even J values is observed between the successive lines in the rotational Raman spectra of $^{14}N_2$ (Fig. 6.6). In other words, the lines at even J values have greater intensity than those at odd J values. In the rotational Raman spectra of $^1H_2$, the intensity ratio of 3:1 is observed between the successive lines.

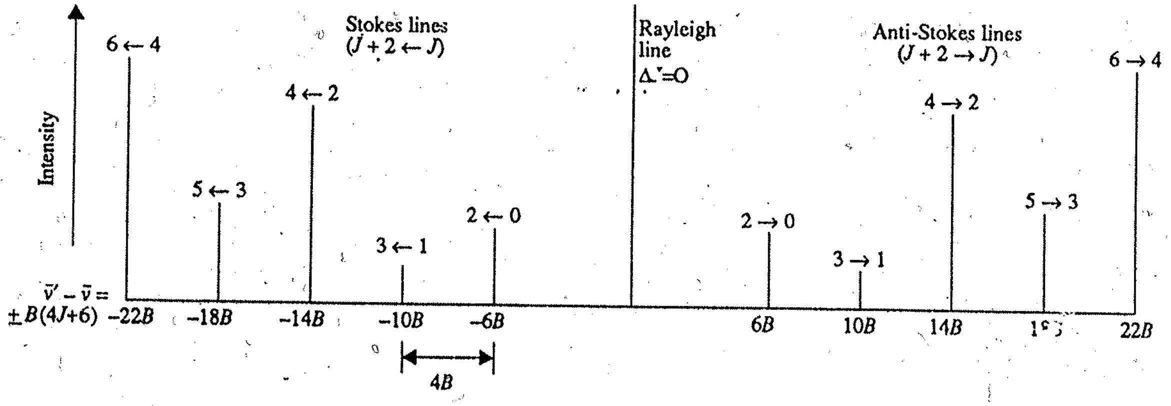

Fig. 6.6: Rotational Raman spectra of $^{14}N_2$.

While using rotational Raman spectra of H_2, N_2 etc. for obtaining molecular parameters, it should be borne in mind that $\Delta \bar{\nu} = 4B$.

Example 4

For hydrogen molecule, the spacing between the S-branch lines in the Raman spectrum is 243.2 cm^{-1}. Calculate the bond length of hydrogen.

Mass of hydrogen atom = 1.673×10^{-27} kg

For hydrogen molecule, the spacing between the lines $(\Delta \bar{\nu}) = 4B$

$$4B = 243.2\ cm^{-1}$$

$$= 2.432 \times 10^4\ m^{-1}$$

$$B = 6.008 \times 10^3\ m^{-1}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.626 \times 10^{-34}}{8 \times (3.143)^2 \times 6.008 \times 10^3 \times 2.998 \times 10^8} \text{ kg m}^2$$

$$= 4.655 \times 10^{-48} \text{ kg m}^2$$

$$\mu = \frac{m_H \cdot m_H}{m_H + m_H} = \frac{m_H}{2}$$

$$= 8.365 \times 10^{-28} \text{ kg}$$

$$r = \left(\frac{I}{\mu}\right)^{1/2} = \left(\frac{4.655 \times 10^{-48}}{8.365 \times 10^{-28}}\right)^{1/2} \text{ m} = 7.46 \times 10^{-11} \text{ m}$$

$$= 74.6 \text{ pm}$$

The spherical top molecules (like CH_4 and SF_6) on rotation along any axis would not produce a change in the polarizability of the molecules. Hence the spherical top molecules do not exhibit rotational Raman spectra. We shall not discuss the rotational Raman spectra of symmetric top and asymmetric top molecules due to their complexity.

In the next section, we shall discuss the vibrational Raman spectra of molecules. You may try to answer the following SAQ before proceeding to the next section.

SAQ 2

Calculate I and carbon-oxygen bond distance (r_{C-O}) for CO_2 (g), knowing that B is 39.5 m^{-1}

Hints: $I = 2 \times \text{mass of oxygen atom} \times (r_{C-O})^2$

$$\text{Mass of oxygen atom} = \frac{0.016}{6.023 \times 10^{23}} \text{ kg}$$

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6.4 VIBRATIONAL RAMAN SPECTRA

We have seen that the Raman frequencies cover the region of energy which can also bring about the changes in the vibrational energy level of the molecules. Thus, both the infrared and Raman spectra will give us information about the vibrational changes in the molecule. However, since the origin of spectra is different in the two cases, we can get information through Raman spectra about those molecules which are inaccessible to infrared spectra.

Each vibrational change will be accompanied by rotational change. Hence, the vibration spectra is truly a vibration-rotation spectra; but the rotational changes are observed only in the gaseous state, where the molecules are far apart from each other and, have complete freedom of rotation. Thus, only under high resolution, molecules in gaseous state give Raman spectra with rotational fine structure. In this section, we shall deal with the vibrational Raman spectra only.

As discussed in Unit 4 on vibrational spectra, we can express the vibrational energy as

$$\varepsilon_{\text{vib}} = (v + 1/2)\,\overline{v}_{\text{osc}} - (v + 1/2)^2\,\overline{v}_{\text{osc}} X \text{ cm}^{-1};\ (v = 0, 1, 2, \ldots.) \qquad \ldots.(6.10)$$

where v is the quantum number associated with the vibrations of the molecule and $\overline{v}_{\text{osc}}$ is the harmonic frequency in wavenumber which is equal to v_{osc}/c. You can refer to Eq. 4.28 of Unit 4 for understanding the significance of v_{osc}. Also X is the anharmonicity constant.

For any vibrational transition, the selection rule is

$$\Delta v = \pm 1, \pm 2 \ldots\ldots$$

Restricting ourselves to only fundamental vibration, where $\Delta v = +1$, the transition takes place from $v = 0$ to $v = +1$. The intensity of other transitions will be very weak and can be neglected.

For vibrational Raman spectrum, we can write an equation similar to Eqs. 6.4 and 6.8,

$$\overline{v}' - \overline{v} = \pm \Delta \overline{v}_{\text{vib}} \qquad \ldots.(6.11)$$

$\Delta \overline{v}_{\text{vib}}$ is the vibrational Raman shift.

Eq. 6.11 takes into account only the fundamental band; it ignores overtones for the sake of simplicity.

From Eq. 6.11, we can see that the Raman active vibrational frequencies appear as Stokes and anti-Stokes lines on either side of the central exciting line having a frequency v. The Stokes lines as usual would be more intense than anti-Stokes lines.

Example 5

Predict the position of the Raman vibration lines for C–H stretching of an alkane at 2960 cm^{-1}, if Hg radiation of 435.8 nm (22946 cm^{-1}) is used.

Stokes line: Using Eq. 6.11, $\overline{v}' = (22946 - 2960)\text{ cm}^{-1}$

$$\overline{v}' = 19986\text{ cm}^{-1}$$

Anti-Stokes line: Using Eq. 6.11,

$$\overline{v}' = (22946 + 2960)\text{ cm}^{-1}$$

$$= 25906\text{ cm}^{-1}$$

For molecules having centre of symmetry, there is a generalisation – known as the rule of mutual exclusion – which is quite useful in identifying them. This has been discussed in the following subsection.

Mutual Exclusion Principle

The mutual exclusion principle states that any molecule which has centre of symmetry will not have any vibrational mode which is both Raman as well as infrared active. A precise way of stating the mutual exclusion principle is as follows:

For a molecule with centre of symmetry, any given normal vibration may be active in the infrared or in the Raman (or in neither) but not in both.

The portion written within the brackets 'or in neither' means that some of the normal vibrations may be inactive both in Raman and infrared regions. For example, ethylene, which has centre of symmetry, has twelve modes of vibration. Six of these are Raman active and five are infrared active, the remaining mode is neither infrared active nor Raman active. Such modes of vibrations of molecules with centre of symmetry which are totally inactive in both infrared and Raman spectra are called **spectroscopically silent fundamental vibrations.** In benzene, which has a total of thirty normal modes, twenty two are active either in Raman or in infrared. The remaining eight modes are totally inactive in both Raman and infrared. A simplified statement of mutual exclusion principle is given below:

"If a molecule has centre of symmetry, then no modes can be both infrared and Raman active".

As a corollary to the above statement, we can say that if a particular vibration mode of the molecule gives rise to lines at the same frequency in both the infrared and Raman spectra, then the molecule must not have centre of symmetry. In the Appendix of this Unit, we shall discuss this principle in relation to group theory.

Let us consider the application of this simple rule in the interpretation of the spectra of two triatomic molecules, CO_2 and SO_2. The two peaks at 2349 and 667 cm^{-1} in the infrared spectrum of CO_2 are found to be absent in the Raman spectrum of the molecule. We may expect a single Raman peak for this molecule at 1340 cm^{-1} due to symmetric stretch. In fact, two peaks of similar intensity appear at 1388 cm^{-1} and 1286 cm^{-1} which are due to Fermi resonance between ν_1 (symmetric stretching frequency) and $2\nu_2$ (twice the bending frequency) as explained in Sec. 5.3 of the last unit. **The Fermi resonance bands are not covered by mutual exclusion principle since it applies to fundamental modes only.** Thus, it must be noticed that the fundamental modes of CO_2 which are infrared active are Raman inactive.

Our conclusion is that CO_2 molecule must have centre of symmetry in accordance with the mutual exclusion principle. This is in agreement with the fact that CO_2 is a linear molecule with a symmetric structure and its dipole moment is zero.

In the case of SO_2, we get three peaks around 519, 1151 and 1361 cm^{-1} in both the Raman and infrared spectra. These observations indicate that SO_2 molecule has no centre of symmetry and we shall use this fact in Sec 6.7 in discussing its structure.

It has also been observed that the symmetric vibrations give rise to intense Raman lines but the antisymmetric vibrations produce weaker lines in the spectrum. Frequencies at which these vibrations will occur can be calculated with the help of quantum mechanics which we are not going to discuss in this course.

Answer the following SAQ's before going through Sec. 6.5.

SAQ 3

C_2H_2 has two IR bands and three Raman bands, none of them occur at the same wavenumber. Further, one of the IR bands shows a simple PR structure. Comment on the structure of C_2H_2.

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SAQ 4

What type of spectral pattern would you expect from IR and Raman spectra, if the structure of N_2O is N–N–O but not N–O–N ? Verify your answer with the case study discussed in Sec. 6.7.

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6.5 VIBRATION - ROTATION RAMAN SPECTRA

Relatively a very small number of molecules have been studied for which vibrational Raman spectra show rotational fine structure.

For the simplest case of a diatomic molecule, the selection rules for vibration-rotation Raman spectra are as follows:

$$\Delta J = 0, \pm 2 \text{ and } \Delta v = \pm 1.$$

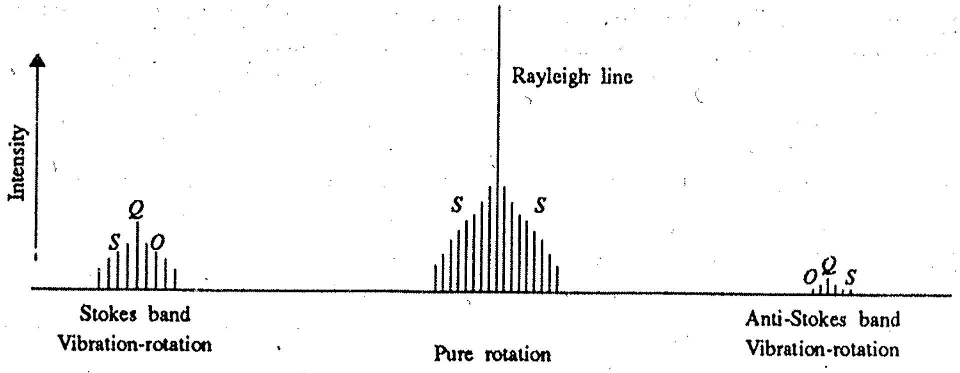

Fig. 6.7: The schematic diagram of the vibration-rotation Raman spectrum of a diatomic gas.

The transitions for which $\Delta J = -2$ give rise to O-branch while those for which $\Delta J = 0$ give rise to Q-branch and finally, if $\Delta J = +2$, S-branch occurs. In Fig. 6.7, the schematic diagram of the vibration-rotation Raman spectrum of a diatomic gas is shown. The presence of a strong Q-branch in the Raman spectra is noteworthy. The lines in O and S-branches of the Raman spectrum could be analysed to yield B, moment of inertia and bond length.

6.6 POLARIZED RAMAN SPECTRA

Before explaining polarized Raman spectra, we should understand the terms, plane polarized light and depolarization ratio. You may have studied in Sec. 6.10 of Unit 6 of Atoms and Molecules Course that when monochromatic light is passed through a nicol prism, the outcoming light vibrates in only one particular plane. Such a type of light is called plane polarized light. When plane polarized light is passed through another nicol prism, the intensity of the transmitted light depends on the way the polarizing axes of the two prisms are oriented towards each other. If the polarizing axes of the two prisms are parallel to each other, the intensity of the transmitted light is maximum. When the two axes are perpendicular, no light passes through the second nicol prism. If the incident light falling on the second nicol prism is only partially polarized, then the intensity of the transmitted light perpendicular to the plane of polarization ($I_\perp$) is minimum but not zero. In the case of partially polarized light, it is useful to define the ratio of intensity of light transmitted perpendicular to the plane of maximum polarization ($I_\perp$) to the intensity of light transmitted parallel to the plane of maximum polarization ($I_{||}$). This ratio is called depolarization ratio (ρ) which is given as follows:

$$\rho = \frac{I_\perp}{I_{||}} \qquad .....(6.12)$$

The depolarization ratio is quite useful in determining whether a Raman line is polarized or not. A Raman line is said to be polarized, if the value of ρ lies between 0 and 6/7. If ρ is more than 6/7, a Raman line is said to be depolarized.

The number of polarized Raman lines can be obtained from the experimental values of ρ which could help us in assigning the vibrational modes to the experimentally observed frequencies. In general, it can be stated that **a symmetric vibration gives rise to a polarized (or partially polarized) Raman line while an antisymmetric vibration gives a depolarized line.** The use of polarized Raman lines will be illustrated in Sec. 6.7.

SAQ 5

Polarized Raman spectra of $CHCl_3$ give the following data for three of the bands:

S.No	**Raman band/cm^{-1}**	**$I_\perp$**	**$I_{||}$**
i)	357	5.8	79.2
ii)	660	1.3	83.2
iii)	760	4.7	6.0

Identify those which are polarized.

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6.7 APPLICATIONS OF IR AND RAMAN SPECTROSCOPY

We can derive useful structural information from Raman and infrared spectra of molecules. However, we must realise that Raman and infrared spectra are complementary to each other in many ways as shown in Table 6.1.

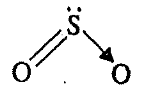
Table 6.1: Characteristics of Raman and Infrared Spectra

	Raman		Infrared
1.	Raman spectrum is the result of scattering of light by the molecules.	1.	Infrared spectrum is because of the absorption of radiation by the molecules.
2.	It depends on the changing polarizability of the molecule.	2.	It depends on the oscillating dipole moment in the molecule.
3.	Homonuclear diatomic molecules are rotationally and or vibrationally active.	3.	Homonuclear diatomic molecules are inactive.
4.	Water can be used as a solvent.	4.	Water is less likely to be used as a solvent since it is opaque to infrared radiations.

Using the case of SO_2 molecule, we now show how the structure of a molecule could be determined using IR and Raman spectra. Let us also explain how the polarized Raman spectra could be used in assigning vibrational modes to the frequencies observed in the spectra.

In sec. 6.4, we have mentioned that SO_2 gives three absorption bands at 519, 1151 and 1361 cm^{-1} both in IR spectra and Raman spectra and that it does not have centre of symmetry. Further, a linear polyatomic molecule is expected to show at least some IR bands with P and R branches as exhibited by diatomic molecules (See Fig. 4.11 of Unit 4). These PR bands (or contours) arise due to vibrations causing a dipole change parallel to the principal axis of symmetry. In the IR spectra of SO_2, no band shows simple PR structure. Hence, SO_2 molecule is not linear and it must have a bent shape.

In the Appendix, we shall examine the Raman activity of the three vibrational modes of triatomic molecules (H_2O or SO_2) belonging to C_{2v} group.



In Table 6.2, the symmetry species are given in terms of group theory symbols.

Further, the bands at 519 and 1151 cm^{-1} are Raman polarized. This indicates that these bands are due to symmetric vibrations. If we make a reasonable assumption that stretching frequencies are larger than bending, then 519 cm^{-1} is assigned to symmetric bending vibration while 1151 cm^{-1} is assigned to symmetric stretching mode. The band at 1361 cm^{-1} is Raman depolarized which indicates that it can be assigned to the antisymmetric stretching mode. Thus we assign the modes of vibration to the observed frequencies of SO_2; also we infer that it is angular in shape.

The symmetry species of each mode of vibration is denoted in the respective figures. For understanding the characters of these symmetry species, you may consult the character tables for C_{2v}, C_{3v}, $C_{\infty v}$ and $D_{\infty h}$ given at the end of the Appendix of this unit. Even without understanding the basis of group theory symbols, you can try to use them, if you follow the Appendix materials. If by chance you don't follow the Appendix materials, don't lose confidence! You can still follow the main portion of the unit excluding the Appendix.

For a few molecules, IR and Raman active vibrations are discussed in Table 6.2.

Table 6.2: IR Active and Raman Active Vibrations of Some Molecules

Molecule (or ion)	CO_2	N_2O	H_2O or SO_2	NH_3 (or ClO_3^-)
Fig. No.	6.2	6.8	6.1	6.9
Geometry	Linear (symmetric)	Linear (asymmetric)	Angular	Pyramidal
Point group	$D_{\infty h}$	$C_{\infty v}$	C_{2v}	C_{3v}

Total number of modes	4	4	3	6
Fundamentals	3	3	3	4
Symmetry species	Σ_g^+ Σ_u^+ Π_u	$2\Sigma^+$ Π	$2A_1, B_1$	$2A_1, 2E$
IR active species	Σ_u^+, Π_u	$2\Sigma^+$ Π	$2A_1, B_1$	$2A_1, 2E$
Raman active species	Σ_g^+	$2\Sigma^+$ [Π (bending) too weak to be observed]	$2A_1, B_1$	$2A_1, 2E$
Polarized vibration	Σ_g^+ (symmetric stretching)	Σ^+ (symmetric stretching)	$2A_1$ (symmetric stretching and bending)	$2A_1$ (symmetric stretching and out-of-plane symmetric bending)

N.B: Π_u, Π and E: Doubly degenerate vibrations

Let us illustrate the use of Table 6.2 in structure determination. Care should be taken to interpret Raman spectra since one or more bands may be missing due to weak intensity (or these bands may be spectroscopically silent).

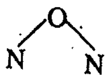
Case study of N_2O

We shall illustrate as to how the structure of N_2O has been established using infrared and Raman spectral data given in Table 6.3.

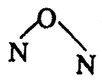
Table 6.3: Infrared and Raman Spectral Data of Nitrous Oxide

$\bar{\nu}/cm^{-1}$	Infrared	Raman
589	strong; PQR band	—
1285	very strong; PR band	very strong
2224	very strong; PR band	strong

The four possible structures of N_2O are given below:



I



II

N—O—N

III

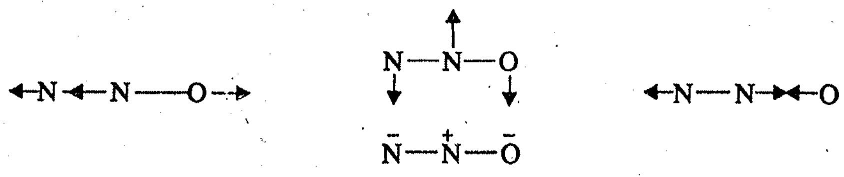
N—N—O

IV

The presence of two bands with simple PR contours indicate that the molecule is linear. Hence the structures I and II are ruled out.

The appearance of (at least) two bands (1285 and 2224 cm^{-1}) in both infrared and

Raman spectra indicates that the molecule does not have centre of symmetry. As per Table 6.2, we may expect all the three bands to appear in the infrared and Raman spectra. It is possible that the third band at 589 cm^{-1} is too weak that it is not observed in Raman spectrum. Hence, it is clear that N_2O has the structure IV. Let us try to indicate the vibrational modes of N_2O (Fig. 6.8).



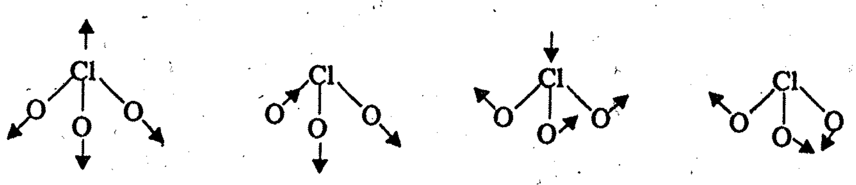
Stretching (Σ^+) Bending (Π) Stretching (Σ^+)

Fig. 6.8: Vibrational modes of N_2O

As another example, you may verify the structure of ClO_3^- ion as pyramidal using the data given in Tables 6.2 and 6.4 . The vibrational modes of ClO_3^- ion are given in Fig. 6.9.

Table 6.4: Infrared and Raman Spectra of ClO_3^- ion

$\bar{\nu}_{Raman}/cm^{-1}$	$\bar{\nu}_{IR}/cm^{-1}$
450 (depolarized)	434
610 (polarized)	624
940 (depolarized)	950
982 (polarized)	994



Symmetric stretching (A_1)

Antisymmetric stretching (E)

Out-of-plane symmetric bending (A_1)

Antisymmetric bending (E)

Fig. 6.9: Vibrational modes of ClO_3^- ion.

The main advantage of Raman spectroscopy lies in the fact that it can be studied in the visible region of the spectrum unlike microwave or infrared spectroscopy. With the introduction of laser beam as a Raman source, low frequency vibrations can also be easily studied. Rotations and vibrations of molecules which cannot be studied with microwave or infrared techniques are easily handled by Raman spectroscopy. For instance, the structural parameters of homonuclear diatomic molecules can be obtained using Raman spectra.

Raman spectra finds a lot of applications in the structure determination of organic compounds. It can be successfully used for the analysis of a mixture of compounds which are otherwise difficult to identify without separation into constituents. In general, IR is more suitable for molecular vibrations of organic compounds having frequencies above 650 cm^{-1} . Raman spectra could be studied even upto 100 cm^{-1} and is therefore, quite suited for studying weak vibrations such as metal-ligand stretchings, most of which lie below 600 cm^{-1}. Further, the polar solvents like water can be used in recording Raman spectra. Let us study three more applications of Raman spectra.

(1) Dissociation constants of mineral acids

By monitoring the intensity of absorption bands due to nitrate ion and nitric acid using Raman spectrum, it is possible to obtain the dissociation constant of nitric acid.

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

Similarly the dissociation constants of H_2SO_4 and HSO_4^- also have been studied. It has been found that the concentration of SO_4^{2-} ion is small in sulphuric acid except in very dilute solutions.

(2) Structure of complex ions in solution

One of the important applications of Raman spectra is to identify the structure of complex ions of mercury, thallium and silver ions in solution. The existence of mercurous ion as Hg_2^{2+} and not as Hg^+ has been established through the Hg–Hg stretching frequency observed in the Raman spectrum of its ions. Similar results have been obtained for thallous (Tl_2^{2+}) ions also.

(3) Strength of metal-ligand bonding

The totally symmetric vibrations (Fig. 6.10) of the tetrahedral complex ions (like $ZnCl_4^{2-}$, $CdCl_4^{2-}$, $HgCl_4^{2-}$, etc) and the octahedral complexes (like SiF_6^{2-}, PF_6^-, SF_6) can be studied using Raman spectra. These are all IR inactive. From their Raman spectra, metal-ligand bond stretching force constants and hence, information about the strength of the metal- ligand bond can be obtained. It is seen that the oxyanions such as PO_4^{3-}, SO_4^{2-} etc. have much larger force constants. This is taken as an evidence that there is $d\pi - p\pi$ bonding between the central atom and the oxygen atom in addition to the σ bonding.

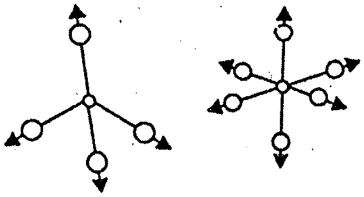


Fig. 6.10: Totally symmetric vibrations of ML_4 and ML_6 complexes.

SAQ 6

A molecule AB_2 has three prominent IR absorption bands and one Raman band; for the Raman band, the vibrational Raman shift coincides with one of the three IR bands. The rotational fine structure of the IR bands is complex and does not show simple PR contour. What is the shape of the molecule ?

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6.8 SUMMARY

In this unit we explained the origin of Raman spectrum in terms of classical as well as quantum mechanical models arriving at the same results. Next we discussed the rotational, vibrational and vibration-rotation Raman spectra in detail. The relevant selection rules were also given. The principle of mutual exclusion was stated and its importance in the elucidation of molecular structure was given. A brief outline of the utility of the study of polarized Raman lines was given. Finally a few applications of Raman spectroscopy were discussed.

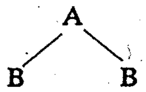
6.9 TERMINAL QUESTIONS

1) If the fundamental vibrational frequency of a particular ketone occurs at 1730 cm^{-1}, determine the position of Raman lines. The ketone is irradiated with argon laser of wavelength 514.53 nm.

2) As per Table 5.3 of Unit 5, the C – H stretching range is 2962-2853 cm^{-1} for an alkane. Assuming that argon laser of wavelength 514.53 nm (19435 cm^{-1}) is used, find the upper and lower wavenumbers for the positions of the Stokes lines for C–H stretching.

3) Why is that the intensity of Stokes lines generally greater than the anti-Stokes lines ?

4) How can you differentiate between the following two structures using IR and Raman spectra :



B – A – B ?

5) Which of the following molecules would give pure rotational Raman spectrum :

H_2, H_2O, SF_6, CH_4 and N_2 ?

6) The vibrational Raman shift for C – H bending vibration is 1460 cm^{-1}. For argon laser of wavenumber 19435 cm^{-1}, predict the position of Stokes and anti-Stokes lines corresponding to C – H bending vibration.

6.10 ANSWERS

Self Assessment Questions

1) A molecular rotation or vibration will be Raman active, only if it is accompanied by polarizability change.

2) $$I = \frac{h}{8\pi^2 Bc}$$

$$= \frac{6.626 \times 10^{-34}}{8 \times (3.143)^2 \times 39.5 \times 2.998 \times 10^8} \text{ kg m}^2$$

$$= 7.08 \times 10^{-46} \text{ kg m}^2$$

But as per the hints given,

$$I = \frac{2 \times 0.016}{6.023 \times 10^{23}} \times (r_{C-O})^2 \text{ kg m}^2$$

$$r_{C-O} = \left[\frac{(7.08 \times 10^{-46} \times 6.023 \times 10^{23})}{0.032}\right]^{1/2} \text{m} = 1.15 \times 10^{-10}\,\text{m}$$

$$= 115 \text{ pm}$$

3) Since none of the bands appear in both IR and Raman spectra at the same wavenumber, C_2H_2 must have centre of symmetry. The presence of an IR band with a simple PR structure brings out the linear structure. Hence C_2H_2 has the linear symmetrical structure as shown below:

$$H-C\equiv C-H$$

4) The structure N – N – O does not have centre of symmetry whereas N – O – N has. Hence, if the structure N – N – O is correct, one or more bands must occur at the same wavenumber in both IR and Raman spectra.

5) ρ values at all these three bands are less than 6/7 and these bands are polarized.

6) The molecule does not have centre of symmetry. It does not have linear structure. Hence, AB_2 must be angular.

Terminal Questions

1) We have to find the position of both Stokes lines and anti-Stokes lines. As per Eq. 6.4, $\bar{\nu}'$ for Stokes line $= \bar{\nu} - \Delta\bar{\nu}$.

$$= \left(\frac{1}{514.53 \times 10^{-9}} - 1.730 \times 10^{5}\right) \text{m}^{-1}$$

$$= (1.9435 \times 10^{6} - 1.730 \times 10^{5})\ \text{m}^{-1}$$

$$= 1.7705 \times 10^{6}\ \text{m}^{-1}$$

$$= 17705\ \text{cm}^{-1}$$

Similarly $\bar{\nu}'$ for anti-Stokes line $= \bar{\nu} + \Delta\bar{\nu}$

$$= 2.1165 \times 10^{6}\ \text{m}^{-1}$$

$$= 21165\ \text{cm}^{-1}$$

2) As per Eq. 6.4, $\bar{\nu}'$ for the Stokes lines lie between (19435 - 2962) cm^{-1} and (19435-2853) cm^{-1}, i.e., between 16473 cm^{-1} and 16582 cm^{-1}

3) There are more molecules in the ground state than in the excited state. The former class gives rise to the Stokes lines, while the latter gives rise to the anti-Stokes lines. Hence, Stokes lines are more intense than the anti-Stokes lines.

4) The molecule with angular symmetrical structure can be expected to exhibit three IR bands and three Raman bands, all the three being common; the molecule with linear symmetrical structure has no band appearing in both IR and Raman spectra.

5) The spherical top molecules SF_6 and CH_4 could not exhibit pure rotational Raman spectrum; others can.

6) Use Eq. 6.11,

Stokes line : (19435 - 1460) $\text{cm}^{-1} = 17975\ \text{cm}^{-1}$

Anti-Stokes line: (19435 + 1460) $\text{cm}^{-1} = 20895\ \text{cm}^{-1}$

6.11 APPENDIX

In this Appendix, we shall show how group theory helps in identifying Raman active vibrations and in understanding the mutual exclusion principle.

Raman active vibrational modes

Group theory can be used to find out whether a particular vibrational mode will be Raman active or not. In the case of vibrational Raman spectra, a particular vibration mode will be active only if the polarizability of the molecule changes during vibration. In terms of the polarizability operator α, the transition moment integral can be obtained using the term, $\int \psi_b \, \alpha \, \psi_a \, d\tau$, where ψ_a and ψ_b are the wave functions corresponding to ground state and the excited state, respectively. In this term, α is one of the following quadratic or binary functions of the cartesian coordinates:

$$x^2, y^2, z^2, xy, yz, zx, (x^2 - y^2).$$

A vibration will be Raman active, if it belongs to the same symmetry species as a component of polarizability. **A vibration transition may give rise to a Raman band, only if the symmetry species of the product of the functions $\psi_a \psi_b$ is the same as one of $x^2, y^2, z^2, xy, yz, zx$ or any combination of these.** In that case, the transition moment integral will have nonzero value and the vibrational mode is Raman active.

This rule can be applied to find out the Raman activity of the vibrational modes of H_2O and NH_3.

H_2O

In Unit 5, we have mentioned that for H_2O (as also for SO_2) molecule, two of the vibrational modes belong to A_1 symmetry and the third one belongs to B_1 symmetry and all these are IR active. Let us now see whether these are Raman active.

(i) Vibrational modes with A_1 symmetry

From the C_{2v} character table, we see that the vibrational modes with A_1 symmetry belong to the same irreducible representation as x^2, y^2 or z^2. Hence the vibrational modes with A_1 symmetry are Raman active.

Since SO_2 belongs to C_{2v} group (just like H_2O molecule), two of the vibrational modes belong to A_1 symmetry and the third one belongs to B_1 symmetry. Also all these three modes are active both in infrared and Raman spectra.

(ii) Vibrational mode with B_1 symmetry

The vibrational mode with B_1 symmetry belongs to same irreducible representation as xz; hence this mode also will be Raman active.

NH_3

In unit 5, we have mentioned that for NH_3 molecule, two of the vibrational modes belong to A_1 symmetry and the other two to E symmetry. From the C_{3v} character table, we see that (i) the vibrational modes with A_1 symmetry belong to the same irreducible representation as z^2 or $x^2 + y^2$, and (ii) the vibrational modes with E symmetry belong to the same irreducible representation as $(x^2 - y^2, xy)$ or (xz, yz). Hence all the four vibrational modes of NH_3 are Raman active.

Let us next explain the mutual exclusion principle using group theory.

The mutual exclusion principle

Point groups of molecules with centre of symmetry have two sets of irreducible representations. The representations which are symmetric with respect to inversion are called g ('gerade') representations, while those which are antisymmetric to inversion are called u ('ungerade') representations. Let us explain as to how to identify a particular representation as u or g.

By inversion operation, the coordinates x, y or z become $-x$, $-y$ or $-z$ i.e., these undergo a sign change on inversion.

$$x \xrightarrow{\text{inversion}} -x$$

$$y \xrightarrow{\text{inversion}} -y$$

$$z \xrightarrow{\text{inversion}} -z$$

i.e., x, y and z coordinates are antisymmetric with respect to inversion. But the quadratic or the binary functions of coordinates do not undergo a sign change on inversion i.e., these are symmetric with respect to inversion.

$$x^2 \xrightarrow{\text{inversion}} (-x) \cdot (-x) = x^2$$

$$xy \xrightarrow{\text{inversion}} (-x) \cdot (-y) = xy$$

This is true of all binary or quadratic coordinates and their combinations.

In the light of the definition given for g and u functions, the coordinates x, y and z which are antisymmetric to inversion belong to u representation whereas the quadratic and binary coordinates, x^2, y^2, z^2, xy, etc. belong to g representation (since these are symmetric with respect to inversion).

The selection rule for IR active vibration which we have studied in the Appendix of the last unit can be stated as follows:

A vibration will be IR active, if the excited mode has the same symmetry as one of the cartesian coordinates (x, y and z).

Using this, we can infer that in the molecules with centre of symmetry, the vibrational modes belonging to u symmetry species are IR active.

Similarly using the selection rule for Raman spectra that a normal vibration will be Raman active if the vibrational mode has the same irreducible representation as one of the quadratic or binary coordinates, we can infer that in case of molecules with centre of symmetry, vibrational modes belonging to g symmetry species are Raman active.

In short, in molecules with centre of symmetry, a vibrational mode may be active either in Raman or in infrared but not in both. This is the mutual exclusion principle stated in Sec. 6.4.

You can use Table 6.2, Figs. 6.1, 6.2, 6.8 and 6.9 and the character tables C_{2v}, C_{3v}, $C_{\infty v}$ and $D_{\infty h}$ (given at the end of this Appendix) and verify that

(i) IR active vibrations belong to the same symmetry species as x, y or z.

(ii) Raman active vibrations belong to the same symmetry species as any of the quadratic or binary functions of the cartesian coordinates.

For instance, from Table 6.2, Fig. 6.2 and the character table for $D_{\infty h}$ group, we can infer that the symmetric stretching vibration of CO_2 is Raman active since it belongs to $\sum_g^+$ symmetry to which also quadratic and binary functions, $x^2 + y^2$ and z^2, belong. Similarly, bending and antisymmetric stretching of CO_2 are IR active since these two belong to Π_u and $\sum_u^+$ to which the cartesian coordinates (x, y) and z also belong. Why don't you verify the entries in Table 6.2 regarding the IR and Raman active vibrations of N_2O, H_2O and ClO_3^- ion also ? Use the relevant figures and the character tables of point groups as mentioned in Table 6.2.

Character Tables of C_{2v}, C_{3v}, $C_{\infty v}$ and $D_{\infty h}$ groups

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	xy
B_1	1	–1	1	–1	x, R_y	xz
B_2	1	–1	–1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	–1	R_z	
E	2	–1	0	(x, y) (R_x, R_y)	$(x^2 - y^2, xy)$ (xz, yz)

$C_{\infty v}$	E	$2C_\infty^\phi$	…….	$\infty\sigma_v$		
$A_1 \equiv \sum^+$	1	1	…….	1	z	$x^2 + y^2, z^2$
$A_2 \equiv \sum^-$	1	1	…….	–1	R_z	
$E_1 \equiv \Pi$	2	$2\cos\phi$	…….	0	$(x, y); (R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	$2\cos 2\phi$	…….	0		$(x^2 - y^2, xy)$
$E_3 \equiv \Phi$	2	$2\cos 3\phi$	…….	0		
…….	…. …….		…….	……		

$D_{\infty h}$	E	$2C_\infty^\phi$	……	$\infty\sigma_v$	i	$2S_\infty^\varphi$	……	∞C_2		
$\sum_g^+$	1	1	……	1	1	1	……	1		$x^2 + y^2, z^2$
$\sum_g^-$	1	1	……	–1	1	1	……	–1	R_z	
Π_g	2	$2\cos\phi$	……	0	2	$-2\cos\phi$	……	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\phi$	……	0	2	$2\cos 2\phi$	……	0		$(x^2 - y^2, xy)$
……	…..	……	……	……	……	……	……	……		
$\sum_u^+$	1	1	……	1	–1	–1	……	–1	z	
$\sum_u^-$	1	1	……	–1	–1	–1	……	1		
Π_u	2	$2\cos\phi$	……	0	–2	$2\cos\phi$	……	0	(x, y)	
Δ_u	2	$2\cos 2\phi$	……	0	–2	$-2\cos 2\phi$	……	0		
……	……	……	……	……	……	……	……	……		

Further Reading

1. **J.R.Dyer, Application of Absorption Spectroscopy of Organic Compounds, Eastern Economy Edition, Prentice-Hall of India Pvt.Ltd.**

2. **D.H.Williams and Ian Fleming, Spectroscopic Methods in Organic Chemistry. Tata Mc Graw Hill Publishing Co. Ltd. 4thEd.**

3. **C.N Banwell, Fundamentals of Molecular Spectroscopy, 3rd Ed, Tata McGraw Hill Publishing Co. Ltd.**

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UGCHE -10
Spectroscopy

Block

3

ELECTRONIC SPECTRA AND INSTRUMENTATION

ELECTRONIC SPECTRA AND INSTRUMENTATION

In Block 1 of this course, you studied the basic concepts of spectroscopy and the rotational spectra. Block 2 dealt with the vibrational spectra of diatomic molecules, infrared spectra of polyatomic molecules and the Raman spectra. In this block, you will study about the electronic spectra and the instrumentation in optical spectroscopy.

Unit 7 deals with a discussion of electronic spectra of diatomic and polyatomic molecules. In this unit the Born-Oppenheimer approximation will be discussed. You will learn to write the term symbols for ground and excited states of diatomic molecules and the selection rules for transitions in diatomic molecules. The Franck-Condon principle, which helps in understanding the variation in intensities of spectral lines, will then be discussed. You will also learn the different types of transitions possible in the electronic spectra of polyatomic molecules. Various terms used in electronic spectra will also be defined. The rules to predict the position of absorption maxima in conjugated dienes and enones will then be presented. The unit will conclude with a discussion of effects of solvents on electronic spectra.

In Unit 8, we will discuss the colour and the electronic spectra of transition metal complexes. An attempt will be made to explain the origin of colour in transition metal complexes and their electronic absorption spectra in the light of *d*–*d* and charge-transfer electronic transitions. The crystal field theory and the ligand field theory will be briefly described to explain the nature of metal-ligand interactions in transition metal complexes. Finally the various processes, by which an excited electronic state gets deactivated will be discussed.

Unit 9 deals with the salient features of various instruments used for recording rotational, vibrational, electronic and Raman spectra. We also describe the methods of preparing a sample for recording these spectra. The experimental techniques employed for recording nmr, esr and mass spectra are quite different from the ones employed for recording rotational, vibrational, electronic and Raman spectra. Hence, the experimental techniques associated with nmr, esr and mass spectra will be described in the respective units in Block 4 of this course.

Objectives

- After studying this block, you should be able to :
- derive term symbols for diatomic molecules,
- predict the allowed transitions between different states in diatomic molecules,
- apply Franck-Condon principle and explain the variation in intensities of spectra lines,
- explain the $n-\pi^*$, $n-\sigma^*$, $\sigma-\sigma^*$, $\pi-\pi^*$ transitions using diagrams,
- calculate dissociation energy of molecules in the ground state,
- apply Woodward rules to predict the wavelength of absorption maxima for conjugated dienes and trienes,
- apply Fieser and Scott rules to predict the wavelength of absorption maxima for α,β –unsaturated ketones,
- explain the effect of solvent on $n-\pi^*$ and $\pi-\pi^*$ transitions in electronic spectra,
- describe the elements of crystal field theory,
- explain why and how, the *d*-orbitals of transition metal ions show energy splittings,
- explain the electronic spectra of transition metal complexes,

- describe charge-transfer spectra,
- use the Jablonski diagrams to explain the various processes by which an excited electronic state gets deactivated,
- explain how fluorescence and phosphorescence take place in natural chemical systems,
- describe the different components of various spectrometers,
- explain the terms, signal to noise ratio and resolving power,
- describe the various sampling techniques,
- correlate slit-width with resolving power,
- differentiate between single beam and double beam spectrometers,
- draw block diagram of a spectrometer.

UNIT 7 ELECTRONIC SPECTRA–I

Structure

7.1 INTRODUCTION

In Units 4 and 5, we have discussed the IR spectra of diatomic and polyatomic molecules, respectively. We have learnt about the mass effects, electronic effects, solvent effects and hydrogen bonding effects on IR vibrational spectra. We have also learnt the usefulness of IR spectra for molecular structure determination. In Unit 6, we have studied the application of Raman spectroscopy in determination of molecular structure. A comparative study of Raman and IR spectra has also been included in Unit 6. This study helps us to identify different kinds of structures of molecules.

The study of IR, Raman and microwave spectra still does not give answer to the question 'why certain substances are coloured?' For example, the green colour of vegetation is due to a compound chlorophyll. Transition metal complexes, such as $[Ti(H_2O)_6]^{3+}$, are coloured. The answer to the origin of colours in substances and information about excited states of molecules can be obtained from a study of their electronic spectra which occur in the visible (400 – 800 nm) and ultraviolet (200 – 400 nm) regions of electromagnetic spectrum. Unit 7 deals with a discussion of electronic spectra of diatomic and polyatomic molecules. This study will be followed by a discussion of electronic spectra of transition metal complexes in Unit 8.

In this unit, we will state the Born-Oppenheimer approximation. We will recapitulate the molecular orbital treatment for determining the electronic states of diatomic molecules. We will learn to write the term symbols for ground and excited states of diatomic molecules. The selection rules for transitions in diatomic molecules will then be outlined. The Franck-Condon principle will also be stated. This principle is used to understand the variation in intensities of electronic spectra. The different types of transitions possible in the electronic spectra of polyatomic molecules will then be discussed. The terms chromophore, auxochrome, hypsochromic and bathochromic effects, hyperchromic and hypochromic effects will be defined. The rules to predict the position absorption maxima in conjugated dienes, and enones will then be presented. The unit will conclude with a discussion of effect of solvent on $n - \pi^*$ an $\pi - \pi^*$ transitions in carbonyl and unsaturated compounds.

Objectives

After studying this unit you should be able to:

- describe the molecular orbital approach for diatomic molecules,
- write the ground and excited state configurations for diatomics,
- derive term symbols for diatomic molecules,
- predict the allowed transitions between states in diatomics,
- apply Franck-Condon principle and explain the variation in intensities of spectra of CN^- radical, CO and I_2 molecules,
- explain using diagrams the $n - \pi^*$, $n - \sigma^*$, $\sigma - \sigma^*$, $\pi - \pi^*$ transitions,
- define chromophore, auxochrome, hypsochromic and bathochromic effects, hyperchromic and hypochromic effects in electronic spectra,
- calculate dissociation energy of molecules in the ground state,
- apply Woodward rules to predict the absorption maximum for conjugated dienes and trienes,
- apply Fieser and Scott rules to predict the absorption maximum for α, ß unsaturated ketones, and
- explain the effect of solvent on $n - \pi^*$ and $\pi - \pi^*$ transitions in electronic spectra.

7.2 BORN-OPPENHEIMER APPROXIMATION

The structure of electronic spectra involves the change of at least three quantum numbers simultaneously, namely electronic, vibrational and rotational quantum numbers. This follows the Born-Oppenheimer approximation that rotational (E_R), vibrational (E_v) and electronic (E_e) energy levels are independent of one another. The total energy E is written as

$$E = E_e + E_v + E_R$$

A change in the total energy as a result of electronic transition in a molecule is

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_R$$

In wave numbers the change is represented as

$$\Delta \nu = \Delta \nu_e + \Delta \nu_v + \Delta \nu_R$$

The approximate orders of magnitude of these changes are

$$\Delta \nu_e \approx \Delta \nu_v \times 10^3 \approx \Delta \nu_R \times 10^6 \text{ cm}^{-1}$$

Thus each electronic level comprises a number of vibrational levels and each vibrational level consists of several rotational levels, as is shown in Fig. 7.1.

From these values of relative order of energies, we find that the vibrational changes give a 'coarse structure' and the smaller rotational changes give a 'fine structure' to the electronic spectra. Since rotational energy changes are minimum, these energy changes are neglected and electronic band system is considered in terms of transitions between electronic levels each consisting of a series of vibronic levels of the same kind.

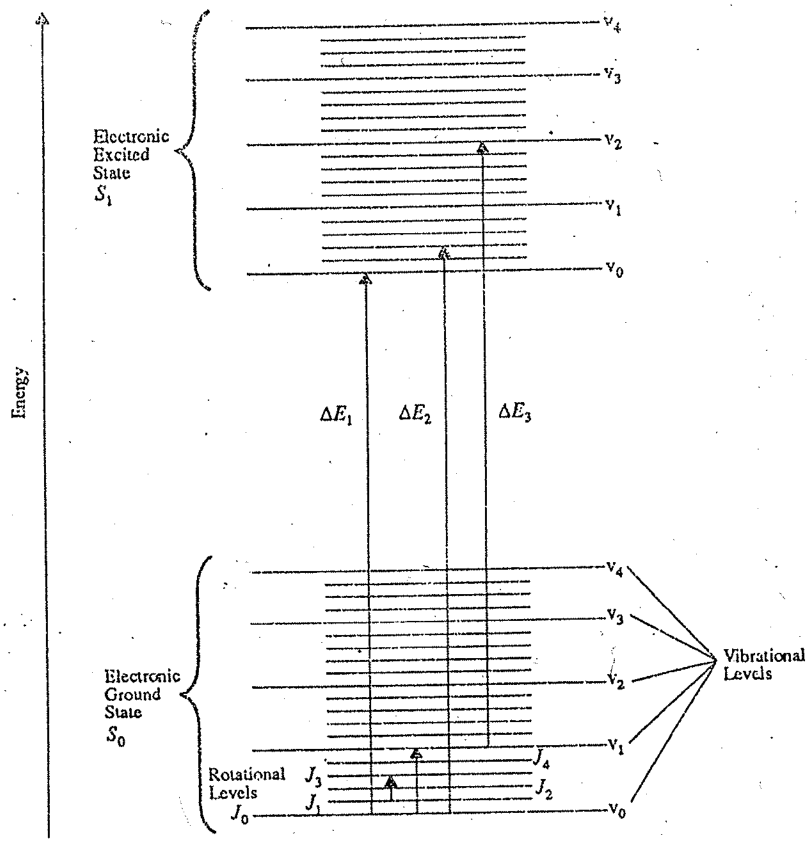


Fig. 7.1 : Rotational, vibrational and electronic energy levels in a molecule.

7.3 ELECTRONIC STATES OF DIATOMIC MOLECULES

In Unit 1 of this course, you studied that in an atom various electronic states can arise from a given electronic configuration due to coupling of orbital angular momentum and spin angular momentum of electron. You also studied that the atomic spectra arise due to transition between different electronic energy states. Similarly for molecules various electronic states can arise from a given electronic configuration of a molecule. The electronic configuration of a molecule can be derived on the basis of molecular orbital theory which you studied in Unit 5 of the CHE-01 course.

7.3.1 Molecular Orbital Treatment of Diatomic Molecules

According to the molecular orbital theory there exists a set of molecular orbitals which embrace all the nuclei forming the molecule. You have studied in the Atoms and Molecules (CHE - 01) course that the molecular orbitals can be created by linear combination of atomic orbitals (LCAO) of appropriate energy. Fig. 7.2 depicts the shape of σ and π molecular orbitals formed by the LCAO method. More complex orbitals, δ, ϕ etc., can be formed by interaction between *d*, *f* atomic orbitals. But this need not concern us; the simple molecules with which we shall deal with use σ and π orbitals only.

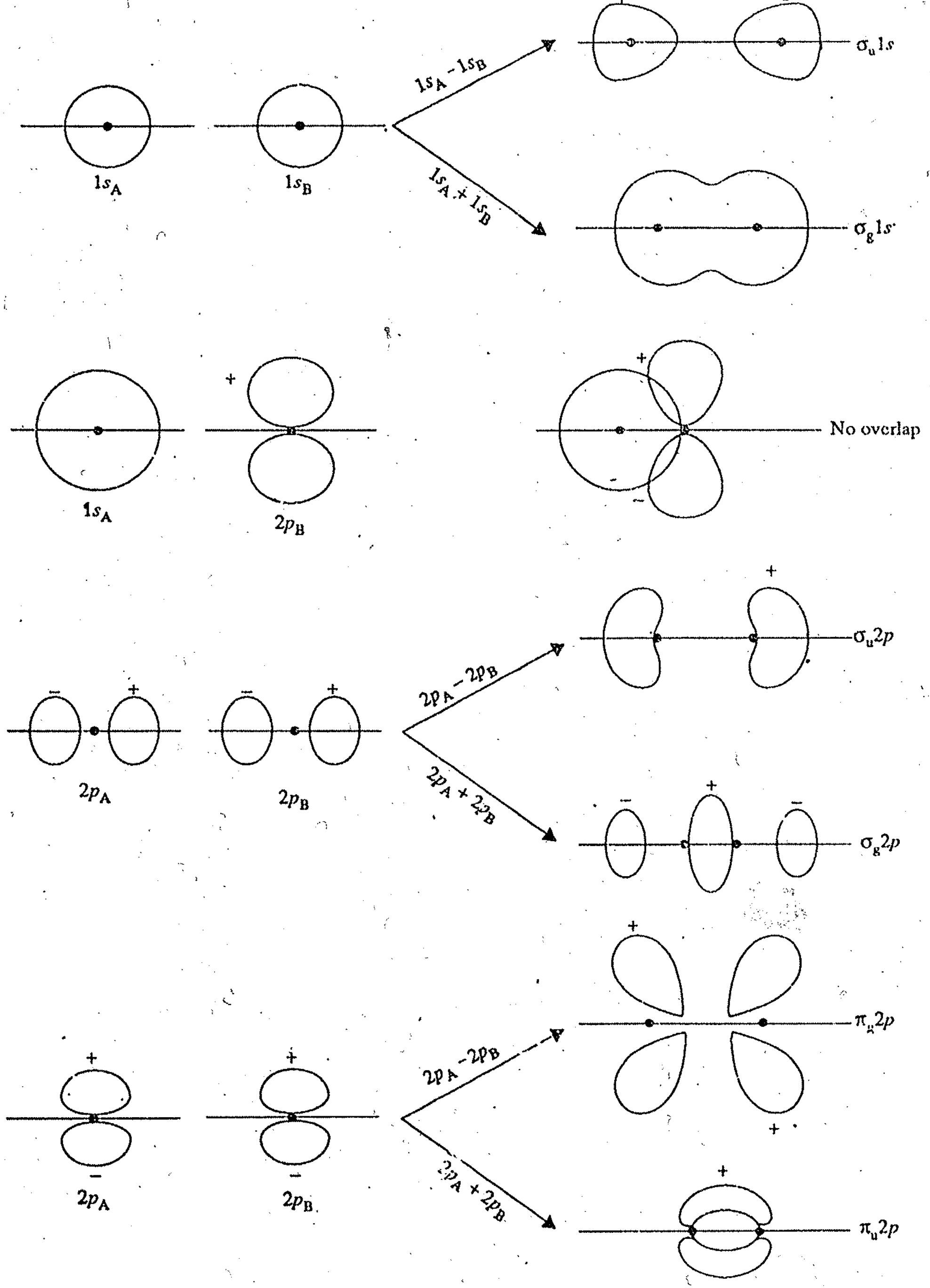


Fig.7.2 : Formation of σ and σ^*, π and π^* molecular orbitals by LCAO.

Various molecular orbitals have different energies and are characterised by the four quantum numbers similar to the atomic orbitals. The principal quantum number, n and the azimuthal or subsidiary quantum number, l are retained from the atomic orbitals and have the same significance here also. But the magnetic quantum number, m_l, is replaced by a new quantum number λ, which represents (in the units of $h/2\pi$), the component or the projection of electronic orbital angular momentum along the inter-nuclear axis. λ can take same values for molecules as m_l has for the atomic orbitals, i.e. $\lambda = 0, \pm 1, \pm 2, \pm 3,...$ When $\lambda = 0$, the molecular orbitals are symmetric for rotation about the inter-nuclear axis (i.e., the line joining the two nuclei) and hence are called σ orbitals. When $\lambda = \pm 1$, orbitals are known as $\pi\pm$ orbitals. The $\pi\pm$ molecular orbitals are antisymmetric for rotation about the molecular axis, that is, if we rotate the molecular orbital by 180°, they change sign (see Fig. 7.2). Similarly, $\lambda = \pm 2, \pm 3,...$ etc. represent $\delta \pm, \phi \pm, ...$etc. molecular orbitals. The different types of molecular orbitals with their symbols and λ values are listed below:

MO symbols σ π δ ϕ ....

λ Values 0 ±1 ±2 ±3 .....

Note that the designations $\sigma, \pi, \delta, \phi$ are not strictly analogous to atomic designations s, p, d, f which depend on l and not on m_l values. Also note that except for σ orbital when $\lambda = 0$, for all other orbitals with $\lambda \neq 0$, there are two possible values of λ, $+\lambda$ and $-\lambda$, i.e., each electronic state is doubly degenerate.

The spin quantum number s is similar to that for the atomic orbitals, and m_s, the component of spin angular momentum, can take the values ± ½.

The order of energy of molecular orbitals has been determined from the spectroscopic data. The energy level diagrams for homonuclear diatomic molecules are shown in Fig. 7.3, where we also indicate to the right and left, the atomic orbitals which combine to form each molecular orbital. Fig. 7.3(a) shows the order of energies of the MOs of the larger molecules such as N_2, O_2 and F_2, wherein the energies of $\sigma 2p$ and $\pi 2p$ orbitals are very close to one another. For lighter molecules such as Li_2, B_2 and C_2, the order of energies of these orbitals is reversed, i.e., $\pi 2p$ becomes lower in energy than the $\sigma 2p$ orbital, Fig.7.3 (b).

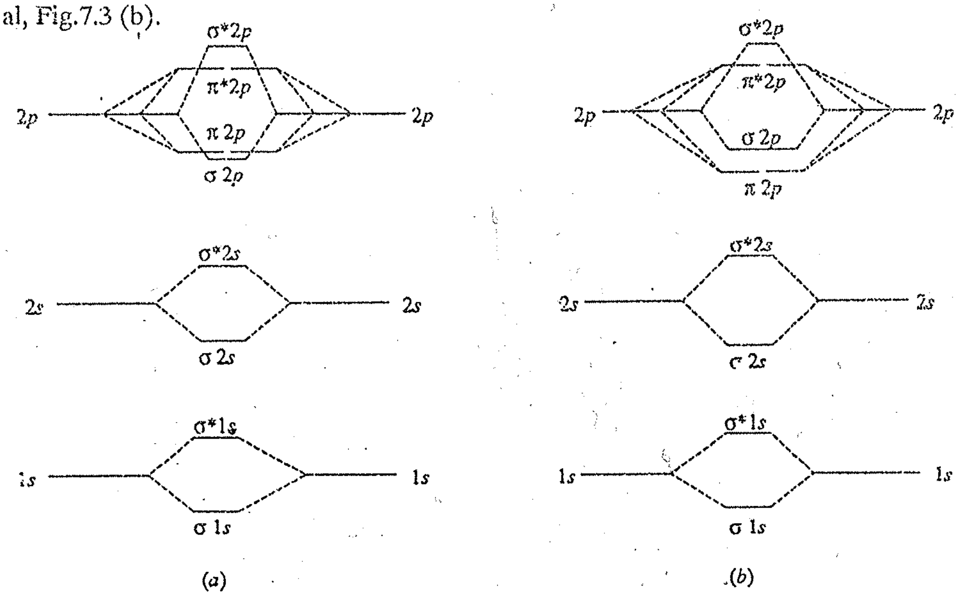


Fig. 7.3 : Energy level diagram for (a) N_2, O_2 and F_2 molecules (b) Li_2, B_2 and C_2 molecules.

Electronic configuration of a diatomic molecule can be derived by filling the electrons in molecular orbitals. Essentially the same rules apply to their filling as to their filling of atomic orbitals. That is

i) the electrons occupy the available molecular orbitals one at a time, the lowest energy orbital being filled first (**aufbau principle**),

ii) each molecular orbital can accommodate a maximum of two electrons, provided their spins are opposite (**Pauli's exclusion principle**),

iii) no pairing of electrons in orbitals of equal energy will take place unless there is atleast one electron in each of them (**Hund's rule of maximum multiplicity**).

7.3.2 Molecular Term Symbols

As for atoms, the electronic state of the molecule depends on the net or total electronic arrangement. The electronic arrangement of the molecule as a whole can be best characterised by the component of total orbital angular momentum along the inter-nuclear axis and the total spin angular momentum. For a molecule, the total orbital component along the molecular axis is denoted by the quantum number Λ, which is the sum of the quantum numbers for each individual electron (λ_i). Thus,

$$\Lambda = \Sigma \lambda_i \text{ where summation is over all electrons.}$$

The following symbols (capital Greek letters) are used to represent the various Λ values for a molecule:

Symbol	: Σ	Π	Δ	Φ	......
Λ Value	: 0	± 1	± 2	± 3	......

The total electron spin angular momentum of a molecule is represented by the total spin quantum number S. The multiplicity of a molecular state is, as for atoms, $2S+1$ and this is usually indicated as an upper prefix to the term symbol.

The values of Λ and S of a molecular state are represented in the form of a term symbol as :

$$^{2S+1}\Lambda$$

In addition, the term symbol has a subscript and a superscript on the right side. The subscript (g or u) indicates whether on inversion through the centre of symmetry the orbital changes sign or not. This is referred to as parity. In a homonuclear diatomic molecule the overall parity is equal to the product of individual parities. If two occupied orbitals are gerade (g), their product is also gerade (g). If the two occupied orbitals are ungerade (u), their product is also gerade (g). However, the product of one gerade and one ungerade orbital will be ungerade, i.e.,

$$g \times g = g$$

$$u \times u = g$$

$$g \times u = g$$

The superscript (+ or −) on the right side of the molecular term symbol denotes the behaviour of the orbitals under reflection in a plane containing the nuclei. The σ molecular orbitals have a perfect cylindrical symmetry and are always symmetric (i.e., remain unchanged) with respect to this operation and are given a + sign. Therefore, any molecular wave function that is a product of σ type orbitals will be Σ^+. The Σ^- state arises when two electrons with parallel spin reside in π or δ molecular orbitals. The Π and Δ states are not classified + or − ; these states always occur as degenerate pairs.

7.3.3 Deriving Term Symbols

In determining the term symbols of many-electron diatomics, the following rules should be kept in mind:

- All filled orbitals (e.g., $\sigma^2, \pi^4, \delta^4$) are $^1\Sigma_g^+$.
  This is because there is no orbital angular momentum from a closed-shell, net spin is zero and the overall parity is g. The last remark follows from the rule that in a many-electron molecule the overall parity is obtained from the product of the parities of each electron using

  $$g \times g = g; = u \times u = g, \text{ and } g \times u = u.$$

- The state of the "hole" is the state of the electron. As for atoms, the state can be determined from the holes that must be filled to complete a orbital. Thus π^1 and π^3 will have the same term symbol, so will have the δ^1 and δ^3 orbitals.

The following examples will illustrate the general procedure for determining the term symbols:

$(\sigma_g)^1 : \Lambda = \Sigma\lambda_i = \lambda = 0$, hence the state is Σ. $S = ½$, $2S + 1 = 2 \times ½ + 1 = 2$. Hence a doublet state. Since, the electron is in a σ molecular orbital which is of g type, hence the subscript will be g. The orbital does not change sign under reflection in the molecular plane, hence a + superscript. So the term symbol should be $^2\Sigma_g^+$. Similarly for $(\sigma_u)^1$, the term symbol should be $^2\Sigma_u^+$

$(\sigma_u)^2$: $= \Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$, hence again a Σ state. As both the electrons are in the same molecular orbital, they have different m_s values. Thus, $M_S = (m_s)_1 + (m_s)_2 = (½) + (-½) = 0$. With $M_S = 0, S = 0$, and $2S + 1 = 1$. Hence, a singlet state. The product of two ungerade functions is gerade ($u \times u = g$), parity is g. Since the electrons are in a σ orbital, the right superscript will be +. Therefore, the term symbol is $^1\Sigma_g^+$.

$(\pi_u)^1$: The electron could be in either the $\pi+$ ($\lambda = +1$) orbital or the $\pi-$ ($\lambda = -1$) orbital. Therefore, $\Lambda = \lambda = \pm 1$, and the state is Π. Since, the molecular orbital has only one electron, $S = ½$, hence multiplicity ($2S + 1$) is 2. Parity is u. Therefore, the term symbol is $^2\Pi_u$.

$(\pi_u)^3$: There are two possible configurations:

$$(\pi+)^2 (\pi-)^1, \Lambda = \lambda_1 + \lambda_2 + \lambda_3 = 1 + 1 - 1 = +1$$

$$(\pi+)^1 (\pi-)^2, \Lambda = \lambda_1 + \lambda_2 + \lambda_3 = 1 - 1 - 1 = -1$$

Therefore, $\Lambda = \pm 1$ and the state is Π. Also, the state function is a product of three ungerade functions, hence ungerade ($u \times u \times u = u$). Since, the electrons in filled molecular orbital $(\pi+)^2$ or $(\pi-)^2$ are paired, there is no net spin contribution from this orbital. There is only one electron present in $(\pi+)^1$ or $(\pi-)^1$ molecular orbital, hence $S = ½$. Therefore, the multiplicity $2S + 1 = 2 \times ½ + 1 = 2$. Hence, the term symbol is $^2\Pi_u$. Note that this is identical to the term symbol for the $(\pi_u)^1$ configuration.

7.3.4 Ground and Excited State Term Symbols of Diatomics

Now, we will derive the term symbols for the ground and excited states of three molecules, namely hydrogen, H_2, the lithium hydride, LiH and the oxygen molecule, O_2. Let us consider the H_2 molecule first.

H_2: The ground state electronic configuration of H_2 is $(\sigma_g 1s)^2$. As both the electrons are in a σ orbital, $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$, hence the state will be Σ. Since electrons are paired, the net spin S is $= 0$. Hence, multiplicity ($2S + 1$) is 1. Both the electrons are in the same orbital which is of g-type. Hence, the overall parity is $g \times g = g$ and the subscript is g. Both the electrons are in σ orbital which does not change sign under reflection in molecular plane. Hence, the superscript is a +. Thus we have the ground state of hydrogen represented by the spectroscopic term symbol, $^1\Sigma_g^+$.

Let us now consider the first excited state of the H_2 molecule having configuration $(\sigma_g 1s)^1 (\sigma_u 1s)^1$. The value of $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$, hence again the state will be Σ. One electron is in an orbital of g parity, while the other is in that of u parity. The overall parity is $g \times u = u$, the subscript is u. The orbitals do not change sign under reflection in molecular plane, hence superscript is (+) × (+) = +. Further, the electrons can have parallel or antiparallel spins, therefore, net spin S can be 1 or 0. The corresponding multiplicities ($2S + 1$) can be 3(triplet) or 1 (singlet). Therefore, the term symbol will be $^1\Sigma_g^+$ or $^3\Sigma_g^+$. You can similarly obtain the term symbols for other excited states of the hydrogen molecule.

LiH : Now, we consider LiH, which is a heteronuclear diatomic molecule. The ground state electronic configuration of LiH is $K\,(\sigma_g 2s)^2$, where K is used to denote two electrons in the 1*s* orbital. $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$, hence it belongs to a Σ state. The net spin (S) is zero, so multiplicity $2S + 1$ is one. The orbitals remain unchanged under reflection in molecular plane, overall reflection symmetry will be $(+) \times (+) = +$. So we will have the $+$ superscript in the term symbol. A heteronuclear diatomic molecule has no centre of symmetry and hence the term symbol will not have the subscript symbol g or u. Therefore, the ground state term symbol for LiH is $^1\Sigma^+$.

The excited state of LiH may have electronic configuration $k\,(\sigma_g 2s)^1\,(\sigma_g 2p)^1$. The value of Λ is again 0, hence a Σ state. S can be either 0 (opposite spins) or 1 (parallel spins), hence multiplicity $(2S + 1)$ will be 1 or 3. Both $\sigma_g\, 2s$ and $\sigma_g\, 2p$ orbitals remain unchanged under reflection, hence overall reflection symmetry will be $(+) \times (+) = +$. Therefore, the term symbols for the above excited state of LiH will be $^1\Sigma^+$ and $^3\Sigma^+$. There can be several other excited states also.

O_2: Let us now consider the ground state term symbol for the oxygen molecule having the configuration $(\sigma_g\, 1s)^2\,(\sigma_u^*\, 1s)^2\,(\sigma_g\, 2s)^2\,(\sigma_u^*\, 2s)^2\,(\sigma_g 2p)^2\,(\pi_u\, 2p)^4\,(\pi_g^*\, 2p)^2$. As you know the completely filled molecular orbitals contribute nothing to the total orbital angular momentum and total spin angular momentum and the overall parity is g, we have to consider the contribution of $(\pi_g^*\, 2p)^2$ orbitals only. The following configurations are possible:

$$\left.\begin{array}{l} (\pi+)^2\,(\pi-)^0 : \Lambda = \lambda_1 + \lambda_2 = 1 + 1 = 2 \\ (\pi+)^0\,(\pi-)^2 : \Lambda = \lambda_1 + \lambda_2 = -1 - 1 = -2 \end{array}\right\}\ a\ \Delta\ \text{state.}$$

$$(\pi+)^1\,(\pi-)^1 : \Lambda = \lambda_1 + \lambda_2 = 1 - 1 = 0,\ \text{a}\ \Sigma\ \text{state.}$$

The electrons in the Δ state must be paired since they are in the same spatial orbital. Hence, $S = 0, 2S + 1 = 1$; it is a singlet $(^1\Delta)$ state.

For the Σ state, the two electrons being in different molecular orbitals with value of $\lambda = \pm 1$, can have same m_s values (i.e. parallel spins) or different m_s values (i.e. antiparallel spins). The net spin S will be 1 or 0, respectively, giving rise to both triplet as well as singlet states, $^3\Sigma$ and $^1\Sigma$. Since, the overall parity is $g \times g = g$, the terms are $^3\Sigma_g$ and $^1\Sigma_g$. Thus for O_2, the ground state must be either $^1\Delta$, $^3\Sigma_g$ or $^1\Sigma_g$.

According to Hund's rule, the ground state has the highest spin multiplicity. The ground state is therefore, $^3\Sigma_g$. As stated earlier, when two electrons with parallel spin reside in π or δ molecular orbitals, it gives rise to Σ^- states. Thus, the complete ground state term symbol for O_2 is $^3\Sigma_g^-$; the other Σ state is $^1\Sigma_g^+$.

Note that the term symbols for π^2 configuration are $^1\Delta$, $^3\Sigma_g^-$ and $^1\Sigma_g^+$. The term for the ground state is $^3\Sigma_g^-$.

You should note that the $\pm$ symmetry is considered only for Σ states. This is because for the states with $\Lambda \neq 0$, reflection of the wave function in a plane through the nuclei changes the sign of λ. That is, one member of the degenerate pair of states is transformed into the other.

We have listed in Table 7.1, term symbols arising from various electronic configurations of diatomic molecules.

Table 7.1 : Electronic Terms of Diatomic molecules.

Configuration	**Terms**
$\sigma\sigma$	$^1\Sigma^+, {}^3\Sigma^+$
$\sigma\pi; \sigma\pi^3$	$^1\Pi, {}^3\Pi$
$\pi\pi; \pi\pi^3$	$^1\Sigma^+, {}^3\Sigma^+, {}^1\Sigma^-, {}^3\Sigma^-, {}^1\Delta, {}^3\Delta$
$\pi\delta; \pi^3\delta; \pi\delta^3$	$^1\Pi, {}^3\Pi, {}^1\Phi, {}^3\Phi$
σ	$^2\Sigma^+$

Configuration	Terms
$\sigma^2; \pi^4; \delta^4$	$^1\Sigma^+$
$\pi; \pi^3$	$^2\Pi$
π^2	$^1\Sigma^+, {}^3\Sigma^-, {}^1\Delta$
$\delta; \delta^3$	$^2\Delta$
δ^2	$^1\Sigma^+, {}^3\Sigma^-, {}^1\Gamma$

Before we describe selection rules for the electronic spectra of diatomic molecules, you may like to attempt the following SAQ.

SAQ 1

State whether the following are true or false. Write either T or F at the end of each statement in the box provided. If false, write the correct statement in the margin.

(a) If the molecular orbital for a homonuclear diatomic molecule has a subscript g, it indicates that the orbital is symmetric to [illegible]. ☐

(b) For oxygen molecule having π-electrons the state may be either Σ or Δ ☐

(c) For LiH molecule the spectroscopic term symbol will have a subscript g or u on the right side. ☐

(d) The spectroscopic term symbol for H_2 in the ground state is $^2\Sigma_g^+$ ☐

(e) The ground state of oxygen molecule is a triplet state. ☐

(f) When the axial component of total angular momentum has a value 3, the state is called a Φ state. ☐

7.3.5 Selection Rules for Spectra of Diatomics

The following selection rules apply to electronic transitions in diatomic molecules:

1. Λ, the component of total angular momentum along the inter-nuclear axis can have the same value for ground and excited states ($\Delta\Lambda = 0$) or $\Delta\Lambda = \pm 1$. Hence, transitions between Σ and Σ or between Π and Σ or between Π and Δ states are permitted. Transitions between Δ and Σ or between Φ and Π states are not permitted.

2. $\Delta S = 0$, i.e., the electron does not change its spin during transition. Only transitions between two singlet or two doublet or two triplet states are allowed. This rule breaks down for molecules with heavy nuclei.

3. Σ^+ states can undergo transitions only into other Σ^+ states (or, of course, into Π states) whereas Σ^- can go only into Σ^- (or Π) state. Symbolically,

$$\Sigma^+ \longleftrightarrow \Sigma^+,\ \Sigma^- \longleftrightarrow \Sigma^-, \Sigma^+ \not\longleftrightarrow \Sigma^-,$$

4. In homodiatomic molecules the parity for the excited state should be different from that of the ground state. $g \longleftrightarrow u$ and $u \longleftrightarrow g$ transitions are permitted; $g \longleftrightarrow g$ or $u \longleftrightarrow u$ transitions are forbidden, i.e.,

$$g \longleftrightarrow u,\ g \not\longleftrightarrow g,\ u \not\longleftrightarrow u$$

We list in Table 7.2 some of the allowed electronic transitions for diatomic molecules.

Table 7.2: Allowed Transitions for Diatomic Molecules.

Homonuclear	Heteronuclear
$\Sigma_g^+ \longleftrightarrow \Sigma_u^+$	$\Sigma^+ \longleftrightarrow \Sigma^+$
$\Sigma_g^- \longleftrightarrow \Sigma_u^-$	$\Sigma^- \longleftrightarrow \Sigma^-$
$\Pi_g \longleftrightarrow \Sigma_u^+$	$\Pi \longleftrightarrow \Sigma^+$
$\Pi_u \longleftrightarrow \Sigma_g^+$	$\Pi \longleftrightarrow \Sigma^-$
$\Pi_g \longleftrightarrow \Sigma_u^-$	$\Pi \longleftrightarrow \Pi$
$\Pi_u \longleftrightarrow \Sigma_g^-$	$\Pi \longleftrightarrow \Delta$
$\Pi_g \longleftrightarrow \Pi_u$	$\Delta \longleftrightarrow \Delta$
$\Pi_g \longleftrightarrow \Delta_u$	$\Delta \longleftrightarrow \Phi$
$\Pi_u \longleftrightarrow \Delta_g$	$\Phi \longleftrightarrow \Phi$
$\Delta_g \longleftrightarrow \Delta_u$	etc.
etc.	

Before we proceed further, you may like to try the following SAQ to test your understanding of the concepts discussed in this section.

SAQ 2

Use the words given below to fill in the blanks in the following statements:

singlets, forbidden, multiplicity, same, parity

(a) The component of the angular momentum along the internuclear axis can have the__________ value for the ground and excited states of the molecule.

(b) Transitions between two __________are permitted.

(c) In homodiatomics the__________ for the excited state must be different from that of the ground state.

(d) The transition $\Sigma^+ \longleftrightarrow \Sigma^-$ is __________ in electronic spectra of diatomics.

(e) During an electronic transition, the ground and excited states must have the same spin__________

We have learnt in Section 7.2 that the vibrational energy changes give rise to the coarse structure in electronic spectra. The appearance of the vibrational structure in an electronic band can be explained in terms of the Franck-Condon principle. The next section deals with this principle.

7.4 FRANCK-CONDON PRINCIPLE AND INTENSITIES OF ELECTRONIC SPECTRA

The Franck-Condon principle states that since the time required for a molecule to execute a vibration (about 10^{-12} sec) is much longer than that required for transition of electrons (about 10^{-15} sec.), during electronic transitions the nuclei do not appreciably alter their positions. This means that the internuclear distance remains unaltered during the transition. The meaning of Franck-Condon principle can be understood by considering the potential energy curves in Figure 7.4. Before the absorption the molecule is in the ground vibrational state of the ground electronic state. The nuclei are located at the equilibrium separation R_e. When the transition occurs, the molecule is excited to the state represented by the upper curve. According to the Franck Condon principle the nuclear framework remains constant during the excitation, and so we may represent this transition by a vertical line (Fig. 7.4).

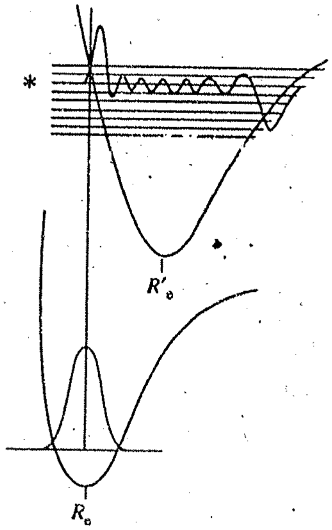


Fig. 7.4 : Representation of a vertical vibronic transition

Thus we say that the electronic transition is vertical. A vertical transition indicates that an electronic transition occurs without change of nuclear geometry. The vertical transition cuts through several vibrational levels of the upper electronic state. The level marked * is the one in which the nuclei are most probably at separation R_e. This happens to be the most probable level for the termination of the transition. However, we have many other vibrational levels nearby which have an appreciable probability of nuclei being at R_e. Hence, transitions occur to all vibrational levels in this region. But most intensely to the level marked by *.

The intensities of bands in electronic spectra can be quantitatively predicted by calculating the Franck condon factor, (which is beyond the scope of this course).

It can be shown with the help of quantum mechanical calculations that the intensity of a band is related to the difference in the nuclear separations R_e and R'_e for the ground and excited electronic states, respectively. Three cases of electronic spectra arise depending on the relative values of R_e and R'_e. These are as follows:

Case 1 : $R'_e = R_e$ (Fig. 7.5 a)

Case 2 : $R'_e > R_e$ (Fig. 7.5 b)

Case 3 : $R'_e >> R_e$ (Fig. 7.5 c)

Case 1: Fig. 7.5 a shows the near ultraviolet spectrum of CN^- radical. The potential energy minima lie very nearly one above the other. The 0–0 band has maximum intensity. 1–0, 2–0, 3–0 bands decrease in intensity. The equilibrium bond lengths (R_e, R'_e) and vibrational wavenumbers (w, w') for the 0–0 band for CN^- radical are given below:

$$R'_e = 0.11506 \text{ nm}, \qquad w' = 2164.1 \text{ cm}^{-1}$$

$$R_e = 0.11718 \text{ nm}, \qquad w = 2068.7 \text{ cm}^{-1}$$

Case 2 : Fig. 7.5 b shows the spectrum of CO. The minimum of the upper potential energy lies at a moderately greater R_e value (0.01–0.02 nm) than the lower potential energy. The 0–3 band has maximum intensity and other bands on both sides have decreased intensity. The equilibrium bond lengths and vibrational wave numbers are given below:

$$R'_e = 0.1235 \text{ nm}, \qquad w' = 1515.6 \text{ cm}^{-1}$$

$$R_e = 0.1128 \text{ nm}, \qquad w = 2170.2 \text{ cm}^{-1}$$

Case 3 : The minimum of the upper potential energy curve lies at a considerable distance away from that of the lower potential energy curve in the spectrum of I_2 (Fig. 7.5 c). In this case, transition takes place to a very high vibrational level in the upper state, which corresponds to the continuum level. The continuum level has very high energy and the molecule undergoes dissociation. The 0 – 0 band is absent in this spectrum.

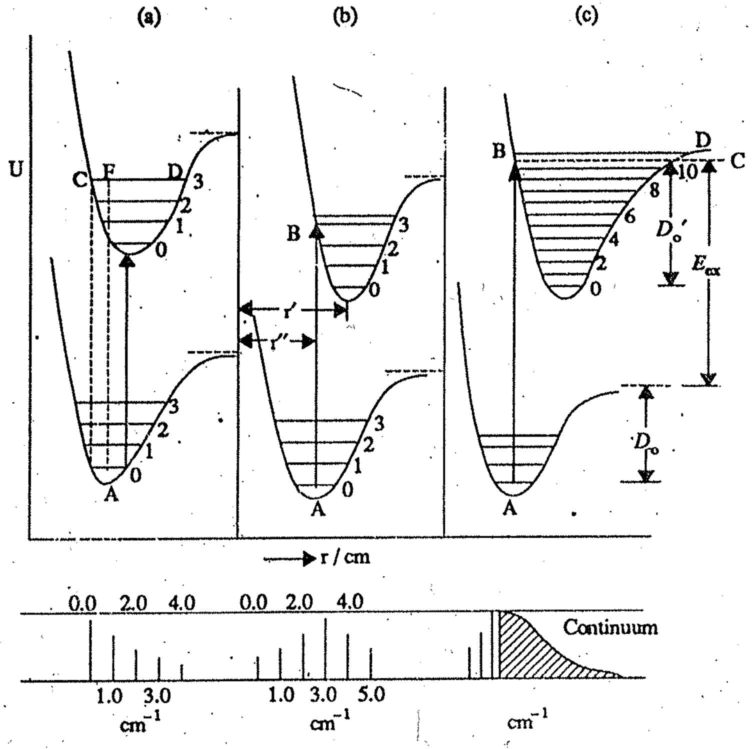


Fig. 7.5 : Application of Franck-Condon principle to the spectra of (a) CN^- radical (b) CO molecule (c) I_2 molecule.

Spectra corresponding to case 3 are useful in obtaining the dissociation energy of the molecule in the ground state. From the excited state, if a diatomic molecule dissociates into atoms, one of the atoms from fragmentation will be in the ground state and the other will be in the excited state. The energy of dissociation into atoms in the ground state (D_0) can be obtained if we know the energy corresponding to continuum (hcw_m) and the excitation energy (E_{ex}). The formula for D_0 is

$$D_0 = hcw_m - E_{ex}$$

This energy corresponds to that of one photon. To obtain the energy for one mole in kcals, we must multiply D_0 by ($N_0/4.2 \times 10^{10}$) where N_0 is the Avogadro number. The following example illustrates the computation of dissociation energy for ground state for I_2 molecule.

Example 7.1

The limit of continuum absorption for iodine gas occurs at 499.5 nm. The excitation energy for the iodine atom is 0.94 ev. Compute the ground state dissociation energy for I_2.

Solution :

$$w_m = 1/\lambda = 1/(499.5 \times 10^{-7}) = 10^7/499.5 \text{ cm}^{-1}$$

$$hcw_m = 6.6256 \times 10^{-27} \times 2.998 \times 10^{10} \times 10^7/499.5 = 3.976 \times 10^{-12} \text{ erg}$$

$$E_{ex} = 0.94 \text{ ev} = 0.94 \times 1.6 \times 10^{-12} \text{ erg} = 1.504 \times 10^{-12} \text{ erg}$$

$$D_0 = hcw_m - E_{ex} \text{ per photon}$$

$$= 3.976 \times 10^{-12} - 1.504 \times 10^{-12} \text{ erg per photon}$$

$$= (3.976 - 1.504) \times 10^{-12} \text{ erg per photon}$$

$$= 2.472 \times 10^{-12} \text{ erg per photon}$$

To obtain the energy in kcal per mole this value is multiplied by $N_0/4.2 \times 10^{10}$

$$D_0 = 2.472 \times 10^{-12} \times 6.023 \times 10^{23}/4.2 \times 10^{10} \text{ kcal per mole}$$

$$= 2.472 \times 6.023 \times 10/4.2 = 35.4496 \text{ kcal per mole}$$

We have learnt the Franck-Condon principle and its application to electronic band spectra of different diatomic molecules. You may now solve the following SAQ.

SAQ 3

Fill in the blanks in the following statements using the words given below:

continuum, unaltered, dissociation.

a) According to Franck-Condon principle the internuclear distance remains___________ during an electronic transition.

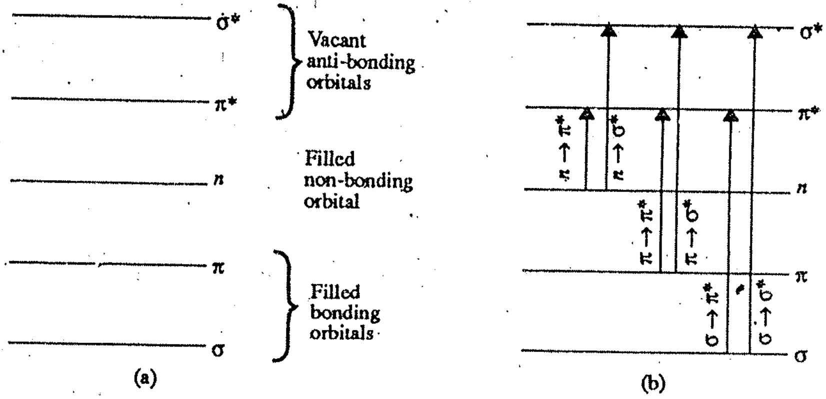
b) When the nuclear separation R'_e for the excited electronic state is very much different from that for the ground electronic state, the molecule undergoes ___________.

c) The dissociation energy in the ground state for a molecule can be computed if we know the wave number for ___________ level and the excitation energy of the molecule.

7.5 ELECTRONIC SPECTRA OF POLYATOMIC MOLECULES

Unlike diatomic molecules, the rotational fine structure is not observed in polyatomic molecules and the vibrational structure is present in the form of broad bands. The absence of rotational fine structure in polyatomics is due to the closely spaced rotational energy levels and high values of moments of inertia. Hence, spectra of polyatomics have poorer resolution as compared to spectra of diatomics. In spite of this limitation, spectra of polyatomics provide important information about electronic structure.

We make use of molecular orbital theory to understand theoretical aspects of spectra of polyatomics. In electronic transitions of polyatomics, we encounter three types of molecular orbitals: σ and σ^*, π and π^*, and n (nonbonding) orbitals. Orbitals without $*$ are bonding orbitals and those with $*$ are antibonding orbitals. The energy levels of all these molecular orbitals, in increasing order of energy, are shown in Fig.7.6.



(a) (b)

Fig. 7.6 : Schematic diagram of (a) order of molecular orbital energies (b) possible electronic transitions.

When a molecule absorbs energy in the UV or visible region, an electron from a specific MO is excited to another of higher energy. The possible transitions of the electron between the MO's are:

$$\sigma - \sigma^*,\ n - \sigma^*,\ n - \pi^*,\ \pi - \pi^*,\ \pi - \sigma^* \text{ and } \sigma - \pi^*.$$

The order of decreasing energy for these transitions is as follows:

$$\sigma - \sigma^* > \sigma - \pi^* \approx \pi - \sigma^* > \pi - \pi^* \approx n - \sigma^* > n - \pi^*$$

Of all the possible transitions, the last three are responsible for absorptions in the region 200-800 nm, whereas others require much higher energy.

$\sigma - \sigma^*$ transition : Fig. 7.6 reveals that this transition requires very high energy. The absorption spectra obtained appear in the far ultraviolet region (< < 200 nm). Molecules which give this type of spectrum are saturated hydrocarbons and other compounds in which all valence electrons are involved in single bond formation. Since a spectrometer generally cannot measure below 185 nm, the region involving $\sigma - \sigma^*$ transitions is relatively of less importance for chemical analysis.

$n - \sigma^*$ transition : The spectra corresponding to $n - \sigma^*$ transition appear in the near UV or visible region. Compounds containing non-bonding or lone-pair electrons show this transition. For example, methyl alcohol vapour shows an absorption maximum at 183 nm. Methyl chloride and methyl amine show absorption maxima at 173 nm and 213 nm, respectively.

$n - \pi^*$ transition : This type of transition is exhibited by unsaturated molecules containing non bonding electrons. Certain organic groups like $>C=N-$, $-N=O$, $>C=O$ show this type of transition and we obtain absorption maxima for these systems at wavelengths greater than 280 nm. Groups such as $>C=N-$, $-N=O$, $>C=O$, $-COOH$ causing absorption at wavelengths greater than 175 nm are referred to as chromophores. More information on chromophores will be presented a little later.

$\pi - \pi^*$ transition : Band due to $\pi - \pi^*$ transition appears in the spectra of compounds containing $>C=C<$, $-C\equiv C-$, $>C=O$ and $>C=N-$ functional groups. Ethylene and acetone exhibit $\pi - \pi^*$ transition at 165 and 150 nm, respectively. The $\pi - \pi^*$ transition is highly affected by conjugation.

You have studied in Unit 8 of the CHE-01 course, that the absorption bands in ultraviolet and visible spectra are characterised by two main parameters which are

i) **λ_{max} Value:** The value of the wavelength at which absorption maximum occurs is called the λ_{max} value. This corresponds to the wavelength of the radiation whose energy is equal to that required for an electronic transition. As different transitions require different energies, their λ_{max} values are different.

ii) **ε_{max} Value :** ε value, which is known as molar absorptivity or molar extinction coefficient, is a measure of extent of absorption or intensity of absorption. The ε value is characteristic of a particular compound at a given wavelength. Usually for the wavelength of maximum absorption (λ_{max}), molar absorptivity is expressed as ε_{max}.

The intensity of absorption can be expressed as transmittance (T), which is defined as the ratio of the intensity of the radiation transmitted from the sample (I) to that of the radiation incident on the sample (I_o), i.e.,

$$T = I/I_o$$

Intensity of absorption is more conveniently expressed in terms of absorbance (A), which is the logarithm of reciprocal of transmittance (T), i.e.,

$$A = \log_{10}(1/T) = \log_{10}(I_0/I)$$

Absorbance of a band is related to the sample thickness and the concentration of the absorbing species. The relationship is expressed in the form of Beer-Lambert law as shown below:

$$A = \varepsilon cl = \log_{10}(I_0/I)$$

or $$\varepsilon = \frac{A}{cl}$$

where ε = molar absorptivity or molar absorption constant

c = concentration of solute

l = sample thickness or path length through the sample

Absorbance is a dimensionless quantity. Concentration (c) is usually expressed in mol dm^{-3} and path length (l) in cm, hence ε has the units of dm^{3} mol^{-1} cm^{-1}. If we use SI units of mol m^{-3} for concentration and m for path length, the units of ε will be m^{2} mol^{-1}. We can obtain the values of ε in m^{2} mol^{-1} units from those in dm^{3} mol^{-1} cm^{-1} units in the following manner: $\varepsilon = \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1} = 10^{-3}\ \text{m}^3\ \text{mol}^{-1}\ (10^{-2}\ \text{m})^{-1} = 10^{-1}\ \text{m}^2\ \text{mol}^{-1}$

Values of ε in SI units can, therefore, easily be obtained from published values in dm^{3} mol^{-1} cm^{-1} by dividing the numerical quantity in latter units by 10.

Absorption bands with ε_{max} value $> 10^3$ m^{2} mol^{-1} are considered to be high intensity or strong bands, whereas those with ε_{max} values $< 10^2$ m^{2} mol^{-1} are known as low intensity or weak bands.

7.6 SOME IMPORTANT TERMS USED IN ELECTRONIC SPECTROSCOPY

Chromophore:

In a number of molecules the absorption of a photon can be traced to the electrons of certain covalently unsaturated groups. Such groups, for example carbonyl in aldehydes or ketones which are responsible for electronic absorption, are referred to as chromophores. Other examples of chromophores are $>C=C<$, $-C \equiv C-$, $-COOH$, $-N=O$, $-NO_2$, $-N=N-$ and so on. Chromophore in Greek means colour bringer and the presence of a chromophore often accounts for colours of substances. The following table lists the absorption maxima for some typical chromophores.

Table 7.3 : Absorption Data for Isolated Chromophores

Chromophoric Group	System	Example	Transition	λ_{max} nm	ε_{max} m^{2} mol^{-1}	Solvent
Ethylenic	$RCH=CHR$	Ethylene	$\pi \rightarrow \pi^*$	165	1500	Vapour
Acetylenic	$R-C\equiv C-R$	Acetylene	$\pi \rightarrow \pi^*$	173	6000	Vapour
Carbonyl	$RR_1C=\dot{O}$	Acetone	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	188 279	900 1.5	n-Hexane
Carbonyl	$RHC=O$	Acetaldehyde	$n \rightarrow \pi^*$	290	1.6	Heptane
Carbonyl	$RCOOH$	Acetic acid	$n \rightarrow \pi^*$	204	6.0	Water
Amido	$RCONH_2$	Acetamide	$n \rightarrow \pi^*$	< 208	–	–
Azomethine	$>C=N-$	Acetoxime	$\pi \rightarrow \pi^*$	190	5000	Water
Nitrile	$-C\equiv N$	Acetonitrile	$\pi \rightarrow \pi^*$	< 160	–	–
Azo	$-N=N-$	Azomethane	$n \rightarrow \pi^*$	347	0.45	Dioxane

Contd.

Chromophoric Group	System	Example	Transition	λ_{max} nm	ε_{max} $m^2\ mol^{-1}$	Solvent
Nitroso	$-N=O$	Nitroso-butane	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	300 665	10 2.0	Ether
Nitrate	$-ONO_2$	Ethyl nitrate	$n \rightarrow \pi^*$	270	1.2	Dioxane
Nitro	$-NO_2$	Nitromethane	$n \rightarrow \pi^*$	271	1.86	Alcohol
Nitrite	$-ONO$	Amyl nitrite	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	218.5 346.5	112	Petroleum ether

Auxochrome

A saturated group with nonbonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption is called an auxochrome, e.g., OH,NH_2 and Cl. The auxochrome, though by itself is unable to impart colour to a compound. The auxochromic effect depends on the ability of the chemical group to donate electrons into conjugated system. This has been most studied with aromatic systems and the spectral shifts of monosubstituted aromatic compounds have been correlated with electron donating power of auxochromes. The electron donating power of some common auxochromes decreases in the order

$O^- > NHCH_3 > NH_2 > OH > Cl > CH_3 > NH_3^+ = H$

In this list the effect of protonating the NH_2 group should be noted, the proton binds the nonbonding (lone pair) electrons on the nitrogen of the amino group and prevents them from interacting with the benzene π-electron system. Thus, the λ_{max} value for aniline ($C_6H_5NH_2$) and the anilinium ion ($C_6H_5NH_3^+$) are 230 nm and 203 nm, respectively as compared to 204 nm for benzene.

Bathochromic or red shift : A shift of the absorption maximum towards longer wavelength (lower frequency)produced by a change of medium or by the presence of an auxochrome, is called bathochromic shift or red shift.

Hypsochromic shift or Blue shift : A shift towards shorter wavelength (higher frequency) caused by a change of medium or by removal of conjugation is referred to as hypsochromic shift or blue shift. For example, the conjugation of the lone pair of electrons on the nitrogen atom of aniline with the π-bond system of the benzene ring is removed by protonation. Aniline absorbs at 230 nm, but in acid solution the main peak is shifted to 203 nm due to the presence of anilinium ions.

Hypochromic effect : An effect leading to decreased absorption intensity is called hypochromic effect.

Hyperchromic effect : An effect leading to increased absorption intensity is called hyperchromic effect.

7.7 ABSORPTION DUE TO ETHYLENIC AND CARBONYL CHROMOPHORE

In this section we shall discuss the electronic absorptions of only two of the more important chromophores in little more detail. These are the ethylenic and the carbonyl chromophores. In addition, we shall have only a brief look at the absorptions of the acetylenic and the benzenoid chromophores.

7.7.1 Ethylenic Chromophore

As you know ethylene has five σ bonds (four C–H and one C–C) and one π bond. If we denote σ molecular orbitals as σ_1, σ_2 etc., and consider only the twelve valence electrons, the ground state electronic configuration of ethylene is $(\sigma_1)^2 (\sigma_2^*)^2 (\sigma_3)^2 (\sigma_4^*)^2 (\sigma_5)^2 (\pi)^2$. If we consider only the highest σ orbital, the ordering of the molecular orbitals is as shown in Fig. 7.7.

In ethylene only four electronic transitions are possible which are $\pi - \pi^*, \sigma - \sigma^*, \pi - \sigma^*$ and $\sigma - \pi^*$. Out of these the latter two are symmetry forbidden. Of the other two, as you can see from the Figure 7.7, the $\pi - \pi^*$ transition would require less energy. In ethylene in the vapour phase the $\pi - \pi^*$ transition appears at 165 nm (ε_{max} = 1000 m^2 mol^{-1}). The transition is out of the normal range of most spectrometers.

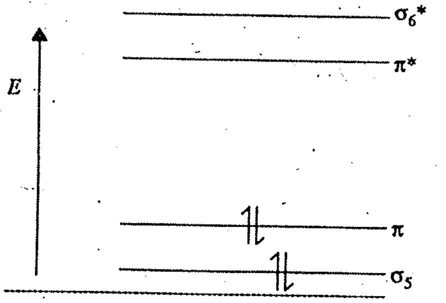


Fig.7.7: Orbital energy diagram for ethylene.

Alkyl substitution of the ethylenic compound moves the absorption to longer wavelengths (bathochromic shift). The effect is progressive as the number of alkyl groups increases. Attachment of a heteroatom (bearing nonbonded electrons) to the ethylenic linkage also gives rise to a red or bathochronic shift. Nitrogen and sulphur are the most effective heteroatoms shifting the absorption well into the near ultraviolet region. For example methyl vinyl sulphide ($CH_3SCH=CH_2$) absorbs at 228 nm. The absorptions of cyclic monoolefins resemble those of the open chain olefins and the absorption has no relationship to ring size. When there are two or more isolated ethylenic bonds in a molecule, it absorbs at the same position as the single ethylenic chromophore. The intensity of absorption, however, is proportional to the number of isolated chromophoric groups in the molecule.

As the absorption due to isolated ethylenic chromophore takes place in far ultraviolet region, electronic spectroscopy has thus little use in detecting isolated double bond. Conjugation markedly affects the position of absorption due to the >C=C< chromophore giving rise to a bathochronic shift. Thus, the λ_{max} value for $\pi - \pi^*$ transition for the 1, 3-butadiene is 217 nm as compared to 185 nm for the 1, 5-hexadiene.

$CH_2=CH-CH=CH_2$	$CH_2=CH-CH_2-CH_2-CH=CH_2$
1, 3-butadiene	1, 5-hexadiene
λ_{max} 217 nm	λ_{max} 185 nm
ε_{max} 2100 m^2 mol^{-1}	ε_{max} 2000 m^2 mol^{-1}

This relatively large increase in the wavelength of absorption due to conjugation can be explained as follows. In ethylene the two 2*p* atomic orbitals combine to form a set of π and π^* molecular orbitals. In conjugated dienes such as 1,3-butadiene, when π and π^* molecular orbitals of two ethylenic linkages are close enough, overlap can occur. As a result a combination of two π molecular orbitals gives two delocalised orbitals of lower and higher energy (π_1 and π_2). Similarly the two π^* orbitals give rise to two delocalised π^* orbitals of different energies (π_3^* and π_4^*) (Fig.7.8). Thus, the lowest energy $\pi_2-\pi_3^*$ transition in 1, 3-butadiene occurs at a longer wavelength (217 nm) as compared to the lowest energy $\pi-\pi^*$ transition of 1, 5-hexadiene (185 nm).

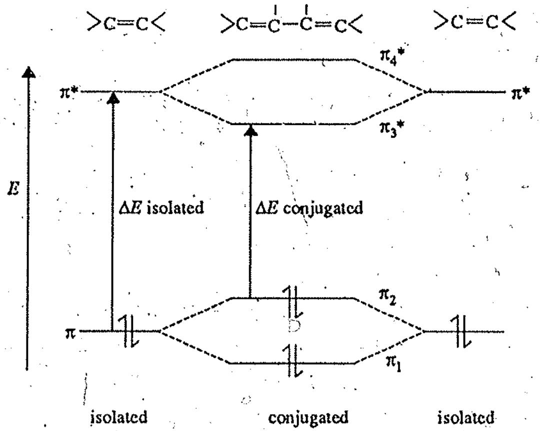


Fig.7.8 : Molecular orbital energy relationship between π-orbitals of isolated and conjugated dienes.

As the extent of conjugation increases, it lowers still further the energy of transition from the highest occupied π orbital to the lowest unoccupied π^* orbital, thereby the λ_{max} value increases.

Table 7.4 gives the wavelengths of some conjugated polyenes that demonstrate this effect.

Table 7.4 :Absorption bands of conjugated polyenes $H(CH=CH)_nH$

n	λ_{max}/nm
2	217
3	268
4	304
5	334
6	364
7	390
8	410

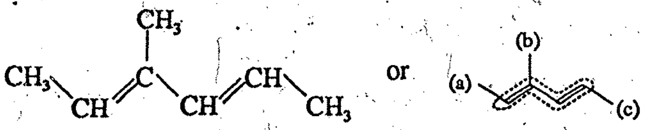
The effects of substituents and geometry on the absorption bands of conjugated dienes are fairly consistent. A set of empirical rules has been formulated by Woodward to predict the absorption of open chain (acyclic) and six-membered ring dienes. These rules have been modified by Feiser and Scott. The rules are summarised in Table 7.5.

Table 7.5 : Woodward Rules for predicting $\pi-\pi^*$ Absorption in Dienes

Value assigned to parent open chain diene			217 nm
Value assigned to parent heteroannular diene			214 nm
Value assigned to parent homoannular diene			253 nm
Increments for			
a)	each alkyl substituent or ring residue		5 nm
b)	each exocyclic double bond		5 nm
c)	each double bond extending conjugation		30 nm
d)	auxochrome	– O(acyl)	0 nm
		– O(alkyl)	6 nm
		– S(alkyl)	30 nm
		– Cl, –Br	5 nm
		– $N(alkyl)_2$	60 nm
		Calculated λ_{max} =	Total

In order to be able to apply these rules you must be able to identify the types of structures referred to in Table 7.5. The basic chromophore unit is 1, 3-butadiene which is considered the parent acyclic (or non-cyclic) diene: $CH_2{=}CH{-}CH{=}CH_2$ or 

If saturated alkyl groups are attached to the diene, then an additional contribution for each group is added, e.g., $\pi-\pi^*$ absorption in 1, 2, 4-trimethylbutadiene(I) is analysed in terms of the rules as follows:



$CH_3{-}CH{=}C(CH_3){-}CH{=}CH{-}CH_3$

(I)

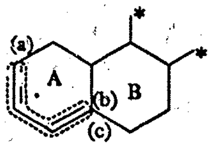
Base value for acyclic diene (I) = 217 nm

For three methyl groups, add 3 × 5 = +15 nm

Predicted λ_{max} for $\pi-\pi^*$ transition = 232 nm

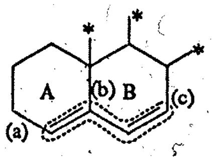
Observed λ_{max} for $\pi-\pi^*$ transition = 231 nm

If the diene system is contained in a single ring, it is termed homoannular, e.g., compound (II). On the other hand if it is spread over two rings, it is said to be heteroannular, e.g., compound (III).



(II)

Homoannular diene



(III)

Heteroannular diene

For Compound (II) we have a base value of = 253 nm

For three ring residues (a), (b) & (c): add 3 × 5 nm = +15 nm

The lower double bond in A is attached to but is outside ring B, i.e., it is exocyclic to ring B, add 5 nm = +5 nm

Predicted λ_{max} value = 273 nm

Observed λ_{max} value = 275 nm

Note that the groups marked with a * do not contribute as they are not directly attached to the diene system.

For compound (III) we have a base value of = 214 nm

For three ring residues (a), (b), (c): add 3 × 5 nm = +15 nm

The double bond in ring A is in exocyclic position to ring B: add 5 nm = +5 nm

Predicted λ_{max} value = 234 nm

Observed λ_{max} value = 235 nm

Thus in all the three cases, the predicted λ_{max} values are in very good agreement with the observed values.

7.7.2 Acetylenic and Benzenoid Chromophore

The electronic spectra of the acetylenic and the benzenoid chromophore are more complex than those of the ethylenic chromophore. These cannot be explained by following the model presented for the ethylenic chromophore. They exhibit three absorption bands each as shown below.

Acetylene: 152 nm (strong), 182 nm (moderate), 220 nm(weak)
Benzene: 184 nm (strong), 204 nm (strong), 254 nm (weak).

In each case, you can see, the lowest energy absorption band is weak, which is characteristic of a forbidden transition, e.g., $n-\pi^*$. But there are no non-bonding electrons in these molecules. Thus all the three transitions arise from $\pi-\pi^*$ transitions. Acetylene and benzene are highly symmetrical molecules having degenerate molecular orbitals. Transitions between degenerate orbitals in these cases give rise to the complexity in their electronic spectra.

7.7.3 Carbonyl Chromophore

You know that the carbonyl group contains, in addition to a pair of σ electrons, a pair of π electrons and two pairs of nonbonding electrons. Saturated aldehydes and ketones exhibit three absorption bands due to $\pi-\pi^*$, $n-\sigma^*$ and $n-\pi^*$ transitions (Fig.7.9). Two bands appear in the far ultraviolet region near 150 nm and 190 nm region and are due to the $\pi-\pi^*$ and $n-\sigma^*$ transitions, respectively. The third band is due to the forbidden $n-\pi^*$ transition which appears as a weak band ($\varepsilon_{max} < 3.0\ m^2\ mol^{-1}$) in the near ultraviolet region in the 270–300 nm region. In formaldehyde the $n-\pi^*$ absorption band is found at 310 nm. In contrast to the situation in alkenes, alkyl substitution moves this absorption to higher energy. Thus in acetaldehyde and acetone this band appears at 290 nm and 279 nm, respectively. Auxochromes such as Cl, OH and NH_2 cause a larger shift in the carbonyl $n-\pi^*$ absorption to shorter wavelengths. The shift in absorption results from a combination of resonance and inductive effects. The resonance effect (π-electron release) of the lone pair of the substituent raises the energy of the π^* orbital, but leaves the nonbonding electrons of the carbonyl group unchanged in energy (Fig. 7.10 (a)). The negative inductive effect (σ-electron withdrawal) lowers the energy of the nonbonding orbital by making the carbon atom of the group more positive (Fig. 7.10 (b)). The overall shift arises from the sum of these two effects.

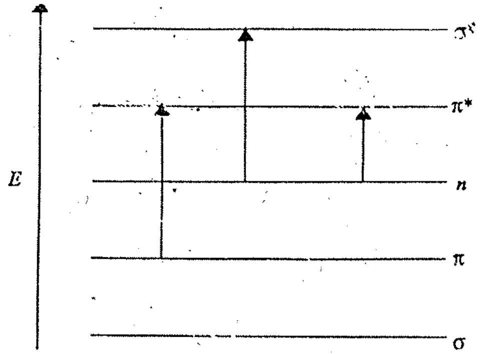


Fig.7.9: Electronic transitions of a carbonyl group in aldehydes and ketones.

When a carbonyl group of a ketone is conjugated with a carbon-carbon double bond ($>C=C<$), the compound is known as an enone or α,β-unsaturated ketone, e.g., methyl vinyl ketone ($CH_3COCH=CH_2$). Conjugation has an effect on the energy of $\pi-\pi^*$ transition similar to that in alkenes. As the energy of the π^* orbital is lowered

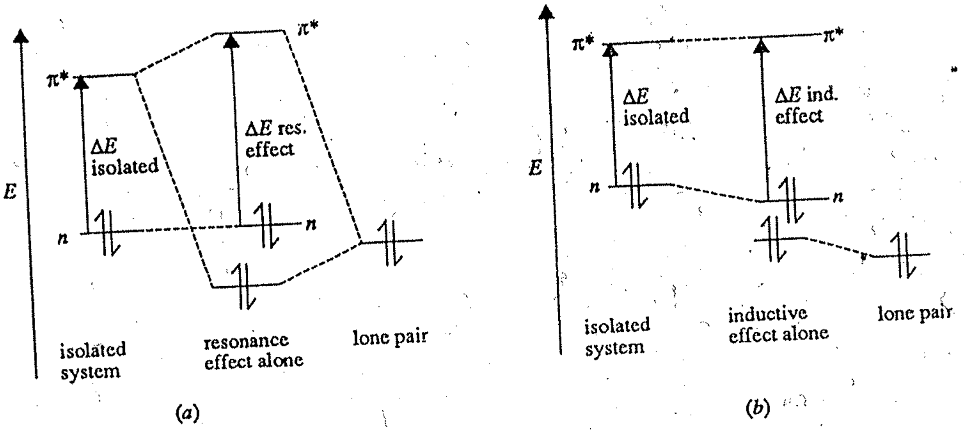


Fig. 7.10: Schematic diagram of a) the resonance effect alone and b) the inductive effect alone of a substituent on the $n-\pi^*$ transition of a carbonyl group.

by conjugation (Fig.7.11), the $\pi-\pi^*$ and $n-\pi^*$ absorptions move to longer wavelengths. Thus for propenal ($CH_2=CH-CHO$), the $\pi-\pi^*$ and $n-\pi^*$ absorptions occur at 202 nm and 336 nm, respectively.

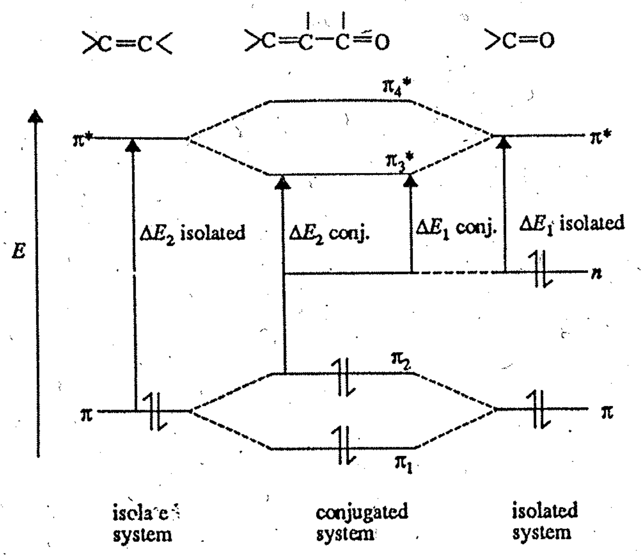
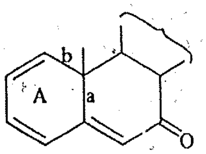


Fig. 7.11 : Orbital energy relationships between isolated and conjugated C=C and C=O groups.

As with the conjugated dienes, there are empirical rules to predict the position of the $\pi-\pi^*$ band in enones. These rules were put forth by Woodward and modified by Feiser and Scott. These rules are summarised in Table 7.6.

We will now apply the rules for α,β unsaturated ketones to predict the absorption maximum in compound IV.



IV

Value for parent α,β-unsaturated ketone	= 215 nm
for β-substituent (marked a); add 12 nm	= + 12 nm
for *w*-substituent (marked b); add 18 nm	= + 18 nm
for two double bonds extending conjugation; add 2 × 30 nm	= + 60 nm
for homoannular diene component; add 39 nm	= + 39 nm
for exocyclic double bond ; add 5nm	= + 5 nm
calculated λ_{max} value	= 349 nm

Three λ_{max} values have been observed for this compound and these are 230 nm, 278 nm and 348 nm. The longest wavelength peak is in excellent agreement with the calculated value.

Table 7.6: Feiser and Scott rules for predicting $\pi-\pi^*$ absorption in α,β – unsaturated ketones (enones) and aldehydes

Value for parent acyclic ketone			215 nm
Value for parent six-membered ring ketone			215 nm
Value for parent five membered ring ketone			202 nm
Value for parent unsaturated aldehyde			207 nm
Increments for			
a) each double bond extending the conjugation			30 nm
b) each alkyl group or ring residue		α	10 nm
		β	12 nm
		γ and higher	18 nm
c) auxochromes	(i) –OH	α	35 nm
		β	30 nm
		δ	50 nm
	(ii) –OAc	α,β,δ	6 nm
	(iii) –OMe	α	35 nm
		β	30 nm
		γ	17 nm
		δ	31 nm
	(iv) –Salk		85 nm
	(v) –Cl	α	15 nm
		β	12 nm
	(vi) –Br	α	25 nm
		β	30 nm
	(vii) NR_2	β	95 nm
d) exocyclic double bond			5 nm
e) homodiene component			39 nm
Calculated λ_{max} value			= Total

The next section describes the effect of solvent on electronic spectra.

7.8 SOLVENT EFFECTS ON ELECTRONIC SPECTRA

As with vibrational spectra, the phase of the sample or the solvent used while measuring the spectrum can make a marked difference on electronic spectra. Broadly, there are two extremes; the vapour phase and non-polar solvents on the one hand, and polar and hydroxylic solvents on the other. Let us consider the effect of solvent on $\pi-\pi^*$ and $n-\pi^*$ transitions one by one.

$\pi-\pi^*$ transitions

When a polar solvent is used, the dipole-dipole interaction with the solvent molecules lowers the energy of the excited state more than that of the ground state (Fig. 7.12). This is due to the fact that excited states are more polar than ground states. The energy difference between the excited and ground states is reduced. This leads to a small red shift of the absorption maximum in polar solvents. Thus the $\pi-\pi^*$ transition shows a red shift of the order of 10–20 nm when the solvent is changed from hexane to ethanol.

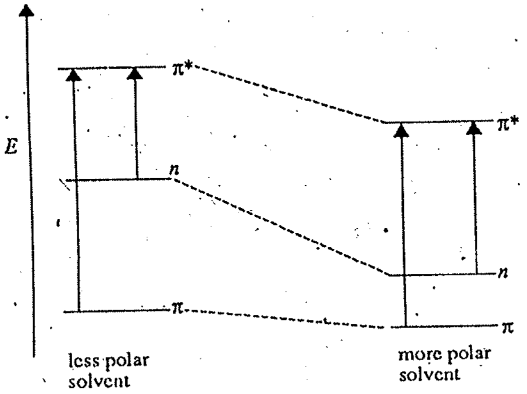


Fig. 7.12 : Solvent effects on $n-\pi^*$ and $\pi-\pi^*$ transitions.

$n - \pi^*$ transitions

Solvent effect for $n - \pi^*$ transitions is opposite to that found for $\pi-\pi^*$ transitions. Polar solvents cause a shift to lower wavelengths (blue shift) relative to non-polar solvents or the vapour phase. The effect is particularly pronounced in hydroxylic solvents. The lone-pair electrons in the non-bonding orbital hydrogen bond or otherwise interact strongly with the polar solvent, leading to a lowering in energy of the non-bonding orbital whereas π^* orbital is affected much less (Fig.7.12). The result is an increase in the transition energy on going from a less polar to a more polar solvent. For example, in hexane solution, acetone shows absorption maximum at 279 nm whereas in aqueous solution, the absorption maximum is at 264.5 nm.

You may now try to answer the following SAQ.

SAQ 5

Fill in the blanks in the following statements using the words given below:

Polar, red, increased, decreased

a) The $\pi-\pi^*$ transition shows a ____________ shift in more polar solvents.

b) The $n-\pi^*$ transition shows a blue shift in more __________ solvents.

c) hyperchromic effect means that the intensity of an absorption is ____________

d) hypsocromic effect means that the intensity of an absorption is ____________

7.9 SUMMARY

In this unit, you have learnt the molecular orbital treatment of diatomic molecules. You have also studied about the ground and excited state configurations and term symbols of diatomics. Selection rules for transition between different energy states have also been described.

We have discussed the Franck-Condon principle and its application to explain variation in intensities of spectra of different kinds of molecules. You have learnt some important definitions of terms used in electronic spectroscopy. We have also discussed the rules to predict absorption maxima in conjugated dienes, trienes and α,β-unsaturated aldehydes and ketones. We now summarise that we have learnt in this unit.

- When we write the molecular term symbols for homodiatomics, we must find out the effects of symmetry operations such as reflection and inversion on these molecules.

- Spin multiplicity of the excited and ground states must be the same for a transition in a diatomic molecule.
- The parity must change during a spectroscopic transition in a diatomic molecule with centre of symmetry.
- The $\pi-\pi^*$ transition is strong in carbonyl compounds since it is electronically allowed whereas the $n-\pi^*$ transition is weak since it is magnetically allowed.
- The rules of Woodward modified by Feiser and Scott help us in predicting the absorption maxima for conjugated dienes, trienes and α,β-unsaturated aldehydes and ketones.
- The $\pi-\pi^*$ transition shows a red shift in more polar solvents. The $n-\pi^*$ transition shows a blue shift for a solvent which is more polar.

7.10 TERMINAL QUESTIONS

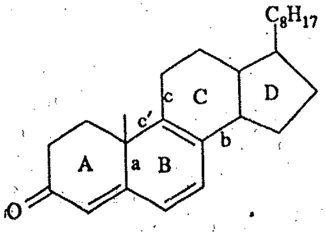
1) Obtain the molecular term symbols for the following three excited states of hydrogen molecule:

   $(\sigma_g 1s)^1 (\sigma_g 2s)^1; (\sigma_g 1s)^1 (\sigma_g 2p)^1; (\sigma_g 1s)^1 (\pi_u 2p)^1$

2) In the ultraviolet absorption spectrum of oxygen, continuum absorption begins at 56876 cm^{-1}. The excitation energy of oxygen atom is 15868 cm^{-1}. Find the dissociation energy of the O_2 molecule in the ground state in kcal/mole.

3) The dissociation energy for chlorine molecule in the ground state is 239.42 kilojoule per mole. If the excitation energy for chlorine is 881 cm^{-1}, compute the continuum vibrational wave number for chlorine molecule.

4) Calculate the λ_{max} for the unsaturated ketone (V) using Fieser and Scott rules.



(V)

7.11 ANSWERS

Self Assessment Questions

1) a) F. The correct statement is "if the molecular orbital for a homonuclear diatomic molecule has a subscript *g*, it indicates that the orbital does not change sign on inversion through centre of symmetry.

   b) T.

   c) F. The correct statement is "for LiH molecule, the spectroscopic term symbol will not have a subscript *g* or *u* on the right side because it a heteronuclear molecule which has no centre of symmetry.

   d) F. The correct statement is "the spectroscopic term symbol for H_2 in the ground state is $^1\Sigma_g^+$.

   e) T

   f) T

2) a) same b) singlets c) parity d) forbidden
   e) multiplicity

3) a) unaltered b) dissociation c) continuum

4) a) red b) polar c) increased d) decreased e) increased

Terminal Questions

1. a) Since, both the electrons are σ electrons, $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$. It gives rise to a Σ state. The net spin S can have two values 0 and 1. The corresponding multiplicities $(2S+1)$ will be 1 (singlet) and 3 (triplet). Since, both constituent obritals are of g parity, the overall parity will be $g \times g = g$. Under reflection, the orbitals remain unchanged, hence reflection symmetry will be $(+) \times (+) = +$. The term symbols will be ${}^1\Sigma_g^+$ and ${}^3\Sigma_g^+$.

   b) Since, both the electrons are σ, $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$, we have a Σ state. The net spin S can be 0 or 1, the multiplicity will be 1 or 3. The overall parity will be $g \times g = g$. Under reflection, both the orbitals remain unchanged, hence the reflection symmetry will be $(+) \times (+) = +$. The term symbols will be ${}^1\Sigma_g^+$ and ${}^3\Sigma_g^+$.

   c) Since one electron is in a π orbital, the value of $\Lambda = \lambda_1 + \lambda_2 = 0 \pm 1 = \pm 1$. The state will be Π. Again, since one electron is in a σ_g orbital and the other in a π_u orbital, the overall parity is $g \times u = u$. The net spin S can be 0 or 1, the multiplicity will be 1 or 3. The term symbol will be ${}^1\Pi_u$ or ${}^3\Pi_u$.

2. $D_0 = hc\,(w_m - v_e)$ erg per photon

$$= 6.6256 \times 10^{-27} \times 2.998 \times 10^{10} \times (56876 - 15868)$$

$$= 8.14564 \times 10^{-12} \text{ erg per photon}$$

$$= 8.14564 \times 10^{-12} \times 6.023 \times 10^{23}/4.2 \times 10^{10} \text{ kcal mole}$$

$$= 11.681 \times 10 = 116.81 \text{ kcal/mole}$$

The dissociation energy is 116.81 kcal/mol

3. $D_0 = hcw_m - E_{ex}$

D_0/per photon $= (D_0/6.023 \times 10^{23}) \times 10^{10}$ erg

$$= 239.42 \times 10^{10}/6.023 \times 10^{23}$$

$$= 39.75 \times 10^{-13} \text{ erg}$$

$$E_{ex} = hcw_m$$

$$= 6.6256 \times 10^{-27} \times 2.998 \times 10^{10} \times 881 \text{ erg}$$

$$= 1.7499 \times 10^{-13} \text{ erg}$$

$$w_m = (D_0 + E_{ex})/hc$$

$$= (39.75 \times 10^{-13} + 1.7499 \times 10^{-13})/(6.6256 \times 10^{-27} \times 2.998 \times 10^{10})$$

$$= (39.75 + 1.7499) \times 10^{-13}/(6.6256 \times 2.998 \times 10^{-17})$$

$$= (41.4999 \times 10^{4})/(6.6256 \times 2.998)$$

$$= 20892.4\ \text{cm}^{-1}$$

4. value for parent six membered ring ketone = 215 nm
for two double bonds extending conjugation, add (2 × 30) nm = + 60 nm
for ring residue ß (marked a), add 1 × 12 nm = + 12 nm
for ring residue (marked b), add 1 ×18 nm = + 18 nm
for ring residues (marked c and c′), add 2 × 18 nm = + 36 nm
for one exocyclic double bond in ring marked A, add 1 × 5 nm = + 5 nm
for homodiene component, add 1 × 39 nm = + 39 nm
Calculated λ_{max} = 385 nm

UNIT 8 ELECTRONIC SPECTRA – II

Structure

8.1 INTRODUCTION

In Unit 7, we have developed the basic theory of electronic energy levels of many simple molecules in their ground and excited state configurations. We also discussed the basic selection rules which permit us to observe electronic spectra when these molecules undergo energy transitions from the ground to the excited state. We have also seen that a quantitative understanding of the colours of many chemical substances, and even specific molecular groupings within substances, may be achieved by studying their electronic absorption spectra.

Indeed, one of the most readily perceived properties of chemical substances is their colour. For example, the wealth of colours displayed by a variety of 'everyday' crystalline inorganic materials such as copper sulphate and potassium permanganate has fascinated almost everyone of us right from our school years.

In this unit, we shall first take up the very interesting subject of the colour of transition metal complexes and the interpretation of their electronic absorption spectra in terms of what are called '*d–d*' and 'charge transfer' electronic transitions. We shall then consider the more general question of how an excited electronic state gets 'deactivated', i.e., returns to its ground state by losing its excess energy through various mechanisms.

Objectives

After studying this unit, you should be able to:

- describe the elements of crystal field theory and explain why, and how, the *d*-orbitals of transition metal ions show energy splittings,
- discuss the electronic spectra of transition metal complexes,
- explain charge-transfer spectra,
- use the Jablonski diagram to explain the various processes by which the excited electronic state gets deactivated, and
- to see how fluorescence and phosphorescence become two very important examples of emission spectroscopy in many natural chemical systems.

8.2 MODELS FOR METAL-LIGAND INTERACTIONS

You have learnt earlier (in Block 4) of the CHE-02 course that metal ions of the first transition series, from Ti to Cu in the Periodic table, are able to form a wide range of compounds. In these compounds the outermost 'valence' shell consisting of the five 3*d* orbitals is only partially occupied by electrons. In the 'free' or 'unbound' state of the transition metal (M), these five *d*-orbitals have the same energy (i.e., they are 'degenerate'); this five-fold degeneracy is, however, usually removed by the effects of ligands (L), which are molecules or ions linked to the metal, M. Very simply, transitions of electrons between the component *d*-orbitals of this partially filled shell cause the beautiful colours which are so characteristic of these compounds. We shall see that an understanding of not only the colours of transition metal complexes, but also the geometric arrangement of the ligands around M, can come from the electronic absorption spectra.

The most common ligands (L) are monoatomic or polyatomic negative ions (Cl^-, CN^-, etc.), and neutral polar molecules usually having one or more lone pairs of electrons (H_2O, NH_3, CO, etc.).

In a large number of transition metal complexes the ligands are found to be arranged around M in one of several definite symmetries: octahedral, tetrahedral, tetragonal, or square planar. Further, usually the negative ends of ionic ligands or the lone electron pairs of polar molecular ligands are attracted towards the positively charged metal ion. There are two models which are used to discuss the metal-ligand (L–M) interaction. In the first of these, known as the Crystal Field Theory, which was introduced by Bethe and Van Vleck, we simply consider the interaction as an electrostatic repulsion between the negative charge of the ligands and the electrons of the central metal; that is, the ligands are considered as 'point' electric charges. This model assumes that the bonds between metal and the surrounding ligands are completely ionic.

You may now wonder whether such a purely electrostatic, or 'ionic', model is always realistic. Indeed, it is not, because our every-day chemistry shows us that in some complexes the electrons which we have assumed to be entirely in the atomic *d*-orbitals of metal may actually 'spread out' and spend time in orbitals belonging to ligand, and vice-versa, thus giving considerable covalency to the M – L bonds which are now made up of M – L 'molecular orbitals'. Accordingly, in the second theory (called the Molecular Orbital Theory), the lone pair orbitals of ligand are combined with *s, p* and *d* orbitals of M to give 'bonding' and 'anti-bonding' orbitals. The electrons from the ligands then occupy the bonding orbitals, giving the complex its stability, and the remaining electrons partially fill the anti-bonding orbitals. You will notice, in any case, that both these theories explain the splitting of *d*-orbital degeneracy in different ways, but that they lead to the same general pattern of energy levels. A blend of these two theories is usually termed as Ligand Field Theory.

8.3 BASICS OF CRYSTAL FIELD THEORY

Let us first consider the crystal field approach to octahedral coordination, in which the M–L interaction is well approximated by placing six equal negative charges at the same distance away from the central M ion along the ± *x*, ± *y* and ± *z* axes. Fig. 8.1 indicates that the lobes of the d_{xy}, d_{xz} and d_{yz} orbitals all point between these charges, whereas the d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes which point directly towards the charges. An electron in one of the first group of orbitals will therefore have a lower energy than an electron in one of the latter group of orbitals because of the smaller electrostatic repulsion.

Thus, in the presence of an octahedral crystal field, the five 3*d* orbitals (see Fig. 8.2) split into two groups separated by an energy difference Δ_o; the upper group of two is doubly degenerate (and labelled e_g) and the lower group of three is triply degenerate (and labelled t_{2g}). The energy difference (Δ_o) between the two separated sets of orbitals is of great interest, because it is this Δ_o which is identified with the *d–d* electronic transition of the octahedral complex. In some textbooks, you may find this energy separation written in terms of the notation '*Dq*' (or 10 *Dq*, for convenience). What does this mean? Well, it turns out that the *d–d* energy difference depends on the product of the magnitude of the charge on the ligands, *q*, and the polarizability of the central metal ion, denoted by *D*. Since in practice we will be unable to separate *D* and *q*, we treat the product *Dq* as a single adjustable parameter. And all confusion will vanish if you remember that, in our notation, $\Delta_o = 10\,Dq$.

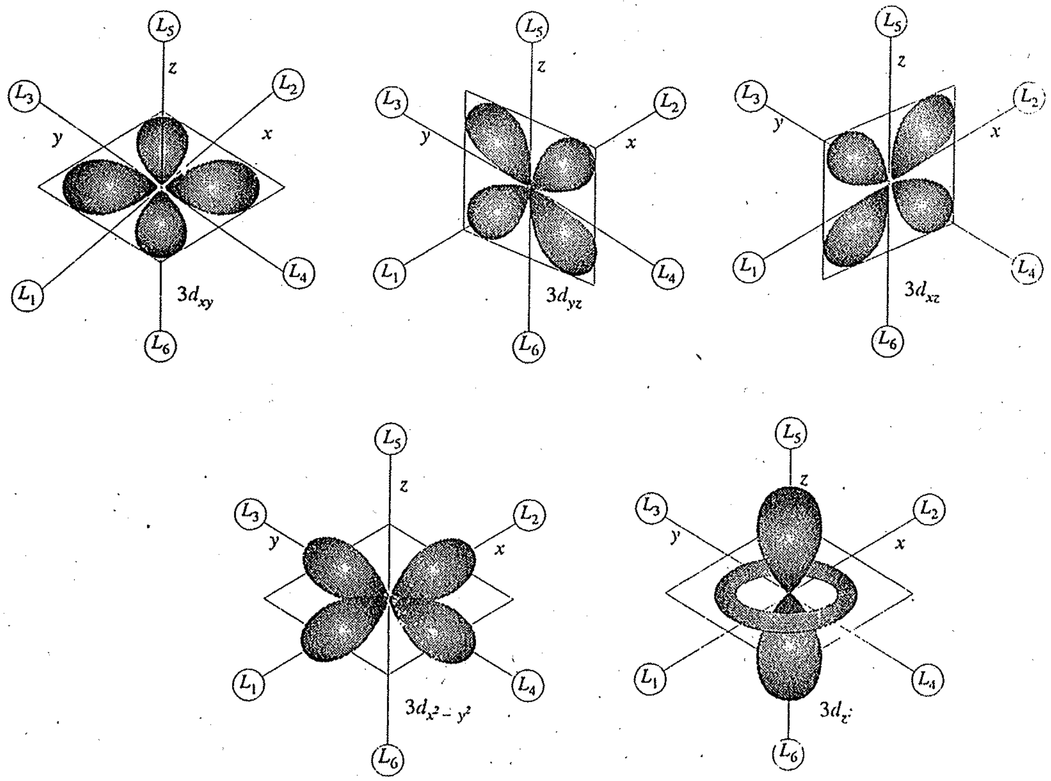


Fig. 8.1 : The orientations of the five 3*d* orbitals when a transition metal ion is surrounded octahedrally by six ligands.

Energy relationships in terms of Δ_o are illustrated in Fig. 8.2, from which it can be seen that the energy of the e_g orbitals increases by an amount 0.6 Δ_o, and that of the t_{2g} orbitals decreases by 0.4Δ_o. Thus, if the 3*d* electrons in an ion M^{2+} of the first transition series are distributed among the available orbitals in such a way as to

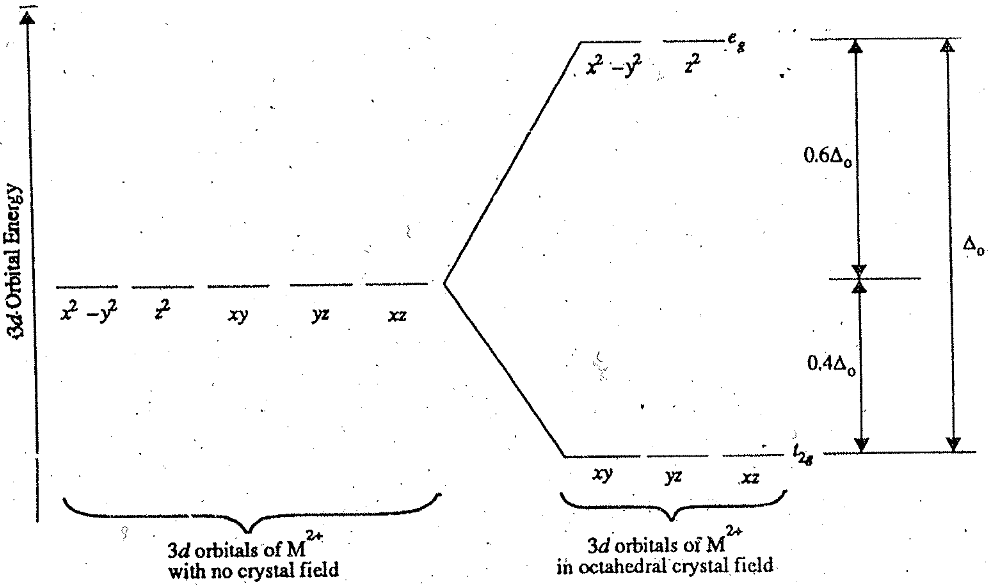


Fig. 8.2 : Effect of an octahedral crystal field on the energies of the five 3d orbitals

maintain the maximum number of electrons in the unpaired ('high spin') condition, a net lowering of the electronic energy will result in all cases except Ca^{2+}, Mn^{2+} and Zn^{2+} as shown in Table 8.1 below.

Table 8.1 : Crystal Field Stabilisation Energies of Ca^{2+} to Zn^{2+} Ions

	Ca^{2+}	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Number of 3*d* electrons	0	1	2	3	4	5	6	7	8	9	10
Distribution for high spin configuration: e_g	–	–	–	–	1	2	2	2	2	3	4
t_{2g}	0	1	2	3	3	3	4	5	6	6	6
Lowering of energy: Δ_o	0	0.4	0.8	1.2	0.6	0	0.4	0.8	1.2	0.6	0

According to this simple electrostatic interpretation, all the M^{2+} ions (with the exception of Ca^{2+}, Mn^{2+} and Zn^{2+}) will, when subjected to an octahedral crystal field, be stabilized by various multiples of Δ_o and this actual energy of stabilisation is named **'crystal field stabilisation energy' (CFSE)**.

At this point you will be naturally curious to know how the *d*-orbital degeneracy will be split in the other most frequently met M–L coordination geometries, namely, the tetragonal, square planar, and tetrahedral geometries. Let us consider them now. Supposing that you pull the two ligands on the ± *z* axis of the octahedron away from the central metal, so that they are more remote from metal than the other four ligands in the *xy* plane, then we achieve a tetragonal arrangement of ligands around metal. The resulting *d*-orbital splitting is shown in Fig. 8.3. The two sets of degenerate orbitals that characterise octahedral splitting are further split; the d_{z^2} now sinks to a lower energy level than $d_{x^2-y^2}$, and the d_{xz}, d_{yz} pair becomes lower than d_{xy} because electrostatic repulsion along ± *z*-axis is now reduced. If the two ligands on the ± *z* axis are then moved away to infinity (the extreme case!), then we have the square planar complex with the splitting shown in Fig. 8.3.

Finally, in the most interesting case of the tetrahedral complexes, the *d*-orbital splitting is actually the reverse of the splitting in the octahedral case! You will visualise this

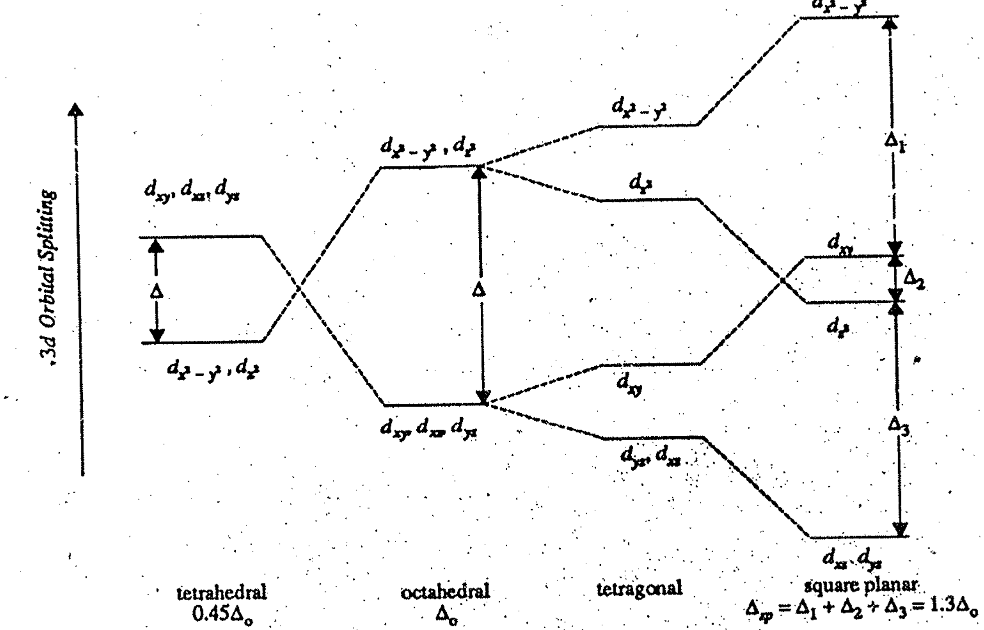


Fig. 8.3 : Crystal field splitting of d-orbitals of metal ion in complexes having different geometries.

more readily by inscribing the tetrahedron in a cube, Fig. 8.4 (a). The four ligands making up the tetrahedron appear as shaded circles at the alternate cube corners. The $d_{x^2-y^2}$ and d_{z^2} orbitals are now degenerate, and point towards the centres of cube faces, and the d_{xy}, d_{yz}, d_{xz} orbitals are degenerate and point at the midpoints of the cube edges.

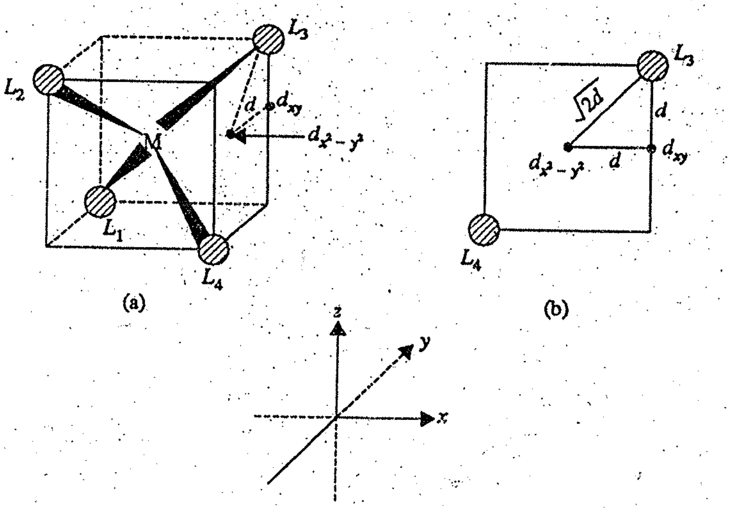


Fig. 8.4: The tetrahedral complex showing that the ligands repel the $d_{x^2-y^2}$ orbitals less than the d_{xy}, d_{yz} and d_{xz} orbitals.

In Fig. 8.4 (b) we examine one face of the cube, on which ligands L_3 and L_4 are located. We see that $d_{x^2-y^2}$ falls at the centre of this face. d_{xy} at the centre of the edge, and L_3 and L_4 at opposite corners. If d is half the edge-length, then L_3 will be at distance d from one lobe of d_{xz} but at distance ($\sqrt{2}$) d from one lobe of $d_{x^2-y^2}$. Consequently, repulsion will be greater at those orbitals that are closer to the ligands, namely, the d_{xy}, d_{yz}, d_{xz} set, than at the other set (d_{z^2} and $d_{x^2-y^2}$). Therefore, for the tetrahedral crystal field, the triply degenerate set (labelled t_2) is higher in energy than the doubly degenerate set (labelled e), just the reverse of the situation for the two sets in the octahedral crystal field case. By the way, you should not fail to note that, in a tetrahedron, there is no centre of symmetry about which the figure can be inverted; therefore, we omit the g-subscript from the t_2 and e symmetry labels. Thus, for the same electron configuration d^n, the energy relationships between octahedral and tetrahedral fields are exactly reversed. This fact greatly facilitates the problems of interpreting electronic spectra.

Analysis of a large number of experimental data for transition metal complexes of various geometries shows the *d–d* splittings to be related as given below:

Square planar	>	Octahedral	>	Tetrahedral
$(1.3\ \Delta_o)$		(Δ_o)		$(0.45\ \Delta_o)$

We now take one very simple, but very typical and 'colourful', example: that of the *d–d* electronic band in a complex with a single *d* electron. An aqueous solution of $Ti_2(SO_4)_3$ is red-purple in colour, and has a single broad absorption maximum in the visible spectral region, around 20,400 cm^{-1} (Fig. 8.5). However, this is a band of rather weak intensity, ($\varepsilon = 0.6\ m^2\ mol^{-1}$)and this is based on an important 'selection rule' which we shall discuss presently. Now our central metal ion is Ti^{3+}, but how is it coordinated, and to what ligands? Note that this is an aqueous solution, having plenty of water molecules to act as ligands! Actually, this electronic absorption band is ascribed to the octahedral complex $[Ti\ (H_2O)_6]^{3+}$, and may be understood as the excitation of the single *d*-electron from the t_{2g} level to the e_g level. This transition can be represented as follows : $(t_{2g})^1\ (e_g)^0 \longrightarrow (t_{2g})^0\ (e_g)^1$

This is what we call a *d–d* transition, or *d–d* absorption band, for which Δ_o = 20,400 cm^{-1}. The spectra of most complexes of the first transition series of elements can be explained with similar orders of magnitude for Δ.

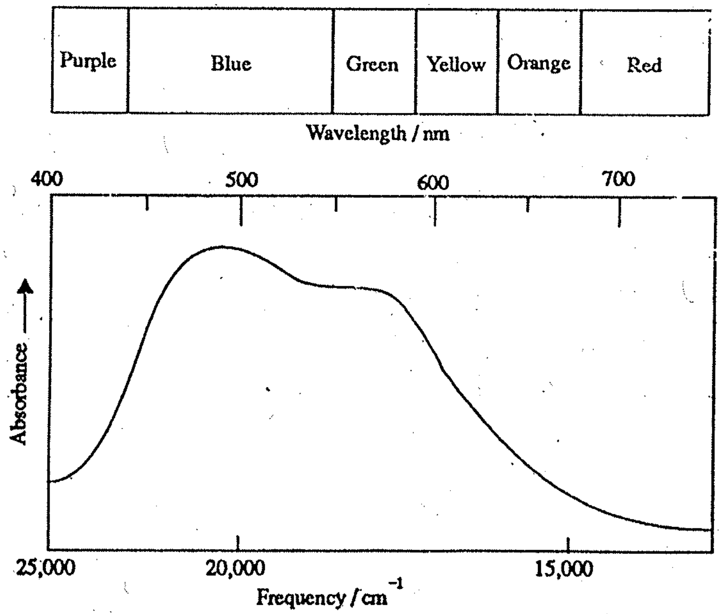


Fig. 8.5 : Visible absorption spectrum of $[Ti(H_2O)_6]^{3+}$.

The spectrum of $[Ti(H_2O)_6]^{3+}$ can be interpreted by means of the colour-scale given in Fig. 8.5. You can see that the complex absorbs strongly in the blue-green region of the visible region. Therefore, it appears purple-red in colour.

We shall examine just one more interesting result of a *d–d* transition from experimental absorption spectra, and by using Table 8.1 we shall also illustrate a sample calculation of crystal field stabilisation energy (CFSE). Our example is solid $NiCl_2$ crystal, in which the Ni^{2+} ion site is surrounded by six Cl^- ligands in an octahedral arrangement. The crystal gives an electronic absorption spectrum peaking at 9270 cm^{-1}. Since the wavenumber corresponding to an energy of one electron volt is 8066 cm^{-1}, and also since 1 eV = 96.5 kJ mol^{-1}, the absorption maximum of 9270 cm^{-1} indicates a crystal field splitting (Δ_o) of (9270/8066) × 96.5 kJ mol^{-1}. The crystal field stabilisation energy for the d^8 Ni^{2+} ion in an octahedral field is (see Table 8.1) 1.2 Δ_o.

Hence,

$$\text{CFSE} = 1.2\,\Delta_o = 1.2 \times \frac{9270}{8066} \times 96.5 = 133\ \text{kJ mol}^{-1}$$

Thus the splitting of $3d$ orbitals leads to a crystal field stabilisation energy of 133 kJ mol^{-1}.

Before we proceed further, you may like to attempt the following SAQ to test your understanding of the concepts developed so far.

SAQ 1

a) State whether the following statements are true or false. Write T or F in the boxes provided.

  i) five-fold degeneracy of d-orbitals is removed by effects of ligands attached to the metal. ☐

  ii) an electron in d_{xy}, d_{yz} or d_{xz} orbitals is lower in energy than that in d_{z^2} or $d_{x^2-y^2}$ orbitals in an octahedral complex. ☐

  iii) an electron in d_{z^2} or $d_{x^2-y^2}$ orbital is higher in energy than that in d_{xy}, d_{yz} or d_{xz} orbital in a tetrahedral complex. ☐

  iv) energy of the e_g orbital decreases by 0.4 Δ_o and that of the t_{2g} orbitals increases by 0.6 Δ_o in an octahedral complex. ☐

b) Fill in the blanks in the following statements using the words given below: centre of symmetry, polarizability, octahedral, point, reverse

  i) The d-orbital splitting for a tetrahedral complex is actually the ________ of the splitting in an octahedral case.

  ii) In a tetrahedron there is no ________________ about which the figure can be inverted.

  iii) The electronic absorption spectrum of $Ti_2(SO_4)_3$ is ascribed to the __________ complex, $[Ti(H_2O)_6]^{3+}$

  iv) The d–d energy difference depends on the product of charge and ___________ of the central metal ion.

  v) In the crystal field theory, ligands are considered as _________ electric charges.

8.4 'FORBIDDEN' VS 'ALLOWED' *d-d* ABSORPTIONS: THE ORIGIN OF 'WEAK' AND 'STRONG' *d-d* BANDS

You will recall from Unit 7 that, by the operation of the Laporte selection rule, a d–d electronic transition is highly forbidden in a free ion; in the case of transition metal complexes also, when the crystal field around the M has octahedral symmetry, the d–d electronic transition is forbidden by the 'parity' selection rule 'even $\nleftrightarrow$ even', or 'gerade $\nleftrightarrow$ gerade', abbreviated as '$g \nleftrightarrow g$'. However, in the real world of chemistry, we sometimes find that rules, like the egg-shell, are "made only to be broken"! Therefore, instead of using the 'go', 'no-go' language of 'allowed' and 'forbidden', we, sometimes find it convenient to speak of 'strongly allowed' and 'weakly allowed' transitions. For example, the $g \nleftrightarrow g$ forbiddenness can be broken the moment the centre of symmetry of our M–L octahedron becomes destroyed by a vibrational displacement of 'odd', or 'u' (ungerade) symmetry. The mechanism is that, in the **displaced arrangement** caused by this vibration, the d orbitals of the central M ion can mix with p (or f) orbitals, and also that the ligand orbitals may contribute unequally to the distorted *d* orbitals. Thus, the totally not-allowed *d-d* transition becomes allowed, though weekly. The rather small value of the absorbance about which we remarked earlier in the case of $[Ti(H_2O)_6]^{3+}$ is in accord with such a vibrationally induced, and therefore weakly allowed, electronic transition. Very suitably, the term 'vibronic transition' has been coined in the literature to describe this band.

If our argument above is correct regarding this so-called 'forbiddenness' of the $t_{2g} \rightarrow e_g$ transition, then in complexes without a centre of symmetry, such as the **tetrahedral** complexes, this mixing of the *d*-orbital with other orbitals can occur even for the equilibrium (i.e., non-vibrating) configuration, giving strongly 'symmetry-allowed' transitions with much larger absorbance values. This is indeed what happens for tetrahedral complexes such as the alkoxides of Cr^{4+}, $Cr(OR)_4$ (which have intense *d–d* bands centred at 15,000 cm^{-1}), proving that our crystal field theory does go far in predicting the behaviour of electronic absorption in transition metal complexes.

8.5 CHARGE-TRANSFER (C.T.) SPECTRA : GENERAL CONSIDERATIONS

The various *d–d* transitions so far discussed are, however, still comparatively weaker in relation to another possible kind of electronic transition called 'charge transfer transition'. Let us illustrate "charge transfer" by choosing a well-known, and again very colourful, example from organic chemistry. When chloroform solutions of chloranil (pale yellow) and aniline (colourless) are mixed, the resulting solution becomes deep purple, and its spectrum shows an absorption which is not possessed by any one of the components of the mixture when in the pure state. At the same time, there is no evidence of any appreciable reaction taking place. This is one example of a Charge-Transfer spectrum, where a photon (or light quantum) is absorbed by a weak complex between an electron 'donor' molecule (D) and an electron acceptor molecule (A) with the consequent shift of electronic charge from D to A. Charge transfer bands are usually broad, structureless bands since the binding energies of the complexes are sufficiently small so that many different configurations may exist in equilibrium with one another.

In the case of inorganic compounds, while colour is generally associated with the presence of a partially filled *d*-shell, many compounds with d^0 or d^{10} configurations are also intensely coloured. Mercury(II) iodide (brick red, d^{10}), the familiar permanganate(VII) ion (intense purple, d^0) and bismuth(III) iodide (red-orange, $d^{10}s^2$) are some examples. In such cases the colour arises, at least in part, as a consequence of the absorption of light which occurs when an electron from a ligand orbital is transferred to a metal orbital and vice versa. Such charge transfer (or electron transfer) processes are termed '**L – to – M**' and '**M – to – L** (inverse)' charge transfer, respectively.

Charge transfer processes are commonly of higher quantum energy than *d-d* transitions and generally lie in the ultraviolet or far ultraviolet spectral region. However, if the metal is easily oxidisable and the ligand readily reducible, or vice-versa, then charge transfer transitions may occur in the visible region. Often, these spectra are very intense and mask the *d–d* transitions. Indeed, the *d-d* spectra of transition metal iodide complexes are notoriously difficult to obtain for this reason, the iodide ion being so readily oxidisable. In the next section we shall explore the effects of 'Metal-Ligand' charge-transfer phenomena a little further, after first 'polishing up' the 'crystal field' model to represent 'ligand field' effects more faithfully.

8.6 EFFECTS OF THE LIGANDS AND 'POLISHING UP' THE CRYSTAL FIELD MODEL : THE LANGUAGE OF LIGAND FIELDS

Our earlier discussion of the simple crystal field theory may now be modified by including three important kinds of 'chemical bonding' involving M and L: (i) L→M sigma-bonding interactions, (ii) L→M pi-bonding interactions, and (iii) M→L "back bonding" (π^*) interactions. For example, in ML_6 octahedral complexes, a strong L→M sigma interaction raises the e_g level, increasing the Δ_o value. On the other hand, the L→M pi-interaction raises the t_{2g} and hence decreases Δ_o. Finally, the M→L (π^*) interaction lowers t_{2g} again, increasing Δ_o. The information contained here represents the general situation for the *d*-orbital splitting for all common geometries which, as we have shown earlier, can be expressed as fractions of Δ_o.

The manner in which various kinds of L and M interact will therefore affect Δ, and hence the stabilisation energies which in the present model we call **Ligand Field Stabilisation Energies** (LFSE, as opposed to the earlier CFSE). For example, good π-electron 'acceptor' ligands such as CN^- and CO favour strong M→L (back-bonding) interaction. As a result, these ligands cause large splittings, in the energy range of 30,000 cm^{-1} or 3.72 eV. In contrast, ligands with a lone-pair of electrons, which we may call 'donors' (to the π-orbitals of metal), cause small splitting about 10,000 cm^{-1} or 1.24 eV. The Br^- and I^- ions are good examples of these. In the intermediate range of splittings, we place ligands such as NH_3 and H_2O which have no π-bonding capacity. At first glance, we may perhaps be surprised that the halogen anions, I^- and Br^-, with their negative charge should cause smaller splittings than a neutral ligand like NH_3. At least our simple electrostatic or 'crystal field' model would tell us that this result is unexpected. But here is where we begin to appreciate that covalence effects are very important. The lone pair of NH_3 is in a well-directed sp^3 hybrid orbital and interacts well with the empty metal (hybrid) orbital. On the other hand, the filled *p*-orbitals on the halide ligand interact quite strongly with the empty *d*-orbitals of M; that is electric charge is transferred from ligand to metal. These L→M interactions therefore, give rise to charge transfer transitions. This transfer lowers the positive charge on the metal and reduces the *D* term in '10 *Dq*'. For the same metal, the greater the reducing power of the ligand, (e.g., $I^- > Br^- > Cl^-$), the lower is the energy at which the charge-transfer band occurs. Similarly, for the same L, the greater the oxidising power of the metal ion, the lower the energy of the charge-transfer band. For transition metal ions carrying the same charge, the value of Δ would decrease as ordered in the series,

$$CO \approx CN^- > NO_2 > \text{'en'} > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-,$$

where the above ions and neutral molecules represent the ligands which may surround the transition metal ion. The above series is known as the **spectrochemical series.**

The electronic spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$, Fig. 8.6, demonstrate, in a simple way, the application of the spectrochemical series. An aqueous solution of $NiSO_4$ is pale green, but when ethylenediamine (en) is added, the colour turns deep blue. The $[Ni(H_2O)_6]^{2+}$ has a minimum in its absorption (or a maximum in its transmittance) where green absorbs, but in all other regions of the visible spectrum it has some absorption, and hence the green colour. On the other hand, $[Ni(en)_3]^{2+}$ absorbs green light strongly and transmits only blue-purple and a little red; hence its deep blue colour.

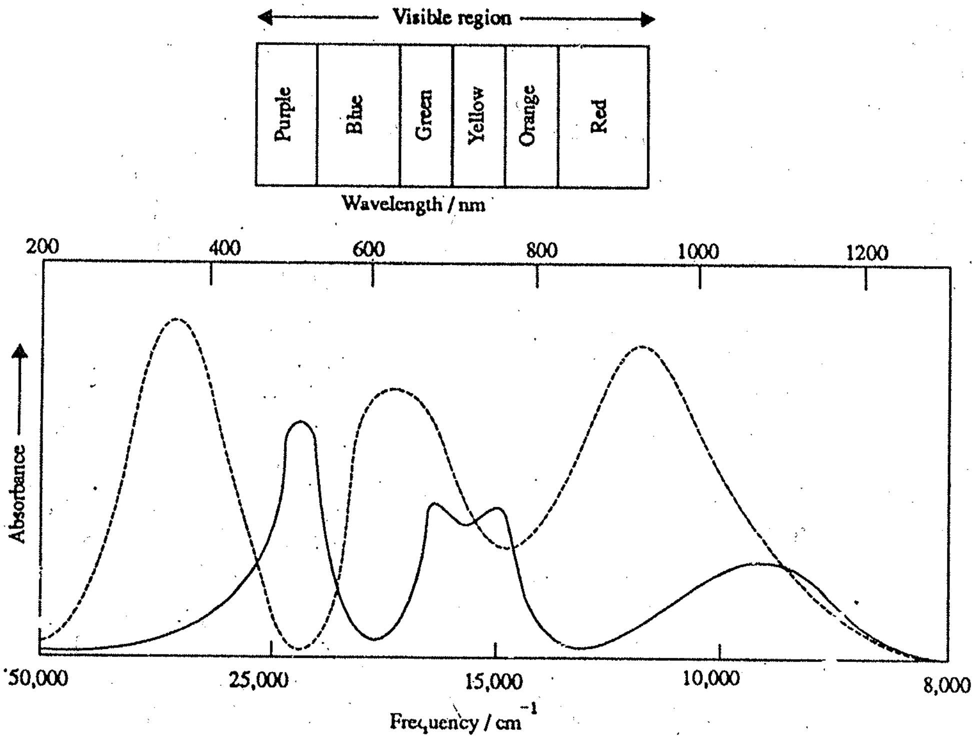


Fig. 8.6 : Electronic absorption spectra of $[Ni(H_2O)_6]^{2+}$ (solid line) and $[Ni(en)_3]^{2+}$ (broken line).

SAQ 2

Although the spectra of $[PtBr_4]^{2-}$ and $[PtCl_4]^{2-}$ are very similar, L→M band in the first complex is at 36,000 cm^{-1}, while in the chloride complex it is at 44,000 cm^{-1}. Suggest a reasonable explanation for this difference.

8.7 DE-EXCITATION PROCESSES IN ELECTRONIC SPECTROSCOPY: THE JABLONSKI DIAGRAMS

In our discussion of electronic absorption spectra so far, we have devoted our attention to the absorption of light energy by a molecule in its ground state. The molecule thus becomes 'excited'. We would now be curious to know what happens to this excess energy in the excited molecule which has absorbed a quantum of light. Let us calculate the time required for a typical absorption process. A light photon travels at a velocity of 3×10^8 m sec^{-1}, or 3×10^{18} Å sec^{-1}. Now, the diameter of a typical molecule with which the light photon interacts is ~ 3 Å. Therefore, the photon will remain 'at' the molecule for $3/(3 \times 10^{18}) = 10^{-18}$ sec. Accordingly, the absorption process has to occur in about 10^{-18} sec or less. In this very small time interval, the nuclei of molecules undergo virtually no motion, and this fact forms the basis of the Franck-Condon principle (Unit 7), according to which most molecules, upon electronic excitation, enter a vibrationally excited level of the excited state.

Virtually all organic molecules (which have filled molecular orbitals), except free radicals, have singlet ground state; these are usually denoted by S_0. We then refer to electronically excited singlets as S_1, S_2, etc., in the order of increasing energies (these together with S_0, are called the singlet manifold) and similarly to a possible manifold of triplets as T_1, T_2, etc. Excitation normally leads to singlet excited states rather than to triplet states because the $S_0 \rightarrow T_1$ transition involves a change in (electronic) spin multiplicity and is **highly forbidden** (Unit 7).

Excitation takes the ground-state molecule from the lowest vibrational level, in which it usually exists, to an excited singlet state. There are several possible excited singlet states S_1, S_2, etc. The various processes by which a molecule in the excited singlet states can become de-excited are illustrated collectively by the **Jablonski diagrams**, e.g. Fig. 8.7. In these diagrams, solid lines represent radiative processes, and wavy lines non-radiative processes. We shall now briefly discuss a number of the possible events which lead to de-excitation or dissipation of the excess energy. The events will be discussed in the order of the increasing time which they require, the first being the fastest.

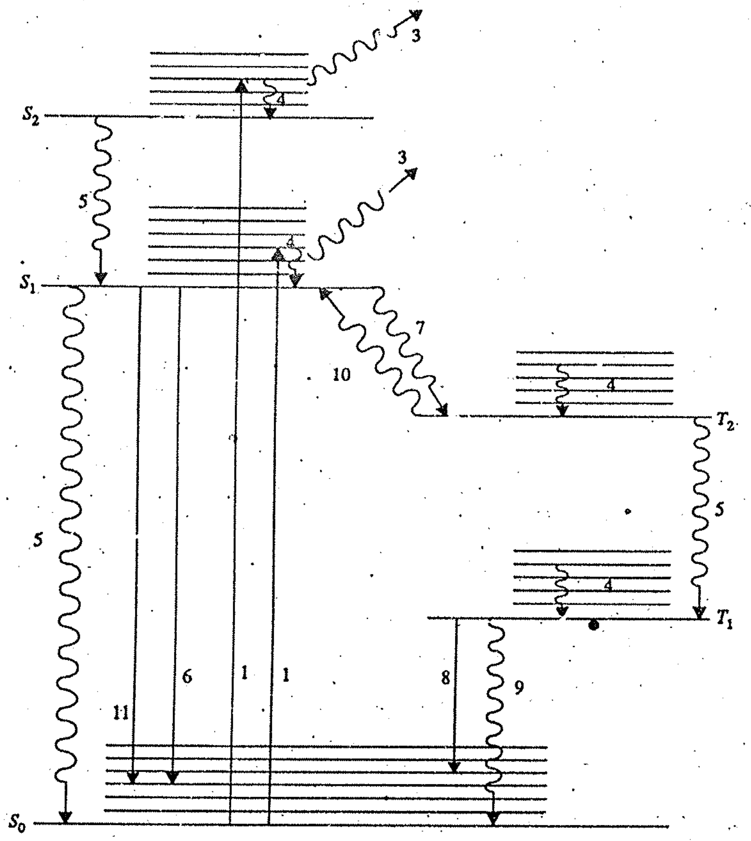


Fig. 8.7 : Jablonski diagram showing processes connecting various electronic states of molecules : (1) absorption, (3) dissociation and predissociation(4) vibrational relaxation, (5) internal and external conversion, (6) fluorescence, (7) intersystem crossing, (8) phosphorescence, (9) quenching, (10) reverse intersystem crossing, (11) delayed fluorescence.

8.7.1 Vibrational Redistribution

After excitation (process 1 in Fig. 8.7), probably the most rapid process to occur in the now electronically and vibrationally excited molecule is a redistribution of the excess vibrational energy among the different vibrational modes (process 2, not shown in Fig. 8.7). It is quite likely to be of major significance in the dissociation and pre-dissociation of large molecules.

8.7.2 Dissociation

Dissociation (Fig. 8.7, process 3) is almost certain to occur, if at all, within the period of time of a few vibrations. For example, if the vibration energy is between 300 and 3000 cm^{-1} the vibrational frequency is between about 10^{13} and 10^{14} sec^{-1}. This, means that the time required for one vibration is, classically, about 10^{-14} to 10^{-13} sec. Given sufficient energy, a diatomic molecule such as H_2 must dissociate in the time of a single vibration, provided some other process (such as a collision) does not intervene.

8.7.3 Predissociation

In polyatomic molecules, there are usually additional states between the attractive and repulsive states shown in Fig. 8.8. An excited state which is not a repulsive state is shown in curve C in this figure. Excitation to a low vibrational level of curve C (arrow a) behaves like a normal electronic transition. But excitation to a high vibrational level of curve C (arrow b) places the molecule energetically above the intersection of curves B and C. Its vibrational motion on curve C, from points x to y and back, passes this intersection point, and there is a fair probability that a molecule will "lose its way" and continue on curve B, which again results in dissociation. This process, called **predissociation**, is very common in heavy diatomic and polyatomic molecules.

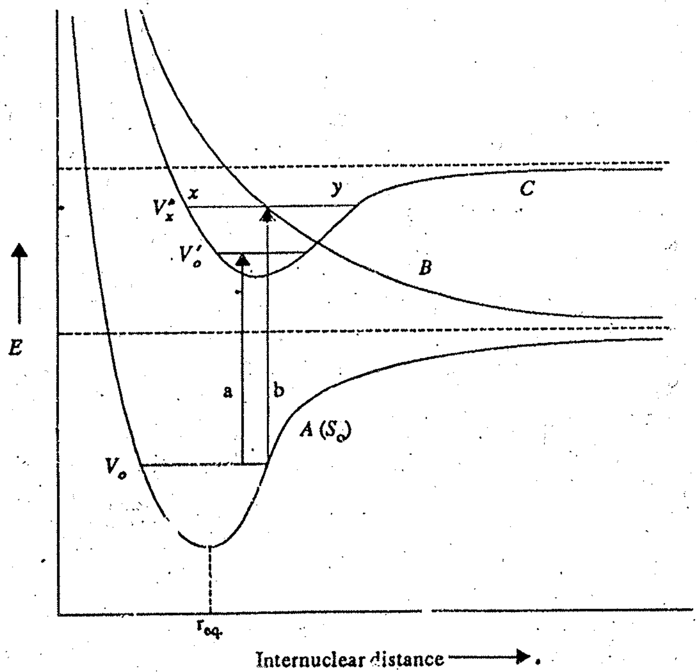


Fig. 8.8 : Potential energy curves for ground and excited electronic states of molecules showing predissociation.

When the molecules are in the higher vibrational excited state, it is also possible that they can undergo rearrangements involving bond formation, bond breaking, or both. However, we must remember that the lifetime in excited singlet states higher than S_1 is very-very short, and even in the lowest vibrational level of S_1 the lifetime is relatively short. Other interesting processes are possible if the molecule can somehow cross over to the T_1 state (in the triplet manifold) where, as we shall see, it has much greater lifetime.

8.7.4 Vibrational Relaxation

In our time scale, the next process (process 4, Fig. 8.7) is vibrational relaxation or the dropping to the lowest vibrational level that does not involve a change in **electronic energy.** The mechanism of this process undoubtedly requires either collision (in the gas-phase) or a collision-like interaction with the environment (in the liquid phase). Gas phase collisions require, depending on gas pressure, about 10^{-13} to 10^{-12} sec or longer, while the liquid-phase collision-like process occurs in about the same time as a vibration (10^{-14} to 10^{-13} sec)

8.7.5 Internal and External Conversion

These processes (shown as number 5 in Fig. 8.7) are slower than those previously discussed and result in the relaxation of the molecule into a lower energy state within a given (i.e., singlet or triplet) manifold.

As originally defined from observations of the luminescence of gases, **internal conversion** is referred to the de-activation (quenching) of excited molecules by collision with other molecules of the same species, while **external conversion** is referred to the de-activation by collision with dissimilar molecules. In solution, this distinction becomes meaningless, of course, and we speak only of internal conversion, referring thereby to a deactivation process in which the electronic excitation energy is dissipated as thermal energy by collision with any other (usually solvent) molecule. We note from Fig. 8.7 that this **non-radiative** conversion occurs between different electronic states.

8.7.6 Fluorescence

All the processes discussed upto this point are relatively very fast, and only in rare cases are they separately observable by spectroscopy. Consequently, our knowledge about these processes is often only by inference.

The emission of radiation (process 6, Fig. 8.7), which results in a transition of the molecule from an excited state to the ground state, **without a change in multiplicity**, is called **fluorescence** and occurs typically in 10^{-8} sec. Therefore, fluorescence practically always occurs from the lowest excited state of the singlet manifold, since this is the only state in the manifold with a lifetime longer than the time required for the various collision dependent relaxation and conversion processes.

Since fluorescence usually occurs from the lowest vibrational state of S_1, and emission like absorption, is always **vertical**, the molecule descends to an excited vibrational level of the ground state, Fig. 8.7. This is just the reverse of the usual case in absorption, in which promotion occurs from the $v = 0$ level in S_0 and the molecule ends up in higher vibrational levels, $v > 0$, in S_1. Accordingly, we expect a "mirror-image" relationship between absorption and fluorescence spectra, with the fluorescence spectrum appearing at longer wavelength (or lower frequency) than the absorption spectrum.

8.7.7 Inter-System Crossing and Phosphorescence

Phosphorescence is another process of de-activation of the excited state. It involves emission of radiation as a result of transition of electron between the states of different spin multiplicities (Fig. 8.7, process 7). This occurs through spin-orbit coupling, in which states with different spin angular momenta and orbital angular momenta mix slightly because they have the same total angular momentum.

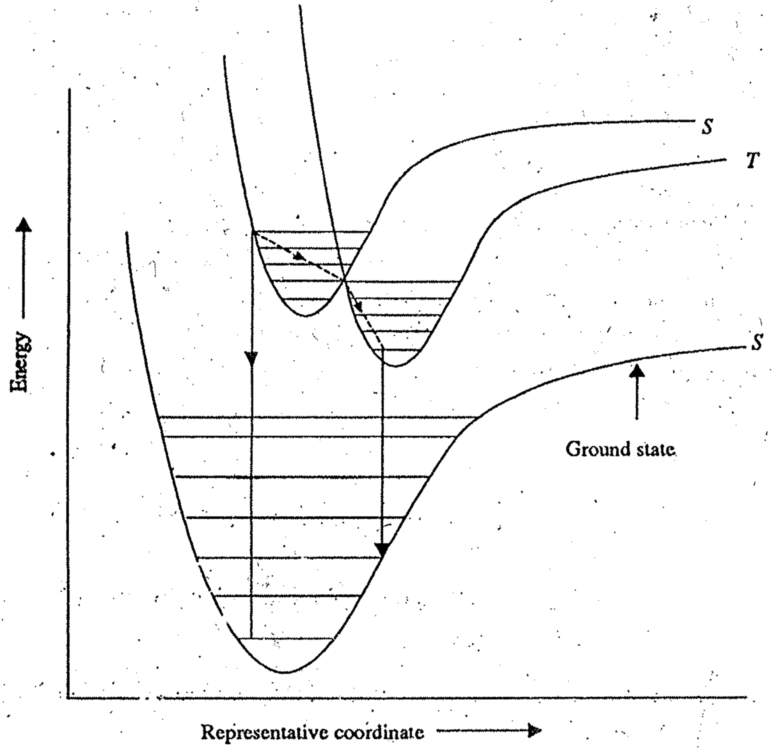


Fig. 8.9 : Potential energy curves of singlet and triplet states involved in phosphorescence

Phenomenon of phosphorescence can be understood in the following manner. Fig. 8.9 represents the arrangement of potential energy curves of singlet S and triplet T states that can lead to phosphorescence. Absorption of radiation can lead to the excitation of electron from the ground singlet state to the excited singlet state. Collision deactivation can then drop the energy past the point where the potential energy curve of the singlet state crosses that of the triplet state. Although internal conversion between states of different multiplicities is not easy, this process, known as inter-system crossing (process 7, Fig. 8.7), can occur leading to the triplet state molecules.

Once a different multiplicity manifold is attained by intersystem crossing (e.g., singlet → triplet), the same relaxation processes are important as were relevant in the original manifold. Following the same reasoning, the molecule will relax to the lowest vibrational level of the lowest electronic state of the new manifold. Once this point is reached, however, the final decay to the ground state is much slower and gives rise to a great variety of phenomena.

Intersystem crossing from the lowest excited singlet to the lowest triplet is one of the most important photochemical processes because of the long lifetime of the lowest triplet. The loss of energy from the lowest triplet to the ground state may occur by a radiative process called phosphorescence (process 8, Fig. 8.7) or by a relaxation process consisting of a reverse intersystem crossing (process 10, Fig. 8.7) involving internal or external conversion. The lowest triplet is difficult to pupulate by direct singlet →triplet absorption and equally difficult to de-populate by emission of radiation. If the non-radiative paths for de-activation are eliminated (for example, by using a very low temperature), the natural radiative lifetime of the triplet can be estimated. Phosphorescence spectra are usually determined in solutions that are frozen at 70-80 K. The phosphorescence spectra occur at longer wavelength (lower frequency) than the fluorescence spectra. Why? (Study the Jablonski diagram carefully).

8.7.8 Fluorescence and Phosphorescence Quenching

The most readily observed, and therefore the most readily studied, are the two radiative processes, **fluorescence** and **phosphorescence**. When they are not observed or, particularly, when they disappear under certain circumstances, they are said to be quenched (process 9, Fig 8.7). What this means is that, in the competition between processes, the radiative one has lost out because some alternative process was more rapid in the systems. Thus, fluorescence competes with internal and external conversion, with intersystem crossing, and possibly with some photochemical processes. Only when fluorescence is more rapid than, or at least as fast as, any of the others, can it be observed. Similarly, phosphorescence competes with relaxation by reverse intersystem crossing to the ground state, delayed fluorescence (process 11, Fig. 8.7), photochemical reactions, and other 'exotic' processes such as triplet-triplet annihilation and excimer fluorescence.

SAQ 3

State whether the following statements are true or false. Write T or F in the boxes provided.

a) In intersystem crossing there is a change in spin multiplicity of states ☐

b) Fluorescence occurs in 10^{-8} seconds ☐

c) The phenomenon of predissociation is very common in heavy diatomic and polyatomic molecules ☐

d) Most of the organic molecules except free radicals are in triplet state ☐

8.8 SUMMARY

In this unit you had studied that in the presence of ligands, the five fold degeneracy of *d* orbitals of a metal ion is removed. By absorption of energy in the visible region of spectra, the electrons can undergo *d–d* transitions. The origin of colours of transition metal complexes can be explained in the light of *d–d* and charge transfer electronic transitions and the crystal field theory. You have also studied various processes by which de-activation of an electronic state takes placed.

8.9 TERMINAL QUESTIONS

1. The e_g orbitals are higher in energy than the t_{2g} orbitals in octahedral environment but the order is reversed in tetrahedral arrangement. Explain.
2. Give the absorption spectrum of $Ti_2(SO_4)_3$ and explain the type of electronic transition taking place.
3. HgS, $KMnO_4$ and K_2CrO_4 – all are intensely coloured, though there is no possibility of *d–d* transitions in them. Explain.

8.10 ANSWERS

Self Assessment Questions

1. a) i) T ii) T iii) T iv) F

   b) i) reverse ii) centre of symmetry

   iii) octahedral iv) polarizability v) point

2. In charge-transfer spectra, the greater the reducing power of the ligand, the lower is the energy at which the charge transfer band occurs. As Br^- ion has a greater reducing power than the Cl^- ion, the charge-transfer bands occur at 36,000 cm^{-1} and 44,000 cm^{-1} in the spectra of $[PtBr_4]^{2-}$ and $[PtCl_4]^{2-}$, respectively.

3. a) T b) T c) T d) F

Terminal Questions

1. See Section 8.3
2. See Section 8.3
3. The intense colours of HgS, $KMnO_4$ and K_2CrO_4 are due to charge-transfer transitions as there is no possibility of *d–d* transition in any of them. The red colour of HgS is due to the transition $S^{2-}(n) \rightarrow Hg(6s)$ i.e., due to the transfer of lone pair electrons of sulphide ion to the empty 6*s* orbital of the mercury (II) ion. The intense colours of $KMnO_4$ and K_2CrO_4 are due to the transfer of lone pair electrons on O^{2-} ion to the empty t_{2g} orbitals on Mn^{7+} and Cr^{6+} ions. You should note that Mn^{7+} and Cr^{6+} are examples of d^0 ions, whereas Hg^{2+} has a d^{10} configuration.

UNIT 9 OPTICAL SPECTROSCOPY: INSTRUMENTATION AND SAMPLING

Structure

9.1 INTRODUCTION

In the earlier units on different kinds of spectra namely – rotational, vibrational, electronic and Raman – we have looked into the origin of a particular spectra and the information it can give us about the molecular structure. However, we had not discussed how these spectra are experimentally obtained. Since there is a lot of similarity in the experimental techniques in obtaining different kinds of spectra, we shall learn them in this unit. At the same time each one of them differs in detail from the other and hence they have been treated separately in different sections. You would notice that nmr, esr and mass spectra have not been included here since their experimental techniques are quite different from the ones discussed in this unit. Hence the experimental techniques associated with nmr, esr and mass spectra are included in their respective units. The spectrum of a sample is recorded with the help of an instrument called spectrometer or spectrophotometer. A spectrometer generally records some function of radiant power (e.g. percent absorption or transmission) **transmitted** through the sample at different wave lengths in the given region. A **spectrophotometer** gives us the ratio of the radiant power of two electromagnetic beams. Since the absorption spectrum is much more intense than the emission spectrum, we generally record the absorption spectrum of a sample. In this unit, we shall deal with absorption spectrometers used in different regions of spectrum.

Objectives

After studying this unit,you should be able to:

- describe the different components of various spectrophotometers,
- explain the various terms like signal to noise ratio, resolving power etc. associated with spectrometers,
- describe the various sampling techniques,
- correlate slit-width with resolving power,
- differentiate between single beam and double beam spectrometers, and
- draw a block diagram of a spectrometer.

9.2 SPECTROSCOPIC COMPONENTS

In this section, we shall discuss the main features of spectrometers, followed by the differences in components as per requirements of the various regions of a spectrum. First of all, we need a suitable source of electromagnetic radiation which must provide a continuous and sufficient radiant energy over the whole region of spectrum under study. Its intensity must also not change during the time when spectrum is being recorded. For different regions of spectrum, we would, naturally, need different sources of radiation and these have been discussed in Sub-section 9.2.1.

Next we shall require some optical devices to guide the radiations on to the sample and to the detector. These include slits, lenses, mirrors, prisms/gratings, monochromators etc. Since monochromators are common to all types of spectrometers, we shall discuss them in Sub-section 9.2.2. Other optical parts are discussed at suitable places simply because the optical set up requirements may be different for different instruments. The sample itself could be in gaseous, liquid or solid state and hence, different sample handling techniques are required. These techniques have been discussed separately in Section 9.3.

Finally, after the radiations have passed through the sample, we detect and record them with the help of detectors. These have been discussed in Sub-section 9.2.3. The detectors are in turn connected to amplifiers and a recorder to produce a plot of absorbance or transmittance as the wavelength or frequency varies. The function of a detector is to convert the radiation falling on it to electrical current which is amplified by the recorder. We can sumup the above information in a block diagram given below (Fig. 9.1.).

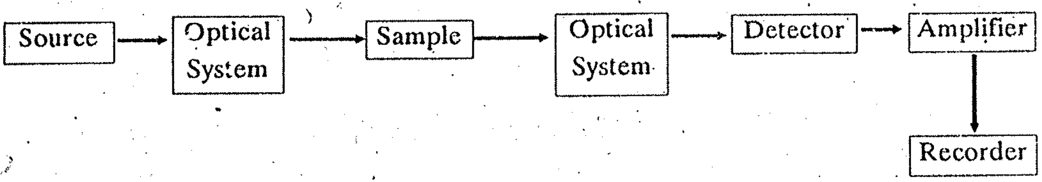


Fig. 9.1 : Block diagram of a spectrometer.

9.2.1 Sources

As stated earlier the source should produce continuous and steady radiations in given region of spectrum. It should also not contain any strong emission lines. Keeping these factors in mind, the following sources have been found useful and are commonly used for different regions.

Microwave : Reflex Klystron valve is the main source of radiations in microwave region. It emits radiations of a narrow range of frequency and therefore, it does not require any monochromator. The frequency of the region is controlled by the voltage applied to the Klystron valve. Thus by slowly changing the voltage, we can scan the whole region of the spectrum. The only difficulty with Klystron valve is that it emits radiations of very small frequency range. Microwaves cannot be directed by optical devices. On the other hand, the microwaves can be directed along a rectangular metal tube called a waveguide.

Infrared : The source for infrared region is usually a filament which is maintained at red or white heat by an electric current. The two most commonly used are known as Nernst glower and Globar filament. The Nernst glower is made of zirconium and yttrium (rare earths) oxides in the form of a hollow rod of approximately 2 mm in diameter and 30 mm in length. It is heated to about 2000°C when it furnishes maximum radiations at about 7000 cm^{-1}. The Globar filament is made of silicon carbide. It is heated to about 1500°C when it furnishes maximum radiation at about 5000 cm^{-1}. It produces less intense radiations than Nernst glower. However, the Globar filament is employed for working at higher wavelengths, the reason being that its radiant power output decreases more slowly than the Nernst glower.

Raman : The common exciting source of Raman spectrometers is a mercury discharge lamp. It gives a series of characteristic lines at 253.7, 365, 404.7, 435 8 and 546.1 nm. A single wavelength is used as a souce. The other wavelengths are cut off by the use of suitable filters. The most commonly used radiation corresponds to 435.8 nm. Since the intensity of Raman spectrum is proportional to the fourth power of the frequency of the exciting line, it is useful to employ high frequency. Too high a frequency may cause photodecomposition or may cause overlap of Raman shifts. Thus a line with optimum value is selected. More recently, however, laser sources have replaced the mercury discharge lamps which provide extreme monochromatic radiations of high intensity. The commonly employed helium-neon laser emits a strong line at 632.8 nm. Except for the high cost, it has all the other advantages like high intensity, monochromatic character and no filter is required. It has the added advantage that it can be used for coloured solutions and much smaller samples.

Ultraviolet and Visible Region: For work in ultraviolet region, a hydrogen discharge lamp is used. It can be used between 200 nm to 375 nm. The intensity of the lamp increases almost threefold by replacing hydrogen with deuterium. Other high intensity lamps are known but are not commonly used due to various difficulties.

For visible region, the common source is the tungsten filament incandescent lamp. It can be used between 350 to 800 nm region and is operated at a temperature of about 3000°C.

9.2.2 Monochromators

In order to restrict the band of wavelength passing through the sample, we require some optical devices known as monochromators. These monochromators consist of a dispersing device which splits the polychromatic beam into a spectrum. The two common devices used for this purpose are prisms and gratings, the only exception being microwave region, where waveguides are used. In addition to a prism or grating, the monochromator has two slits. One of the slits sharply defines the incoming beam. The other exit slit is placed after the dispersing medium and its function is to allow only a narrow beam of radiation to fall on the sample. Two important characteristics of a dispersing device are shown in Fig. 9.2. The nominal wavelength is the wavelength of band centre. The range of wavelengths between two points at which the transmittance is one half of the maximum transmittance is known as band pass width. It is essentially the width of the exit slit. The band pass width depends on the nature of the dispersing unit and the focal length of the monochromator. The band pass width also depends on the ruling of the grating and since it remains constant for a particular grating, the band pass width for a given slit remains constant throughout the spectrum in case of grating spectrometers. In prism spectrometers, the band pass width changes with wavelength because the dispersion of the prism changes with the wavelength. We know from our previous knowledge that the dispersion of polychromatic radiation into a spectrum is caused due to the variation of refractive index with wavelength. Hence, the separation of two wavelengths depends upon the dispersion power of the prism material. The separation of wavelengths is not uniform throughout and the separation becomes smaller at higher wavelengths. Glass and quartz are used as prism materials for the visible spectrum; glass is preferred as prism since its dispersion power is three times than that of quartz. However, glass is not transparent in the ultraviolet region and hence quartz prisms are used for this region.

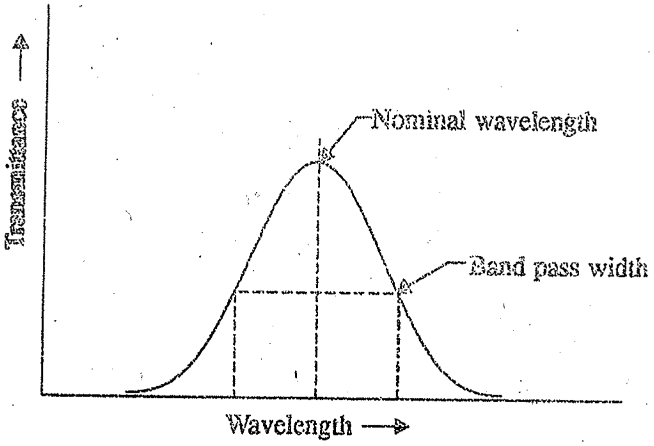


Fig. 9.2: Transmittance characteristics of a monochromator.

The dispersal of a polychromatic beam into a spectrum can also be achieved by means of a grating. A grating consists of a large number of parallel lines on a highly polished surface. Generally, there are about 600 lines per millimeter for ultraviolet and visible regions. Each ruled groove in a grating acts as a scattering centre for light rays and the light spreads out over a range of angles.

9.2.3 Detectors

It is quite obvious that different regions of spectrum would require different detector systems. In this section, we shall discuss the various detectors used for different regions of spectrum.

For microwave region, a quartz crystal is generally employed as a detector. It is mounted on a cartridge made up of a tungsten wisker held in point contact with the crystal. It detects the radiations focussed upon it and converts the microwave power to a direct current output. The signal it gives is amplified and fed to the recorder. It is quite sensitive and easy to use. Instead of quartz crystal, superhetrodyne radio receiver or silicon-tungsten crystal may also be used.

In case of Raman spectrum, especially when mercury arc lamp is used as a source, we must use extremely sensitive detectors. The detectors commonly employed for this purpose are either photomultiplier tubes or a photographic plate. A photomultiplier tube consists of a phototube and a series of electrodes known as diodes. A phototube is simply a glass bulb which is partially coated internally with a thin layer of photosensitive material such as potassium oxide or silver oxide leaving a small portion uncoated to permit the entry of light. The coated layer is attached to the negative end of a battery. A metal ring at the centre of the bulb is made the anode by joining it to the positive end of the battery. The whole bulb is evacuated. When light falls on the cathode, the photosensitive layer emits electrons which are attracted towards the anode and a current flows through the outside circuit.

As mentioned above, in a photomultiplier tube the emitted electrons are made to fall successively on a series of electrodes which are charged successively at higher potentials. Each of these electrodes is covered with a material which emits several electrons for each electron that fall on its surface. The net effect is the amplification of the current many times.

In the case of infrared spectrometers, the detectors are generally of two kinds : (i) Golay cell (ii) bolometer or thermocouple. Both of them are basically thermal detectors which give response at all the frequencies in the region.

Golay cell : When infrared radiations are allowed to fall on a gas enclosed in a small cell, it heats up the gas causing the change in pressure within the cell. These changes in pressure are recorded. This type of cell is bulky and expensive and hence less commonly used. Bolometers and Thermocouples on the other hand make use of photoconductivity phenomenon.

Bolometers: We know that the resistance of a metallic conductor changes with temperature. When infrared radiations fall on a thin metal conductor, its temperature changes which causes a corresponding change in its resistance. The changes in the resistance can be measured with the help of a Wheatstone bridge. The bolometer forms one arm of the bridge and the other balancing arm of the bridge consists of a similar metal strip but which is not exposed to the radiation. If no radiation falls on the bolometer, no current would flow and the bridge would remain balanced. However, when infrared radiations fall on the bolometer, a current would start flowing through the galvanometer due to change in the resistance. The current flowing through the galvanometer would then be directly proportional to the radiations falling on the bolometer.

Thermocouples: In a thermocouple, two wires of different semiconductor materials with high thermoelectric efficiency are joined together at the two ends. The infrared radiations are made to fall at one of the joints (hot junction), the other joint (cold junction) is kept at a constant temperature. This difference of temperature causes an electrical potential difference between the two joints. The potential difference would depend upon the amount of radiation falling on the hot junction and is thus a measure of the radiation.

The ultraviolet or visible spectrophotometers generally contain photomultiplier tube as a detector.

SAQ 1

Fill in the blanks in the following:

i) Intensity of the discharge lamp increases by replacing hydrogen with ....

ii) Tungsten filament lamp is used between .... and .... nm for visible region.

iii) In prism spectrometer, band pass width changes with ....

SAQ 2

What are the detectors for IR spectrometer ? Give their basic principle.

....

....

....

....

9.3 SAMPLE HANDLING TECHNIQUES

All the instruments would require some kind of a container to hold the sample. The first and the foremost characteristic of a container is that it should be transparent to the region in which the spectrum is to be recorded. Secondly, when a spectrum of a sample in solution is to be recorded, the containers or the cells must be made of such a material which is inert to the solvent. The thickness of cell must be uniform. The surface facing the incident radiation must be flat. These are some of the other criteria which must be kept in mind. We shall now discuss various types of cells used for different regions of spectrum.

The Microwave Region

A rectangular tube of copper or silver known as waveguide is used to keep the sample for the microwave region. The tube is closed at both ends by thin mica windows. Holes are made in the tube for introduction of the sample as well as for evacuation of air. The beam direction can be fixed across the tube and hence the waveguide is made of metallic conductor with a rectangular shape.

The Infrared Region

Glass cells cannot be used for the infrared region, since the glass absorbs strongly at most of the frequencies in this region. NaCl and KBr are some of the salts which are transparent in this region of the spectrum. Hence, the cells are constructed from these salts. The NaCl cells are most commonly used for routine work in the region 4000-650^{-1}. These are cheaper than KBr cells. Below 650 cm^{-1}, we must use KBr cells since NaCl absorbs in this region. Depending upon the phase — solid, liquid or gas — the sampling techniques change.

i) Sampling of Gases : The gas samples are contained in a cell approximately 10 cm long with sodium chloride windows at either end. It is kept across the path of infrared beam. These cells are used for gases at a pressure of 1 atm. or greater. For gases at low pressures specially designed cells are used. Since the area provided in the spectrometers is limited, the path length of the beam can be increased by repeated reflections within the cell by means of mirrors.

ii) Sampling of Liquids : For liquid samples, cells with fixed path lengths and variable path lengths are both commercially available. The liquid sample thickness should be between 0.01 to 0.05 mm which would give transmittance between 20-70 percent. The cells of this thickness are made of sodium chloride or potassium bromide rectangular plates sealed by gaskets and clamped together. A drop of liquid is pressed between NaCl/KBr plates which are put in a cell holder and scanned. For solutions, two matched cells are generally employed, one of which contains the solution and the other is filled with pure solvent and scanned through a double beam spectrometer. However, it is difficult to obtain a fully matched pair of cells since the cell material is easily affected by moisture. Under these circumstances, a careful selection of solvents is made such that they are transparent in the desired region of spectrum. The influence of a particular solvent on the solute must be carefully examined before its use.

iii) Sampling of Solids : There are basically two different techniques for handling of a solid sample. One which is most commonly employed is known as **nujol mull technique.** In this case the sample is finely ground to a paste in a small amount of mineral oil (nujol) or hexachlorobutadiene. It forms a fine suspension or mull of the sample in the oil. The mull is pressed between two NaCl/KBr plates to give a thin film of the sample. The two plates are clamped in a holder with open windows on both sides and the whole assembly is kept in the path of the infrared beam. Two spectra of the sample are recorded separately, one with a nujol mull and the other with a hexachlorobutadiene mull. Though hexachlorobutadiene absorbs at a number of frequencies in the infrared region, it is transparent in all those regions where nujol absorbs. Hence, by the combined study of the two spectra, we can get all the frequencies at which the sample absorbs.

The second technique is known as **pellet technique**. In this case a small amount of sample is mixed and ground with about hundred times its weight of potassium bromide. The mixture is transferred to an evacuable die to remove the moisture and then a high pressure is applied to yield a transparent pellet. It is put in a suitable holder and the whole assembly is placed in the line of the infrared beam. The holder may be even a thick folded paper with open slits. A blank KBr pellet of almost the same dimensions is placed in the path of the beam. The results with this technique are not easily reproducible. The resolution, however, is better as compared with the nujol mull method.

Raman Spectra

The type of cell for Raman spectrum varies with the amount of sample used, and the intensity of the source. When the quantity of the sample is small, a **multitraversal** tube is used where the incident beam is allowed to undergo a series of reflections with the help of mirrors before it emerges from the tube. The sample cells are larger for gases as compared to the ones used for liquids.

The usual length of the cylindrical tube may be between 20-30 cm and the diameter 1 to 2 cm with flat ends. The source is usually a mercury discharge lamp. However, when the source is a laser beam, the sample holders are of much smaller capacity of about 1ml and are made of quartz.

U.V. and Visible Region

A good quality glass or quartz can transmit radiations down to 200 nm. Hence, for routine work in the uv and visible region, quartz cells are most commonly employed. Alkali fluorides and clacium fluoride are transparent upto about 100 nm and as such these are used for specific samples where the desired absorption occurs below 200 nm. The thickness of the cell is usually 1 cm and rectangular in shape. They are normally supplied as matched pair.

9.4 MICROWAVE SPECTROMETER

The microwave spectrometer is shown in the form of a block diagram in Fig. 9.3. As shown in the figure, the source of monochromatic radiations in the microwave region is a Klystron whose emission frequency can be varied over a range. Since the frequency depends upon the applied voltage, by varying the voltage we can scan the whole region of microwave spectrum. Moreover, we have already learnt that Klystron emits radiations of narrow frequency range and so we do not need a monochromator in this case.

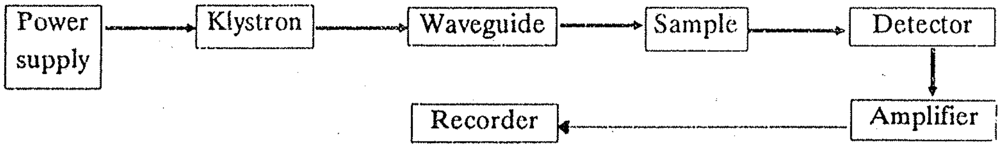


Fig. 9.3 : Block diagram of a microwave spectrometer.

The radiations are made to pass through a waveguide containing the sample in the gaseous state. After passing through the sample, the radiations fall on the detector. A quartz crystal acts as a detector which converts the radiations into electrical signals which are subsequently amplified. The amplified signal is connected to a pen-and-ink recorder. The functional details of various parts have already been discussed in previous sections.

9.5 INFRARED SPECTROMETER

There are two kinds of infrared spectrometers available: Single beam and double beam. A block diagram of the single beam spectrometer is given in Fig. 9.4.

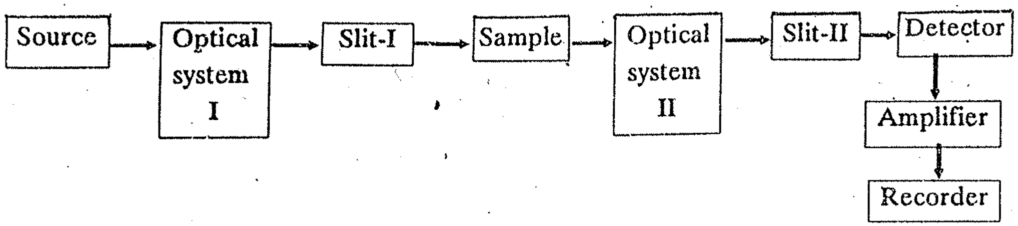


Fig. 9.4 : Block diagram of a single beam infrared spectrometer.

The optical system-I consists of a set of collimating mirror placed near the source. A parabolic mirror is used to produce parallel light rays. Slit-I regulates the amout of incident radiation reaching the sample. The radiations after passing through the sample are analyzed using optical system-II. Optical system II consists of a set of prism or grating, littron mirror and a spherical mirror. The spherical mirror is employed to focus the radiation on to the detector.

Littron Mirror: A plane mirror is placed behind the prism at a suitable angle. When a beam of light passes through the prism, it is reflected back by the mirror. Thus the beam passes through the prism two times thereby doubling the dispersion produced. It is known as double-pass system. We can improve the resolution further if the beam is returned one more time through the prism. This would make a total of four passes. It also reduces the scattered radiation to negligible amount.

Knowing the original intensity and the intensity of radiation after passing through the sample as measured by the detector, you can find out how much radiation has been absorbed. Though the construction of a single beam spectrometer is cheaper and easier than a double beam spectrometer, it is associated with some inherent problems. First, since the intensity of emission of the radiation is not constant throughout the region of spectrum, it must be continuously balanced by varying the slit width which cannot be easily achieved. Secondly, water vapours and CO_2 present in the atmosphere also absorb in certain regions of the spectrum. This absorbance must be subtracted from the spectrum with the help of a blank-run. This 'back ground' spectrum must be repeated with each sample since the percentage of water vapours in the atmosphere is variable. Even this would not solve our problem if our sample shows characteristic absorbance at those frequencies where H_2O or CO_2 absorbs. Hence, these must be completely removed by some means before a spectrum is recorded. Again it cannot be done easily and completely. Finally if the spectrum of the sample is to be recorded in solution, it would show the absorbance peaks due to the solvent. All these problems are taken care of satisfactorily in a double beam spectrometer.

An optical system is used to:

- select the proper frequency of radiation
- guide the radiation in the specified direction
- obtain a good spectrum

Double beam Spectrometer : In the double beam instrument, a plane mirror is placed in front of the source which splits the beam into two equivalent half beams. The two beams are focussed by separate concave mirror systems one passing through the sample while the other reference beam is left empty or allowed to pass through the solvent. A shutter-comb is placed in the path of the reference beam to reduce its intensity such that the two beams are again balanced. The two half beams after recombination with the help of mirror system reach the detector. The signal from the detector is amplified and fed to the recording system. The roles of prism (grating), littron mirror etc. remain the same as in the single beam instrument. Thus the spectrum recorded on the chart paper gives the relative transmittance of the sample.

SAQ 3

State the name of the instrument useful in studying the IR spectra in the solution phase.

9.6 RAMAN SPECTROMETER

A block diagram of a Raman spectrometer is shown in Fig. 9.5.

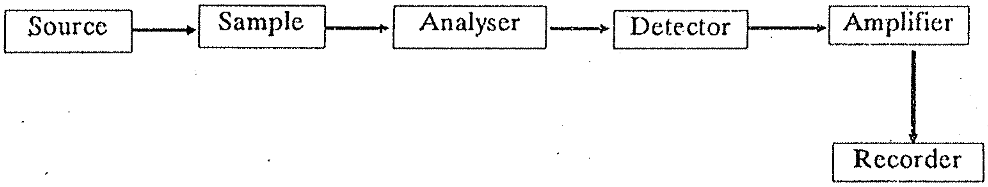


Fig. 9.5 : Block diagram of a Raman spectrometer.

The sample is irradiated with an intense beam of monochromatic light and the scattered radiations are collected at right angles to the incident beam. These are then passed on to the analyser, detector, amplifier and recorder sequentially. Raman intensities are approximately 0.01 percent of the incident light and therefore incident light must be very intense. This is achieved by surrounding the sample tube with four to eight tubular mercury arc lamps. These arcs generate a good amount of heat and hence the Raman tube is protected from the heat by means of a water jacket through which tap water is circulated. Selection of useful lines in the mercury arc lamp is done by placing suitable liquid filters between the source and the sample tube. A cross-sectional diagram of the whole set-up is shown in Fig. 9.6.

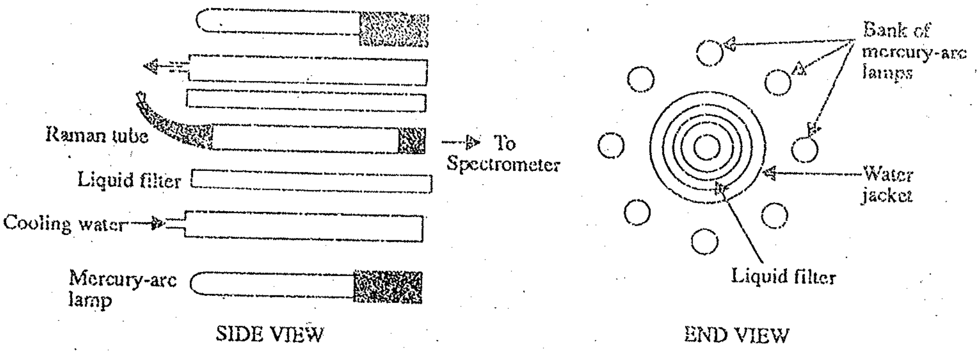


Fig. 9.6 : Arrangement of sample tube and Raman excitation source.

The introduction of laser source, which gives narrow, intense and monochromatic beam, has simplified the arrangement drastically. The laser beam is directly focussed on to the sample. The sample container in this case is a rectangular quartz tube approximately 2 cm in length and 0.5 cm^2 in cross-section with suitably located openings for transferring the solution.

The scattered light after passing through the sample is focussed at the front slit of the spectrometer with the help of two prisms and lenses. The beam from the entrance slit is allowed to fall on two monochromators with the help of spherical mirrors. The gratings are rotated linearly in wave numbers and the wave number setting is read on a counter. The beam then passes through an exit slit to a rotating mirror. The function of the rotating mirror is to direct the beam to two photomultiplier tubes alternately. This arrangement avoids the loss in energy. The signals from the two photomultiplier tubes are combined. Another reference phototube collects a portion of the exciting radiation through an alternative optical path. The two signals from the reference and the Raman beam are amplified and compared. The use of a double monochromator reduces the effect of scattering by dust particles in the sample.

SAQ 4

What is the function of the rotating mirror in Raman spectrometer ?

....

....

9.7 ELECTRONIC (VISIBLE AND ULTRAVIOLET) SPECTROMETER

The basic features of a single beam u.v. - visible spectrometer are shown in Fig. 9.7.

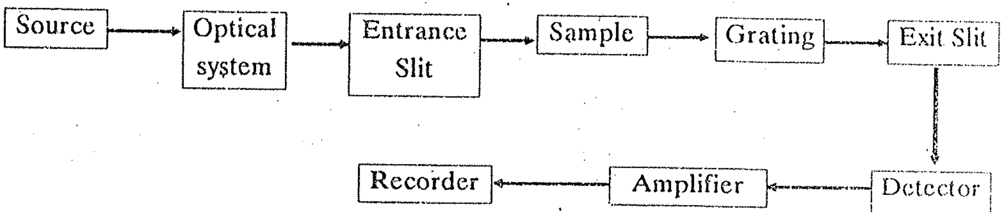


Fig. 9.7 : Schematic diagram of a visible and uv spectrometer.

The radiation from a suitable source is focussed on an entrance slit with the help of lens system. In the single beam spectrometer the beam passes through the sample and falls on a prism or grating which is mounted on a rotating table. After dispersion from the prism or grating, the radiation of the desired wavelength passes through the exit slit and on to a detector. The signal from the detector is amplified and fed to a recorder. In a double beam spectrometer. The beam is split into two equivalent half-beams with the help of lens systems. One part of the beam passes through the sample and the other through the reference cell which contains the solvent. Two parts of the beam emerging out from the sample and reference cells are focussed on to a detector which records the difference in transmittance of the two beams. The signal from the detector is fed into an amplifier. The amplifier commonly employed is a photomultiplier tube. The signal transmitted by the amplifier enters the recorder. The recorder consists of a pen and a chart paper whose movement is synchronised with the movement of the grating. Thus the chart paper plots a graph between the wavelength and absorbance (or transmittance).

The only difference between the u.v. and visible spectrophotometers lies in the choice of the radiation source. For visible region, we use tungsten filament lamp which is useful in the region of 350-800 nm. For ultraviolet region covering the range from 150 to 350 nm, a hydrogen lamp or deuterium lamp is used, which is basically a discharge tube containing hydrogen (or deuterium) gas under pressure. The pressure of the gas is kept high in order to obtain a continuous spectrum otherwise a line spectrum would be obtained. There are a number of other types of discharge tubes available in the market but the one described above is the most commonly used.

Thus we can record the spectrum from say 150 to 800 nm by the same spectrohotometer just by changing the source from hydrogen lamp to tungsten filament lamp. As stated earlier, the electronic spectra can be recorded either on a photographic plate or on a chart paper with the help of a photomultiplier tube as a detector. For any short lived species a photographic plate is more useful since it can record the whole spectrum in a fraction of a second. No detector can operate at such a fast speed. Even unstable species giving very weak signals can be recorded on a photographic plate by increasing the exposure time. These signals can be easily missed by a photomultiplier tube. However, the greatest disadvantage with the photographic plate is its limited resolving power besides being expensive.

Once the spectrum is recorded – which is basically a plot between absorbance (or transmittance) and the wavelength – it can be analysed to get useful information.

9.8 FLUORESCENCE AND PHOSPHORESCENCE SPECTROMETER

The instrument for measuring fluorescence are known as fluorimeters by the British and fluorometer by the Americans. They are further classified as filter fluorometers and fluorescence spectrometer. The difference between the two lies in the way the exciting radiations and the fluorescence (emission) radiations are selected.

The basic components of a filter fluorometer are shown in a block diagram form in the Fig. 9.8.

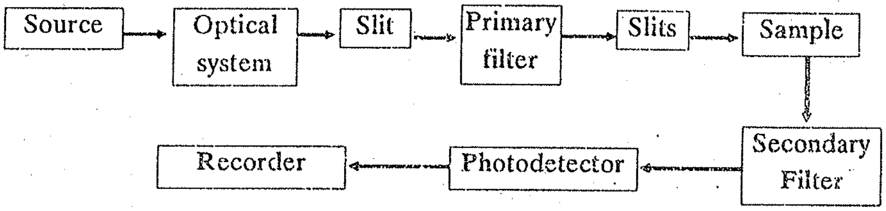


Fig.9.8: Block diagram of a fluorometer.

The source of excitation is usually a mercury discharge lamp. The principal lines of this occur at 366, 405, 436, 546 and 578 nm. We can select any of these exciting lines with the help of a primary filter. The beam after passing through the sample passes through a secondary filter and falls on the photocell placed at right angles to the incident beam in order that it may not be affected by primary radiation. Proper optical system and secondary filters are to be used to absorb the primary radiation and transmit the fluorescent radiation. The intensity of the fluorescence is measured with reference to some standard substance.

In the fluorescence spectrometer, we get rid of the filters by using two monochromators— usually gratings. Thus we can selectively utilise the wave-length of the exciting radiation as well as the fluorescence peaks. Further improvement is made by making use of a beam splitter. A portion of the beam is reflected directly to a monitoring photomultiplier tube and the other portion after passing through sample is detected by fluorescence photomultiplier tube in the usual fashion. The output from the two photomultiplier tubes are fed into a radiation recorder. Thus, we can obtain a true excitation spectrum.

Phosphorescence Spectrometer: Phosphorescence spectrometers are essentially very similar to fluorescence spectrometers. There are however, two basic differences. In order to minimize all the other degradation processes through collision except the phosphorescence transitions, we maintain the sample at liquid nitrogen temperature. Secondly, the substance under study may give both phosphorescence and fluorescence spectrum. Since we want to record only the phosphorescence spectrum, we introduce a device known as phosphoroscope. It introduces a delay between the time when the sample is irradiated and when the phosphorescence is observed. Two commonly employed phosphoroscopes are rotating disk or rotating drum type.

Rotating disk phosphoroscope consists of two slotted disks mounted on a shaft driven by a variable speed motor. The disks are so arranged that the openings in one are in line with the unslotted portion of the other. The sample is placed between the two disks. When the disks are rotated, the sample gets illuminated and then darkened. When it is dark, the phosphorescence passes through the second disk, and can be recorded in the usual manner. In the rotating drum phosphoroscope, the sample is surrounded by a hollow drum having equally spaced slits. The drum is rotated by a variable speed motor. When a slit is in line with exciting radiation, the sample is illuminated and then it gets darkened. The phosphorescence radiation passes through the other slit at right angles to the exciting radiation and then on to the monochromator. The common solvent used for the phosphorescence studies is a mixture of ethyl ether, isopentene and ethanol. At liquid nitrogen temperature, it forms a clear rigid glass.

9.9 SIGNAL TO NOISE RATIO AND RESOLVING POWER

The quality of spectrum would depend on the nature of the substance, type of spectrometer, and the sample handling technique. However, there are a couple of things which if properly handled can yield better spectrum. These are discussed under the heading signal to noise (S/N) ratio and resolving power. As we shall see they are interrelated and indirectly controlled to a certain extent by the slit width of the monochromator.

S/N Ratio: It is a recognised fact that all electronic devices, whether it is a detector or an amplifier, produce fake electronic signals. These singals are non-uniform and random in nature. Such signals are called 'noise' and are inherent weakness of any electronic device. The main reason for the noise is not too difficult to understand. The electrons which are the signal (charge) carriers are not confined to narrow energy value of the signal but spread over a range of energy values due to thermal motion and hence the false signals.

If the noise of the instrument is low in comparison with the signal due to absorption of the sample, it does not interfere and we can neglect it. However, if the absorption due to the sample is very weak it would be lost in the noise of the instrument. Even with sensitive detectors, the signals can be identified easily only if their intensity is three or four times that of the noise.

Resolving Power: We have stated earlier that the electronic spectra never occur at a single frequency. It is always spread over a range of frequencies. Now if there are two absorption peaks very near to each other, we shall be recording the total abssorption due to the two peaks as the radiations pass across the slit. To a certain extent, we can resolve the two peaks if the width of the slit is narrowed but too much resolution will cause unnecessary noise superimposed upon the signal. On the other hand, too little resolution depresses the peak heights and the separation of the bands is less well defined. Obviously, we can operate only with an optimum band width.

The resolution of the bands is also determined by the scan speed, size and the dispersing characteristics of grating or prism, optical design of the instrument etc. We are not going to discuss these factors here.

9.10 SUMMARY

In this unit, we have studied the different sources of radiation and the detectors used for the various spectroscopic regions. We have also analysed the reasons for using different kinds of materials and their limitations. Sample handling techniques also vary in different regions of the spectrum and these have also been discussed briefly. Next, we discussed the working of spectrometers concentrating mainly on the variations in the optical systems of different regions. The role of monochromators and filters has also been indicated. We defined the terms, signal to noise ratio (S/N ratio), slit width and the resolving power. Throughout the text, we have emphasized the point that this discussion should give you a brief idea of instrumentation, so that you may not consider any instrument as a black magic box in which you insert your sample and out comes the result!

9.11 TERMINAL QUESTIONS

1) What do you understand by the term "band pass width" ?

2) What are the sources of radiation for the following spectrophotometers ?

   i) IR ii) Raman iii) UV

3) What is the function of Littron mirror in IR spectrophotometer ?

4) What are the differences between phosphorescence and fluorescence spectrometers ?

5) Draw block diagram of a spectrometer ?

9.12 ANSWERS

Self Assessment Questions

1. i) Deuterium
   ii) 350 nm; 800 nm
   iii) Wave length

2. Golay cell, bolometer and thermocouple are the detectors for IR spectrophotometer. Their basic principles are as follows:

   Golay Cell: Radiation heats up the gas, causing change in pressure within cell. These changes are recorded.

   Bolometer and thermocouple work by photoconductivity phenomenon.

3. Double beam spectrophotometer

4. The function of the rotating mirror is to direct the beam to two photomultiplier tubes alternately.

Terminal Questions

1) The range of wavelengths between two points at which the transmittance is one half of the maximum transmittance is known as band pass width.

2) i) Nernst glower and Globar filament
   ii) Mercury discharge lamp.
   iii) Hydrogen or deuterium discharge lamp.

3) It is used for improving the resolution.

4) Unlike fluorescence spectrometers, phosphorescence spectrometers make use of liquid nitrogen temperature and a device known as phosphoroscope.

5) Please see Fig. 9.1.

Further Reading

1. **J.R.Dyer, Application of Absorption Spectroscopy of Organic Compounds, Eastern Economy Edition, Prentice-Hall of India Pvt.Ltd.**

2. **D.H.Williams and Ian Fleming, Spectroscopic Methods in Organic Chemistry. Tata Mc Graw Hill Publishing Co. Ltd. 4thEd.**

3. **C.N Banwell, Fundamentals of Molecular Spectroscopy, 3rd Ed, Tata McGraw Hill Publishing Co. Ltd.**

NOTES

Uttar Pradesh
Rajarshi Tandon Open University,

UGCHE -10
Spectroscopy

Block

4

RESONANCE SPECTROSCOPY AND MASS SPECTROMETRY

RESONANCE SPECTROSCOPY AND MASS SPECTROSCOPY

In the earlier blocks of this course, you have studied a variety of spectroscopic techniques. In this block, you will study about the Resonance spectroscopy and Mass Spectrometry techniques which are widely used in the structure determination. The last unit illustrates how to arrive at the structure of an unknown compound on the basis of its spectral data.

Both Units 10 and 11 are devoted to resonance spectroscopy. In Unit 10, the Nuclear Magnetic Resonance Spectroscopy has been discussed while Unit 11 deals with the Electron Spin Resonance Spectroscopy. These two techniques are unique in principle in spectroscopy because of the fact that here energy levels are generated by placing the substance being studied in an external magnetic field. In Unit 10, the nuclear magnetic resonance spectroscopy of proton is discussed in detail alongwith its analytical applications. Unit 11 reveals the fundamental concepts associated with Electron Spin Resonance Spectroscopy. Here also, structure-spectra relation has been illustrated using simple examples.

Unit 12 is devoted to Mass Spectrometry. Although this technique is not based on the general principle of absorption of electromagnetic radiation, it is studied alongwith the other spectroscopic techniques because of its important role in structure determination.

Unit 13 contains some representative examples and illustrates how the information from various spectral techniques can be put together like the pieces of a jig-saw puzzle to arrive at the structure of an unknown compound.

Objectives

After studying this block, you should be able to

- explain the principle of nuclear magnetic resonance,
- define chemical shift,
- discuss spin-spin splitting,
- describe the uses of NMR spectroscopy in structure elucidation,
- correlate the NMR spectra of simple molecules with their structure,
- discuss the principle of Electron Spin Resonance Spectroscopy,
- explain nuclear hyperfine splitting in simple radicals,
- illustrate the use of ESR spectral studies in structure elucidation of some simple species,
- explain the technique of mass spectrometry,
- discuss various fragmentation types and factors affecting them,
- describe Mclafferty rearrangement,
- correlate mass spectra of simple molecules with their structure,
- use UV, IR, NMR and mass spectral data to arrive at the structure of a given compound.

UNIT 10 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Structure

10.1 INTRODUCTION

Upto now we have described various spectroscopic techniques in which we measured the energy levels of electronic, vibrational and rotational states of atoms and molecules. In the above cases we simply subjected the system to electromagnetic radiations of appropriate energy (or wavelength) and looked for absorption at specific regions. There is an interesting new branch of spectroscopy, known as *magnetic resonance spectroscopy* where we subject the system to an external magnetic field and examine the **energy levels created in these systems by the magnetic field.** If a system is to produce a number of new energy levels under the influence of a magnetic field, it is obvious that the system itself should have some magnetic properties. For example, systems which have unpaired electrons or 'free' electrons (examples are free radicals and systems containing incompletely filled electron shells) and also systems which have some specific atomic nuclei possessing a permanent magnetic dipole moment, have magnetic properties. The former systems are termed **electron paramagnetic systems,** while the latter are called **nuclear paramagnetic systems.** We shall in this unit address ourselves to the spectroscopic study of paramagnetic nuclei, called Nuclear Magnetic Resonance or NMR and in the next unit describe the electron paramagnetic resonance spectroscopy. In essence, magnetic resonance spectroscopy deals with energy levels of atoms or molecules when these are placed in an external magnetic field.

Objectives

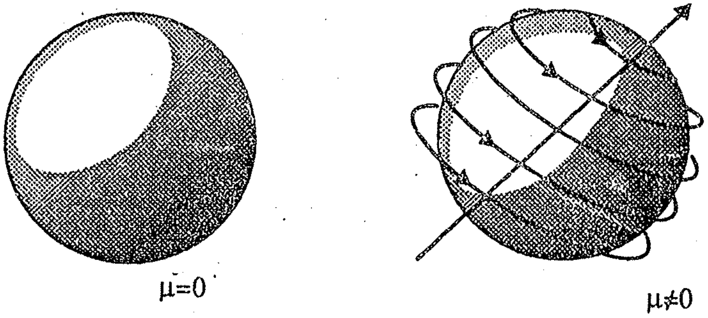
After studying this unit, you should be able to:

- predict whether a nucleus will show magnetic properties or not?
- describe the magnetic moment,
- discuss Larmor precession,
- explain the principle of nuclear magnetic resonance,
- give the schematic representation of the NMR spectrometer,
- describe relaxation phenomenon and its mechanism,
- define chemical shift,
- discuss spin-spin splitting,
- explain time domain NMR,
- describe uses of NMR spectroscopy in structure elucidation, and
- correlate the NMR spectrum of simple molecules with their structure.

10.2 MAGNETIC AND NON-MAGNETIC NUCLEI

10.2.1 Magnetic Moments

Before we describe the Nuclear Magnetic Resonance phenomenon, let us first ask ourselves why some nuclei are magnetic and why some others are not. We know from our previous background, all atomic systems as well as atoms in molecules have a nucleus at the centre with electrons occupying the extranuclear space. We also know that (in order that atoms and molecules are neutral) the nuclei are positively charged. Although **ALL** nuclei are positively charged, only some of them have, in addition, the property of "spinning". This is shown in Fig. 10.1.



Spherical nonspinning nucleus

Spherical spinning nucleus

Fig. 10.1 : A nonspinning and a spinning nucleus.

Nuclear spin is described by the spin angular momentum quantum number, I. The nuclei which exhibit NMR spectra have $I > 0$.

Given below are some generalisations for the spin quantum number of different nuclei:

(i) Nuclei having even number of protons and neutrons have $I = 0$. The examples of such nuclei are ^4He, ^{12}C and ^{16}O.

(ii) Nuclei having odd number of protons and neutrons have integral value of I. For example, ^2H and ^{14}N have $I = 1$.

(iii) Nuclei having odd value for the sum of protons and neutrons have half integral value of I. Thus ^1H and ^{15}N have $I = \frac{1}{2}$ and ^{17}O have $I = \frac{5}{2}$.

The spin characteristics of nuclei are defined by a ***spin angular momentum quantum number***, I. The magnitude of the spin angular momentum $|\mathbf{I}|$ is related to the spin angular momentum quantum number I in the following way.

$$|\mathbf{I}| = \sqrt{I(I+1)}\,\hbar \qquad \ldots(10.1)$$

Remember that we expressed the spin angular momentum of an electron by a similar expression, (Eq. 1.14b) in Unit 1, Block 1. This spin angular momentum is a vector sum of the individual spin angular momentum of the component particles of the nucleus, namely neutrons and protons. The exact way in which the neutrons and protons are vectorially coupled can be understood from nuclear shell models but this is not important for us now. If the nucleus has a spin angular momentum $\mathbf{I} \neq 0$, then this corresponds to a spinning positive charge and any spinning charge will generate a magnetic moment (μ). The magnetic moment, μ, of any nucleus is proportional to its spin angular momentum ($\mathbf{I}$) and is given by the following expression.

$$\mu = \frac{g_N e}{2m} \mathbf{I}$$

where g_N is called the **nuclear g-factor** which is characteristic of the particular nucleus, e is the charge on a proton and m is the mass of the proton. Similarly, the magnitudes of magnetic moment and spin angular momentum are thus related as follows:

$$|\mu| = \frac{g_N e}{2m} \sqrt{I \cdot (I+1)}\,\hbar \qquad \text{(Using I from Eq. 10.1)}$$

$$= g_N \beta_N \sqrt{I\,(I+1)} \qquad \text{...(10.2)}$$

where $\beta_N = \dfrac{e\hbar}{2m}$ and is called **nuclear magneton.**

Note that the quantity $\frac{g_N e}{2m}$ is called the gyromagnetic ratio, γ. Hence, we can say that

$$\mu = \gamma \mathbf{I}$$
$$= \gamma \sqrt{I(I+1)}\,\hbar$$

When the charge of the particle is positive, the magnetic moment vector ($\vec{\mu}$) and the angular momentum vector ($\vec{I}$) point in the same direction. But when the particle is negatively charged (e.g. electron), these two vectors point in the opposite direction.

SAQ 1

Calculate the value of nuclear magneton for proton.
(Given $e = 1.602 \times 10^{-19}$ C, $\hbar = 6.626 \times 10^{-34}$ J s, mass of proton $= 1.672 \times 10^{-27}$ kg)

....

....

....

....

The following table (Table 10.1) lists some of the magnetic nuclei with their spin angular magnetic quantum number I, magnetic moment μ and nuclear g_N factors. The nuclei such as ^{12}C (6 protons + 6 neutrons) and ^{16}O (8 protons + 8 neutrons) have $I = 0$ and are non-magnetic, i.e. they are not affected by a magnetic field.

Table 10.1: Properties of Some Magnetic Nuclei

Name	(% abundance)	Z	M	I	μ (in nuclear magnetons)	g_N
^{1}H	Proton (99.99)	1	1	1/2	2.7928	5.585
^{2}H	Deutron (0.01)	1	2	1	0.8574	0.857
^{13}C	Carbon (1.1)	6	13	1/2	0.7024	1.405
^{19}F	Fluorine (100)	9	19	1/2	2.6288	5.257
^{31}P	Phosphorus (100)	15	31	1/2	1.1317	2.263
^{14}N	Nitrogen (99.63)	7	14	1	+0.4038	0.403
^{15}N	Nitrogen (0.37)	7	15	1/2	−0.2831	−0.567

10.2.2 Quantization

Those nuclei which have a spin angular momentum, are therefore, associated with a magnetic moment, and can be looked at as a small bar magnet. There is, however, a very clear distinction between an ordinary laboratory bar magnet and a "nuclear spin magnet" since the latter is a quantum particle. In other words, while a bar magnet can take up any orientation when placed in an external field corresponding to a continuous variation of the potential energy (Fig. 10.2 a), the nuclear magnetic "quantum bar magnet" is allowed to take **only certain allowed** orientations. Thus, a nucleus with spin quantum number I, can take $(2I + 1)$ orientations in the external magnetic field. If the spin quantum number $I = \frac{1}{2}$, then it can take two $(2I + 1 = 2 \times \frac{1}{2} + 1 = 1 + 1 = 2)$ **orientations only in an external field.** We can easily understand the orientation of spin $\frac{1}{2}$ nuclei, in that they can either align parallel or antiparallel to the external field. No other orientation is permitted. This is schematically illustrated in the Fig. 10.2(b).

It should be noted that although the spins can be classified as parallel or antiparallel to the magnetic field, the magnetic moment vector is not completely aligned or non-aligned to the magnetic field because of the relation

$$\cos\theta = \frac{I_z}{|\mathrm{I}|} = \frac{m_I \hbar}{\sqrt{I(I+1)}\hbar} = \frac{m_I}{\sqrt{I(I+1)}}$$

where θ is the angle between the magnetic moment vector and the direction of the magnetic field. For a proton $I = \frac{1}{2}$ and $m_I = \pm\frac{1}{2}$.

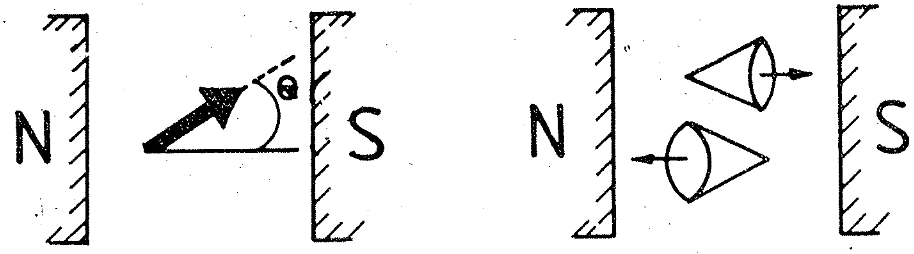
Thus,

$$\cos\theta = \frac{+\frac{1}{2}}{\sqrt{\frac{1}{2}(\frac{1}{2}+1)}} = \frac{\frac{1}{2}}{\sqrt{\frac{3}{2}}} = \frac{1}{\sqrt{3}}$$

and $\theta = 35°15'$

$$\text{and } \cos\theta = \frac{-\frac{1}{2}}{\sqrt{\frac{1}{2}(\frac{1}{2}+1)}} = \frac{-\frac{1}{2}}{\sqrt{\frac{3}{2}}} = -\frac{1}{\sqrt{3}}$$

$\therefore\ \theta = 144°45'$



$E \alpha (3\cos^2\theta - 1)$

(a)

$E = \pm g_n \beta_n B_z m_I$

(b)

Fig. 10.2: (a) The orientation of a macroscopic magnet in a field, where it can take any orientation (θ) and the energy is proportional to $(3\cos^2\theta - 1)$.
(b) The nuclear magnetic moments being quantum mechanical entities are either aligned parallel or antiparallel to the external field.

The component of the magnetic moment of the nucleus in the direction of the applied magnetic field, μ_z is given as follows:

$$\mu_z = \frac{|g_N|\, e}{2m} I_z \qquad \text{...(10.3)}$$

Eq. 10.3 can also be written as $\mu_z = \gamma I_z$

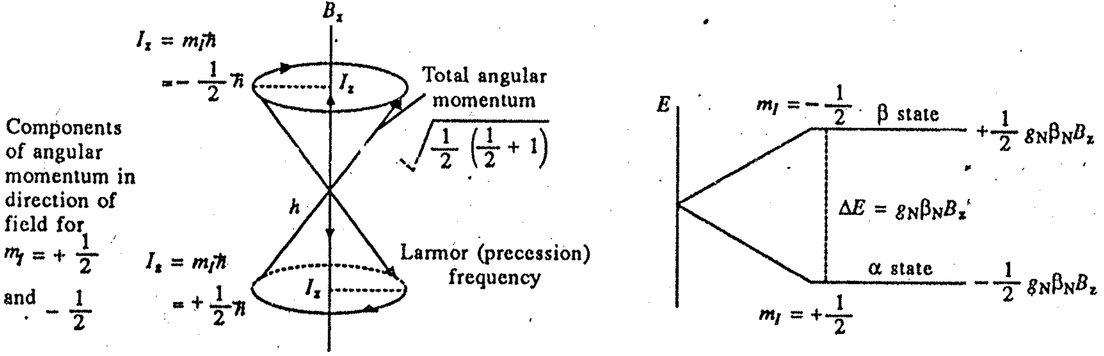
where I_z is the component of spin angular momentum in the direction of the applied magnetic field.

Also I_z can be expressed as follows:

$$I_z = m_I \hbar \qquad \text{...(10.4)}$$

Remember that you studied similar expressions for the case of electron in Unit 1, Block 1.

where m_I is the quantum number for z-component and can take values $-I$, ..., $+I$. This is illustrated in Fig. 10.3 (a).



(a)

(b)

Fig. 10.3: (a) Total angular momentum $I = \sqrt{I(I+1)}\hbar$ for $I = \frac{1}{2}$ and its components I_z ($= m_I\hbar$ for $m_I = +\frac{1}{2}$ and $-\frac{1}{2}$) in the direction of applied magnetic field.
(b) Two energy levels corresponding to $m_I = +\frac{1}{2}$ (lower level) and $m_I = -\frac{1}{2}$ (upper level).

The different values of m_I yield different values of I_z and μ_z in turn.

Thus, we can say for $I = \frac{1}{2}, m_I = -\frac{1}{2}$ and $+\frac{1}{2}$

and $\quad I_z = -\frac{1}{2}\hbar$ and $+\frac{1}{2}\hbar \qquad$ (from Eq. 10.4)

Substituting these values of I_z in Eq. 10.3, we can say that

$$\mu_z = \frac{|g_N|\, e}{2m} \times -\frac{1}{2}\hbar \text{ and } \frac{|g_N|\, e}{2m} \times \frac{1}{2}\hbar$$

$$= \frac{-|g_N|\, e\hbar}{4m} \text{ and } \frac{|g_N|\, e\hbar}{4m}$$

Using β_N for $\frac{e\hbar}{2m}$

$$\mu_z = -\frac{1}{2}|g_N|\,\beta_N \text{ and } \frac{1}{2}|g_N|\,\beta_N$$

Since the energy of the magnetic dipole in a magnetic field of strength B_z is given as

$$E = -\mu_z B_z \qquad \text{...(10.5)}$$

we get, $\quad E = +\frac{1}{2}|g_N|\,\beta_N B_z$ and $E = -\frac{1}{2}|g_N|\,\beta_N B_z$

These energy levels are shown in Fig. 10.3 (b).

$$\mu_z = \gamma I_z$$
$$= \gamma m_I \hbar$$

Hence,

$$E = -\gamma m_I \hbar \; B_z$$

For

$$m_I = \frac{1}{2}, E_\alpha = \frac{-\gamma}{2}\hbar B_z$$

$$m_I = -\frac{1}{2}, E_\beta = \frac{\gamma}{2}\hbar B_z$$

And

$$\Delta E = E_\beta - E_\alpha = \frac{\gamma}{2}\hbar B_z - \left(-\frac{\gamma}{2}\hbar B_z\right)$$
$$= \gamma \hbar B_z$$

Therefore

$$\nu = \frac{\Delta E}{h} = \frac{\gamma \hbar B_z}{h\, 2\pi}$$
$$= \frac{\gamma B_z}{2\pi}$$

In the absence of magnetic field, these two levels have the same energy and are called *degenerate.*

Note that for a proton ($I = \frac{1}{2}$), the lower spin level corresponds to $m_I = +\frac{1}{2}$ and is known as α state. The upper spin state having $m_I = -\frac{1}{2}$, is known as β state. The energy difference between these two spin states is thus given as

$$\Delta E = E_\beta - E_\alpha = \frac{1}{2}|g_N|\,\beta_N B_z - \left(-\frac{1}{2}|g_N|\,\beta_N B_z\right) = |g_N|\beta_N B_z$$

and $\quad \nu = \frac{\Delta E}{h} = \frac{|g_N|\,\beta_N B_z}{h} \qquad$ ...(10.6)

The splitting of the nuclear energy into $(2I + 1)$ levels for a nucleus of spin I is known as the **nuclear Zeeman effect** and is the primary phenomenon in NMR spectroscopy.

10.3 LARMOR PRECESSION AND RESONANCE PHENOMENON

10.3.1 Magnetic Torque and Gyration

Apart from the above understanding that the nuclear magnetic energy levels are split in a magnetic field, it is also important to understand the phenomenological description of the motion of the spins. Thus, the spin of a nucleus (proton) under the influence of an external magnetic field can either align with the field or oppose an external field. In addition to this, it shows **precessional motion.** The precessional motion of a spinning top is shown in Fig. 10.4. The top is spinning about the axis A. In addition the spinning axis A moves slowly around the vertical axis O which is the precessional motion.

Just as a spinning top experiences a gravitational torque and undergoes a precessional motion (gyroscopic motion), the spinning atomic nucleus also undergoes a precessional motion under the influence of the magnetic torque from the external magnetic field.

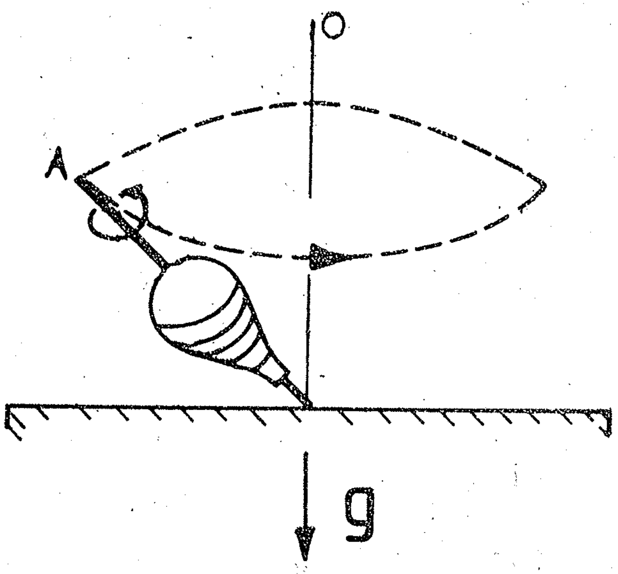


Fig. 10.4: The gyroscopic motion of a spinning top under the influence of the gravitational torque, g.

The precessional motion of a proton can take two orientatious as shown in Fig. 10.5. The lower energy orientation shows the alignment with the field and the higher energy orientation is opposed to the field.

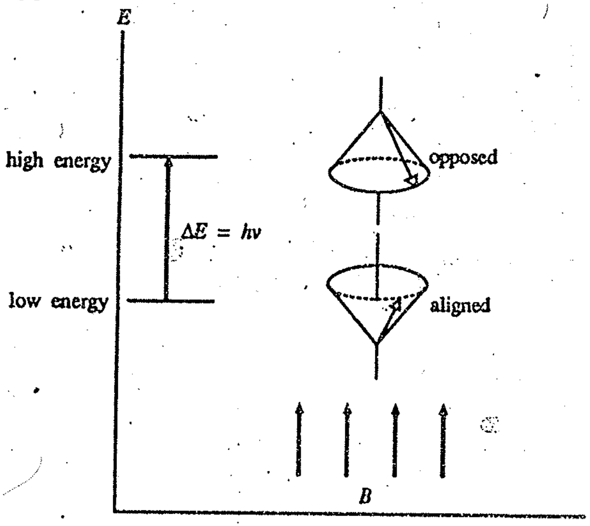


Fig. 10.5: Precession of a nucleus (proton).

The phenomenon of precession is known as *Larmor precession* and the precessional frequency is known as *Larmor frequency*.

Now we have two kinds of motion and frequencies. One, the spinning frequency (around axis A) and the second precessional frequency (around axis O). The spinning frequency does not change but the precessional frequency is proportional to the strength of the applied field. The expression for precessional frequency, ω is given below:

$$\nu = \frac{\gamma B_z}{2\pi} \text{ or } 2\pi\nu = \omega = \gamma B_z \qquad ...(10.7)$$

where γ is the gyromagnetic ratio and B_z is the strength of the applied magnetic field felt by the proton.

You may remember from unit 1, Sec 1.10 that we called ω as Larmor frequency.

If we replace γ in the above equation by $\frac{\mu}{I}$, we get

$$\nu = \frac{\mu B_z}{2\pi I}$$

Substituting the values for μ and I we can write

$$\nu = \frac{g_N \beta_N \sqrt{I(I+1)}.B_z}{2\pi\sqrt{I(I+1)}\hbar}$$

$$= \frac{g_N \beta_N B_z}{2\pi \dfrac{h}{2\pi}}$$

$$= \frac{g_N \beta_N B_z}{h} \qquad \text{...(10.8)}$$

The precessional frequencies for some of the nuclei at selected field strengths are given in Table 10.2.

Table 10.2: Precessional frequencies for some nuclei at various field strengths

B_z/T Nucleus	1.4	1.9	2.3	4.7	7.1	11.7	14.1
^1H	60	80	100	200	300	500	600
^2H	9.2	12.3	15.3	30.6	46.0	76.8	92
^{11}B	19.2	25.6	32.0	64.2	96.9	159.8	192
^{13}C	15.1	20.1	25.1	50.3	75.5	125.7	151
^{14}N	4.3	5.7	7.2	14.5	21.7	36.1	43
^{15}N	6.1	8.1	10.1	20.3	30.4	50.7	61
^{17}O	8.1	10.8	13.6	27.1	40.7	67.8	81
^{19}F	56.5	75.3	94.1	188.2	288.2	470.5	565
^{31}P	24.3	32.4	40.5	81.0	121.5	202.4	243

If you compare Eq. 10.8 with Eq. 10.6, you will note that the precessional frequency is the *same* as the frequency of separation between the two energy levels.

Let us now study the phenomenon of resonance.

10.3.2 Resonance and Nuclear Induction

The Larmor precession which you read above, provides a mechanism by which an electromagnetic radiation can interact with the spinning nucleus. If an electromagnetic radiation of frequency ν. as given by Eq. 10.6 (and is same as in Eq. 10.8) is allowed to interact with the nuclei, then the nuclei from lower energy level may absorb energy and go to the higher energy level.

In an ensemble of nuclei, they distribute themselves between the two energy levels according to the Boltzmann distribution as given below:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}}$$

Since the energies of the upper and lower levels do not differ very much, the number of nuclei occupying these levels *is also not* very different. For example, in case of protons studied using a 200 MHz instrument, the difference in the number of nuclei is *of the order of 1 in 10^5. Because of this small difference in population, the sample has* a net magnetisation M is the direction of the applied field, Fig. 10.6(a).

When

$$\Delta E = 7 \times 10^{-26}\ \text{J}$$
$$k = 1.38 \times 10^{-23}\ \text{J K}^{-1}$$
$$T = 300\ \text{K}$$
$$\frac{N_2}{N_1} \approx e^{-\frac{7 \times 10^{-26}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 300\ \text{K}}}$$
$$\approx e^{-1 \times 10^{-5}}$$
$$\approx 1 - (1 \times 10^{-5})$$

The magnetic dipole moment per unit volume is known as magnetisation.

When the radiofrequency is applied at the right angle to magnetic field, it produces a rotating magnetic field having a component in the (x–y) plane. It is necessary that the frequency of rotation of the rotating magnetic field be exactly the same as the Larmor frequency (Fig. 10.6b). Only when such a condition is met, i.e. the two

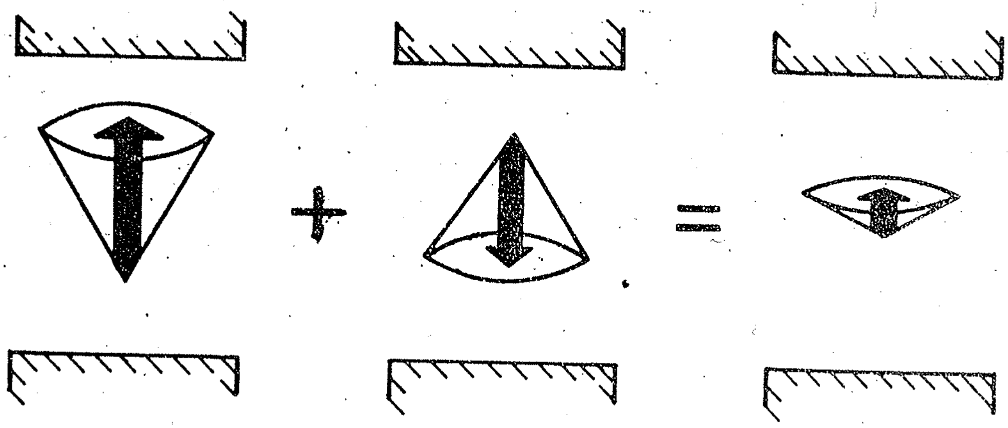


Fig. 10.6: (a) The vector sum of nuclear magnetic moments which are precessing about an axis parallel or antiparallel to the external field, leads, due to Boltzmann distribution, a net excess population in the lower energy state.

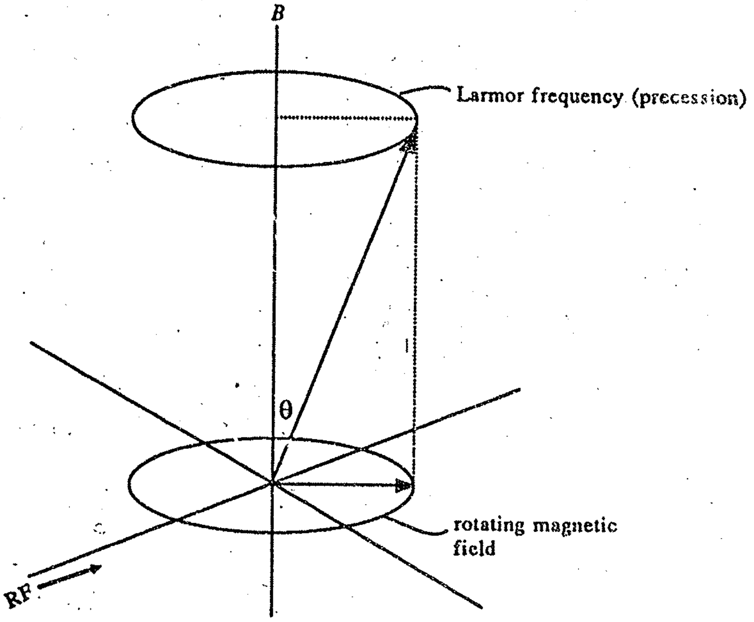
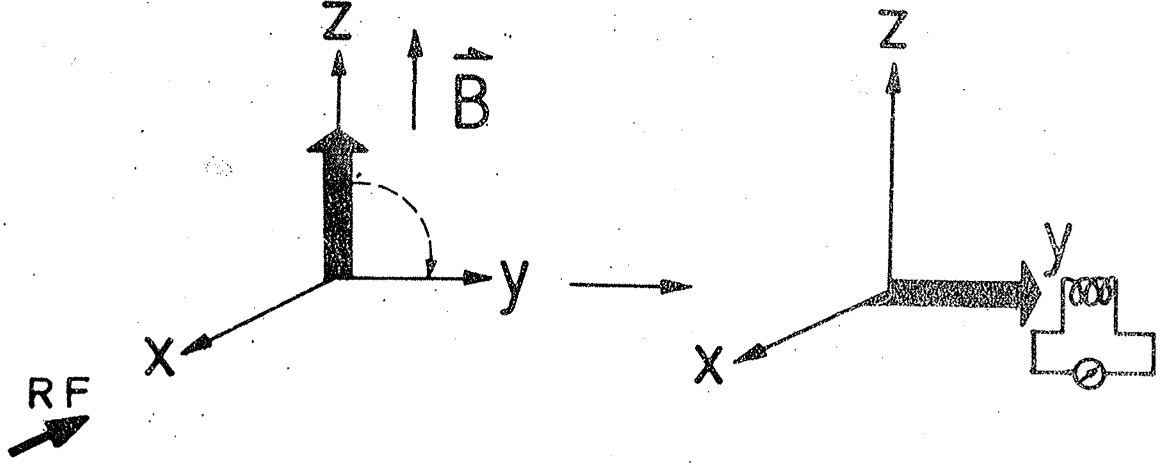


Fig 10.6 (b)

(b) Resonance will be observed when the frequency of rotating magnetic field matches with that of Larmor frequency.



(c) An rf field applied perpendicular to the magnetic field produces a torque rotating the net magnetisation from the z-axis to the transverse plane (x– y) where it can produce a nuclear magnetic induction signal in a tuned coil.

frequencies are in resonance, the nuclei will absorb energy. This is the reason why this phenomenon is called **nuclear magnetic resonance.** Hence, the condition for resonance is

$$h\nu = g_N \beta_N B_z \qquad ...(10.9)$$

The application of the radiofrequency rotates the net magnetisation into the (x–y) plane as is shown in Fig. 10.6(c). This induces a current in the tuned coil. The details of this are given in Sec. 10.4 under instrumentation. Before you study the details of instrumentation of NMR spectroscopy, it is worthwhile to understand the phenomenon of relaxation as given below.

10.3.3 Relaxation Phenomenon

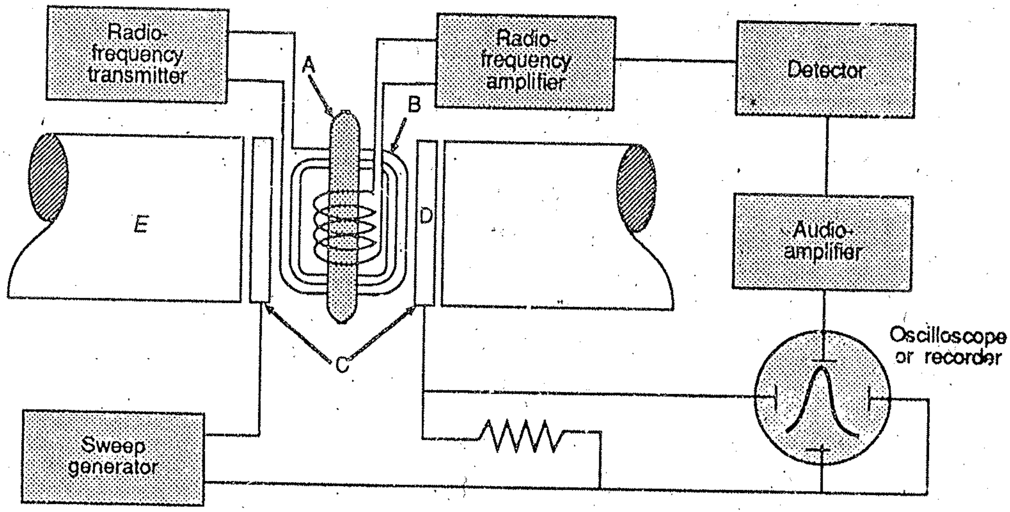
You have studied above that the population of various energy levels is governed by Boltzmann distribution. Absorption of radiofrequency radiation will disturb this distribution. Hence, after some time, the population of lower and higher levels will become equal. When this happens, no more energy will be absorbed. This situation is referred to as the **saturation** of the resonance signal. To record the NMR spectrum, it is necessary that the original equilibrium is restored. This is done by the dissipation of excess energy through **relaxation process.** Two types of relaxation processes are **spin-lattice relaxations** and **spin-spin relaxations.**

The name spin-lattice relaxation originated from the fact that earlier studies were made on solid samples where the relaxation of spin excitation energy occurs due to lattice vibrations. The random motions of the adjacent nuclei set up fluctuating magnetic fields at the nucleus leading to its interaction with the magnetic dipole of the excited nucleus. The result of this overall process is the transfer of energy from the excited nucleus to the neighbouring atoms.

The spin-spin relaxations involve the interaction of spin of one nucleus with the spins of neighbouring nuclei. For example, if there are two nuclei, then one nucleus can flip up and the other can flip down by mutual exchange of spins.

10.4 RECORDING OF NMR SPECTRUM

The schematic representation of an NMR spectrometer is shown in Fig. 10.7.



A, sample tube; B, transmitter coil; C, sweep magnet; D, receiver coil; E, main magnet

Fig. 10.7 : Schematic representation of an NMR spectrometer.

The components of an NMR spectrometer include a magnet, a radiofrequency source and a detection system in addition to the recording device. The sample whose NMR spectrum is to be recorded is dissolved in a suitable solvent and placed in a glass tube

A very small amount of sample is required for recording the NMR spectrum.

having 15 cms length and 0.5 cm diameter. The sample tube is placed between the poles of a magnet. The sample tube is spun to ensure that a uniform magnetic field is experienced by all the nuclei of the sample. When the radiofrequency is applied, the nuclei absorb energy which is detected and recorded. Two alternatives are available here. We can either keep the frequency constant and vary the magnetic field to know the position of resonance or we can keep the magnetic field strength constant and vary the frequency and record the resonance position.

The solvents used for recording NMR spectrum are CCl_4, $CDCl_3$, C_6D_6, d_6 −DMSO, D_2O, $(CD_3)_2SO$.

Modern NMR spectrometers are of Fourier transform type. They are very sensitive and can be used to record the NMR spectra of a variety of nuclei. You will study more about this technique in Sec. 10.11.

In most NMR spectrometers, the frequency is kept fixed and the magnetic field is varied till the resonance condition is reached.

Till now you were studying the principle behind NMR spectroscopy and its instrumentation. Let us now study the reason why this technique is so important to the chemists.

10.5 THE CHEMICAL SHIFT

So far what we have talked about nuclei holds good only when they are bare. For bare nuclei the resonance condition is as given by Eq. 10.9, i.e. $h\nu = g_N \beta_N B_z$.

It implies that all the nuclei of a given type (for example, hydrogen atoms) in a sample should absorb the energy corresponding to the above ν value. If such had been the case, the NMR spectroscopy would have been of no use to the chemists. In real systems, however, the nuclei are surrounded by extranuclear electrons and these can modify the external field by either shielding or deshielding the nucleus.

The circulating electrons produce an induced magnetic field which opposes the applied field (B_z). Hence, the magnetic field experienced by the nucleus (B_{eff}) is given by the following equation:

$$B_{eff} = B_z - B_{induced} \qquad ...(10.10)$$

The induced field is proportional to the applied field and is given by the following expression:

$$B_{induced} = \sigma B_z \qquad ...(10.11)$$

where σ is the shielding constant.

Substituting the value of $B_{induced}$ from Eq. 10.11 into Eq. 10.10, we get

$$\begin{aligned} B_{eff} &= B_z - \sigma B_z \\ &= B_z (1 - \sigma) \qquad ...(10.12) \end{aligned}$$

Note that for an unshielded proton $\Delta E = h\nu = g_N \beta_N B_z$

Hence $\nu = \frac{g_N \beta_N B_z}{h}$

Similarly, for a shielded proton

$\Delta E' = h\nu' = g_N \beta_N B_z (1-\sigma)$

Hence, $\nu' = \frac{g_N \beta_N B_z (1-\sigma)}{h}$

Thus, $\nu' = \nu (1-\sigma)$

Thus, in presence of the extranuclear electronic environment, the resonance condition has to be modified as:

$$h\nu = g_N \beta_N B_z (1 - \sigma) \qquad ...(10.13)$$

This is shown in Fig. 10.8.

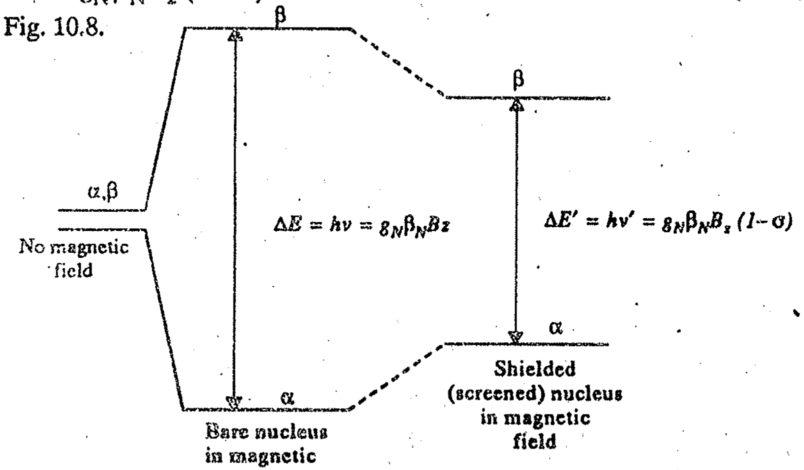


Fig. 10.8 :

Fig. 10.8: Modification of nuclear Zeeman level splitting as a result of electronic shielding.

Positive value of σ means that the nuclei are *shielded* by the electronic environment, while negative σ corresponds to *deshielding* of the nucleus. When shielding occurs, the B_{eff} is **less** than B_z, hence B_z must be increased to bring the nucleus in resonance. On the other hand when deshielding occurs, B_{eff} is more than B_z, resulting in the resonance at **lower** field. Thus, due to shielding (or deshielding) identical nuclei (e.g. H) which have different chemical environment (in other words, different electron density) resonate at **different** values of the applied field. These values being characteristic can be used to identify various types of environment in which the nucleus is present. Since the shift in the position of resonance is due to difference in **chemical** environment, it is called **chemical shift.** Since we cannot measure the NMR of bare nuclei we have to use some reference standard with respect to which we can measure the extent of shielding or deshielding of the external field in various chemical environments. (This is very similar to the choice of the standard hydrogen electrode as the reference for defining electrode potentials of various half-cells in Electrochemistry).

The reference chosen is the molecule Tetramethyl silane, $(CH_3)_4$ Si (TMS). The choice of TMS as reference is due to the fact that it contains 12 protons per molecule, all of which are chemically equivalent. With the consequent high specific proton concentration TMS will give strong NMR absorption even in dilute solutions. Secondly the protons in TMS are highly shielded and hence occur at "higher fields" compared to protons of most organic compounds. This will make the TMS resonance non-interfering with test spectra.

Since the protons of TMS are more shielded as compared to those of most organic compounds, the chemical shift for most organic compounds is a positive number.

Unit of Chemical Shift

Suppose we measure a test sample and TMS using the same magnetic field B_z, the resonance conditions are given by

$$h\nu_{\text{Test}} = g_N \beta_N B_z (1 - \sigma_{\text{Test}}) \qquad \text{...(10.14)}$$

$$h\nu_{\text{TMS}} = g_N \beta_N B_z (1 - \sigma_{\text{TMS}}) \qquad \text{...(10.15)}$$

Thus

$$h\nu_{\text{Test}} - h\nu_{\text{TMS}} = g_N \beta_N B_z (1 - \sigma_{\text{Test}}) - g_N \beta_N B_z (1 - \sigma_{\text{TMS}})$$

$$h(\nu_{\text{Test}} - \nu_{\text{TMS}}) = g_N \beta_N B_z [1 - \sigma_{\text{Test}} - (1 - \sigma_{\text{TMS}})]$$

$$h(\nu_{\text{Test}} - \nu_{\text{TMS}}) = g_N \beta_N B_z [- \sigma_{\text{Test}}] \qquad \text{...(10.16)}$$

By definition $\sigma_{\text{TMS}} = 0$ (Reference)

If we measure the same two samples (Test and TMS) by doubling the field then,

$$2h(\nu_{\text{Test}} - \nu_{\text{TMS}}) = 2g_N \beta_N B_z (- \sigma_{\text{Test}}) \qquad \text{...(10.17)}$$

Now the frequency difference between test and reference gets *doubled*. In order to represent shifts in a universal manner we have to quote these shifts **independent** of the strength of the field. This is achieved by dividing the shift in field (constant frequency measurement) or shift in frequency (constant field measurement) by the respective spectrometer field or frequency and represent it by δ. This makes the shift dimensionless, but makes it a very small value since the shift in field or frequency is nearly 10^6 times smaller than the measuring field or frequency. Therefore, we multiply this dimensionless constant by 10^6 and express it in terms of parts per million (ppm). Thus the chemical shift, δ can be given as

$$\delta = \frac{\nu_{\text{Test}} - \nu_{\text{TMS}}}{\text{Spectrometer frequency}} \times 10^6 \text{ ppm}$$

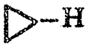
$$= \frac{B_{z_{\text{TMS}}} - B_{z_{\text{Test}}}}{\text{Spectrometer field}} \times 10^6 \text{ ppm} \qquad \text{...(10.18)}$$

Note that there is a change of signs when we use field (B) instead of frequency (ν) in Eq. 10.18.

Table 10.3 shows the chemical shifts for protons in some classes of organic compounds.

Remember that the chemical shift values for protons are related to the electron density around the atom to which they are bonded. If the electron density is high, then the protons are shielded from the magnetic field and hence higher magnetic field is to be applied to achieve resonance. Protons having smaller values of chemical shift are said to appear at **upfield** as compared to those which have higher chemical shift values and are said to appear **downfield**. But you should not forget that both these types of protons are still appearing downfield with respect to TMS.

Table 10.3: Chemical Shifts of Common Proton Groups.

Functional Group		δ
Organometallic	RCH_2M	–1.2–0.1
Cyclopropyl		0.2
Methyl	$-CH_3$	0.9
Methylene	$-CH_2-$	1.3
Tertiary	R_3C-H	1.5
Allylic	$-C=C-CH_2-$	1.7
Alkyne	$-C\equiv C-H$	2-3
Benzylic	$Ar-CH_2-$	2.3-3
Vinyl	$-C=C-H$	4.5-6.0
Aromatic	$Ar-H$	6-8.5
Amino	$RC\underline{H_2}NH_2$ $R-NH_2$	2.0-2.8 1-5
Alkyl halides	$R-CH_2-X$	2-4
Ketones	$R-CH_2-CO-R$	2-2.7
Alcohols	$RC\underline{H_2}-OH$ $R-OH$	3.4-4 1-5
Ethers	$R-O-CH_2-R$	3.3-4
Esters	$R-CO-OCH_2-R$ RCH_2-COOR	3.7-4.1 2-2.2
Aldehydic	$RCO-H$	9-10
Carboxylic acids	$R-COOH$	10-12
Enolic	$-C=C-OH$	15-17

SAQ 2

The chemical shift of protons in a test sample occurs at 2 ppm. What is the difference in Hz between TMS and test proton resonances when measured in a 100 MHz spectrometer and in a 200 MHz spectrometer?

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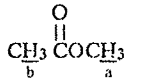
From here onwards, we will focus our discussion mainly on the ^1H – NMR, or proton NMR as hydrogen is present in most of the organic molecules and hence a study of ^1H–NMR helps in their structure elucidation. Before that let us see how does an NMR spectrum look like?

10.6 PRESENTATION OF THE NMR SPECTRUM

Remember that chemically equivalent protons absorb at the same δ value.

The NMR spectrum is recorded on a chart paper. It has at its botton δ scale (in ppm) with δ values increasing from right to left. The 0 (zero) δ value corresponds to TMS. TMS when added as an internal standard to the solution of the sample whose NMR spectrum is to be recorded, shows a signal (peak) at 0 δ as shown in Fig. 10.9. The *lower* δ value means an *upfield chemical shift* and indicates that the proton whose signal appears in this region has high electron density around it. Similarly the *higher* the value of δ for a particular signal, the *higher* the deshielding and *lower* the electron density around the proton giving that signal. Thus, as said earlier, chemically (or magnetically) different protons will show signals at different δ values. Hence, by counting the number of signals, you can say how many chemically different protons are present in the molecule of the sample.

Besides showing the **number** of different kinds of protons, the ^1H – NMR spectrum also tells **how many** protons of each kind are present in a molecule. This is shown by the intensity of the signal. The intensity of a signal is measured in terms of the **area** under that peak. The area under an NMR signal is directly proportional to the number of protons giving rise to that signal. This area is measured by an electronic integrator and is recorded by the instrument on the spectrum as a stepped curve. The height of each step can be counted by counting the number of squares on the graph.


$\underset{b}{\underline{CH_3}}\,\overset{\overset{O}{||}}{C}O\underset{a}{\underline{CH_3}}$

In the light of the above discussion, let us go through Fig. 10.9. It shows *two signals* indicating that *two kinds of hydrogens* are present in methyl acetate.

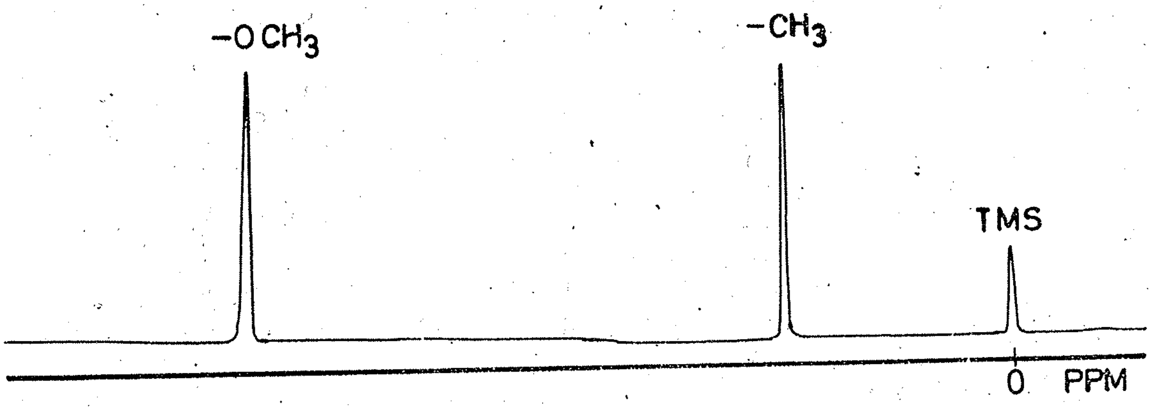


Fig. 10.9: The NMR spectrum of methyl acetate (not drawn to scale) showing two peaks from the two chemically different methyl groups and the TMS at 0 ppm.

One signal is due to the hydrogen atoms of the methyl group attached to the oxygen and the other signal is due to the methyl group attached to the carbonyl group. These two sets of hydrogens are non-equivalent and can be represented by a,b,c..... etc.

The two signals are of equal intensity because the number of protons responsible for them is equal (3 in this case).

Besides giving the above information, the NMR spectrum of a compound can tell how many different protons are present on the neighbouring carbon atom of a particular proton. This is explained in the next section.

Before that attempt the following SAQ to check your understanding of the above concepts.

SAQ 3

Identify the chemically different set of protons in $(CH_3)_2$ CHCHO and label them using letters, a,b,c .... etc.

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10.7 SPIN-SPIN COUPLING

Apart from the phenomenon of chemical shift, protons which are on adjacent atoms can also indirectly interact with each other depending upon the nature and number of the bonds between them. This can be illustrated by studying a portion of the NMR spectrum of a compound having two protons on adjacent carbons as shown in Fig. 10.10.

Protons on adjacent carbons are known as *vicinal* protons.

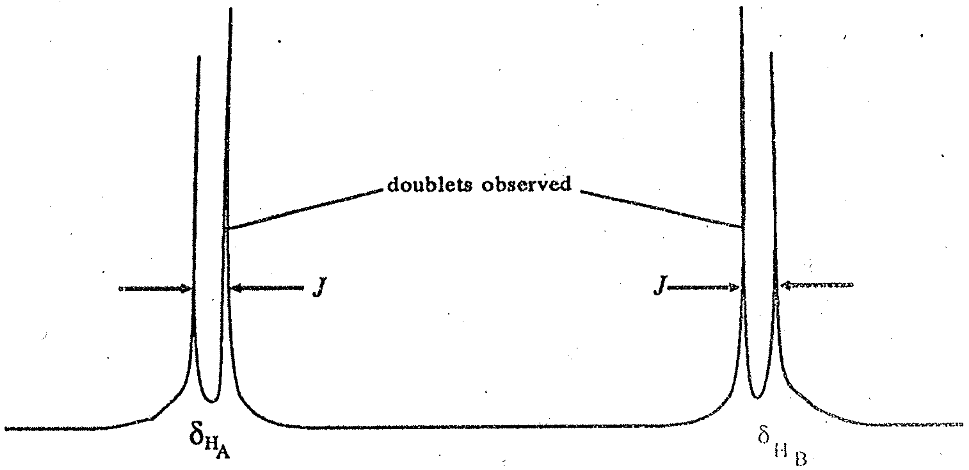


Fig. 10.10 Splitting in the signals of two vicinal protons.

Let the two protons present on the adjacent carbon atoms be represented as H_A and H_B. These two protons when present in different magnetic environments resonate at different position and hence show different values of chemical shifts. The signal due to each proton is split into a *doublet*. This can be explained as follows. For H_A, there are two possibilities of spin orientations of H_B. The spin of H_B can be either aligned (parallel) to H_A or opposed to H_A. In roughly half of the molecules, the spin of H_B is parallel to H_A and in rest half, it is opposed to H_A. In one case H_A proton is deshielded and in other it is shielded. Thus, H_A experiences two different magnetic fields and resonates at two different positions resulting in a doublet in the NMR spectrum. Similarly, H_B also yields a doublet.

Let us consider one more example, i.e. the NMR spectrum of ethanal as shown in Fig.10.11.

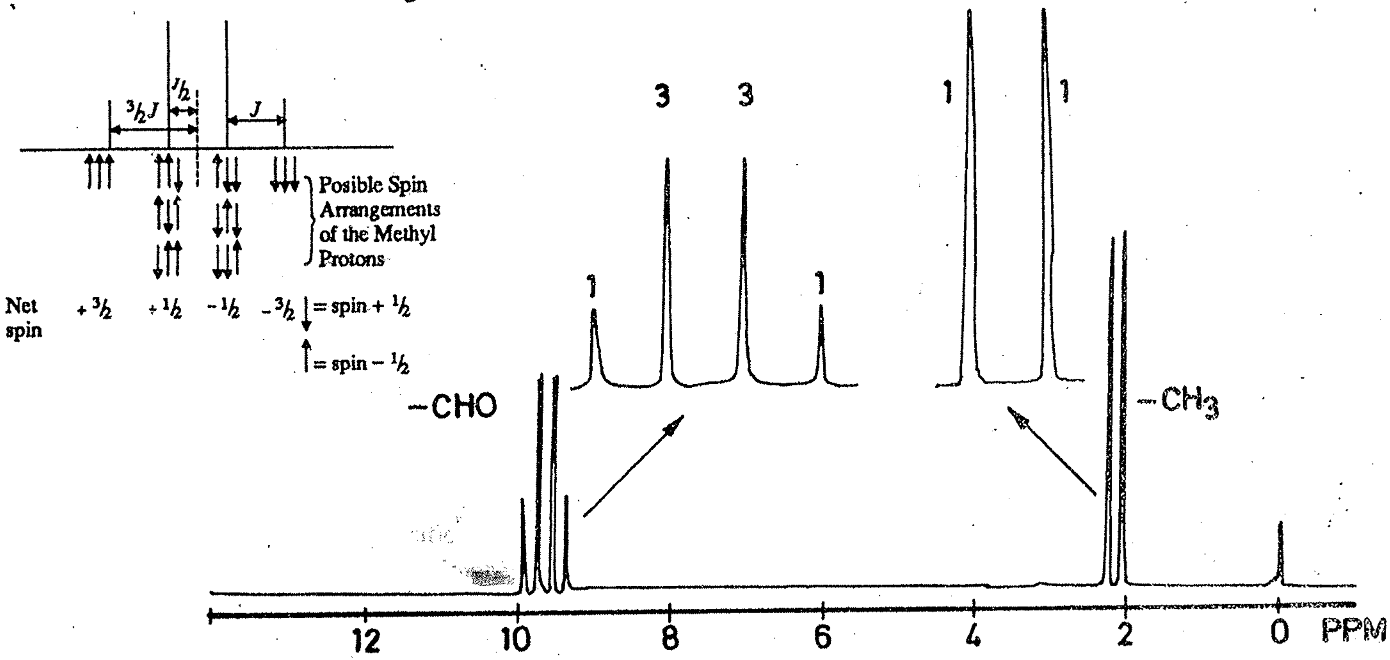


Fig. 10.11: NMR spectrum of ethanal. The spectrum shows a signal at δ 2.12 ppm due to the CH_3 group being split into a doublet due to spin-spin coupling to the aldehyde proton and a quartet at δ 9.9 ppm from the aldehyde proton due to coupling to methyl protons; inset shows the multiplets in expanded scale.

The spectrum consists of two groups of lines. The group occurring at δ 9.9 ppm comes from the aldehyde proton while the lines occurring at δ 2.12 ppm are from the methyl group. The relative intensities of these lines are in the ratio 1:3. However, the aldehyde resonance(lines)occur as an equally spaced quartet (four lines) with relative intensity 1:3:3:1 with a spacing of 3 Hz in between them.

This fine structure or splitting of lines is due to the indirect coupling between aldehyde proton and the methyl protons. This is called *spin-spin coupling* and can be understood as due to a small magnetic field produced at the site of the aldehyde proton by various statistical distributions of the *spin* orientation of the methyl protons. There are three methyl protons and their spins can be aligned parallel or antiparallel to the field as is shown in Fig. 10.12.

STATISTICAL DISTRIBUTION OF ORIENTATIONS

TOTAL SPIN QUANTUM NO. (M_I)	METHYL PROTONS (as seen by CHO proton)			RELATIVE WEIGHTAGE
3/2		↑ ↑ ↑ ($\alpha\alpha\alpha$)		1
1/2	↑ ↑ ↓ ($\alpha\alpha\beta$)	↑ ↓ ↑ ($\alpha\beta\alpha$)	↓ ↑ ↑ ($\beta\alpha\alpha$)	3
–1/2	↓ ↓ ↑ ($\beta\beta\alpha$)	↓ ↑ ↓ ($\beta\alpha\beta$)	↑ ↓ ↓ ($\alpha\beta\beta$)	3
–3/2		↓ ↓ ↓ ($\beta\beta\beta$)		1
	ALDEHYDE PROTON (as seen by CH_3 protons)			
1/2		↑ α		1
–1/2		↓ β		1

Fig. 10.12: **The origin of spin-spin coupling multiplets and their relative intensities. The eight possible orientations of the spin of three methyl protons leads to total spin quantum numbers of 3/2, 1/2, –1/2 and –3/2 with a statistical weight ratio of 1:3:3:1 leading to a quartet splitting of the aldehyde resonance in this ratio. Similar arguments will lead to a 1:1 doublet of the methyl protons by aldehyde proton. If we denote spins with $m_I = +\frac{1}{2}$ by α and those with $m_I = -\frac{1}{2}$ with β, we get notations for the spin orientations as given in brackets.**

The statistical distribution of the methyl proton orientations leading to net m_I (total) of 3/2, 1/2, –1/2, –3/2 has the weightage 1:3:3:1. While the $m_I = 3/2$ configuration can provide a local field, say, of $3/2\,J$, the others will provide $\pm\, 1/2\,J$ and $-3/2\,J$, so that the aldehyde proton will give now four resonances relative to the position of chemical shift (in the absence of coupling) at $\pm 3/2\,J$ and $\pm 1/2\,J$ with intensities 1:3:3:1 and separation J. Thus the aldehyde resonance occurs as a quartet of intensity 1:3:3:1. Here J is known as the **coupling constant** and is measured in Hz.

We now look at the effect of aldehyde proton on the methyl resonance; the former can be either parallel or antiparallel ($m_I = +\frac{1}{2}$ or $-\frac{1}{2}$) giving rise to local field of $\pm J/2$. Thus the methyl resonance is split into a doublet of separation $J = 3$ Hz with equal intensities. Spin-spin coupling can range between few Hz to tens of Hz depending on the hybridization of the bonds involved and the number of bonds intervening the two coupled nuclei under consideration.

On similar grounds, an ethyl group will give a quartet (1:3:3:1) for the methylene resonance and a triplet (1:2:1) for the methyl resonance. This is shown in the NMR spectrum of ethanol in Fig. 10.13.

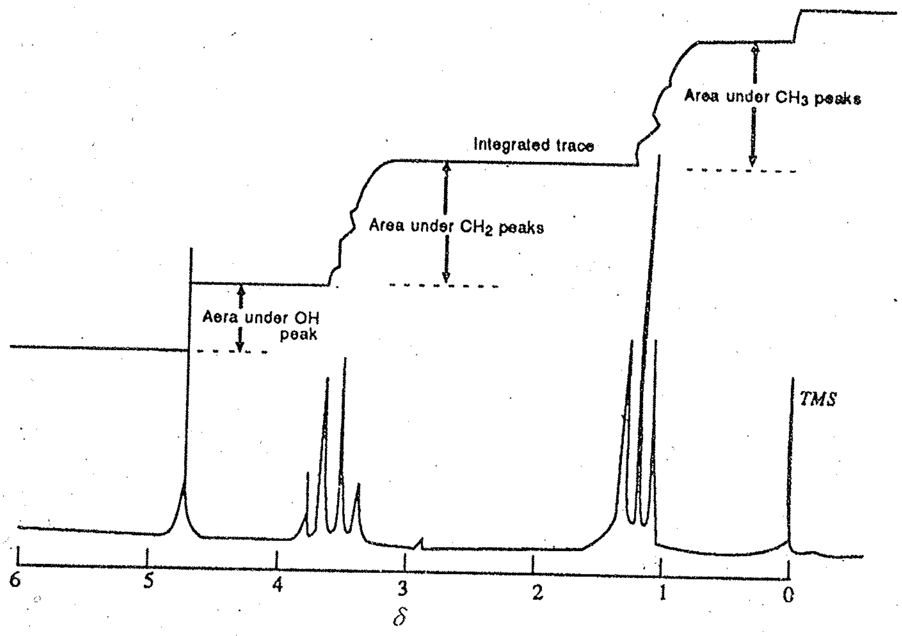
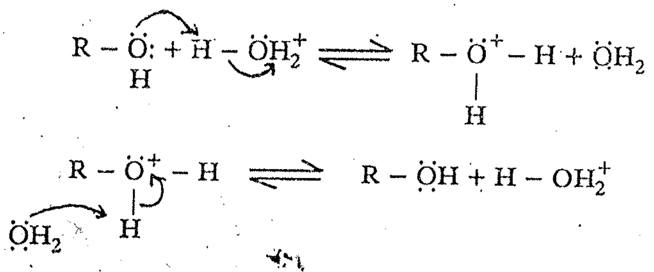


Fig. 10.13 : The NMR spectrum of a solution of ethanol. The methyl and methylene groups are mutually coupled giving a triplet (1:2:1) and quartet (1:3:3:1) respectively, while the OH group, due to rapid exchange does not show any spin-spin coupling with neighbouring protons and no splitting of the signals is observed due to the –OH proton.

The ^1H – NMR spectrum of ethanol was discussed in unit 4 of CHE –05 (Organic chemistry) course also.

If any atom in the molecule undergoes rapid exchange in the intra-or intermolecular way (exchange between solutes or between solvent and solute), then the coupling between the exchanging and rest of the nuclei is averaged to zero. Thus an aqueous solution of alcohol will give spin-spin coupling pattern for the methyl and methylene protons by mutual coupling, while the OH group which undergoes rapid exchange with the solvent water molecules will appear as a single line.

Chemical Exchange



$$R-\underset{H}{\ddot{O}}: + H-\ddot{O}H_2^+ \rightleftharpoons R-\underset{H}{\overset{}{\dot{O}^+}}-H+\ddot{O}H_2$$

$$R-\underset{H}{\dot{O}^+}-H \quad \ddot{O}H_2 \rightleftharpoons R-\ddot{O}H+H-OH_2^+$$

In general, we can say that for n equivalent protons coupled to a particular set of protons, spin-spin coupling leads to splitting of the signal of this set into $(2nI + 1)$

lines with the intensities given by the coefficients of the bionominal expansion of $(x+1)^n$. For ^{1}H – NMR, I for a proton $= \frac{1}{2}$ leading to $2nI + 1 = 2 \times n \times \frac{1}{2} + 1 = n + 1$. Thus, in ^{1}H – NMR spectrum, n equivalent protons will split a signal into $n + 1$ lines. This is shown below in the form of Pascal triangle in Fig.10.14.

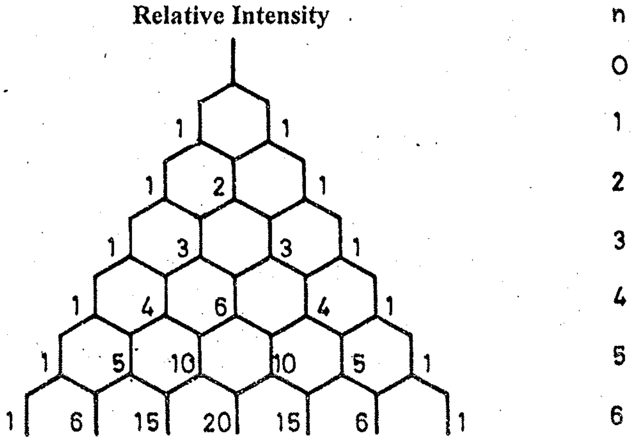
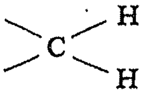
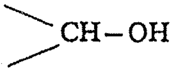
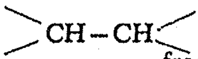
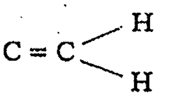
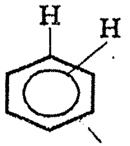
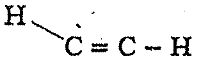
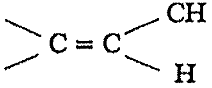
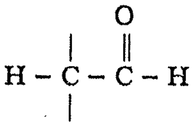
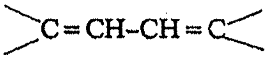
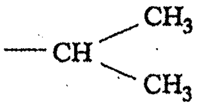
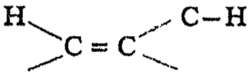


Fig. 10.14: The relative intensities of the spin-spin splitting multiplets for n coupled equivalent protons.

Spin-spin coupling patterns are also transferable between molecules. Thus whenever a molecule contains an ethyl group, the quartet-triplet pattern (as shown for ethyl alcohol) will appear in the NMR spectrum. Table 10.4 lists some characteristic spin- spin coupling constants.

Table 10.4 : Spin-spin coupling constants

Type of compound	J, (Hz)	Type of compound	J, (Hz)
	12-15		5
 (free rotation)	6-8		0-3
	(o) 8 (m) 2-3 (p) 0-1		(cis) 6-14 ($trans$) 11-18
	4-10	 $H-\overset{\vert}{\underset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-H$	1-3
	10-13	Cyclohexane	(a-a)8-9 (a-e) 2-3 (e-e) 2-3
H–C–C≡C–H	2-3		6–7
$-CH_2-CH_3$	7		–2

SAQ 4

How many resonances will occur in the proton NMR of isopropyl chloride and what will be the nature of the spin-spin coupling ?

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$CH_3\overset{Cl}{C}HCH_3$

Isopropyl chloride

SAQ 5

An organic compound with molecular formula C_8H_{10} gives three NMR signals at 7 ppm (singlet), 2.4 ppm (quartet) and 1.2 ppm (triplet) with relative intensities 5:2:3. Identify the compound.

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10.8 FACTORS AFFECTING CHEMICAL SHIFT

(i) Electronegativity of the groups present

Let us study the NMR spectrum of 1,1,2-trichloroethane (Cl_2CHCH_2Cl) as shown in Fig. 10.15.

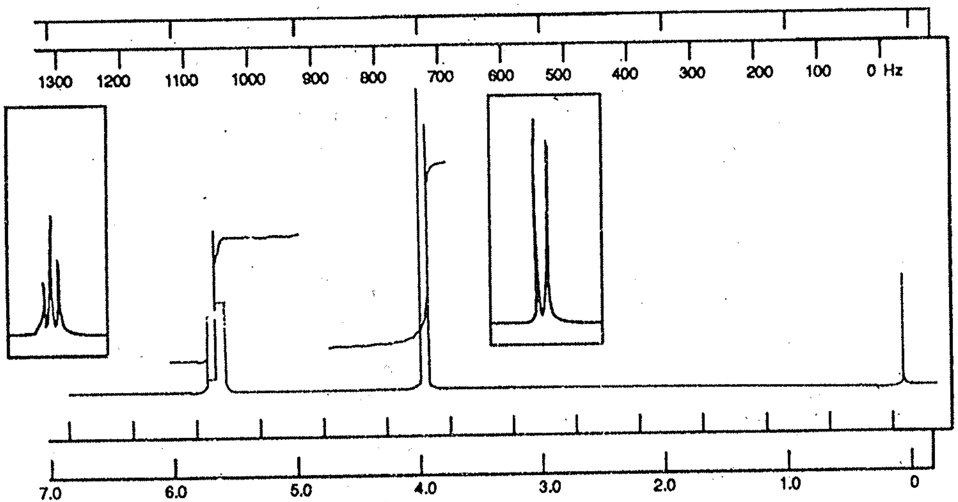


Fig. 10.15 : NMR spectrum of 1,1,2-trichloroethane.

The spectrum shows two groups of signals. The signal due to $C\underline{H}_2$ protons is of double intensity as compared to that for $C\underline{H}$ protons. The signal due to $-C\underline{H}_2$ protons is split due to the adjacent $-C\underline{H}$ proton into a doublet as per the $n + 1$ rule. Similarly, the signal due to $-C\underline{H}$ proton is split into a **triplet** due to two protons of the adjacent

$-CH_2$ group. Also the signal due to $-CH$ protons appears downfield as compared to the signal due to $-CH_2$ proton because the two chlorine atoms attached to the carbon bearing this hydrogen withdraw electrons due to their inductive effect and deshield the proton to a larger extent as compared to the single chlorine atom present on the other carbon atom.

Similarly, the NMR spectrum of ethyl bromide as shown in Fig. 10.16. shows **one triplet** due to methyl protons and one **quartet** due to methylene ($-CH_2$) protons.

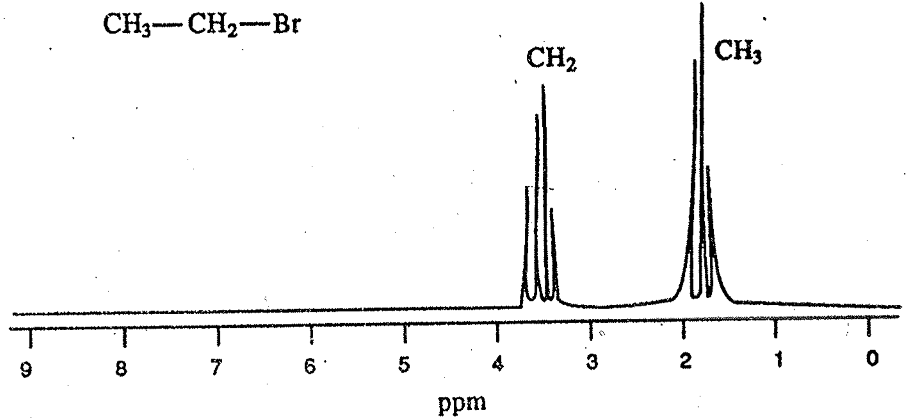


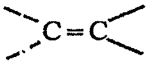
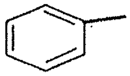
Fig. 10.16 : NMR spectrum of ethyl bromide.

In addition to the *electronegativity* of the groups, the other factor which influences the position of the chemical shift is **magnetic anisotropy.**

(ii) **Magnetic Anisotropy**

Anisotropy means difference in a property depending upon the direction. Thus, anisotropic properties have unequal value in different directions. Various functional groups present in organic molecules containing multiple bonds show this behaviour.

Various classes of organic compounds having multiple bonds are given below:

(i)		alkenes
(ii)	$-C\equiv C-$	alkynes
(iii)	$C=O$	carbonyl compounds
(iv)		aromatic compounds

In these molecules, the circular motion of π electrons in the presence of applied magnetic field, generates an induced magnetic field. The induced magnetic field opposes the applied magnetic field in the centre of the molecule. But it reinforces the applied magnetic field outside the region of π electrons. This is shown in Fig. 10.17.

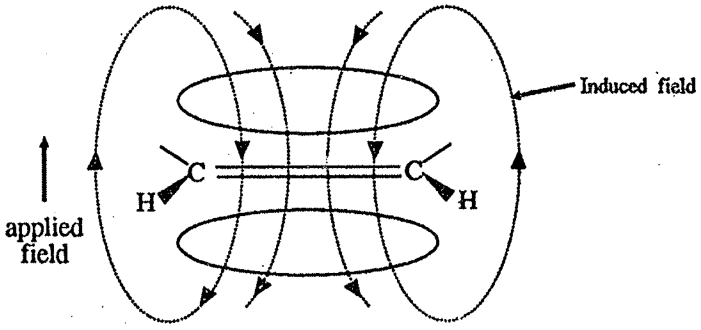
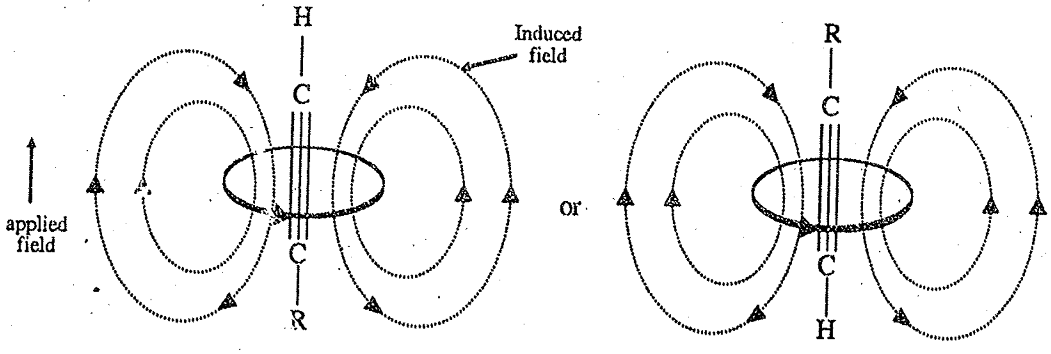


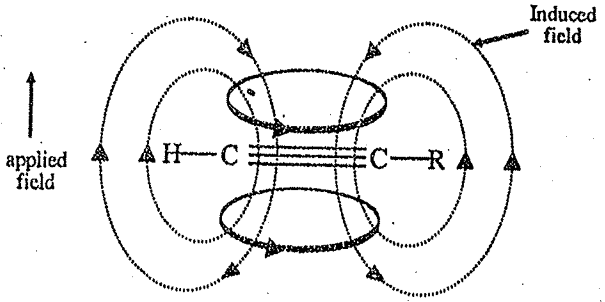
Fig. 10.17 : Direction of induced magnetic field

Thus the H atoms attached to the double bond are **deshielded** and appear downfield in the NMR spectrum at δ 4-8 ppm.

But in case of alkynes, the protons appear *upfield* because the region in which they lie has induced field opposite to the magnetic field, see Fig. 10.18 given below. They appear in the range δ 1.5-3.5.



Shielding of acetylenic protons by a triple bond in parallel orientation to the applied field



Shielding of acetylenic protons by a triple bond perpendicular to the applied field

Fig. 10.18: Direction of induced magnetic field in alkynes.

The aromatic protons of benzene are similar to the protons of the double bond. The direction of the induced magnetic field is shown in Fig. 10.19 for aromatic ring. The aromatic protons are deshielded and appear in the region δ 6-9.

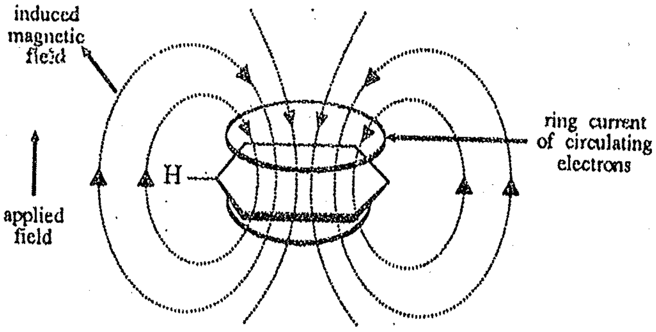


Fig. 10.19 : Effect of ring current in benzene π-system increases effective magnetic field at the proton.

10.9 SPIN DECOUPLING

It is also possible to decouple the spin-spin coupling between two groups of resonances (signals) by sweeping the spectrum while simultaneously applying a second constant frequency at the resonance position of one of the groups. This irradiation scrambles the population of various orientations leading to a net zero magnetization from this group and the spin-spin coupling to this group is decoupled. Spin decoupling can be used to identify the connectivities between groups of spins. This is shown below in Fig.10.20.

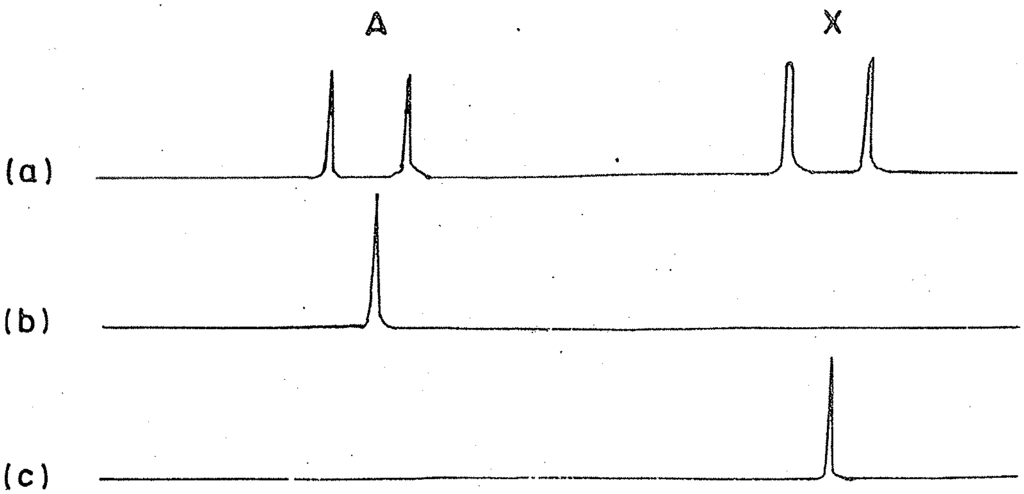


Fig. 10.20: (a) NMR spectrum of a two spin (A and X) system: both A and X showing a doublet coupling pattern. (b) When X nucleus is irradiated and the spectrum measured, resonance of A appears as a singlet since coherent irradiation at X frequency decouples it from the A nucleus. (c) When A nucleus is irradiated and the spectrum measured, X appears as a singlet.

10.10 NMR OF NUCLEI OTHER THAN PROTONS

Other nuclei such as ^{31}P, ^{19}F and ^{13}C can also be studied by NMR. Both ^{31}P and ^{19}F have $I = \frac{1}{2}$ and are 100% abundant in this state. Their spectra can be measured in the same ways as for protons. ^{31}P and ^{19}F compounds can be analysed in terms of their characteristic chemical shifts and spin-spin coupling to neighbouring nuclei.

However as far as ^{13}C is concerned, it is very difficult to obtain good spectra due to the following reasons. The natural abundance of ^{13}C is only 1.1% and the remaining ^{12}C isotope is non-magnetic. Besides, the magnetic moment is $\frac{1}{4}$ of that of a proton. It can be shown that in a given magnetic field, the sensitivity of NMR detection is proportional to the (Resonance frequency)^3 × abundance. ^{13}C spectra are approximately 1/6400 times weaker than proton spectra for identical molar concentrations, so that normal detection by field sweep or frequency sweep gives practically no spectrum. One can measure isotopically enriched ^{13}C compounds, but these are prohibitively expensive. The way to circumvent this difficulty is to resort to the practice of time domain NMR and Fourier transform techniques, which we shall very briefly and in a qualitative manner describe below.

10.11 TIME DOMAIN NMR

Normally we let the ensemble of molecules in a strong magnetic field and sweep the radio-frequency slowly, so that sequentially different chemically shifted protons are brought to resonance and we obtain the spectrum as a function of frequency. This sequential way of obtaining spectrum subjects the system to a single monochromatic radiation at a time and searching for NMR absorption. In order to obtain well resolved spectrum, we have to sweep the frequency slowly giving sufficient time for the recorder to react. Typically several minutes or even hours will be required to record one spectrum, even when the concentration of the spins are high.

However, if we subject the system to a radiofrequency "pulse" (i.e., a high power radiofrequency source is electronically pulsed-switched on and off-within a time interval of a few microseconds), it can be shown mathematically as well as in reality that this sudden "gating" of the radiofrequency can produce a wide range of spectral distribution in a single shot. By pulsing the radiofrequency transmitter, we produce and subject all nuclei, irrespective of their chemical shifts, simultaneously to a broad spectrum of frequencies leading to the so called "multichannel excitation". It is possible, therefore, to simultaneously "tip" all different chemically shifted nuclei into the *x-y* plane in a very short time (much less compared to spin-lattice and spin-spin relaxation). The resulting magnetization vectors will induce current simultaneously in the receiver coil which will produce a time varying signal from each and every different type of nuclei at their characteristic frequencies. The resulting induced signal known as *free induction decay* (FID) will gradually decay in a sinusoidal fashion depending on chemical shift, spin-spin coupling and spin-spin relaxation. This time-domain signal when mathematically Fourier transformed will produce the full NMR spectrum that would otherwise be obtained by the conventional way of slowly sweeping the frequency through the entire spectrum. Schematically this is shown in Fig. 10.21.

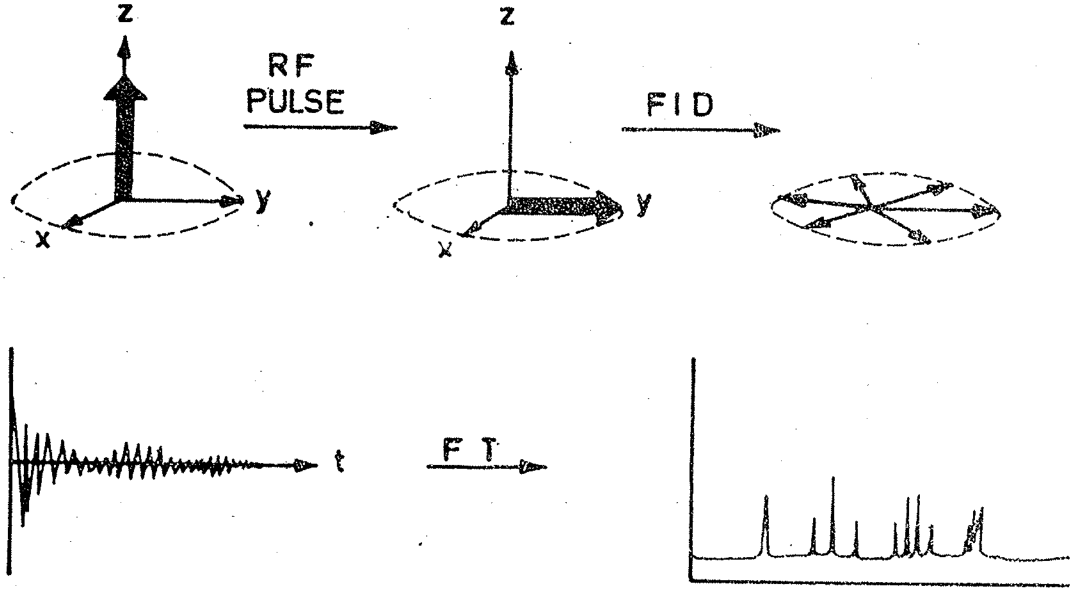


Fig. 10.21: Schematic representation of the pulse NMR method. An intense RF pulse applied close to resonance will bring all nuclei into resonance irrespective of their chemical shifts. All these precessing magnetic moments will produce a free induction decay signal (FID) which upon Fourier transformation will produce the full spectrum which would otherwise be obtained by a slow scan of the spectrum.

The whole process which corresponds to multichannel excitation followed by multichannel detection can be accomplished in a few seconds. This process can be repeated several hundred times and spectra coherently added to produce a good signal to noise ratio even from ^{13}C or ^{1}H at micromolar concentrations. In the pulsed Fourier transform method it can be shown that while the signal from nuclear resonances will add linearly proportional to the number of co- added spectra, the noise being a random process will only add proportional to the square root of the number of co-added spectra.

Thus if a ^{13}C spectrum has a signal to noise ratio of 1:1 (i.e., the signal cannot be distinguished from noise) after co-adding one hundred spectra we get a meaningful spectrum, of signal to noise ratio of 10. This is illustrated in Fig. 10.22.

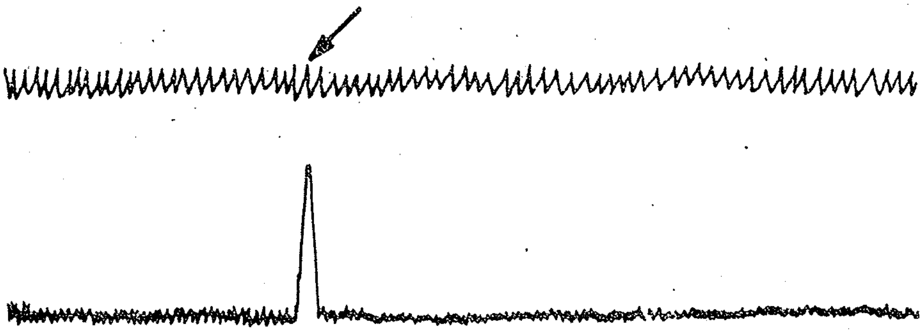


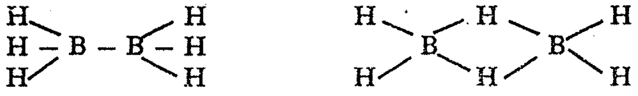
Fig.10.22: Schematic representation of the dramatic improvement in the signal to noise ratio from 1:1 (top spectrum) to nearly (10:1 when 100 spectra are co-added).

With the advent of commercially available pulse– FT spectrometers, almost all magnetic nuclei in the periodic table, irrespective of their magnetic moment and low natural abundance, are now accessible for NMR study.

Let us now study some analytical applications of NMR study.

10.12 REPRESENTATIVE EXAMPLES WITH ANALYTICAL APPLICATIONS

The NMR spectrum of B_2H_6, diborane, gives two groups of resonances for protons. The two possible structures for diborane are shown in Fig. 10.23.



(a) (b)

Fig. 10.23 : Two possible structures for diborane, B_2H_6. The NMR results will show that structure (b) is correct.

Structure (a) contains two equivalent BH_3 units and is expected to give a single resonance (all protons are equivalent), while structure (b) has two bridged protons and four terminal protons and is expected to give two different resonances, as observed. Hence structure (b) is supported by NMR.

The spectrum of *N, N*-dimethylnitrosoamine shows two different methyl resonances at room temperature and at high temperatures it shows only one resonance corresponding to the middle point of the room temperature spectrum. This can be understood as follows. At room temperature, there is only restricted rotation about the *N–N* bond so that statistically 50% of methyl groups are *trans* to N = O bond. Therefore, the methyl groups (a) and (b) have different chemical shifts. When free rotation sets in at high temperatures, the two methyl groups interchange rapidly between *cis* and *trans* configurations, so that on a "time average" they are identical and neither is *cis* or *trans* leading to an equivalence and a single transition, (see Fig. 10.24).

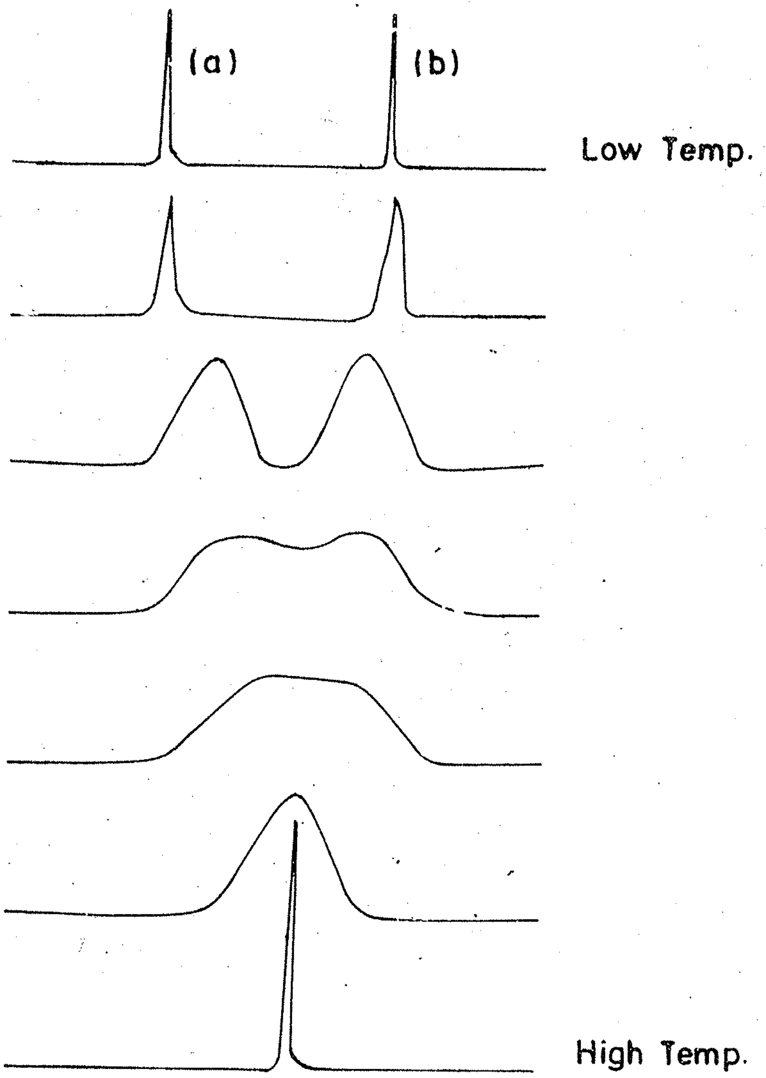
The rate of rotation of C-N bond, k is given as

$$k = \frac{1}{2\tau}$$

where τ is the mean lifetime of a particular configuration and can be measured at any temperature. The activation energy ΔE for rotation can then be calculated using the Arrhenius equation

$$\ln k = !\ A - \frac{\Delta E}{RT}$$

where A is a constant characteristic of the reaction.



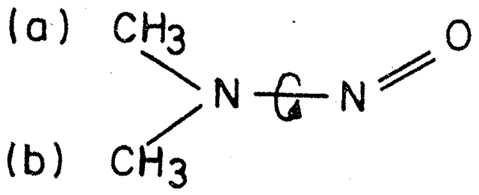


Fig. 10.24: The effect of hindered internal rotation and subsequent free rotation about the N-N bond in N, N-dimethylnitrosoamine as a function of temperature. At low temperature, the two methyl groups appear as two distinct peaks. As the rotation sets in, they undergo slow exchange leading to broadening of the lines, and when the exchange frequency is higher than the shift difference (in the static spectrum) they are no longer distinguishable.

10.13 SUMMARY

In this unit, you studied about the magnetic behaviour of common nuclei. Then the principle of NMR spectroscopy was discussed. The details of instrumentation were described followed by relaxation phenomenon. A detailed account of chemical shift and spin-spin interactions was presented. The NMR spectrum of nuclei other than hydrogen was briefly introduced. Due emphasis was given on the time domain NMR keeping in view its importance in the recent times. Finally, some examples illustrating the use of NMR spectroscopy were taken.

10.14 TERMINAL QUESTIONS

1. Predict qualitatively the NMR of propargyl bromide, $HC \equiv CH - CH_2 - Br$ if the spin-spin coupling is 2.7 Hz.
2. Predict the nature of the ^{31}P and ^{1}H spectrum of trimethyl phosphine, $(CH_3)_3P$, if the coupling between ^{31}P and ^{1}H is 8 Hz.

3. Predict the nature of the NMR spectrum for the isomers of butyl chloride, assuming coupling only between protons on adjacent carbons.

10.15 ANSWERS

Self Assessment Questions

1.
$$\beta_N = \frac{e\hbar}{2m} = \frac{(1.602 \times 10^{-19}\ \mathrm{C})\ (6.626 \times 10^{-34}\ \mathrm{J\ s})}{2 \times 2\pi \times 1.672 \times 10^{-27}\ \mathrm{kg}}$$
$$= 5.050 \times 10^{-27}\ \mathrm{J\ T^{-1}}$$

2. The chemical shift $\delta = 2$ ppm

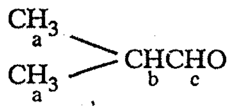
By definition

$$2 = \frac{\nu_{\mathrm{TEST}} - \nu_{\mathrm{TMS}}}{\text{spectrometer frequency}} \times 10^6$$

At 100 MHz

$$\Delta\nu = \frac{2 \times 100 \times 10^6}{10^6} = 200\ \mathrm{Hz}$$

Similarly, for 200 MHz, $\Delta\nu = 400$ Hz

3.

$\underset{a}{CH_3}\,\underset{a}{CH_3} > \underset{b}{CH}\underset{c}{CHO}$

4. Isopropyl chloride has the formula $(CH_3)_2\,CHCl$. The two methyl groups are identical, while the CH group is different. Therefore, there are two groups of resonances. The resonance from the two methyl groups will give a 1:1 doublet through coupling with the CH proton. The resonance of CH proton will be split into a seven line pattern (septet) whose relative intensities are 1:6:15:20:15:6:1 (refer to Fig. 10.14).

5. The peaks at δ 2.4 and δ 1.2 ppm consisting of a quartet and triplet are from an ethyl group. The peak at δ 7 ppm corresponds to protons attached to a benzene ring. From the relative intensities, if there is one ethyl group, then there is one C_6H_5 group. Together the molecule is likely to be ethyl benzene. If it is so, the molecular formula is $C_6H_5CH_2CH_3 = C_8H_{10}$. Hence, the compound is ethyl benzene.

Terminal Questions

1. Propargyl bromide contains two types of protons. The $\equiv C\underline{H}$ protons are like in acetylene and will occur at δ 2.2 ppm and the $-C\underline{H}_2\,Br$ protons will occur around δ 3.68 ppm. The $C\underline{H}_2$ resonance will occur as a doublet (1:1) and the CH resonance as a triplet (1:2:1). The splitting between the doublet and triplet is 2.7 Hz.

2. The ^1H–NMR spectrum will give a resonance corresponding to a single chemical shift due to all three equivalent methyl groups, split into a doublet with a spacing of 8 Hz due to P, with intensities 1:1.

The ^{31}P spectrum will give a resonance corresponding to chemical shift of ^{31}P split into 10 lines from 9 equivalent protons of methyls with intensity distribution given by 1:9:36:84:126:126:84:36:9:1.

3. Normal butyl chloride, $CH_3 - CH_2 - CH_2 - CH_2 - Cl$ will give four resonances. The methyl group will give triplet (from adjacent $-CH_2$, the next methylene will be a triplet of quartet (4 × 3), the next methylene will be a triplet of triplet (3× 3), and the last methylene adjacent to Cl will give a triplet.

Isobutyl chloride will give a single resonance from two equivalent methyls, split into a doublet (CH), the CH group will give a resonance split into a septet of triplets (7 × 3) and the last CH_2 group will give a doublet.

Tertiary butyl chloride, $(CH_3)_3 - C - Cl$, will give a single line from three equivalent methyls and there will be no spin-spin coupling.

UNIT 11 ELECTRON SPIN RESONANCE SPECTROSCOPY

Structure

1.1 INTRODUCTION

In the last unit, you have studied about the Nuclear Magnetic Resonance (N.M.R.) Spectroscopy. We hope that you have clearly understood the principle of N.M.R. spectroscopy and other concepts explained there. We assume that you can apply the knowledge gained about N.M.R. spectroscopy in structure elucidation of simple molecules.

Similar to the nuclei of some atoms, the free or unpaired electrons have spin and show magnetic properties. Thus, systems containing unpaired electrons can be studied by a technique, called Electron Spin Resonance (E.S.R.) spectroscopy in a manner similar to N.M.R. spectroscopy. Therefore, we will reuse here some of the concepts of Unit 10.

In this unit, we will first introduce you to the principle behind E.S.R. spectroscopy. Then we will familiarise you with the instrumentation. After that you will know how an ESR spectrum looks like? We will then discuss nuclear hyperfine interaction using simple examples. Finally we will focus our attention on the applications of ESR spectral studies.

Objectives

After studying this unit, you should be able to:

- discuss the principle behind ESR spectroscopy,
- give the condition for absorption of radiation in ESR spectral studies,
- describe salient features of instrumentation used in ESR spectrum recording,
- explain nuclear hyperfine splitting in simple radicals,
- give the significance of *g* values, and
- illustrate the use of ESR spectral studies in the structure elucidation of some simple molecules.

11.2 PRINCIPLE

Similar to the case of a nucleus having spin and magnetic moment, the electron has spin and magnetic moment. When the electron is kept in a magnetic field, the magnetic dipole precesses about the axis of the applied field with the frequency called *Larmor precession* similar to the case of a nucleus. Parallel to the treatment of NMR, here also there are two spin states differing in energy. When an electromagnetic radiation of suitable frequency is applied, the transition from one spin state to another takes place.

You may recall that an electron has both orbital angular momentum and spin angular momentum. However, in case of molecules, only the constributions from spin angular momentum are important. Within a molecule, there are strong internal electric fields directed along the chemical bonds. In a diatomic molecule such a field is directed along the inter-nuclear axis. This internal field holds the orbital angular momentum of the electrons in fixed orientations. They cannot line up with an external magnetic field and their contribution is not significant. Thus, orbital angular momentum is said to be quenched. Thus, the major contribution comes from spin angular momentum.

Similar to NMR spectroscopy, for an assembly of unpaired electrons, the ratio of electron population in two levels is given by Boltzmann distribution and is expressed as $\frac{N_\alpha}{N_\beta} = e^{-\Delta E/RT}$

The ratio of populations in two energy levels are calculated by substituting the ΔE values in the above equation and here also the lower energy level is slightly more populated. It is this excess population which is responsible for the net upward transitions resulting in the phenomenon of electron spin magnetic resonance. Thus, the following species may show an ESR spectrum:

(i) Free radicals having odd number of electrons

(ii) Odd electron molecules, e.g. NO, NO_2, ClO_2 etc.

(iii) O_2 in triplet state

(iv) Some transition metal complexes, organometallic compounds and catalysts containing metal ions having incomplete *3d, 4d* or *5d* orbitals

(v) Rare earths and actinides having incomplete *4f, 6d* , etc. orbitals

(vi) Some impurities

SAQ 1

Which of the following would show an ESR spectrum?

(i) $\cdot\, CH_3$ (ii) N_2 (iii) CO_2 (iv) $\cdot\, C_6H_6^-$

....

....

11.3 THE FUNDAMENTAL EQUATION

You are aware from Unit 1, Block 1 that an electron has spin which can be designated by the spin quantum number, *s*. The spin quantum number has a value of $\frac{1}{2}$. You may also recall that the magnitude of the spin angular momentum $|\vec{s}|$ of the electron can be represented as

$$|\vec{s}| = \sqrt{s(s+1)}\,\hbar$$

If we substitute $s = \frac{1}{2}$ in the above equation, we get

$$s = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar = \sqrt{\frac{1}{2} \times \frac{3}{2}}\,\hbar = \frac{\sqrt{3}}{2}\,\hbar$$

You are also aware that this spin angular momentum (s) of the electron can have its components (s_z) in the direction of the magnetic field (in the z direction) which are half integral multiples of $\hbar$, i.e.

$$s_z = m_s \hbar$$

where m_s can take values $+\frac{1}{2}$ and $-\frac{1}{2}$.

The magnetic moment of the electron $|\mu_e|$ can also be expressed as follows

$$|\vec{\mu}_e| = \gamma \vec{s}$$

You are also aware from Sec. 10.2, (Unit 10) that a spinning charge generates a magnetic moment. The magnetic moment of the electron μ_e is related to its spin angular momentum (s) by the following equation.

$$\left|\vec{\mu}_e\right| = -\frac{g_e e}{2m}\left|\vec{s}\right|$$

Note that the negative sign indicates that the magnetic moment vector is in the opposite direction to that of the angular momentum vector.

Substituting the value of s from above equation, we get

$$\left|\mu_e\right| = -\frac{g_e e}{2m}\sqrt{s(s+1)}\,\hbar$$

$$\left|\mu_e\right| = -\frac{g_e e \hbar}{2m}\sqrt{s(s+1)} = -g_e \beta_e \sqrt{s(s+1)} \qquad \text{...(11.1)}$$

where

β_e is the *Bohr magneton* and is equal to $\frac{e\hbar}{2m}$. Here, e and m are the charge and mass of the electron, respectively.

g_e is a dimensionless constant and is called the electron g factor. It has a value 2.00232 for a free electron.

You may remember that in Unit 10, a similar equation, Eq. 10.1, was used for the case of a nucleus. From Eq. 11.1, the component of the magnetic moment in the direction of the field (μ_z) will be related to the component of the angular momentum in the z direction (m_s) by the following equation.

$$\mu_z = -g_e \beta_e m_s \qquad \text{...(11.2)}$$

[illegible]

$$E = -\gamma m_s \hbar B_z$$

The interaction of the magnetic moment (μ_z) with the applied field of strength B_z applied along z axis is given by their product.

$$\text{Interaction} = E = -\mu_z B_z \qquad \text{......(11.3)}$$

$$= g_e \beta_e m_s B_z \quad \text{(using Eq. 11.2)}$$

The value of Bohr magneton can be calculated by substituting the values for the various constants.

$$\beta_e = \frac{e\hbar}{2m_e}$$

$$= \frac{(1.602\times10^{-19}\ \text{C})(6.626\times10^{-34}\ [illegible])}{2\times2\pi\ [illegible]}$$

$$= \frac{(1.602\times10^{-19}\ \text{C})(6.626\times10^{-34}\ \text{J s})}{4\times3.14\ (9.109\times10^{-31}\ \text{kg})}$$

$$= 9.274\times10^{-24}\ \text{C J s kg}^{-1}$$

$$= 9.274\times10^{-24}\ \text{A s J s kg}^{-1}$$

$$= 9.274\times10^{-24}\ \text{A s}^2\ \text{J kg}^{-1}$$

$$= 9.274\times10^{-24}\ \text{J T}^{-1}$$

$$1\ \text{T} = 1\ \text{kg s}^{-2}\ \text{A}^{-1}$$

T represents tesla, the SI unit of magnetic flux density.

Remember that m_s can take values from $+s$, ..., $-s$. For a single electron, $s = \frac{1}{2}$ and $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$. Corresponding to the two values of m_s as $+\frac{1}{2}$ and $-\frac{1}{2}$, the two values of energy can be obtained using Eq. 11.3 as follows.

$$E = +\frac{1}{2} g_e \beta_e B_z \quad (\text{for } m_s = +\tfrac{1}{2}) \qquad \text{...(11.4)}$$

and

$$E = -\frac{1}{2} g_e \beta_e B_z \quad (\text{for } m_s = -\tfrac{1}{2})$$

Thus, the electron spin has two energy states in a magnetic field. These energy states are shown in Fig. 11.1.

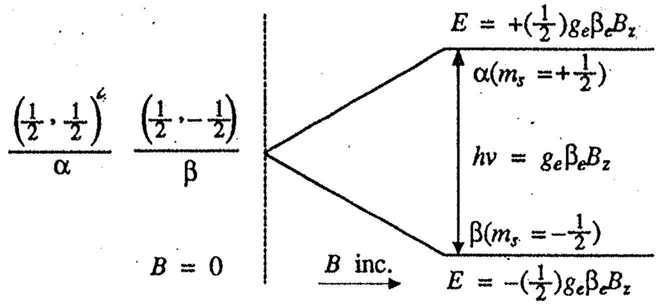


Fig. 11.1: Two energy levels of an electron in the presence of magnetic field.

You can see in Fig. 11.1 that the lower energy state corresponds to $m_s = -\frac{1}{2}$ which is in contrast with the case of nuclei about which you studied in Unit 10. This lower energy state is represented by β and can be designated by its quantum numbers (s, m_s) as $\left(\frac{1}{2}, -\frac{1}{2}\right)$. In this state, the magnetic moment is *parallel* to the applied field. Similarly, the higher energy state can be denoted by α and can be designated by quantum numbers $\left(\frac{1}{2}, \frac{1}{2}\right)$. In this state, the magnetic moment is *antiparallel* to the applied field.

In the absence of the magnetic field, the two states (α and β) have the same energy and are said to be *degenerate*.

Note that the basic equations for ESR follow the same pattern of NMR.

It is also evident from Fig. 11.1 and Eq. 11.4 that the energy difference between the two states is as given below:

$$\Delta E = g_e \beta_e B_z \qquad \text{.......(11.5)}$$

Application of an electromagnetic radiation (oscillating field) perpendicular to the applied field B_z, induces transitions from the lower to the higher energy state provided the following resonance condition is satisfied:

$$h\nu = \Delta E = g_e \beta_e B_z \qquad \text{.........(11.6)}$$

where ν is the frequency of the applied radiation.

From Eq. 11.6, we can say that

$$h\nu = g_e \beta_e B_z$$

$$= \frac{g_e e \hbar}{2m} B_z$$

$$= \gamma \hbar B_z$$

and

$$\nu = \frac{\gamma \hbar B_z}{h}$$

$$= \frac{\gamma h B_z}{h \cdot 2\pi}$$

$$= \frac{\gamma B_z}{2\pi}$$

Eq. 11.6 shows that the energy separation between the two levels and hence frequency of the radiation absorbed (ν), is proportional to the applied field, (B_z). Therefore, you may say that e.s.r. spectra can be studied by using the radiation of any frequency provided we use the appropriate applied field. Most commonly, fields of 0.34 T and 1.25 T are used. The corresponding frequencies for the free electron being 9.5×10^9 Hz and 35×10^9 Hz.

Spectrometer frequency (ν/Hz)	
X-band	9.5×10^9
K-band	23×10^9
Q-band	35×10^9

1 GHz = 10^9 Hz

So the frequencies mentioned on R.H.S can also be written as 9.5 GHz, 23 GHz and 35 GHz.

The frequency 9.5 GHz lies in the X-band of the microwave region and the frequency 35 GHz lies in the Q band of the microwave region. The details of instrumentation of an ESR spectrometer are given in the next section.

To test yout understanding of the above discussion, try the following SAQ.

SAQ 2

A specimen of ZnO shows a strong esr line at the frequency 9.45 GHz. Calculate the g-value of the line.

....

....

11.4 ESR SPECTROMETER

The layout of ESR spectrometer is shown in Fig 11.2, you can see that the ESR spectrometer is similar to the NMR spectrometer in principle. You can see in Fig. 11.2 that the source of microwave radiation is klystron. The radiation obtained from source is channeled through a waveguide to the sample which is kept in the magnetic field. When the transitions between spin levels take place, the energy from the microwave radiation is absorbed. The absorbed radiation is then detected by a phase-sensitive detector and the spectrum is recorded as a derivative spectrum. Let us study next section to know what do we mean by a derivative spectrum.

The ESR spectrometer is similar to an NMR spectrometer. But since the Bohr magneton (β_e) of an electron is about 10^3 fold larger than that for the nuclei, the frequency required for the ESR experiment falls in the microwave region of the electromagnetic radiation instead of radiofrequency region as was the case for an NMR experiment. Also the ESR spectra are not represented as absorption curves (as is the case with NMR spectra) but as derivative curves.

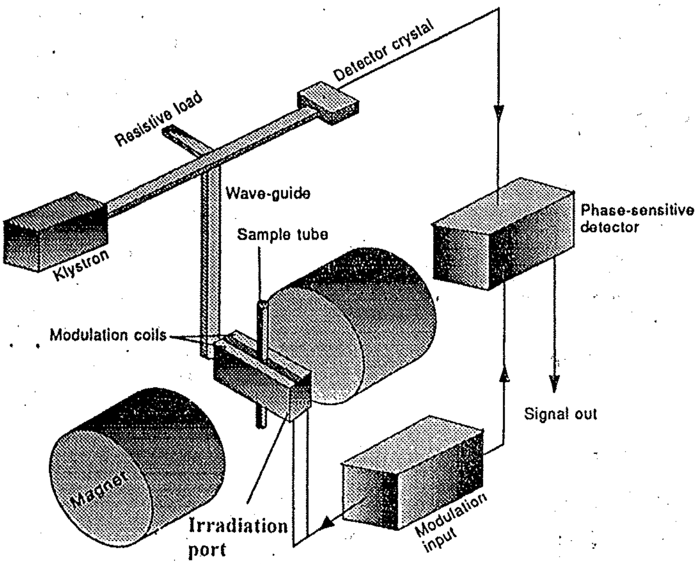


Fig. 11.2: The ESR spectrometer.

11.5 PRESENTATION OF THE ESR SPECTRUM

The ESR spectrometer operates at a fixed microwave frequency and the magnetic field is swept. The ESR spectra are not presented as absorption curve which was the case for NMR spectrum but as derivative curves as said earlier. The first derivative (i.e. slope) of the absorption curve is plotted against the strength of the magnetic field. Such a comparison of spectral presentation is shown in Fig. 1.3. Fig. 1.3 (a) shows an absorption curve whereas Fig. 1.3 (b) shows the derivative curve.

ESR Spectrum can be recorded for gases, solutions, powders, single crystals and frozen solutions.

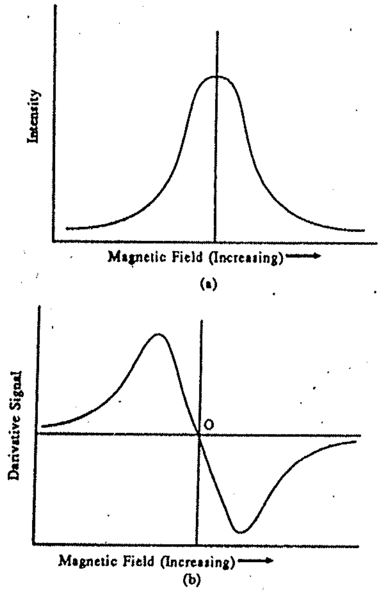


Fig. 1.3: (a) An absorption curve.
(b) A derivative curve.

In case of an ESR spectrum, the absorption signal is broad and it is difficult to know the point of maximum absorption. The recording of spectra as a derivative is useful because it helps to identify the point of maximum absorption which is obtained as a point of intersection of two lines. This point is shown as point O in Fig. 1.3 (b). We will now discuss the ESR spectrum of some simple systems.

11.6 THE ESR SPECTRA OF SOME SIMPLE SYSTEMS

If the applied magnetic field (B_z) is the only magnetic field acting on the unpaired electron, the ESR spectrum would show a single line with a frequency specified in terms of the g value (as given by Eq. 11.6, $h\nu = g_e \beta_e B_z$)

Such is the case of the ESR spectrum of SO_3^- anion where *no magnetic nuclei* are present and the observed spectrum is a single line.

You have studied in Unit 10 that coupling between the nuclear spins (spin-spin coupling) causes a splitting of the nuclear magnetic energy levels resulting in the splitting of signals in NMR spectra. Similarly when the magnetic nuclei are present in the system, the spin of the electron interacts with the magnetic moments of the nuclear spin. This leads to the splitting of the spectral line into a number of lines and is known as the *nuclear hyperfine interaction.*

Note that the positive values ($+\frac{1}{2}$) of spin quantum number (m_s for electron and m_I for nucleus) are designated as α and negative values ($-\frac{1}{2}$) are represented by β. Thus, we can represent the energy levels obtained after hyperfine splitting by specifying their (m_s, m_I) values or using α, β notation. The subscripts e and p in α_e, β_e and $\alpha_p \beta_p$ denote electron and proton, respectively. A third way of representing the spin of an electron or a proton and thus specifying various energy levels is, by using arrows as ↑ or ↓. This notation was used in Unit 10, Fig. 10.10.

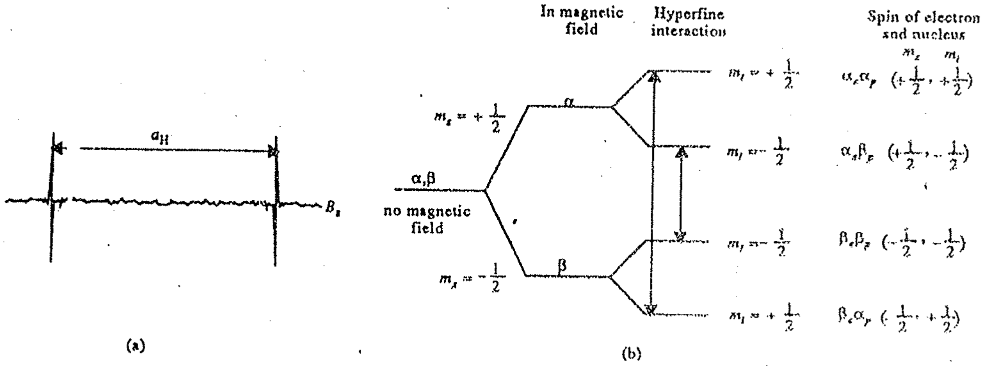
1T = 10^4G

Note that the hydrogen atom represents the case of an interaction between an electron and a single proton in the magnetic field.

Let us study the case of hydrogen atom to understand hyperfine interaction.

11.6.1 ESR spectrum of Hydrogen Atom

The ESR spectrum of hydrogen atom shows two equally intense lines which are 506.8 G apart. This is shown below in Fig. 11.4(a).



(a) (b)

Fig. 11.4: (a) ESR spectrum of hydrogen atom.
(b) The energy levels obtained as a result of nuclear hyperfine interaction.

The origin of these two lines as a result of splitting due to nuclear hyperfine interaction can be explained as follows. In the presence of magnetic field, an unpaired electron has two energy levels corresponding to two spin states denoted by $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$.

If we consider the interaction of these levels with a single nuclei (as in the case of hydrogen) having $m_I = +\frac{1}{2}$ and $-\frac{1}{2}$, we get four energy levels as shown in Fig. 11.4 (b). The selection rules for the transitions are

$$\Delta m_s = \pm 1 \text{ and } \Delta m_I = 0.$$

The transitions which are allowed by these selection rules are also shown in

Fig. 11.4(b). The energies of the two allowed transitions are given by the following expression.

$$\Delta E = h\nu = g_e \beta_e B_z \pm m_I a$$
$$= g_e \beta_e B_z \pm \frac{1}{2} a \qquad \text{......(11.7)}$$

where a is **hyperfine splitting constant** and has the value 1420.4 MHz for hydrogen atom.

Since an electron can approach the proton much more closely than can another proton, the coupling is much stronger and the splitting of ESR spectral lines is much greater than those of NMR spectral lines. Hence in proton NMR spectra, the coupling constant is of the order of 10 Hz whereas in ESR spectra, the hyperfine splitting constant is of the order of 10 MHz.

Let us now study a little more complex systems.

11.6.2 ESR Spectra – Some More Examples

Let us now study the case of deuterium. The nuclear spin quantum number $I = 1$ in this case. Hence, there are three values of the component of angular momentum vector m_I as given below.

$$m_I = I, (I-1), \text{........} 0, \text{......}, -(I-1), -I \qquad \text{......(11.8)}$$
$$= +1, 0, -1$$

Similar to the case of hydrogen atom, the interaction of nuclear spin with both the values of m_s of electron ($\pm 1/2$) yields six energy levels as shown in Fig. 11.5 (a).

By applying the selection rules, the three allowed transitions are as shown in Fig. 11.5 (a). This leads to the splitting of the signal into 3 components as shown in Fig. 11.5 (b). In general, we can say that if an electron interacts with a nucleus of spin I the ESR signal splits into $(2I + 1)$ components.

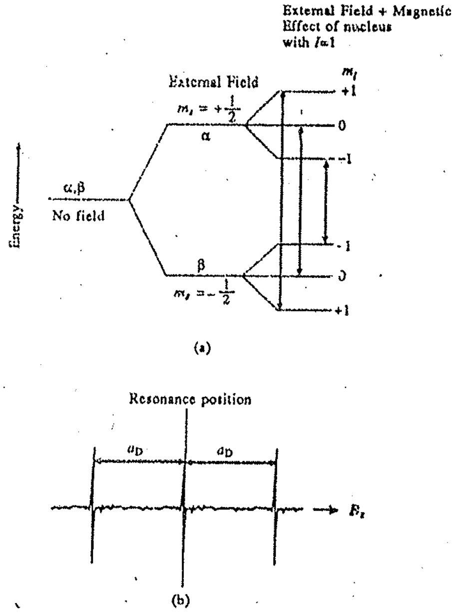


Fig. 11.5: (a) Energy levels of deuterium arising due to nuclear-electron interaction, (b) ESR spectrum of deuterium.

We will now discuss the ESR spectra of some species which contain **more than one** magnetic nuclei.

Let us first consider a single electron in presence of two protons. The two protons interact equally with the electron and give rise to six energy levels. By using the selection rules $\Delta m_s = \pm 1$ and $\Delta m_I = 0$, three transitions are possible as shown in Fig. 11.6. These three transitions will show three signals in the ESR spectrum.

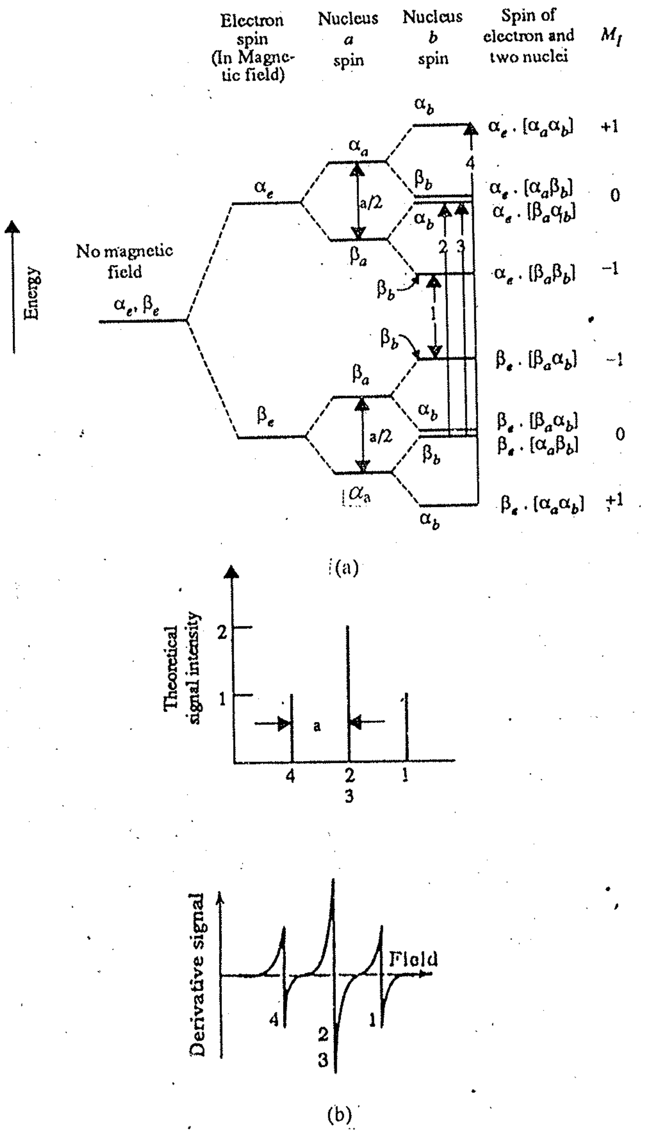


Fig. 11.6 (a) ESR energy level diagram for the interaction of one electron with two protons. (b) ESR spectrum.

The simplest example of such a species is methyl radical, $\cdot CH_3$. It contains three **equivalent** hydrogen atoms. Thus, net $I = 1/2 + 1/2 + 1/2 = 3/2$ in this case. Hence $m_I = \frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ in the direction of the applied magnetic field. Interaction of each of these m_I values with $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ will yield **eight** energy levels as shown in Fig. 11.7 (a).

The application of selection rules tells us that 4 transitions are allowed. These transitions are shown in Fig. 11.7 (a). The ESR spectrum of methyl radical obtained as a result of these transitions is shown in Fig. 11.7 (b). You can see that the signals are **not** of equal intensity and their ratio of intensity is 1: 3: 3: 1. This pattern of splitting and intensity can be understood easily if we add the splitting caused by each equivalent nucleus **in turn.** This is shown in detail in Fig. 11.7 (c) for one, two and three protons. Note that in this case since the hyperfine splittings are same (i.e. hyperfine splitting constant is having the same value), there was equal spacing between the splitted lines. For such cases where equivalent protons are involved, Pascal triangle can be used for determining the number of lines obtained after splitting and

Since both the electron and the proton have spin quantum number $\frac{1}{2}$, the splitting pattern due to hyperfine splitting in ESR spectra resembles to that of spin-spin splitting in case of NMR spectra.

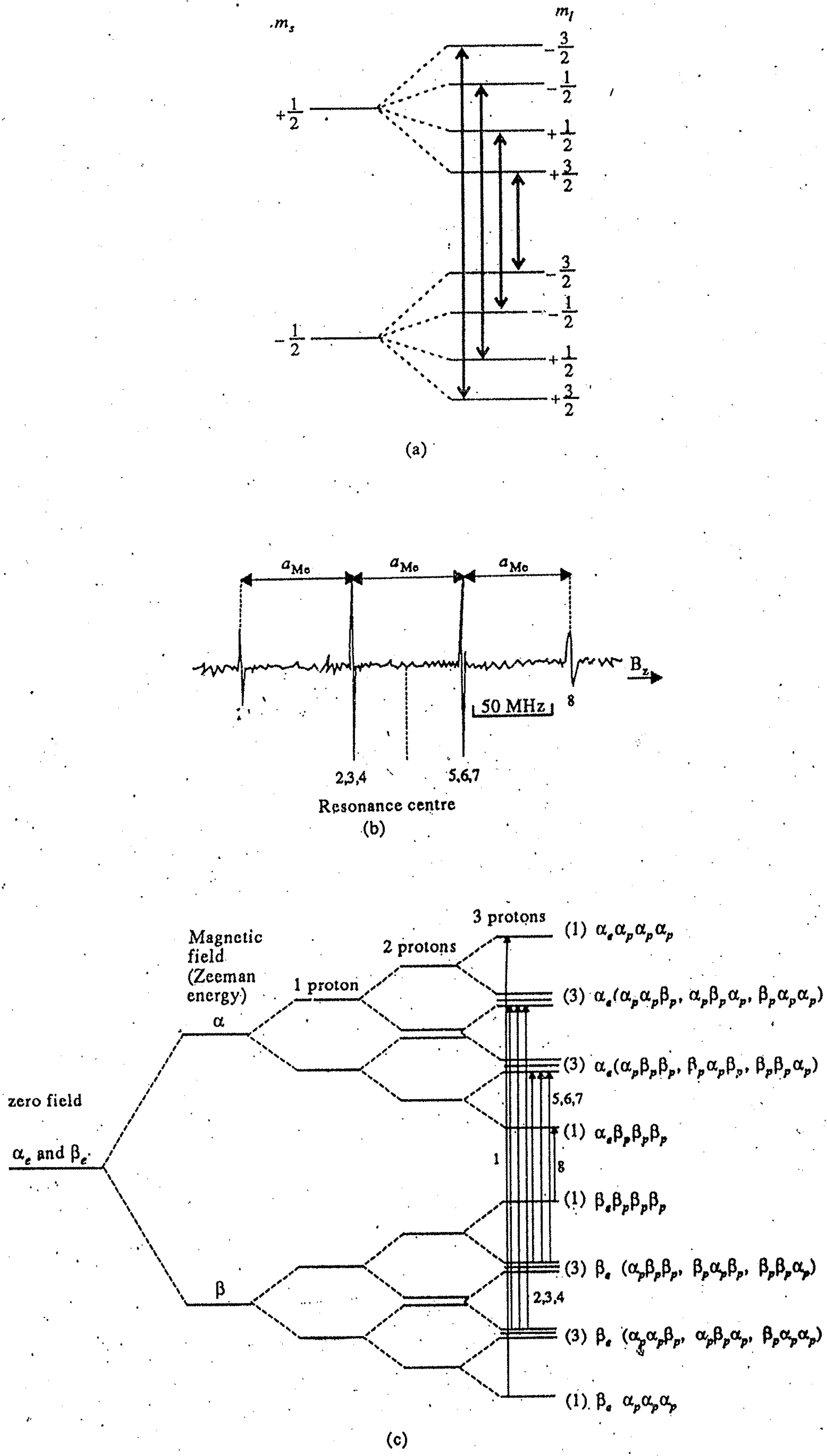


Fig. 11.7: (a) The energy levels and allowed transitions in methyl radical.
(b) ESR spectrum of methyl radical. The numbers indicate the transition shown in part (c).
(c) Identical splitting caused by three equivalent protons.

their relative intensity. This is shown below.

Pascal triangle

Number of Equivalent protons	Intensity ratio	Number of lines observed
0	1	1
1	1 1	2
2	1 2 1	3
3	1 3 3 1	4
4	1 4 6 4 1	5
5	1 5 10 10 5 1	6
6	1 6 15 20 15 6 1	7
7	1 7 21 35 35 21 7 1	8
8	1 8 28 56 70 56 28 8 1	9

Thus for *n* equivalent nuclei having spin quantum number *I*, the interaction with an ESR spectral line will lead to its splitting into $2nI + 1$ components.

For a proton

$I = \frac{1}{2}$, So $2nI + 1 = 2 \times n \times \frac{1}{2} + 1$

$= n + 1$.

Thus, *n* equivalent protons will split an ESR signal into $n + 1$ components.

Let us come to a little different case of *non-equivalent* protons. Consider a simple system where there are two *non- equivalent* protons interacting with an electron. Firstly, the original line will be split by the first proton to a doublet. Let us denote the splitting constant due to the interaction with first proton by a_1. This is depicted in Fig. 11.8 (a). Then, the second proton again splits each line of the doublet into two lines and this time we represent the splitting constant as a_2 . Since a_1 and a_2 are different, we get 4 lines. You can compare this splitting pattern with that obtained with two *equivalent* protons as predicted by Pascal triangle. This is shown in Fig. 11.8 (b).

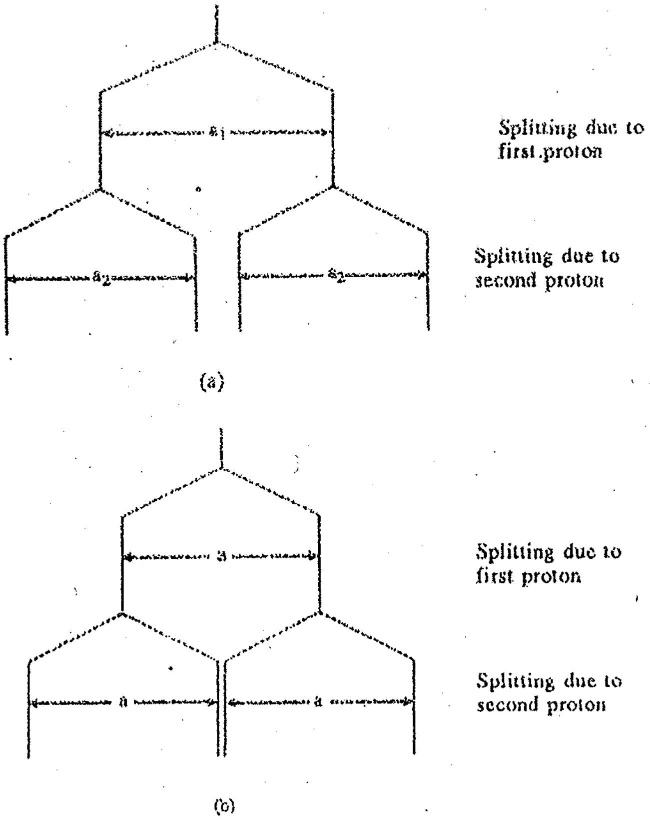
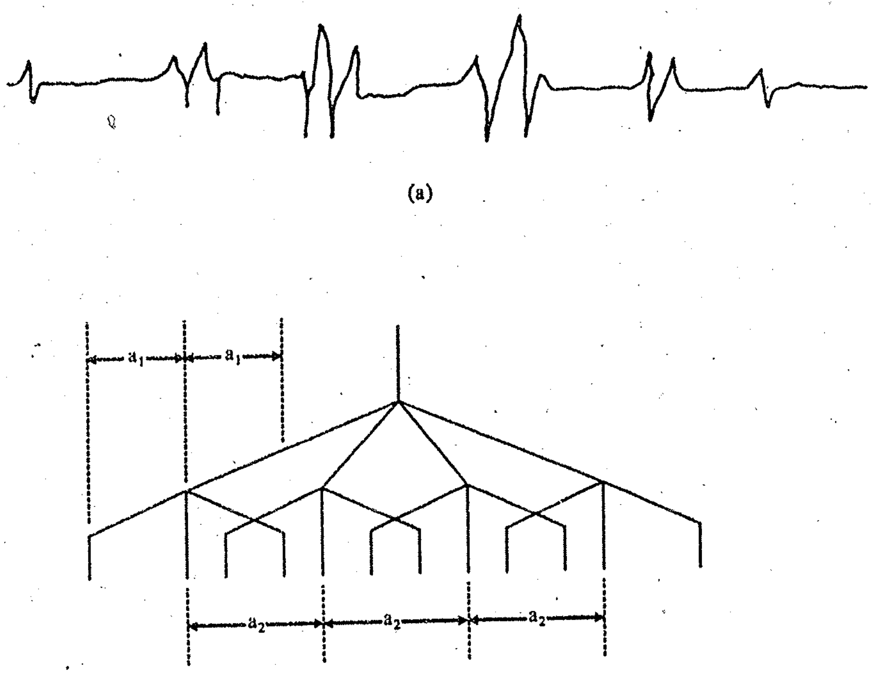


Fig. 11.8: (*a*) Splitting by two non-equivalent protons.
(b) Splitting by two equivalent protons.

[illegible] take the example of ethyl radical, C_2H_5 which has two sets of protons having different splitting constants. We can write ethyl radical as $\cdot CH_2CH_3$. The ES spectrum of ethyl radical is shown in Fig. 11.9 (a).

The pattern of lines observed in the spectrum can be explained if we first consider the splitting of the signal due to two CH_2 protons. This will lead to a triplet having the intensity in the ratio of 1:2:1. Let the splitting constant for this be denoted as a_1 as shown in Fig. 11.9 (b). Each component is further split by methyl (CH_3) protons into four components having intensity in the ratio 1: 2: 2: 1. The splitting constant is denoted as a_2.

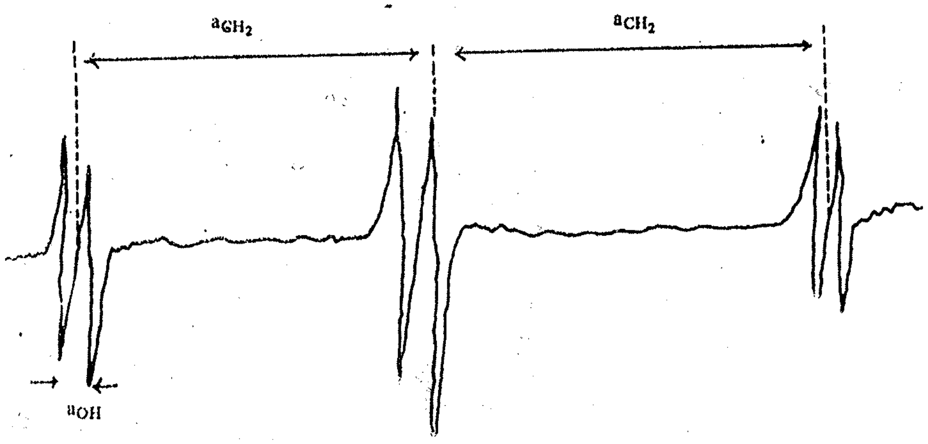


(a)

(b)

**Fig. 11.9: (a) The ESR spectrum of ethyl radical.
(b) Splitting pattern of the ESR spectrum.**

Similarly, in case of $\cdot CH_2OH$ radical the signal in the ESR spectrum is first split due to the two protons of CH_2 group into a triplet in the ratio 1: 2: 1. Then, each component of this triplet is further split into a doublet by coupling with the H of the OH group. The observed spectrum thus looks as shown below in Fig. 11.10.



We can thus generalise that when the splitting is caused by both a [illegible] nuclei of spin I_i and a set of m equivalent nuclei of spin I_j, then the number of lines is given by $(2n\,I_i + 1)\,(2m\,I_j + 1)$.

After understanding the above discussion, answer the following SAQ.

SAQ 3

Predict the number of components and their intensities in the ESR spectrum of $\cdot C_6H_6^-$.

....

....

11.7 THE g VALUE

You are aware of the g value of free electron from Eq.11.1 where we represented it by g_e. You have also seen that g_e is related to the energy difference, ΔE according to Eq. 11.5. Thus, we can describe the variation in ΔE in terms of changing g_e values. This is in contrast to NMR spectroscopy where we kept g_N fixed and introduced shielding constant (σ) to describe the different resonance energies. Since for NMR, we had $B_{eff} = B_z(1-\sigma)$ and $\Delta E_{NMR} = g_N \beta_N B_{eff} \Delta m_I = g_N \beta_N (1-\sigma) B_z \Delta m_I$.

Similarly, $\Delta E_{ESR} = g_e \beta_e B_{eff} \Delta m_s = g_e \beta_e (1-\sigma) B_z \Delta m_s$ ...(11.9)

If we combine g_e and $(1-\sigma)$ in Eq. 11.9 and write it as g;

[i.e. $g = g_e(1-\sigma)$], then we can write Eq. 11.9 as follows.

$$\Delta E_{ESR} = g\,\beta_e B_z \Delta m_s \qquad \text{......(11.10)}$$

You are already aware that for a free electron g is represented as g_e and is equal to 2.00232. But, when we talk about the g factor of a radical or a complex in the context of the resonance condition given by Eq. 11.5, we mean g which is inclusive of shielding constant as

$$g = g_e(1-\sigma)$$

The g value of a substance gives information about its electronic structure and hence can be used in its identification just like chemical shifts in the NMR spectra.

It may also be mentioned here that the g value we were referring above (Eq. 11.5) was for **isotropic** systems, i.e. systems which were *without* directional properties. But the systems which are **anisotropic**, i.e. systems which *have* directional properties (e.g. a crystal), show different g values depending upon its direction of measurement. For such a system, when g values are measured by applying the field along the three coordinate axes, they are termed as g_{xx}, g_{yy} and g_{zz}. Again, we can refer the g value as $g_{\parallel}$ (g parallel) or $g_{\perp}$ (g perpendicular) depending upon whether we are measuring g values parallel to the axis of symmetry or perpendicular to it. You can understand this with the help of the following diagram, (Fig. 11.11).

Fig. 11.11 shows a as the axis of symmetry. When we measure g along this axis, we represent it as $g_{\parallel}$ and designate it as g_{zz}. The other two g values along the other two principle axes perpendicular to g are called $g_{\perp}$ and are designated as g_{xx} and g_{yy}.

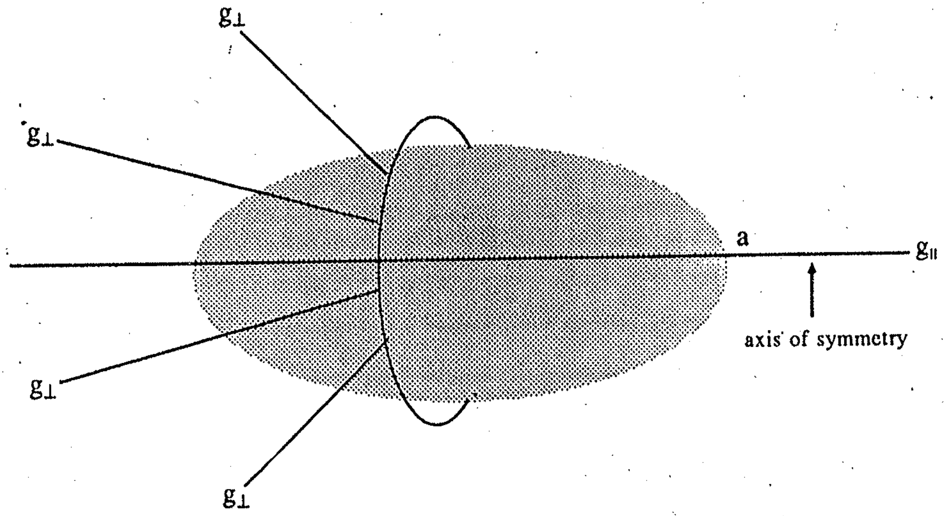


Fig. 11.11: $g_{\parallel}$ and $g_{\perp}$.

The g values for organic radicals are almost isotropic and differ very little from g_e for the free electron. This is illustrated below in Table 11.1.

Table 11.1: The g value of some organic radicals

radical	g value
$\cdot CH_3$	2.00255
$\cdot CH_2CH_3$	2.0026
$\cdot CH_2OH$	2.0033
$\cdot CH_2CHO$	2.0045
$\cdot CH_2COCH_3$	2.0042

The g values of some species such as $RO\dot{O}$, $R_2N\dot{O}$ and inorganic radicals differ from g_e. This is because the unpaired electron is localised in a particular orbital giving rise to spin orbital coupling. Some examples of inorganic radicals being $3d^3$ ions (V^{2+}, Cr^{3+} and Mn^{4+} having g values in the range 1.98-1.99) and $3d^5$ ions (Fe^{3+}, Mn^{2+} and Cr^+ have g values close to 2.00).

11.8 SOME APPLICATIONS OF ESR SPECTRAL STUDIES

The study of ESR spectrum has wide applications as given by the following examples:

(i) Study of Free Radicals:

Free radicals can be studied by ESR spectroscopy even in small concentrations. The hyperfine structure of the ESR spectrum is a kind of fingerprint that helps to identify the radical present in a sample. Besides using nuclear hyperfine splitting to explain the number of magnetic nuclei present nearby the unpaired electron as discussed in Sec. 11.5, it can also help in mapping the unpaired spin density. This can be done by using McConnell Equation as given below:

$$a = Q\rho \qquad .....(11.11)$$

Here a is the observed hyperfine splitting constant, Q is the hyperfine splitting constant (or coupling constant) for unit density and ρ is the electron density.

For example, in case of hydrogen atom $a = 50$ mT and ρ for $1s$ orbital is 1; hence $Q = 50$ mT.

For $\cdot CH_3$ radical, $a = 2.3$ mT. Using $Q = 50$ mT, ρ can be calculated as

$$\rho = \frac{2.3}{50} = 0.046.$$

This means electron spends 5% of its time in 1s orbital of each hydrogen atom and remaining 85% of its time near carbon.

(ii) **In the Study of Organometallic Compounds:**

The ESR spectra of the single electron reduction product of $SFeCo_2(CO)_9$ and $PhCCo_3(CO)_9$ show 15 line spectrum ($a = 5$ G) and 22 line spectrum ($a = 10$ G), respectively. This thus indicated the delocalisation of the added electron on the cobalt atoms present.

Thus, 2 Co in $SFeCo_2(CO)_9$ will give $2 \times 2 \times 7/2 + 1 = 15$ lines and 3 Co in $PhCCo_3(CO)_9$ will give $2 \times 3 \times 7/2 + 1 = 22$ lines.

(iii) **Transition Metal Complexes**

Here, observed g values help to determine wheather unpaired electron is localised on transition metal atom or on adjacent ligand.

11.9 SUMMARY

In this unit, you studied that

- ESR transitions occur in the microwave region of the electromagnetic spectrum and are accompanied by a change in the spin of the unpaired electron.
- ESR spectra are recorded as derivative curves.
- The coupling of the electron and nuclear spins results in nuclear hyperfine interaction. This results in the splitting of ESR line. The splitting is denoted by the hyperfine splitting constant, a. The splitting pattern helps in the determination of structure of the free radical.
- The g-factor for the electron is a universal constant and has the value $g = 2.00232$. The deviation from this g value indicates the departure from free radical behaviour (delocalisation).

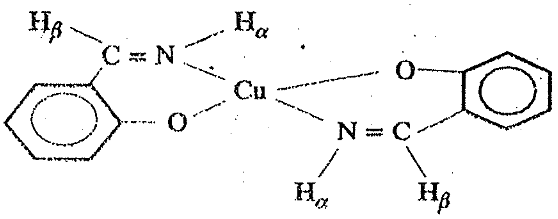
11.10 TERMINAL QUESTIONS

1. The benzene anion has $g = 2.0025$. At what magnetic induction B_z would its ESR spectral line be centred at frequency 9.350 GHz?
2. How many ESR spectral lines are observed if an unpaired electron, delocalised on two non-equivalent protons, is placed in magnetic field?
3. An ESR spectrum shows only three lines. Explain how it could arise from:
   (a) Hyperfine coupling to two nuclei with spin $= 1/2$
   (b) Hyperfine coupling to a nucleus with spin $= 1$.
4. The ESR spectrum of a radical with a single magnetic nucleus is split into four lines of equal intensity. What is the spin of the nucleus?
5. How many lines would you expect in the ESR spectra of bis (acetylacetonato) copper (II) if I for copper is $\frac{3}{2}$?

6. Predict the ESR spectrum pattern for $NO(SO_3)_2^{2-}$ radical if $I = 1$ for nitrogen which is here the only nucleus having spin.

7. In the ESR spectrum of $K_3Mo(CN)_8$, 25% isotopes of Mo show spin $I = \frac{5}{2}$. Predict the pattern of lines around a central line from 75% non-magnetic isotope.

8. The ESR spectrum of bis (salicylaldiminato) copper (II)



showed four main groups of lines, each of which contains 15 lines.

I for Cu $= \frac{3}{2}$,

I for N $= 1$

and I for H $= \frac{1}{2}$

Assume H_α are not participating in hyperfine splitting and explain the origin of lines.

11.11 ANSWERS

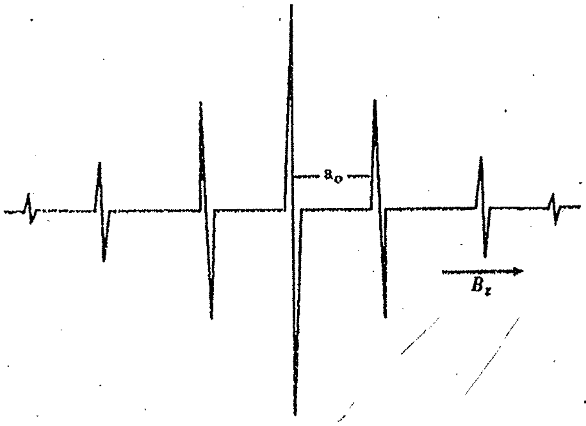
Self Assessment Questions

1. (i) $\cdot CH_3$ and (iv) $\cdot C_6H_6^-$.

2. $g = \frac{h\nu}{\beta B_z}$ (from Eq.11.6)

$$= \frac{(6.626 \times 10^{-34}\text{ J s})\,(9.55 \times 10^{9}\text{ Hz})}{(9.274 \times 10^{-24}\text{ J T}^{-1})\,(0.1569\text{ T})} = 4.3$$

3. According to the Pascal triangle when the number of protons is six, there will be 7 lines in the ESR spectrum having the intensity in the ratio 1: 6: 15: 20: 15: 6: 1.



Terminal Questions

1. $B_z = \dfrac{h\nu}{\beta g}$

$$= \frac{(6.626 \times 10^{-34}\ \text{J s})\ (9.35 \times 10^{9}\ \text{Hz})}{(9.27408 \times 10^{-24}\ \text{A m}^2)\ (2.0025)}$$

$= 3.334 \times 10^{-1} = 0.3334$ T
$= 3334$ G (1 T $= 10^4$ G)

2. In the presence of a magnetic field the unpaired electron will have two energy levels giving rise to a single ESR line. This line will split further into a doublet due to the first proton $\left(I = \frac{1}{2}\right)$. This doublet will further split into two doublets due to second proton, because each proton has different hyperfine splitting constant. The splitting due to two non-equivalent protons is shown in Fig. 1.8(a). With selection rules $\Delta m_I = 0$, four lines will be observed in the ESR spectrum.

3. (a) For two equivalent nuclei ($I = 1/2$) gives the total $I = 1$; so $(2nI + 1)$ rule gives $2 \times 1 \times 1 + 1 = 3$ lines, with an intensity distribution of 1: 2:1.

(b) In case we have a nucleus with spin $I = 1$; then by using $2nI + 1$, we get $2 \times 1 \times 1 + 1 = 3$ lines in the spectrum. These lines will be of equal intensity.

4. Since we have obtained 4 lines of equal intensity in ESR spectrum suggesting interaction of a single nucleus. By using the equation $2nI + 1$ where $n = 1$, we have $2 \times 1 \times I + 1 = 4$

$$2I + 1 = 4$$

$$2I = 3$$

$$I = \frac{3}{2}$$

So, the spin of the nucleus interacting would be $\frac{3}{2}$.

5. 4 lines using $2nI + 1$.

6. $I = 1$; hence $2nI + 1 = 2 \times 1 \times 1 + 1$
$= 3$ lines with equal intensity

7. Around a central line, six smaller signals (three on each side) should appear from 25% Mo having $I = \frac{5}{2}$ because

$$2nI + 1 = 2 \times 1 \times \frac{5}{2} + 1$$
$$= 6$$

8. Four main group of lines originate from Cu ($I = \frac{3}{2}$) hyperfine coupling.

No. of lines in each of these four major peaks $= (2nI_i + 1)\ (2mI_j + 1)$

$$= (2 \times 2 \times 1 + 1)\ (2 \times 2 \times \frac{1}{2} + 1)$$

$$= 5 \times 3 = 15$$

UNIT 12 MASS SPECTROMETRY

Structure

12.1 INTRODUCTION

In the last two units (Units 10 and 11 of this block), you studied about the spin magnetic resonance spectroscopy. You learnt there that the spin magnetic resonance spectroscopy helps in structure elucidation. You may also remember that rotation, vibration, Raman and electronic spectroscopy are the other techniques which help in the determination of molecular structure. You have already studied about these techniques in detail in the various units of earlier blocks of this course. In this unit, we will introduce to you one more technique which is useful in the determination of structure of atoms and molecules as well as atomic and molecular masses. This technique is known as **mass spectrometry.**

In this unit, we will first explain the principle of mass spectrometry. Then we will tell you about the salient features of a mass spectrometer. This will be followed by a discussion on how a mass spectrum is presented and how to deduce information available from the mass spectrum. You will also be told about the fragmentation types of various species and factors affecting fragmentation. We will also discuss McLafferty rearrangement.

Finally we will illustrate the applications of mass spectrometry by taking some simple examples.

Objectives

After studying this unit, you should be able to:

- explain the principle involved in the mass spectrometry,
- highlight the important features of a mass spectrometer,
- draw a typical mass spectrum and explain the information derived from it,
- discuss various fragmentation types and factors affecting fragmentation,
- explain the McLafferty rearrangement, and
- correlate the mass spectra of simple systems to their structure.

12.2 PRINCIPLE

Mass spectrometry is based upon a principle which is different from that underlying the various forms of spectroscopy which you studied earlier. Most of the spectral techniques which we discussed in the earlier units involved absorption of energy from various regions of electromagnetic spectrum. But, in mass spectrometry the sample is bombarded with high energy electrons which knock off an electron from the sample leading to a positively charged **radical ion**, $[M]^{+\cdot}$.

$$M + e^{-} \longrightarrow [M]^{+\cdot} + 2e$$

This radical ion being highly energetic, may fragment further yielding smaller fragments as shown below:

$$\begin{tikzcd} & A^{+} + B^{\cdot} \\ {[M]^{+}} \arrow[ur] \arrow[dr] & \\ & C^{+} + D^{\cdot} \end{tikzcd}$$

The radical ion and other fragments are separated according to their m/z ratio where m is the mass and z is the charge of the ion. The record of m/z values of these species verses their relative abundance is known as **mass spectrum** of the sample. You will study in the later sections of this unit that mass spectrum of a sample gives important information about the structure of its atoms or molecules. Although the mass spectrometry differs **in principle** from other spectroscopic techniques, it is considered alongwith them because it complements the information regarding the structure of the atoms and molecules obtained by other spectroscopic techniques.

12.3 THE MASS SPECTROMETER

Fig. 12.1 (a) shows the basic features of a simple mass spectrometer while Fig. 12.1 (b) shows the components of a modern high resolution mass spectrometer.

Fig. 12.1 (a) shows a **vapour inlet** from where sample vapours are introduced to the **ionisation chamber.**

Various methods of ionisation are available as given below:

(i) Electron Ionisation or Electron Impact (abbreviated as EI)
(ii) Chemical Ionisation (CI)
(iii) Fast Atom Bombardment (FAB)

Note that the radical cation is both a radical as well as a cation.

(i) In *electron ionisation* method, the sample vapour is bombarded with high energy electrons having energy about 1.12×10^{-17} J. The electron on striking the sample M, takes away one electron from it and the sample gets ionised as shown below:

$$e^{-} + M \longrightarrow \underset{\text{radical cation}}{[M]^{+\cdot}} + 2e^{-} \quad \ldots (12.1)$$

A very low pressure (10^{-4} N m^{-2}) is maintained in the ionisation chamber so that collisions between ions and unionised atoms or molecules are at a minimum level.

In EI method, we study the molecular ion and fragment ions.

(ii) In *chemical ionisation* method, a reagent gas (such as CH_4 or NH_3) is passed into the ionising chamber where it **ionises, fragments** and **collides** with neutral molecules to yield CH_5^{+} or NH_4^{+} reagent ions. This process is shown below for methane.

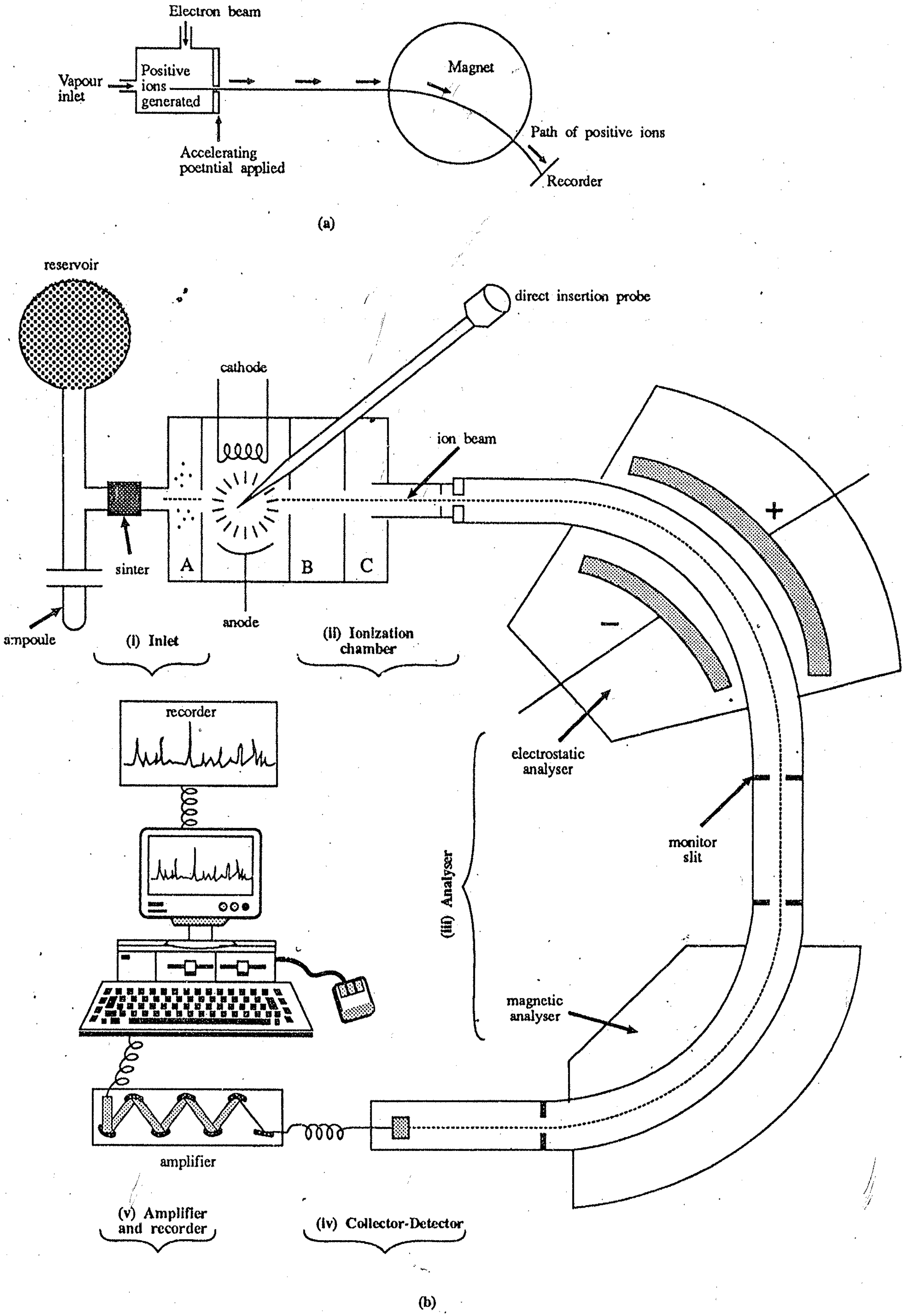


Fig. 12.1 : Mass Spectrometer: (a) Basic features.
(b) High resolution double focussing instrument.

$$CH_4 + e^- \longrightarrow CH_4^{\dot{+}} + 2e^- \qquad \text{(ionisation)} \quad \ldots (12.2)$$

$$CH_4^{\dot{+}} + \longrightarrow CH_3^+ + H\cdot \qquad \text{(fragmentation)} \quad \ldots (12.3)$$

$$\left.\begin{array}{ll} & CH_4^{\dot{+}} + CH_4 \longrightarrow CH_5^+ + \dot{C}H_3 \\ \text{and} & CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \end{array}\right\} \begin{array}{l}\text{(collision with neutral} \\ \text{molecule, } CH_4) \quad \ldots (12.4)\end{array}$$

These reagent ions protonate the sample to yield MH^+ ions which are **one unit higher** in mass than the sample.

In CI method, we study MH^+ ions.

$$M + CH_5^+ \longrightarrow MH^+ + CH_4$$

Chemical ionisation is a milder method of ionisation as compared to electron ionisation. This is also useful in the determination of relative molar mass (mol. wt.) because fragmentation of MH^+ is very little in this case. However, in EI method $M^{\dot{+}}$ undergoes extensive fragmentation and hence is not observed most of the time in mass spectra. But the fragmentation is otherwise helpful in structure determination of the sample.

(iii) **Fast atom bombardment** involves the bombardment ot the sample with high energy xenon atoms. This method is used for large or involatile molecules. The ionisation is carried out in solution phase and hence thermally unstable compounds can be studied by using this technique.

$$\underset{\substack{\text{ionic}\\ \text{compound}}}{A^+B^-} \xrightarrow{Xe} A^+ + B^- \qquad \ldots (12.5)$$

Now you have learnt a lot about what can happen in the ionisation chamber. Let us look at Fig. 12.1(a) again. The ions are generated in the ionisation chamber. The ions are then passed through **accelerating plates**. The accelerating plates accelerate only the positively charged ions. **The negative ions and neutral particles are not accelerated** but are continuously removed. From the accelerating plates, the positive ions pass through the **analyser tube** where a magnet is used which reflects them along a curved path. By varying the magnetic field, ions of different masses can be recorded.

The term high resolution will be explained in the next section.

Fig. 12.1 (b) shows a high resolution double focusing mass spectrometer. You can see that the basic features of the instrument are same as in Fig. 12.1 (a). But in addition it has an **electrostatic analyser** which carries out a preliminary focusing and then the ions are passed through the magnetic analyser. This is known as **double focusing.** The ions are then allowed to enter the **collector detector** system where they impinge upon an electron multiplier detector and produce a current. The current is amplified by an **amplifier** and is proportional to the intensity of the ions. The current so produced is fed to a **computer** which processes the data and then usually records it in the form of a bar graph using a recorder.

Let us now study how does a typical mass spectrum look and what are its salient features.

SAQ 1

Calculate the *m/z* values for $\overset{+}{C}H_3$, $\overset{+}{O}CH_3$ and $\overset{+}{O}CCH_3$.

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12.4 THE MASS SPECTRUM: VARIOUS IMPORTANT FEATURES

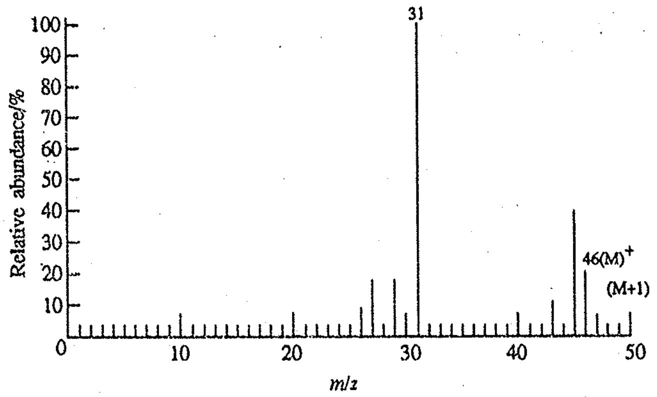


Fig. 12.2: Mass spectrum of ethanol.

Fig. 12.2 shows the mass spectrum of ethanol. You can see that the mass spectrum is a plot of relative abundance (on y–axis) of positively charged ions verses their mass to charge (m/z) ratio (on x–axis). Since most of the particles are singly charged ($z = 1$), the m/z of these ions is equal to their masses. You have learnt in the previous sections that loss of an electron from a molecule yields a radical cation, i.e.

Relative abundance is also known as intensity.

$$\mathrm{M} + e^- \longrightarrow \underset{\substack{\text{radical}\\ \text{cation}}}{\mathrm{M}^{\dotplus}} + 2e^-$$

This radical cation is also known as **molecular ion.** The mass of $\mathrm{M}^{\dotplus}$ can be taken as equal to that of M because the mass of the electron lost is negligible. Thus, if we get the value of m/z of M^+ from the mass spectrum, we get the molecular weight of M.

The mass spectrum of ethanol shows a peak at m/z 46. Let us see if it corresponds to its molecular ion or not? Let us add the relative atomic masses of atoms present in ethanol (C_2H_5OH) as given below.

$$\begin{aligned} &2 \times \text{atomic mass of carbon} + 6 \times \text{atomic mass of H} + 1 \times \text{atomic mass of O} \\ &= (2 \times 12) + (6 \times 1) + (1 \times 16) \\ &= 24 + 6 + 16 \\ &= 46 \end{aligned}$$

Thus, the peak at $m/z = 46$ corresponds to the molecular ion of ethanol which is $(C_2H_5OH)^{\dotplus}$. But this is not the peak of highest intensity.

The peak of highest intensity is called the **base peak.** The base peak in the mass spectrum of ethanol is at m/z 31. The intensity of the base peak is assigned a value of 100 and the intensities of other peaks are expressed relative to that of the base peak.

You can see in the figure that there is a small peak at m/z 47 also. This can be called as M + 1 peak. But where from it has come? The origin of this peak can be understood if we take into account the natural abundance of the constituent atoms. Most of the elements exist in nature as predominantly one isotope. But some elements exist as more than one isotope (Table 12.1) and carbon is one such element. Carbon exists in nature a $^{12}_{6}C$ as well as $^{13}_{6}C$. The natural abundance of $^{13}_{6}C$ is 1.1% as compared to $^{12}_{6}C$. If $^{13}_{6}C$ is present in ethanol molecule, it will show an M+1 peak. Similarly, O also occurs as $^{17}_{8}O$ isotope and H also occurs as $^{2}_{1}H$ isotope. The presence of an isotope of these elements would also lead to M+1 peak. Similarly, if the molecule contains two $^{13}_{6}C$ atoms or a $^{13}_{6}C$ and $^{2}_{1}H$ or $^{18}_{8}O$ atoms, the mass spectrum would show an M+2 peak also. The other peaks in the spectrum appear due to the fragmentation of the molecular ion.

Table 12.1 shows the natural abundance of isotopes of some common elements.

Table 12.1 : Natural abundance of isotopes of some elements.

Isotope	Abundance %	Isotope	Abundance, %	Isotope	Abundance, %
^{1}H	99.985	^{2}H	0.015		
^{12}C	98.89	^{13}C	1.11		
^{14}N	99.63	^{15}N	0.37		
^{16}O	99.76	^{17}O	0.04	^{18}O	0.20
^{32}S	95.0	^{33}S	0.76	^{34}S	4.2
^{19}F	100				
^{35}Cl	75.5			^{37}Cl	24.5
^{79}Br	50.5			^{81}Br	49.5
^{127}I	100				

You can see in Table 12.1 that Br exists as two isotopes: ^{79}Br and ^{81}Br in the ratio 50.5 and 49.5. Thus, in the mass spectrum of bromomethane (CH_3Br) shown in Fig. 12.3, you can see an M+2 peak of almost equal intensity as M^+ peak.

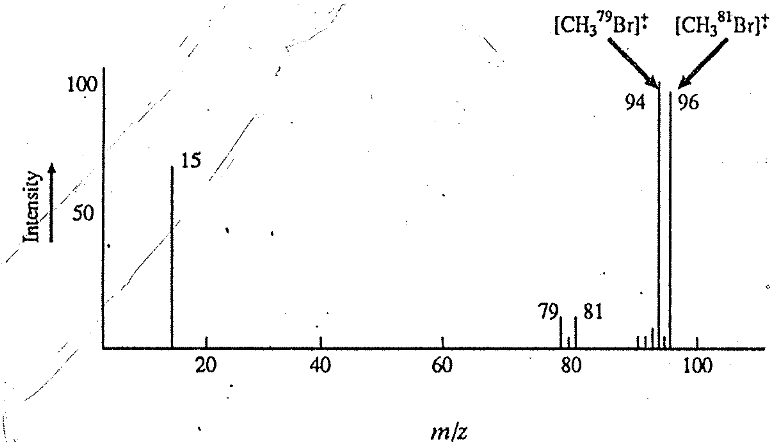


Fig. 12.3: Mass spectrum of bromomethane.

Similarly when chlorine is present in the molecule, the pattern in the spectrum near M^+ region will be as shown below:

$$\frac{M}{M+2} = \frac{3}{1}$$

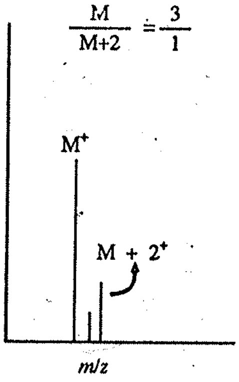


Fig. 12.4: Pattern of mass spectrum near M^+ region for a molecule containing a chlorine atom.

Note that the intensity of M+2 peak is about one third of M^+ peak. In case a compound contains a nitrogen atom, it shows an odd numbered molecular ion peak. This is called the **nitrogen rule**. In case, the number of nitrogen atoms is even, a molecular ion peak having an even mass will be observed.

So far we have discussed the *m/z* values which differed from each other by one unit. This is termed as **unit resolution.** Thus, by unit resolution, we should be able to differentiate a peak of say *m/z* 400 from that of *m/z* 399 or 401. To determine the resolution of an instrument, two adjacent peaks in the mass spectrum having approximately the same intensity are chosen and are designated as M_n and M_m where M_n represents the higher mass number peak out of the two. The resolution R is then given by the following equation:

$$R = \frac{M_n}{M_n - M_m} \qquad \dots (12.6)$$

There are two kinds of instruments available:

i) Low Resolution and (ii) High Resolution

Arbitrarily; low resolution instruments are categorised as those which can resolve masses upto 2000. The high resolution instruments, on the other hand can differentiate the mass 500 from 499.95. Thus, by using a high resolution mass spectrometer it is possible to differentiate between the following species:

	m/z
CO	27.9949
$CH_2{=}CH_2$	28.0313
N_2	28.0061

These molecular masses are calculated using the following atomic masses:

^{1}H	-	1.00782
^{16}O	-	15.9949
^{14}N	-	14.0031

Using low resolution instrument all these species yield the peak at *m/z* 28 and could not be differentiated.

Thus using high resolution mass spectrometer one can chose the correct structure out of the various possibilities.

12.5 FRAGMENTATION PATTERNS

You are aware that the molecular ion formed undergoes fragmentation. Fragmentation involves the lose of free radicals or small neutral molecules from the molecular ion. It is important to note that the fragmentation does not take place in a random way but it takes place in such a fashion that the most stable fragments possible are formed. We will now discuss the common fragmentation patterns by taking the example of some organic compounds.

12.5.1 Simple Cleavage

Let us start with the simple case of alkanes. The mass spectrum of *n*–hexane is shown in Fig. 12.5.

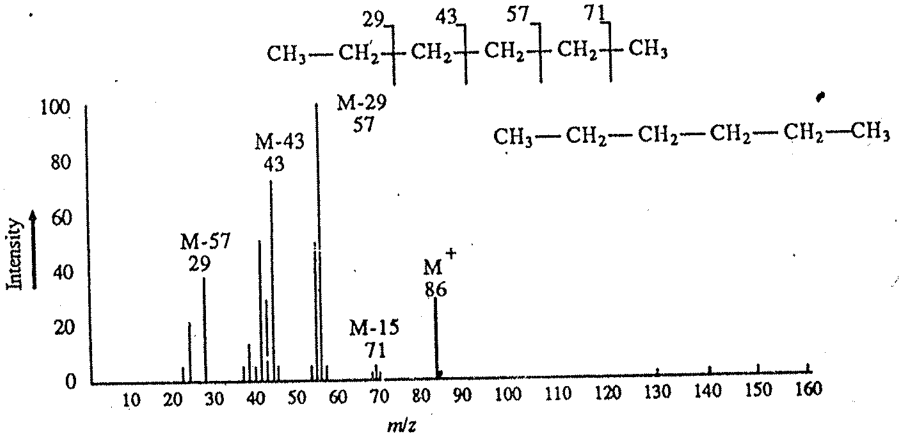


Fig. 12.5: Mass spectrum of *n*–hexane.

Molecular ion of *n*–hexane can be written as follows:

$$[CH_3CH_2CH_2CH_2CH_2CH_3]^{\dot{+}}$$

You can see a peak at m/z 86 corresponding to the molecular ion.

Let us find out the base peak. It appears at m/z 57. Its origin can be explained if we consider the loss of 86–57 = 29 units as C_2H_5 radical from $M^{\dot{+}}$ ion giving the *n*–butyl cation as follows:

$$\underset{m/z\ 86}{[CH_3CH_2CH_2CH_2CH_2CH_3]^{\dot{+}}} \longrightarrow \underset{\substack{n\text{–butyl cation}\\ m/z\ =\ 57}}{[CH_3CH_2CH_2\overset{+}{C}H_2]} + \underset{\substack{\text{ethyl radical}\\ \text{(not detectable)}}}{\cdot\ C_2H_5}$$

Note that the positive charge is carried by one fragment and the odd electron is on the other fragment. The reverse could have also happened, i.e. the ethyl cation and butyl radical could have formed as given below:

$$[CH_3CH_2CH_2CH_2CH_2CH_3]^{\dot{+}} \longrightarrow \underset{\text{(not detectable)}}{CH_3CH_2CH_2\dot{C}H_2} + \underset{m/z\ 29}{\overset{+}{C}H_2CH_3}$$

Thus, we can expect a peak at m/z 29 due to $\overset{+}{C}H_2CH_3$. **Remember that it is the positively charged ion which is detected by mass spectromety.** If you look at Fig. 12.5, you can find a peak at m/z 29 also.

The cleavage could have taken place in the middle of the molecule also as shown below:

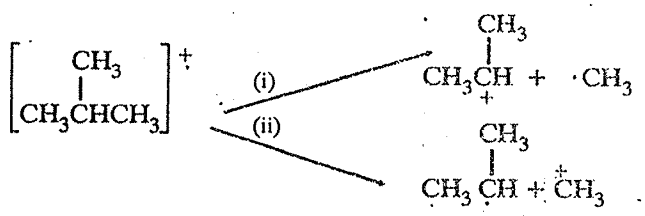
$$[CH_3CH_2CH_2 - CH_2CH_2CH_3]^{\dot{+}} \longrightarrow \underset{m/z\ 43}{CH_3CH_2\overset{+}{C}H_2} + CH_2CH_2CH_3$$

You can see a weak peak at m/z 71 which corresponds to M–15 fragment. This indicates the loss of $\cdot CH_3$ radical as 15 units. The peak is weak because the $\cdot CH_3$ radical produced is not very stable. The other possibility of charge being carried by methyl as $\overset{+}{C}H_3$ is not observed.

$$[CH_3CH_2CH_2CH_2CH_2 - CH_3]^{\dot{+}} \begin{array}{l} \nearrow \underset{(m/z\ =\ 71)}{CH_3CH_2CH_2CH_2\overset{+}{C}H_2} + \cdot CH_3 \\ \searrow CH_3CH_2CH_2CH_2\dot{C}H_2 + \underset{\text{not observed}}{\overset{+}{C}H_3} \end{array}$$

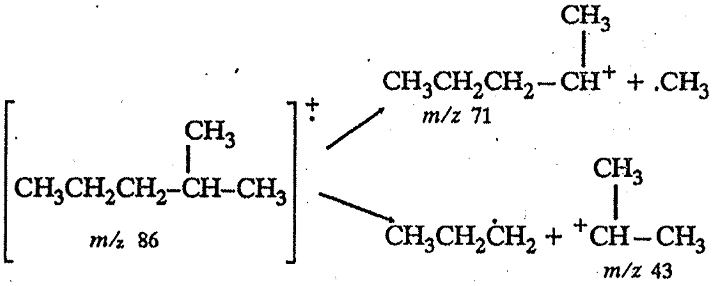
Out of the above two pathways possible, first one takes place indicating that **the stability of the cation is more important than the stability of the radical.** Thus, fragmentation yields the more stable $CH_3CH_2CH_2CH_2\overset{+}{C}H_2$ cation and not $\overset{+}{C}H_3$ cation.

Stability of cation is also observed in case of **branched alkanes.** In branched alkanes, fragmentation primarily occurs at the branch. For example in 2–methylpropane,



$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3CHCH_3 \end{array}\right]^{\dot{+}} \begin{array}{l} \xrightarrow{(i)} \begin{array}{c} CH_3 \\ | \\ CH_3\underset{+}{C}H \end{array} + \cdot CH_3 \\ \xrightarrow{(ii)} \begin{array}{c} CH_3 \\ | \\ CH_3\,\dot{C}H \end{array} + \overset{+}{C}H_3 \end{array}$$

fragmentation occurs predominantly via the first pathway because the cation obtained is more stable as compared to the methyl cation obtained in the second pathway. Similarly, for 2–methylpentane fragmentation at branches can lead to peaks at m/z 71 and m/z 43 as shown below:



Note that both the carbocations (*m/z* 71 and 43) are secondary carbocations and are stable. You can locate these peaks in the mass spectrum of 2–methylpentane shown in Fig. 12.6.

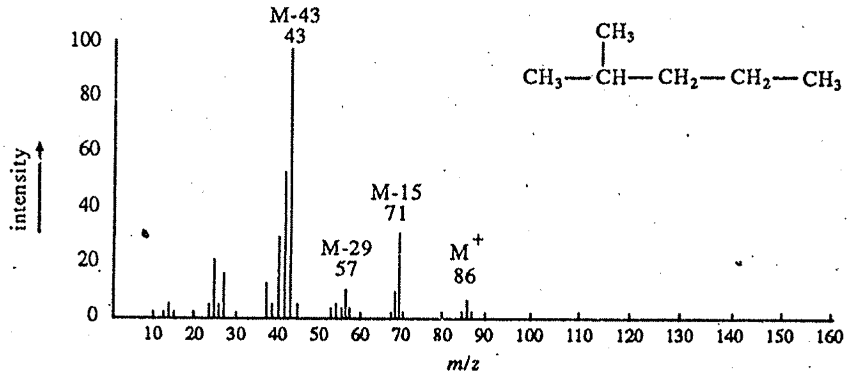


Fig. 12.6: Mass spectrum of 2–methylpentane.

You can also observe from the above examples that alkanes show homologous series of M–14 fragments due to the lose of CH_2 groups.

SAQ 2

Explain the origin of peaks at *m/z* 114, 85, 71, 57 in the mass spectrum of *n*–octane.

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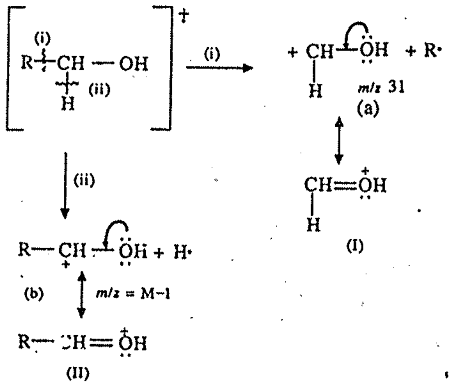
12.5.2 Effect of a Heteroatom

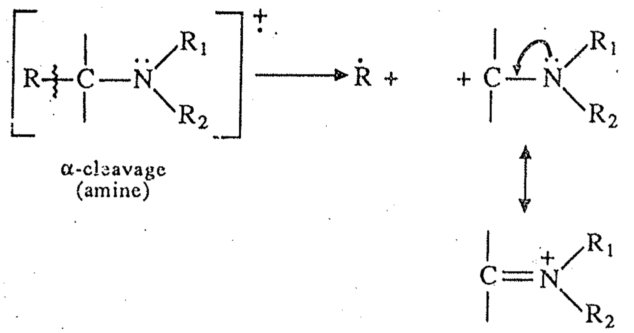
Mass spectra of compounds containing heteroatoms (N, O, halogens etc.) show

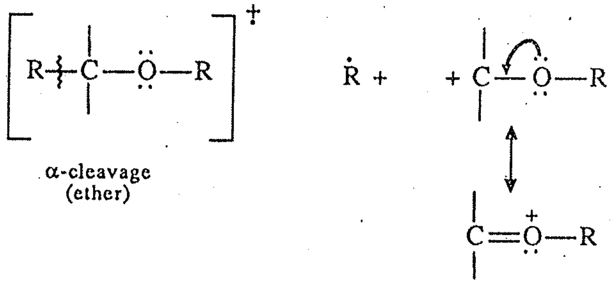


α-cleavage, i.e. cleavage of bond to the carbon that is α to the heteroatom. For example, two such α cleavages are shown above in case of alcohol.

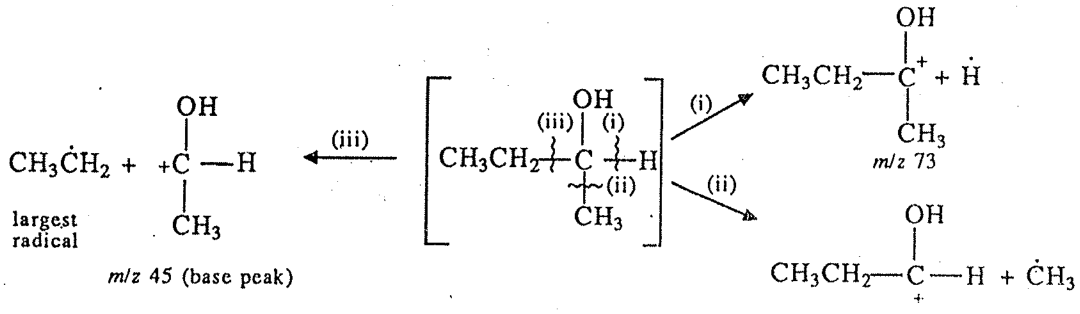
The resulting cations (a) and (b) can resonance stabilise to structures (I) and (II), respectively. It is here in this resonance stabilisation that the role of heteroatom comes into play. The unshared pair of electrons on the heteroatom helps in delocalisation of the positive charge which helps to stabilise the carbocations (a and b) formed initially.

The α–cleavage rule applies to compounds containing –NRR′, –SR, –OR, –Cl and carbonyl functional groups. Two such examples follow.

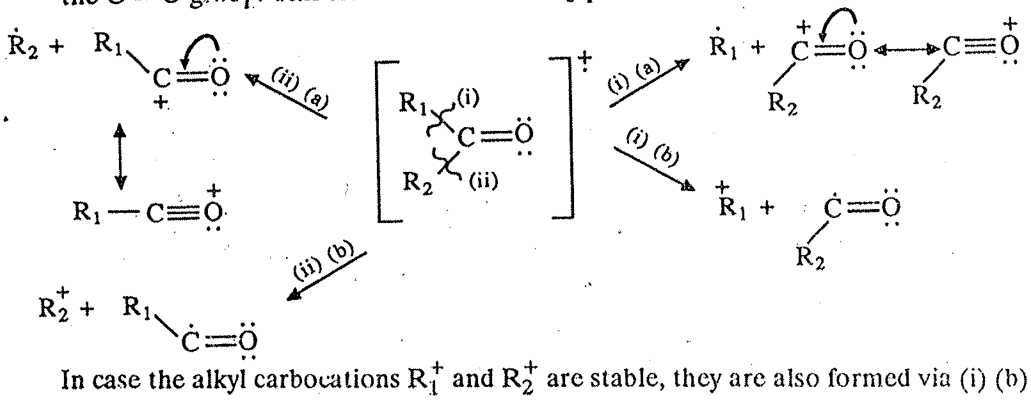

α-cleavage
(amine)


α-cleavage
(ether)

It is also worth considering here the fact that where **more than one site** of α–cleavage is possible, the ejection of **largest** alkyl radical gives the largest peak. We can understand this by taking the following example. In the case of 2–butanol, the most abundant peak is at m/z 45 resulting from the ejection of ethyl radical.



In case of carbonyl compounds, $\begin{matrix}R_1\\R_2\end{matrix}\!\!>C = O$, cleavage can occur on either side of the C = O group. This leads to the following possibilities:

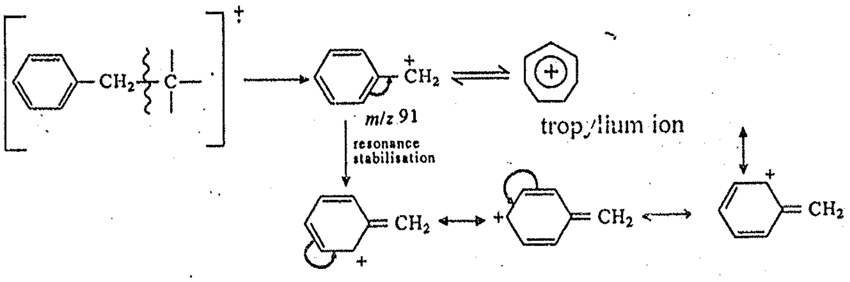


In case the alkyl carbocations R_1^+ and R_2^+ are stable, they are also formed via (i) (b) and (ii) (b) pathways.

12.5.3 Formation of Resonance Stabilised Cations

Molecular ions of alkenes and alkylbenzenes fragment to yield resonance stabilised cations. In alkenes, the bond β to the double bond is cleaved to yield a resonance stabilised allyl cation. Similarly, the following fragmentation of the alkylbenzenes takes place because the resulting benzylic cation, which is stabilised by resonance, is also in equilibrium with the tropylium ion.

$$[R \nmid CH_2-CH=CH_2]^{+\cdot} \longrightarrow R^{\cdot} + [\overset{+}{C}H_2-CH=CH_2 \longleftrightarrow CH_2=CH-\overset{+}{C}H_2]$$



The mass spectrum of butylbenzene shown in Fig. 12.7 exibits a peak at m/z 91 and it is in fact the base peak.

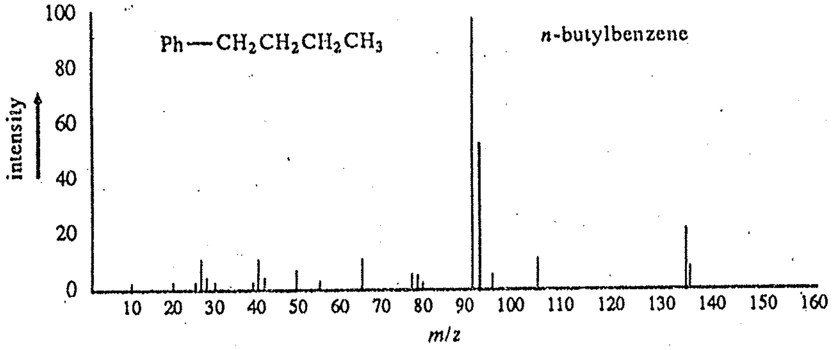


Fig. 12.7 : Mass spectrum of butylbenzene

SAQ 3

The mass spectrum of *trans* 2–hexene shows peaks at m/z 84 and 55. Account for them.

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12.5.4 Loss of Small Molecules

Small stable molecules such as H_2O, CO_2, CO, C_2H_4 etc. can be lost from a molecular ion. For example, alcohols easily lose H_2O molecule and show prominent M–18 peak.

The loss of H_2O from alcohols is so facile that no molecular ion peak is observed in their mass spectrum. Mass spectrum of 2–methyl –2–butanol as shown in Fig. 12.8 illustrates this point.

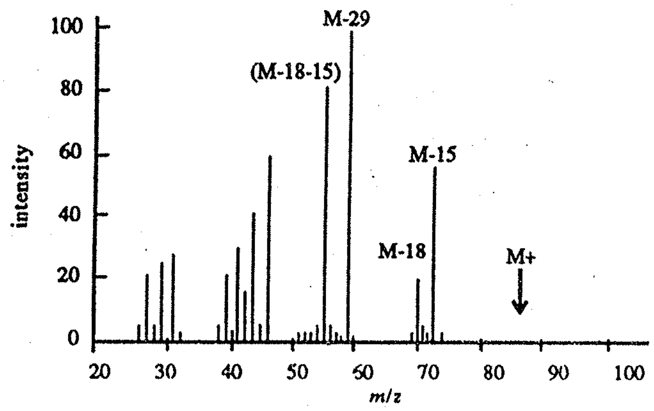
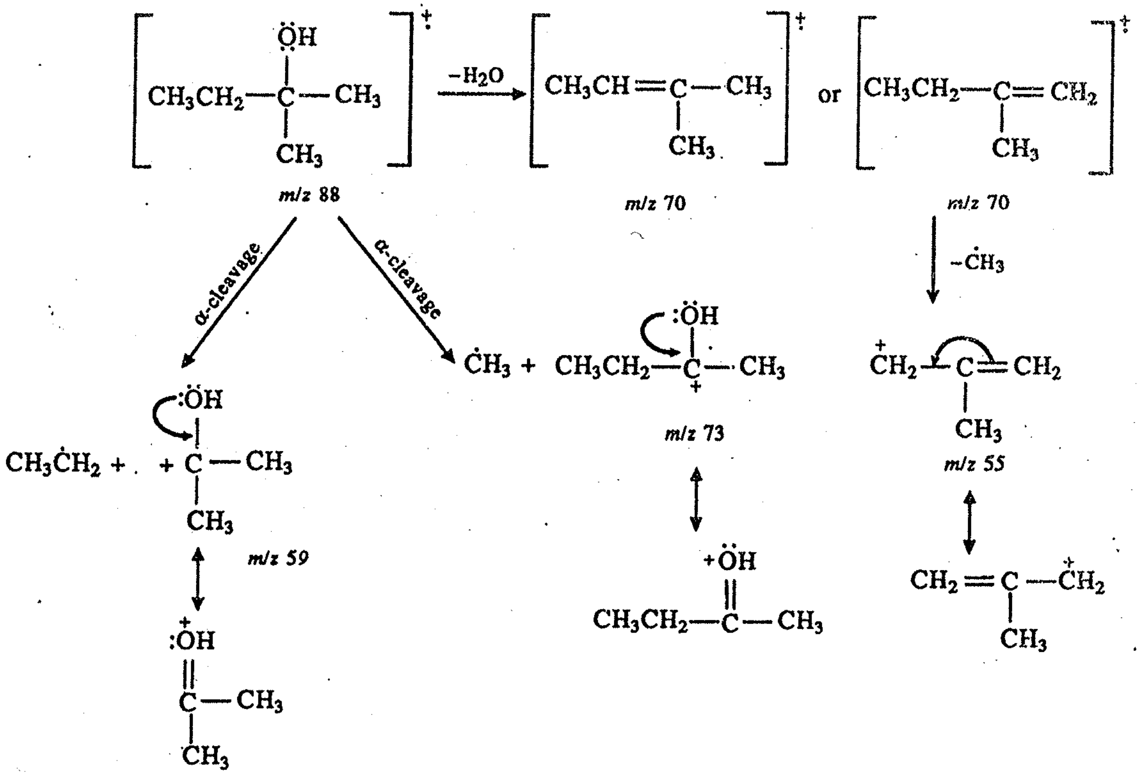


Fig. 12.8: Mass spectrum of 2-methyl-2-butanol.

The following fragmentation pathways explain the origin of various peaks in the mass spectrum.

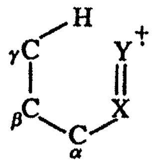


12.5.5 Rearrangement

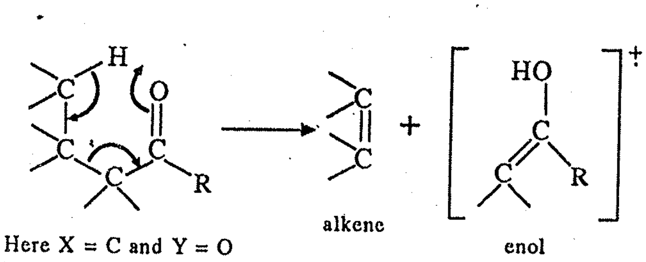
You might have observed in the earlier examples that a molecular ion with an even mass value cleaves to give fragment ions with **odd** mass values and vice–versa. But if the **even** mass molecular ion yields fragments of **even** mass and **odd** mass molecular ion yields fragments of **odd** mass, it indicates that a **rearrangement** has taken place.

In case the mass difference between expected and the observed fragment ion is of one unit, rearrangement involving migration of hydrogen atom can be expected.

A rearrangement known as **McLafferty rearrangement** is commonly observed in the compounds having the following structure where X and Y can be C, O, S, N and P.



Let us take the example of an aldehyde or a ketone having γ–hydrogen. It can undergo the McLafferty rearrangement as shown below:



Here X = C and Y = O
When R = H, aldehyde
R = Alkyl, ketone

Here X = C and Y = O

when R = H, aldehyde

R = alkyl, ketone

The mass spectrum of butanal ($CH_3CH_2CH_2CHO$) is shown in Fig. 12.9. It shows

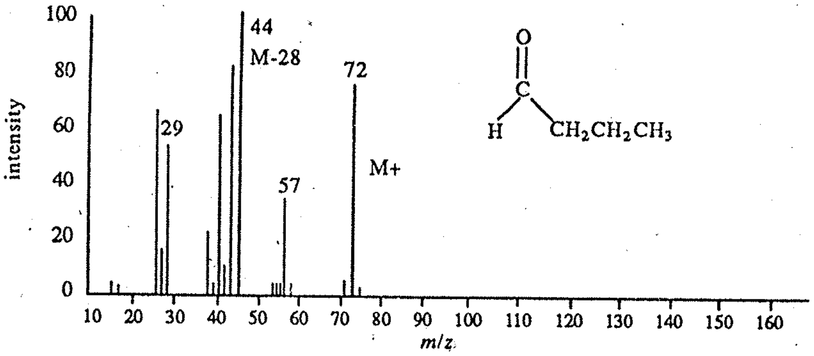
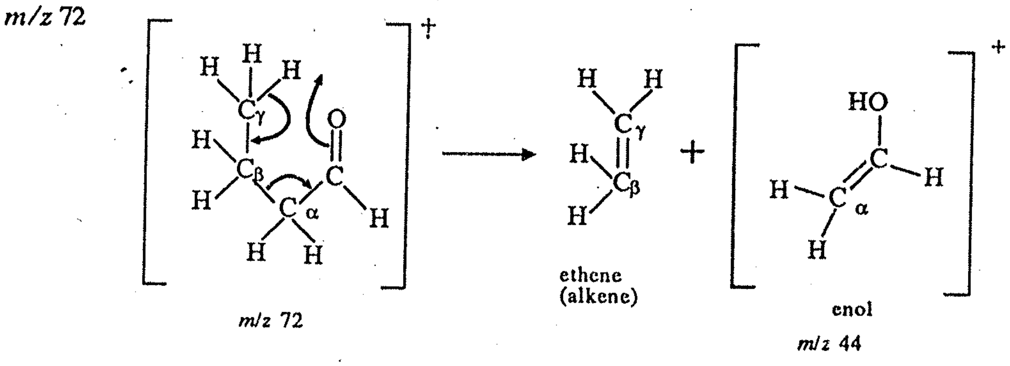


Fig. 12.9: Mass spectrum of butanal.

prominent peaks at *m/z* 72, 57, 44 and 29. These peaks can be explained as follows:

m/z	fragments
72	M^+
57	loss of $\dot{C}H_3$, $(M-CH_3)^+$ fragment
29	loss of $\dot{C}H_3CH_2CH_3$, $(M-C_3H_7)^+$ fragment

The peak at *m/z* 44 (M–28) is an even mass peak from the **even** mass number molecular ion and hence indicates a rearrangement. The McLafferty rearrangement explains this peak as follows:



Similarly carboxylic acids and esters can also undergo McLafferty rearrangement provided they have γ–hydrogen.

SAQ 4

The mass spectrum of pentanoic acid shows a peak of m/z 60 involving McLafferty rearrangement. Write the structures for the fragments formed.

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12.6 SUMMARY

Let us now summarise the important points which you studied in this unit.

- Mass spectrometry is different in principle from the other spectroscopic techniques.
- It involves the bombardment of atoms and molecules with high energy electrons which yields a molecular ion by the lose of an electron. This forms the basis of electron ionisation.The molecular ion itself being energetic can undergo fragmentation
- Chemical ionisation and fast atom bombardment provide alternative means of ionisation.
- Mass spectrum is a plot of relative abundance of various positively charged fragments vs their m/z values.
- The peak corresponding to molecular ion gives the molecular mass.
- The base peak is the peak of highest intensity.
- The pattern of peaks near the molecular ion region i.e., M+1, M+2 peaks etc. gives important information about the nature of heteroatoms present.
- Various fragmentation patterns involve simple cleavage, α–cleavage, loss of small molecules, formation of resonance stabilised cations and rearrangements.
- McLafferty rearrangement involves a γ–hydrogen and a double bond between C, O, N, S, P atoms.

12.7 TERMINAL QUESTIONS

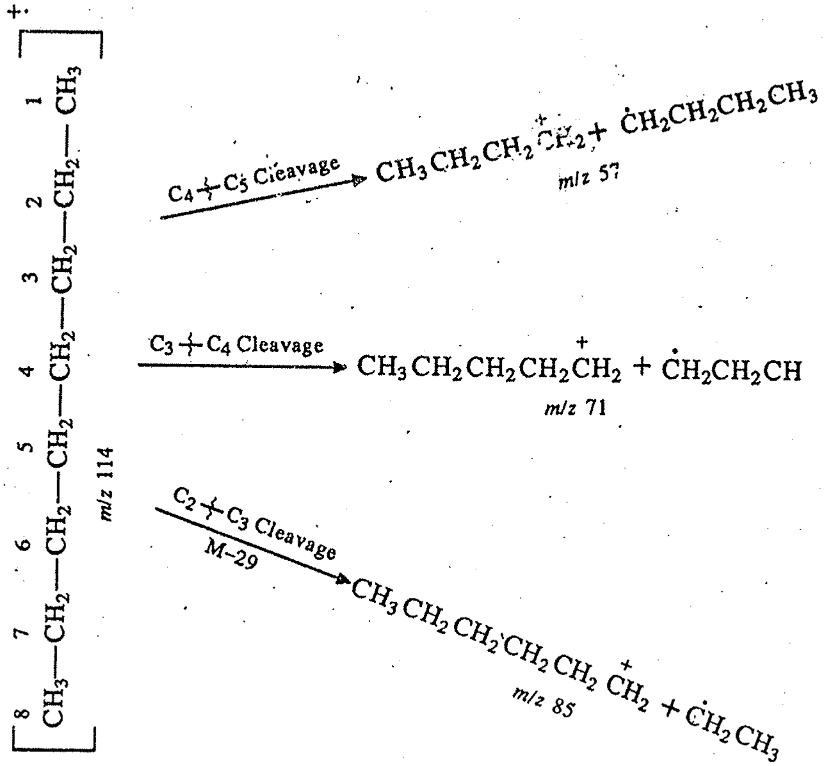
1. The mass spectrum of chloroethane shows two peaks at m/z 64 and 66. The peak at m/z 66 is of one third intensity as the peak at m/z 64. Which one is the molecular ion peak? Account for the origin of the other peak.
2. The mass spectrum of phenyl ethanone ($C_6H_5COCH_3$) shows the peaks at m/z 120, 105 and 77. Show how these peaks arise in the mass spectrum.
3. A compound shows the molecular ion peak at m/z 107. What is the nature of the compound?

12.8 ANSWERS

Self Assessment Questions

		m/z
1.	$^+CH_3$	15
	$^+OCH_3$	31
	$^+OCCH_3$	43

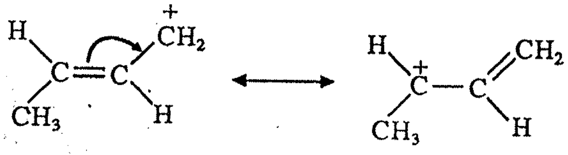
2.



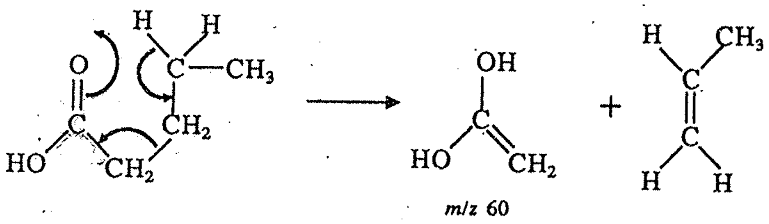
3. *trans*–2–hexane : peak at m/z 84 is due to $[M]^+$ and that at

m/z 55 is due to $[M - CH_2CH_3]^+$

which is resonance stabilised allylic cation as shown below:



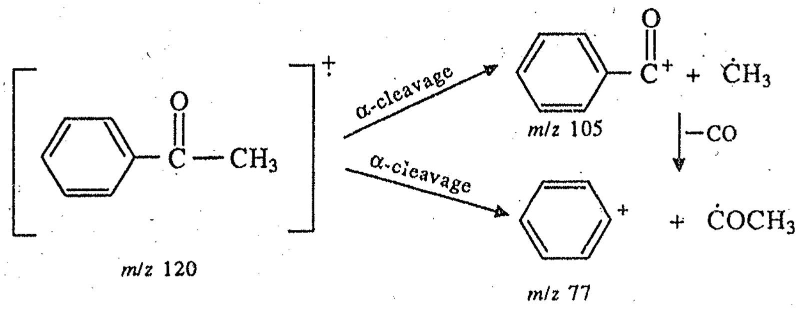
4.



Terminal Questions

1. The peak at m/z 64 is the molecular ion peak having ^{35}Cl isotope. The other peak is M+2 peak having ^{37}Cl isotope.

2.



3. It contains one nitrogen atom.

UNIT 13 EXERCISES IN PROBLEM SOLVING USING IR, UV, NMR AND MASS SPECTRAL TECHNIQUES

Structure

13.1 INTRODUCTION

So far we have studied various spectroscopic techniques such as IR, UV-VIS, NMR and mass spectrometry. The knowledge you have gained so far provides the framework for learning advanced concepts of the subject, but deeper understanding of spectroscopy can be gained through actual application of your knowledge in solving problems related to structure elucidation. In this unit we will discuss the simple applications of IR, UV, NMR spectroscopy and mass spectrometry in arriving at the structures of organic compounds. Thus if you have learnt the previous units carefully, namely 1-12 of this course, you will be able to correlate the information from various spectral techniques with the structure of an organic compound.

It is always advisable to collect all the available spectral data of the compound before making a tentative (or even definite) structural assignment. The order in which the information from various spectral techniques could be used is not a very rigid one. But, it is better to start with the mass spectral data and know the molecular weight. The UV spectrum can then be analysed to know the extent of conjugation present. This can be followed by the study of IR spectrum which will indicate the nature of carbon skeleton and functional group (s) present. The information obtained so far from above spectral techniques is supplemented by studying the NMR spectrum which reveals the number of various kinds of protons present in a molecule.

We will use the same approach in this unit to illustrate spectra- structure relationship by taking a few simple molecules as examples.

Objectives

After studying this unit, you should be able to :

- use mass spectrum of a given compound to know its molecular weight and other structural features,
- calculate the index of hydrogen deficiency (the sum of multiple bonds and ring systems),
- identify the carbon skeleton and functional groups present in a compound from its IR spectrum,
- predict the extent of unsaturation present in a compound from its UV spectrum

using λ_{max} and ε values,

- count the exact number of various non-equivalent protons and predict their chemical environment using the NMR spectrum;
- use the UV, IR, NMR and Mass spectral data to arrive at the structure of a given compound.

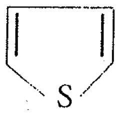
13.2 MOLECULAR FORMULA AND INDEX OF HYDROGEN DEFICIENCY

Before attempting to deduce the structure of an unknown organic substance from its spectral data, we can simplify the problem to some extent by arriving at its molecular formula. The molecular formula of a compound can be obtained by knowing its empirical formula and molecular weight. You must be aware from your previous knowledge that qualitative and quantitative elemental analysis yields empirical formula. Then, molecular formula can be obtained as given below:

Let $$n = \frac{\text{Mol. wt.}}{\text{Empirical formula wt.}}$$

Then molecular formula $= n \times$ Empirical formula.

When the molecular formula is determined, the *index of hydrogen deficiency* (IHD) may be used to know the number of multiple bonds and ring systems. If the IHD is one, it shows that there is either a double bond or one ring system. If IHD is two, it indicates two double bonds or two rings or one double bond and one ring system or a triple bond. Similarly IHD three means either three double bonds or three rings or their combination thereof. Now the question is how to find the IHD? It is very simple: In the molecular formula, substitute CH_3 for each halogen, CH_2 for each O or S and CH for each N or P. For example, the IHD for thiophene C_4H_4S is 3, i.e. by substituting S by CH_2, we arrive at $C_4H_4CH_2 = C_5H_6$ and the molecular formula for the corresponding saturated hydrocarbon is C_5H_{12}. Hence there is a difference of 6H atoms (or 3 hydrogen equivalents) and this number gives IHD as 3. It indicates that 2 double bonds and a ring system could be present in the structure as given below:



(Two double bonds and a ring system)

Similarly, the IHD for C_6H_6 is 4 while that of C_6H_{14} is zero.

13.3 GENERAL APPROACH OF IDENTIFICATION OF ORGANIC COMPOUNDS

Prior to the spectroscopic methods of analysis and identification of compounds, other physical and chemical methods were used for characterising various molecules. The physical methods included the determination of physical constants such as m.pt., b.pt., solubility, refractive index etc.

The various methods used for determination of mol.wt. included the Rast method (involving freezing point lowering), vapour density method for volatile substances and elevation of boiling point etc.

The chemical methods involved the following steps:

(i) Qualitative and quantitative determination of elements present.

(ii) Determination of mol. wt. and molecular formula.

The determination of molecular formula restricts the number of possible structures by limiting the number and nature of functional groups.

(iii) Functional group identification.

(iv) Preparation and identification of suitable derivatives.

(v) Synthesis from known simple compounds.

(vi) Support from degradative studies.

But today spectroscopic methods have replaced the older chemical methods due to the following advantages:

(i) they are less time consuming,

(ii) the results are very accurate,

(iii) only a small amount of sample is needed which can be recovered in most of the techniques.

The determination of structure now-a-days involves the use of data from mass, UV, IR and NMR spectra leading to a variety of information about a given compound. Let us study about this in a little more detail.

I. Mass Spectrum :

You have studied in Unit 12 that by knowing the molecular ion peak from the mass spectrum, we can know the molecular weight of the compound. Also by carefully analysing the other small peaks present near M^+ peak, we can know about the presence of halogens etc. The presence of nitrogen is also indicated in case of an odd numbered molecular ion peak.

Thus when you have mass spectrum of a given compound, you should look for the following information :

(i) Which is the M^+ peak ?

(ii) What is its m/z value ?

(iii) What is the molecular weight of the compound ?

(iv) Whether the molecular weight is odd or even ?

(v) What is the pattern around M^+ region ?

(vi) What are the halogens present and what is their number ?

(vii) Which is the base peak ?

viii) Presence (or absence) of various characteristic peaks resulting due to the fragmentations of various classes of compounds indicating a particular functional group.

Since in the last unit, we did not discuss the characteristic fragmentation patterns of each class of organic compounds, at this stage you have only a limited knowledge to check the information needed in point (viii). But you can identify certain features such as presence of alcohols, heteroatoms, presence of benzyl ($C_6H_5CH_2-$) group, γ - hydrogen (McLafferty rearrangement) etc. in the mass spectrum.

II. The next step is analyse the UV spectrum

You have studied electronic spectra in Units 8 and 9 of Block 3 and you are aware of various electronic transitions which can take place in a compound. Thus, the electronic or UV spectrum yields the information about the presence (or absence) of conjugation present in a compound. But it is of little value as far as the finer structural details are concerned. A few λ_{max} values for simple classes of organic compounds are presented in Table 13.1.

The study of UV spectra is more useful for long chain unsaturated compounds e.g. fatty acids, certain natural products as terpenes, carotenes etc.

Table 13.1: Range of λ_{max} values for various classes of compounds

S.No.	Class	Region of λ_{max} in nm (transition)
1.	Alkanes	140–150 $(\sigma \longrightarrow \sigma^*)$
2.	Akyl chloride Alkyl bromide Alkyl iodide	170–175 $(n \longrightarrow \sigma^*)$ 200–210 (") 255–260 (")
3.	Alcohols and amines	180–185
4.	Aldehydes	180 $(\pi \longrightarrow \pi^*)$ 290–295 $(n \longrightarrow \pi^*)$
5.	Ketones	190 $(\pi \longrightarrow \pi^*)$
6.	Carboxylic acids (saturated)	200–210 $(n \longrightarrow \pi^*)$
7.	Esters	200–205 $(n \longrightarrow \pi^*)$
8.	Amides	205–220 $(n \longrightarrow \pi^*)$
9.	Aromatic compounds	250–280 $(\pi \longrightarrow \pi^*)$

Conjugation shifts the λ_{max} values to higher wavelengths.

Presence of various substituent groups also shifts the λ_{max} value.

Table 13.2 lists some common organic compounds and their λ_{max} values.

Table 13.2: λ_{max} values of some common organic compounds

S.No.	Compound	λ_{max} / (nm)
1.	Ethene	175
2.	Butadiene	217
3.	Hexatriene	258
4.	Ethanal	180, 290
5.	Propanone	190,280
6.	Benzene	204, 254
7.	Aniline	230, 280
8.	Phenol	210,271
9.	Nitrobenzene	270
10.	Resorcinol	277
11.	Pyridine	252
12.	Stilbene (*trans*)	295
13.	Stilbene (*cis*)	280

The *trans*-isomer of an alkene absorbs at longer λ_{max} than the *cis*-isomer.

III. IR Spectrum

You are familiar from unit 5 that the vibrational or IR spectrum of a compound can tell many things about the given compound. Thus, in an IR spectrum you should look into various regions for the following information.

(i) Nature of Carbon skeleton (600–1400 cm^{-1}).

(ii) Presence of various functional groups (1400–4000 cm^{-1}).
(as given in Table 5.3).

(iii) Presence of hydrogen bonding (3200–3600 cm^{-1}).

(iv) Geometry (*cis*– or *trans*–) in case of olefinic compounds.

(v) Substitution pattern for aromatic compounds.

For your convenience, we are enlisting in Table 13.3 the range of frequencies for some classes of organic compounds.

Table 13.3: Characteristic IR frequencies in cm^{-1}

Bond	Class	Frequency
C–H	Alkanes	2850–2960
		1350–1470
C–H	Alkenes	3020–3080
		675–1000
C–H	Aromatic ring	3000–3100
		675–870
C–H	Alkynes	3300
C=C	Alkenes	1640–1680
C≡C	Alkynes	2100–2260
C=C	Aromatic	1500, 1600
C–O	Alcohols, ethers, carboxylic acids, esters	1080–1300
C=O	aldehydes, ketones, carboxylic acids, esters	1690–1760
O–H (free)	Alcohols, phenols	3610–3640
(H–bonded)	Alcohols, phenols,	3200–3600
	carboxylic acids	2500–3000
N–H	Amines	3300–3500
C–H	Monosubstituted aromatic	690–710, 730–770
	o-Disubstituted	735–770
	m-Disubstituted	690–710, 750–810
	p-Disubstituted	810–840

No two different compounds can have the superimposable IR spectra. Therefore, IR spectrum can be used to characterize a compound if it exhibits a superimposable (peak to peak) IR spectrum with that of a known compound, thereby, establishing its identity.

After knowing the presence of functional groups and other features from IR spectrum, finally the NMR spectrum of the compound is analysed to supply the finer structural details.

IV. NMR spectrum

The NMR spectrum was discussed in Unit 10. You know that NMR spectrum or more particularly ^{1}H-NMR spectrum can furnish information about the nature and number of various protons present in a molecule. Thus when you start interpreting the ^{1}H-NMR spectrum of a compound, you should look for the following details in the spectrum.

(i) How many different types of protons are there?

You will find an answer to this question by counting the number of different signals present in the spectrum.

(ii) What is the position of these signals ?

The position of signals will give you hint about the electronic environment of the proton, i.e whether it is linked to an electronegative element or not and is it aromatic, aldehydic, alcoholic, phenolic or carboxylic proton etc.

(iii) What is the ratio of various types of protons ?

This can be found out by analysing the integrals.

(iv) How many neighbouring protons are present around a given proton ?

This information is obtained by observing the spin-spin splitting pattern of a particular signal.

In the rest of the unit, we will present some examples to show how we can use the Mass, UV, IR and ^{1}H-NMR spectral data in solving structural problems.

13.4 APPLICATION OF SPECTRAL DATA TO STRUCTURE ELUCIDATION

Problem 1

A compound showed molecular formula C_4H_8O on the basis of C, H analysis. It exhibited the mass spectrum as shown in Fig. 13.1.

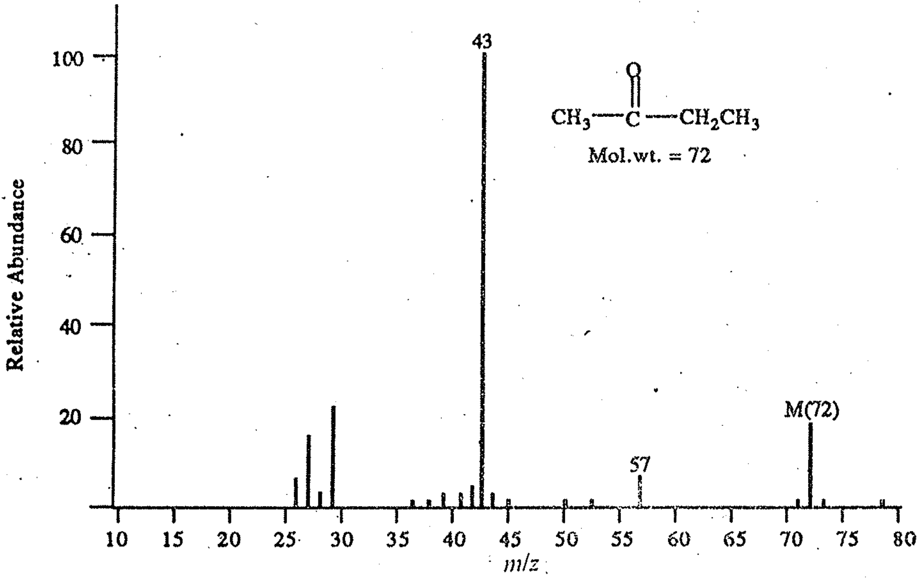


Fig. 13.1: The mass spectrum of compound 1.

The mass spectrum showed a peak at *m/z* 72 which also indicates the C_4H_8O as the molecular formula.

First of all we will calculate the IHD. Since there is one oxygen and it is to be replaced by CH_2 and hence C_4H_8O gives $C_4\ H_8\ CH_2$ or $C_5\ H_{10}$. The corresponding molecular formula for saturated hydrocarbon having 5 carbon atoms is C_5H_{12} (cf, $C_n\ H_{2n+2}$). The difference between C_5H_{10} and C_5H_{12} is two H atoms, therefore, the IHD is one. This shows that either there is one double bond or it is a cyclic compound with one ring.

The base peak in mass spectrum appears at *m/z* 43 which could be due to the loss of 72–43 = 29 units; thus indicating the loss of C_2H_5 (29 units). Another peak at *m/z* 57 indicates the loss of 72–57 = 15 units which could due to the loss of CH_3 group (having mass 15 units). Thus, presence of one ethyl and one methyl group is indicated.

The IR spectrum in Fig. 13.2 shows a strong band at 1716 cm^{-1} which shows the presence of carbonyl (C = O) group.

The presence of carbonyl group thus accounts for the index of hydrogen deficiency (i.e. one double bond C = O) as well as oxygen atom of the molecular formula. Thus, the possibility of cyclic structure is ruled out. The other information which we can get from IR spectrum is not very useful as the bands at 2941–2857 cm^{-1} and 1460 cm^{-1} are due to the C–H stretching and bending vibrations, respectively.

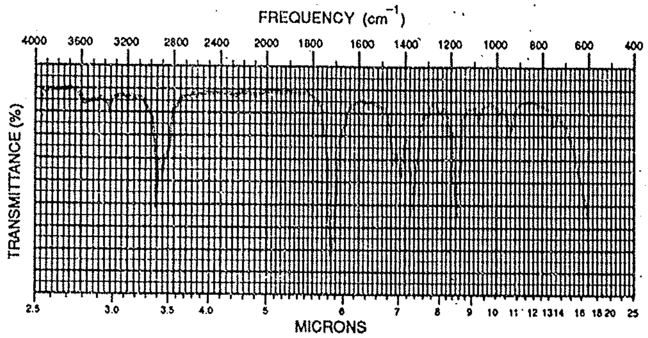


Fig. 13.2: IR spectrum of compound 1.

The presence of carbonyl suggests us to look for its UV spectrum which shows λ_{max} at 274 nm. This indicates that the carbonyl is either in the form of an aldehyde or a ketone. The above information is further supplemented by ^{1}H-NMR spectrum. The ^{1}H-NMR spectrum is shown in Fig. 13.3.

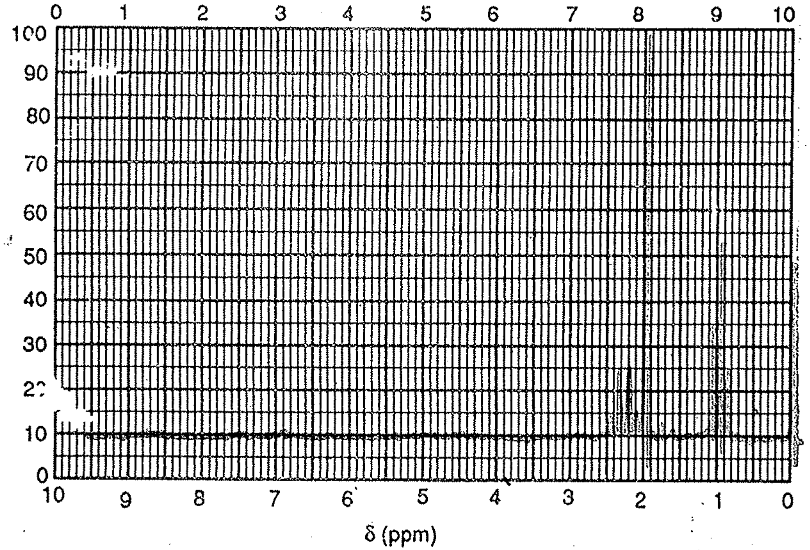
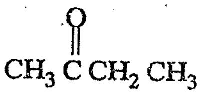


Fig. 13.3: The ^{1}H-NMR spectrum of compound 1.

It shows a triplet at δ 1.0 with $J = 7$ Hz corresponding to 3 protons which indicates that it is coupling with 2 neighbouring protons. A quartet at δ 2.47 ($J = 7$ Hz)is observed which corresponds to 2 protons. The same coupling constant of 7 Hz for both signals show them to be coupled to each other and hence a $CH_3 - CH_2-$ group is indicated. Remember that same was indicated in mass spectrum also. The singlet at δ 2.20 for 3 protons shows the presence of methyl group. The absence of any splitting of methyl signal shows that these protons are not coupled to any other proton; thus indicating that there is no proton on its adjacent carbon atom. Thus, the adjacent carbon could be a carbonyl carbon. So, we can write



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3$$

as the structure of compound 1. Had it been an aldehyde, there should have been a signal around δ 9. The absence of signal in this region rules out the possibility of an aldehyde. Thus, it is a ketone.

Problem 2

The following data is given for a compound. Let us arrive at its structure.

Mol. wt. : 108 (it is not an acidic compound).

UV : λ_{max} 254 nm and 202 nm.

IR : 3420, 3064, 1500 and 1455 cm^{-1}.

NMR : (δ, $CDCl_3$) : 3.85(*s*, 1H), 4.55(*s*, 2H) and 7.25 (*s*, 5H).

The mass spectrum of this compound as exhibited in Fig. 13.4 shows the molecular ion peak at *m/z* 108; thus confirming its molecular weight as 108.

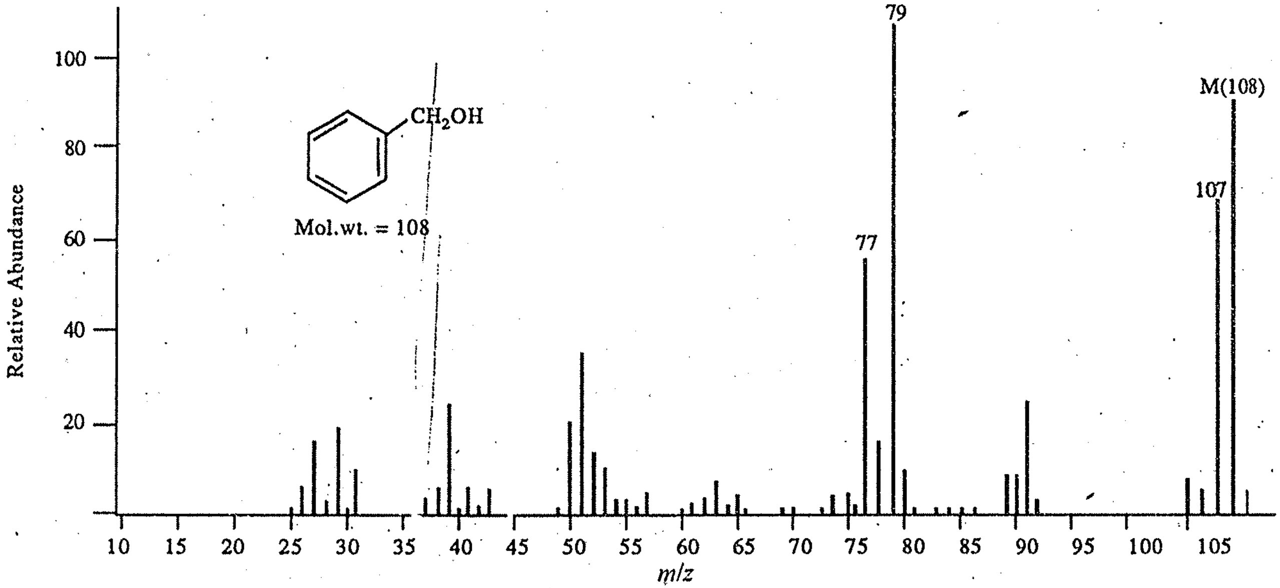


Fig. 13.4: Mass spectrum of compound 2.

In this case only molecular weight is known and hence in the absence of molecular formula no help in structural assignment can be obtained as far as IHD is concerned.

The most important information is from its UV spectrum which exhibits λ_{max} 254 nm and λ_{max} 202 nm showing the presence of benzene ring in the compound. This observation is further supported by its IR spectrum shown in Fig. 13.5.

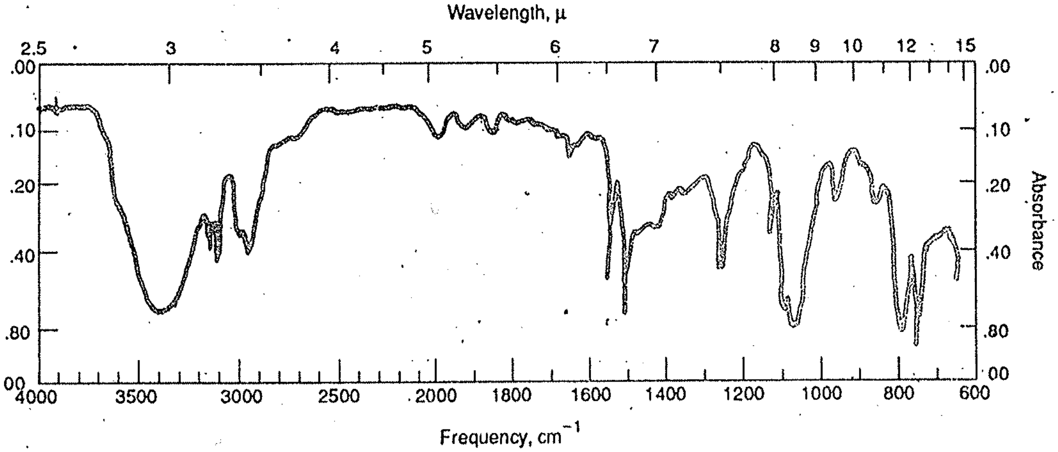


Fig. 13.5: IR spectrum of compound 2.

The band at 3064 cm^{-1} is from C–H stretch of aromatic ring system and those at 1500 and 1455 cm^{-1} are characteristic of aromatic C = C stretching. The broad band at 3420 cm^{-1} may be due to –OH or –NH. Since the band is broad it may be due to hydrogen bonded –OH. When the compound was tested for acidity it was found that it is not acidic. Therefore, hydroxyl is not present on benzene ring because phenols are acidic.

Let us next consider its ^{1}H-NMR spectrum which is shown in Fig. 13.6.

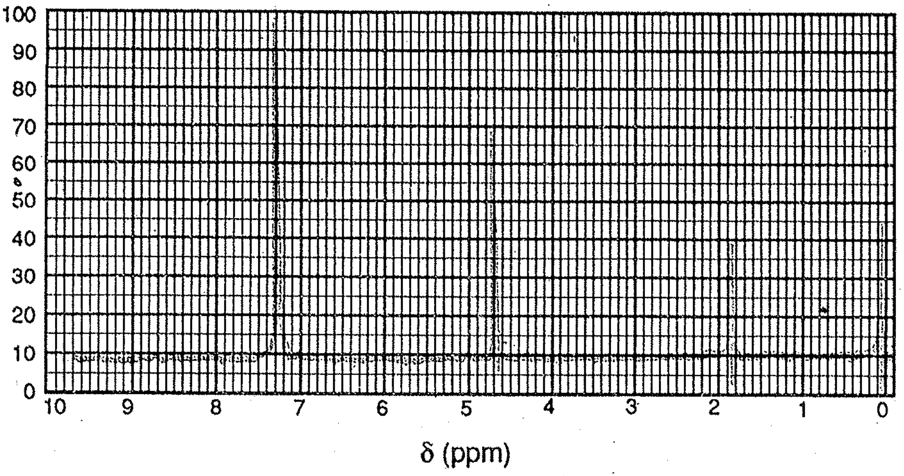


Fig. 13.6: ^{1}H-NMR spectrum of compound 2.

It shows a singlet at δ 7.25 corresponding to five protons. This region indicates the presence of aromatic protons. Thus, this signal indicates 5 aromatic protons of a benzene ring. Only one position of the benzene is thus substituted.

The other information which can be achieved from NMR spectrum is that there are two more singlets. The singlet at δ 1.8 corresponds to one proton indicating it to be a –OH proton. The other singlet at δ 4.7 is due to two protons. Since the protons are in the ratio 1:2:5, the total number of hydrogens is eight. The total mass units of hydrogen and oxygen are 24 and the remainder is 108–24 = 84 mass units. This indicates that there are 7 carbon atoms. Hence the molecular formula comes out to be C_7H_8O. If we substract C_6H_5 of benzene ring and –OH, from C_7H_8O we are left with a CH_2 unit. Hence, the formula of compound 2 is $C_6H_5CH_2OH$.

Let us now go back to its mass spectrum. The mass spectrum shows a prominent (M–1) peak and small (M–2) and (M–3) peaks. The base peak is at *m/z* 79, the other large peaks are at *m/z* 77 and 51. The fragmentation pattern shown in Fig. 13.7 explains the origin of these peaks.

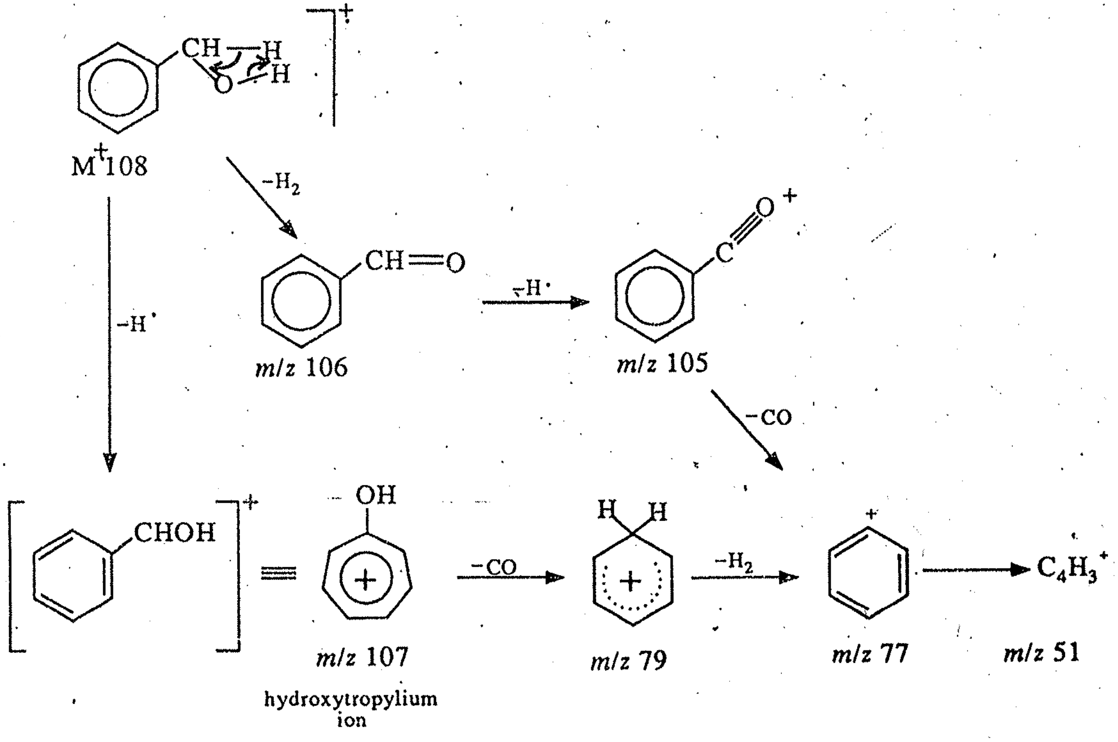


Fig. 13.7: Fragmentation of benzyl alcohol.

Problem 3

Let us now assign the structure to a compound which shows the following spectra.

The mass spectrum of this compound is shown in Fig. 13.8.

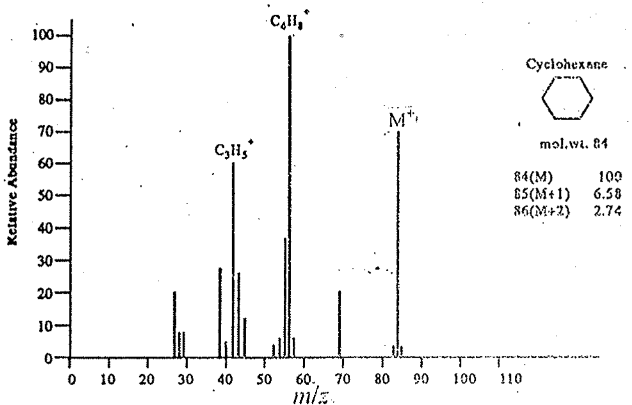


Fig. 13.8: The mass spectrum of compound 3.

It shows an M^+ peak at m/z 84. The base peak appears at m/z 56 and there is another large peak at m/z 41. Thus, there are losses of 28 and 43 mass units, respectively.

Let us now study the IR spectrum as shown in Fig. 13.9.

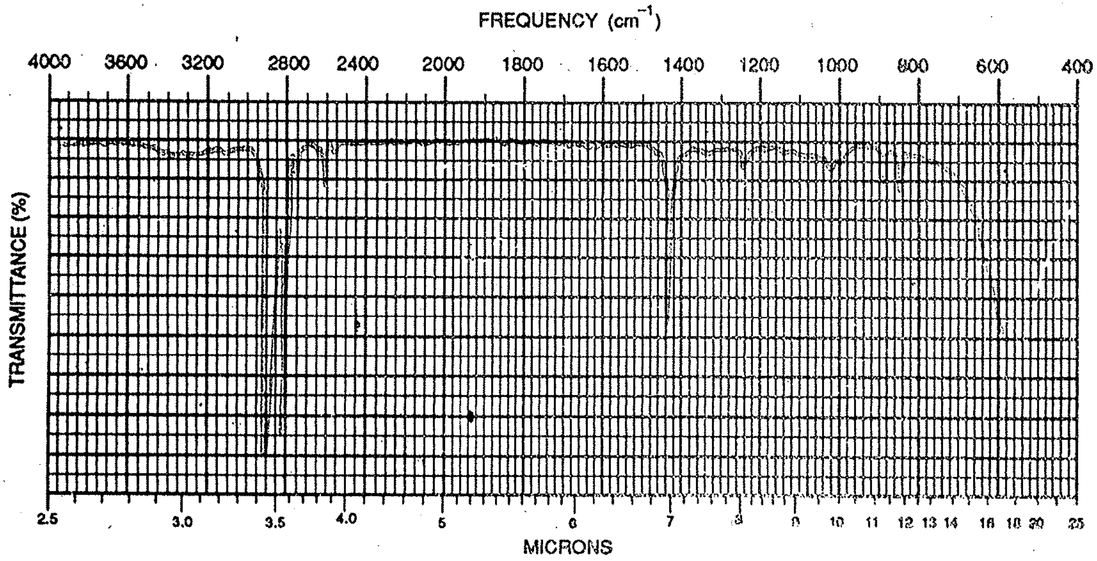


Fig. 13.9: IR spectrum of compound 3.

It shows bands at about 2900 cm^{-1} and 1450 cm^{-1} indicating the presence of a saturated hydrocarbon. The band at 1450 cm^{-1} is characteristic of methylene group (CH_2) for its C–H bending vibrations. The band near 2900 cm^{-1} is due to C–H stretching vibration. The absence of any band in the region 1600–1800 cm^{-1}, attributable to C = C and C = O stretching bands, confirms their absence from the molecular structure.

Let us now take some help from its ^{1}H-NMR spectrum which is shown in Fig. 13.10.

The NMR spectrum is very simple and shows only one singlet at δ 1.42. This indicates that only one kind of protons are present. In other words, it means that all protons are equivalent. This is possible only if the compound is cyclic. Thus, it could be a cyclic saturated hydrocarbon. Since the mol.wt., from mass spectrum was indicated to be 84, it could be C_6H_{12} or cyclohexane. The peaks in the mass spectrum at m/z 56 and 41 could be due to $C_4H_8^+$ and $C_3H_5^+$, respectively.

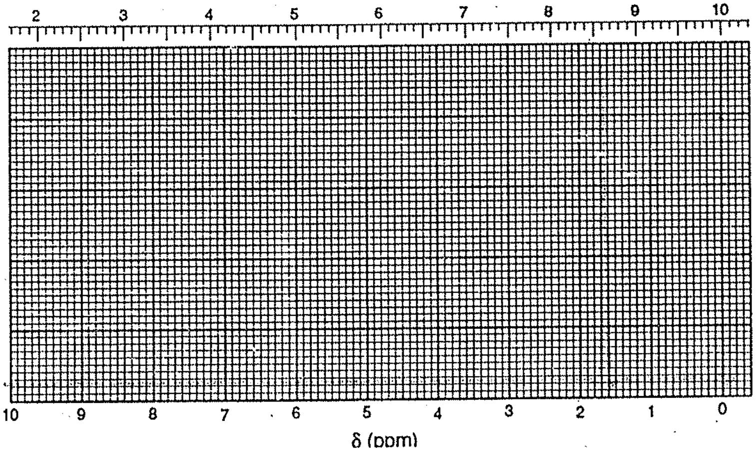


Fig. 13.10: ^{1}HNMR spectrum of compound 3.

The NMR spectrum is very simple and shows only one singlet at δ 1.42. This indicates that only one kind of protons are present. In other words, it means that all protons are equivalent. This is possible only if the compound is cyclic. Thus it could be a cyclic saturated hydrocarbon. Since the mol.wt, from mass spectrum was indicated to be 84, it could be C_6H_{12} or cyclohexane. The peaks in the mass spectrum at *m/z* 56 and 41 could be due to $C_4H_8^+$ and $C_3H_5^+$, respectively.

Problem 4

We will now assign the structure to a compound which has following spectral data :

Mass spectrum : *m/z* = 150 (M^+), 91, 43.

Molecular formula :$C_9H_{10}O_2$.

IR spectrum: 1740, 1220, 1600–1400, 749 and 697 cm^{-1}.

NMR spectrum : (δ , $CDCl_3$): 1.96 (*s*, 3H), 5.0 (*s*, 2H), 7.22 (*s*, 5H).

The compound is found to have molecular formula $C_9H_{10}O_2$, on the basis of its elemental and mass spectral analysis. The mass spectrum presented in Fig. 13.11, shows the M^+ peak at *m/z* = 150.

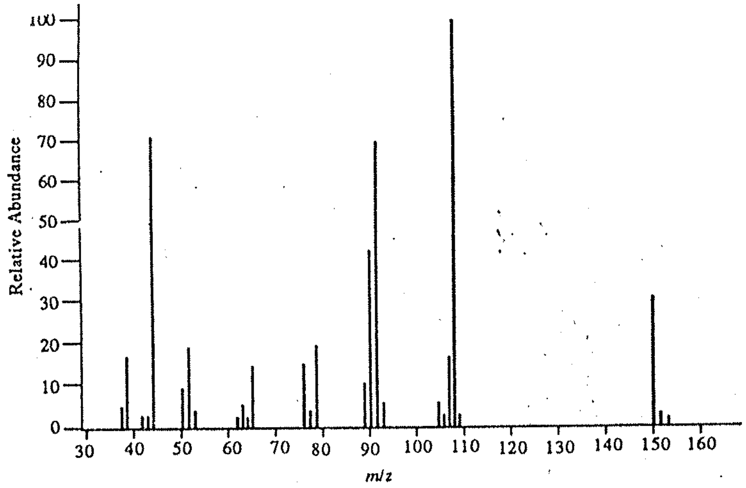


Fig. 13.11: Mass spectrum of compound 4.

The index of hydrogen deficiency for this molecular formula is calculated to be 5.

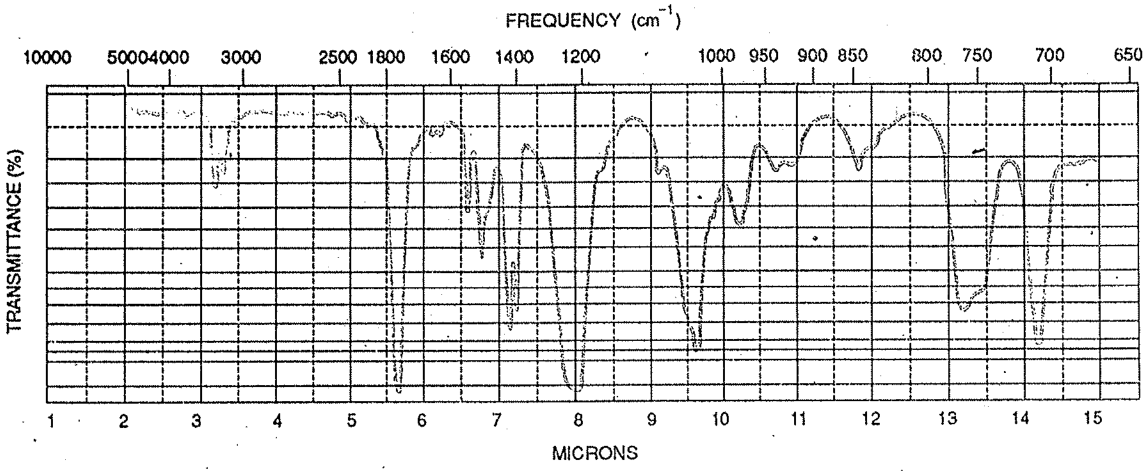


Fig. 13.12: IR spectrum of compound 4.

Its infrared spectrum in Fig. 13.12 shows intense bands at 1740 (C = O) and 1220 cm^{-1} (C–O) which suggest an ester $(-\overset{O}{\overset{\|}{C}}-O-)$ grouping. (Refer Table 13.3).

The band at 1220 cm^{-1} is characteristic of an ethanoate (acetate) ester, i.e. $-\overset{O}{\overset{\|}{C}}-O-CH_3$. The two bands at 749 cm^{-1} and 697 cm^{-1} suggest that it contains a mono-substituted benzene ring. The aromatic C=C is also evident from bands in the 1600–1400 cm^{-1} region.

Let us now look for these features in its ^{1}H- NMR spectrum which is illustrated in Fig. 13.13.

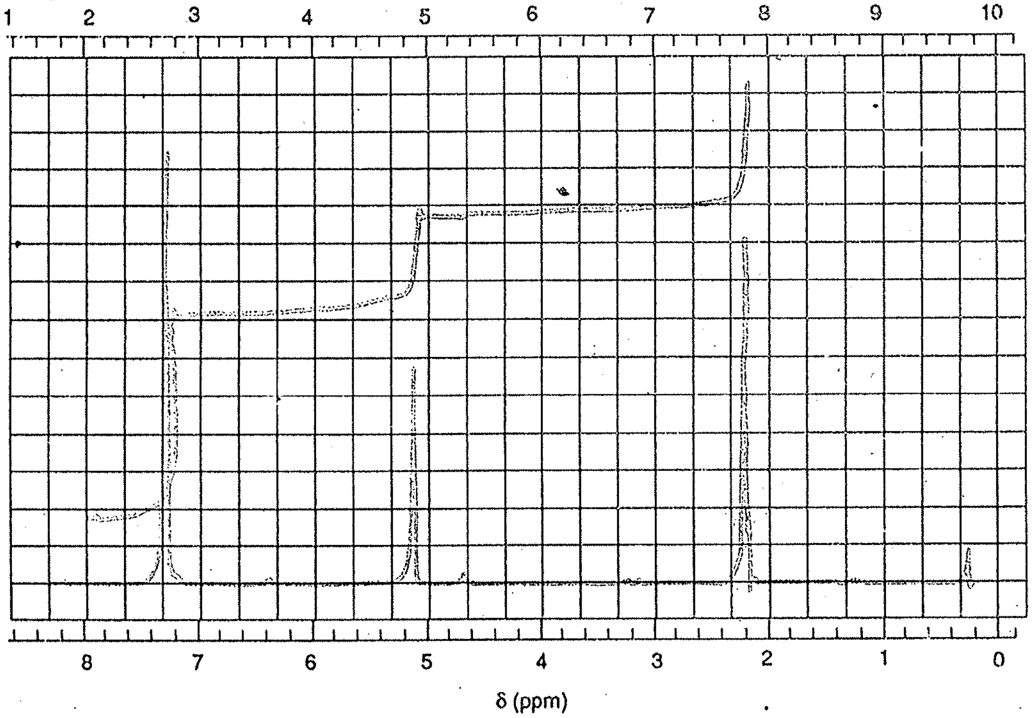


Fig. 13.13: ^{1}H-NMR spectrum of compound 4.

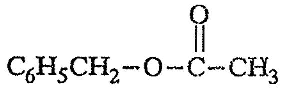
It shows a singlet at δ 7.22 corresponding to 5 protons, thus confirming the presence of a mono-substituted benzene ring. Further, another singlet at δ 1.96 corresponding to 3 protons confirms the presence of three protons of $-\overset{O}{\overset{\|}{C}}-O-CH_3$ groups. The third

signal in the NMR spectrum is also a singlet at δ 5 due to two protons.

Let us now see where these two protons are located ?

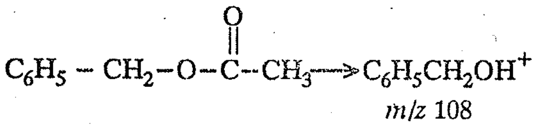
If we subtract C_6H_5- and $CH_3 - \overset{\overset{O}{||}}{C}O-$ from the molecular formula $C_9H_{10}O_2$, we are left with one CH_2 group. Thus, these two protons are $-CH_2-$ protons. The $-CH_2-$ protons appear downfield indicating their linkage to benzene ring on one hand and oxygen on the other.

We can fit the above pieces of information into the following structure:



$$C_6H_5CH_2-O-\overset{\overset{O}{||}}{C}-CH_3$$

The mass spectrum also supports the above structure by showing peaks at $m/z = 43$ due to $\overset{+}{C}OCH_3$ and at 91 due to $C_7H_7^+$. The base peak at m/z 108 can be explained as follows :



$$C_6H_5-CH_2-O-\overset{\overset{O}{||}}{C}-CH_3 \longrightarrow \underset{m/z\ 108}{C_6H_5CH_2OH^+}$$

Problem 5

A compound shows the following spectra. Let us identify its structure.

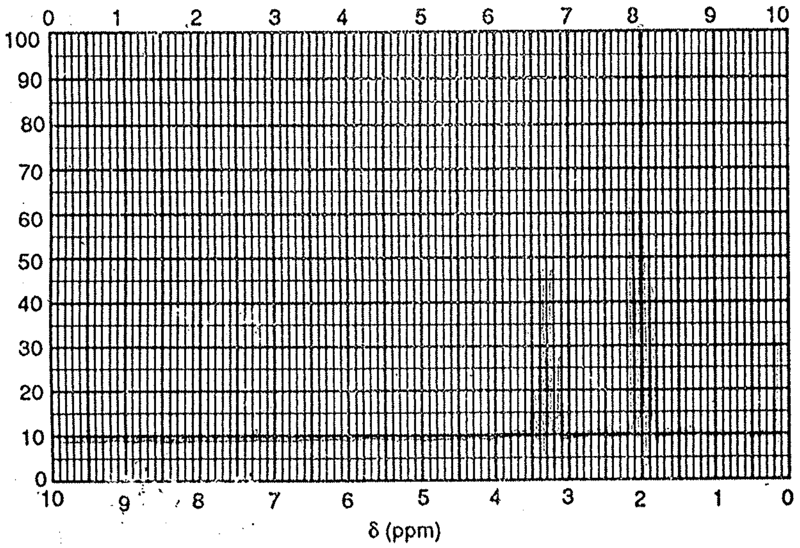


Fig. 13.14: ^{1}H-NMR spectrum of compound 5.

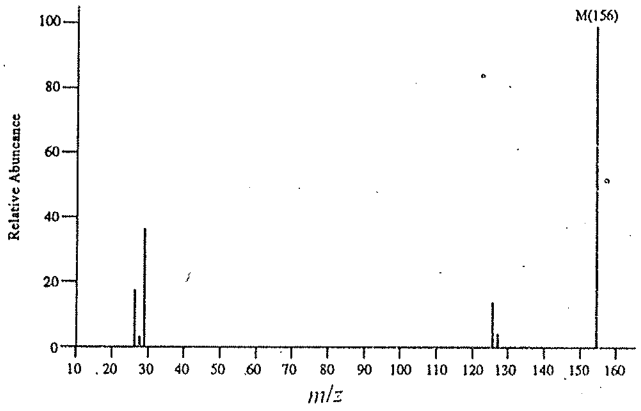


Fig. 13.15: Mass spectrum of compound 5.

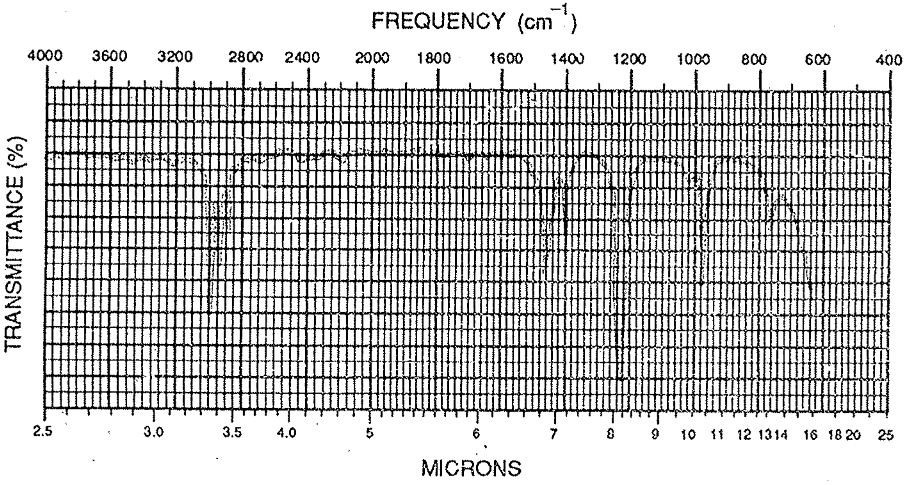


Fig. 13.16: IR spectrum of compound 5.

The ^{1}H-NMR spectrum of the compound shown in Fig. 13.14 exhibits a triplet at δ 1.85 due to 3 protons and a quartet at δ 3.2 due to 2 protons. You must have guessed by now the origin of these signals. These signals correspond to an ethyl group. These are the only signals present in the NMR spectrum. Let us now see to which another group this ethyl group is attached.

We will now study its mass spectrum shown in Fig. 13.15. The mass spectrum shows the molecular ion peak at m/z 156 which is also the base peak in this case. There is another large peak at m/z 29 and this could be due to the ethyl grouping ($C_2H_5^+$). The remaining 127 units could be thought of as due to the presence of Iodine because it has a mass 127. Also there are no M + 2 or M + 4 peaks present, so Cl and Br are ruled out. Flourine also does not fit in this mass data, thus iodine is the only possibility. Thus, this compound could be C_2H_5I.

This structure is further supported by its IR spectrum (Fig. 13.16) which is very simple indicating the simple nature of the compound. In addition to the usual C–H stretching near 3000 cm^{-1}, it shows a strong band at 1200 cm^{-1} which is due to the CH_2 wagging vibration, characteristic of alkyl halides.

Problem 6

A compound having molecular formula $C_5H_8O_3$ shows the following spectra. Let us identify its structure.

UV spectrum – λ_{max} 262 nm

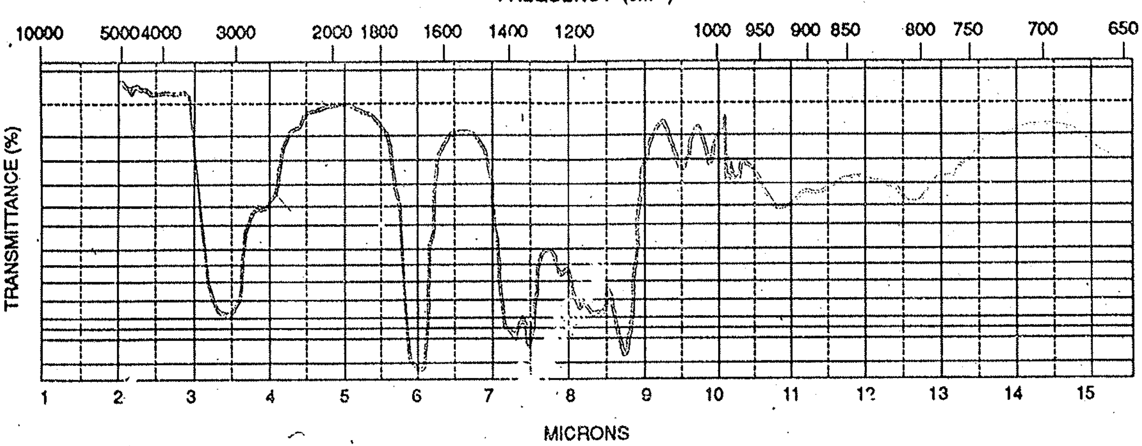


Fig. 13.17: IR spectrum of compound 6.

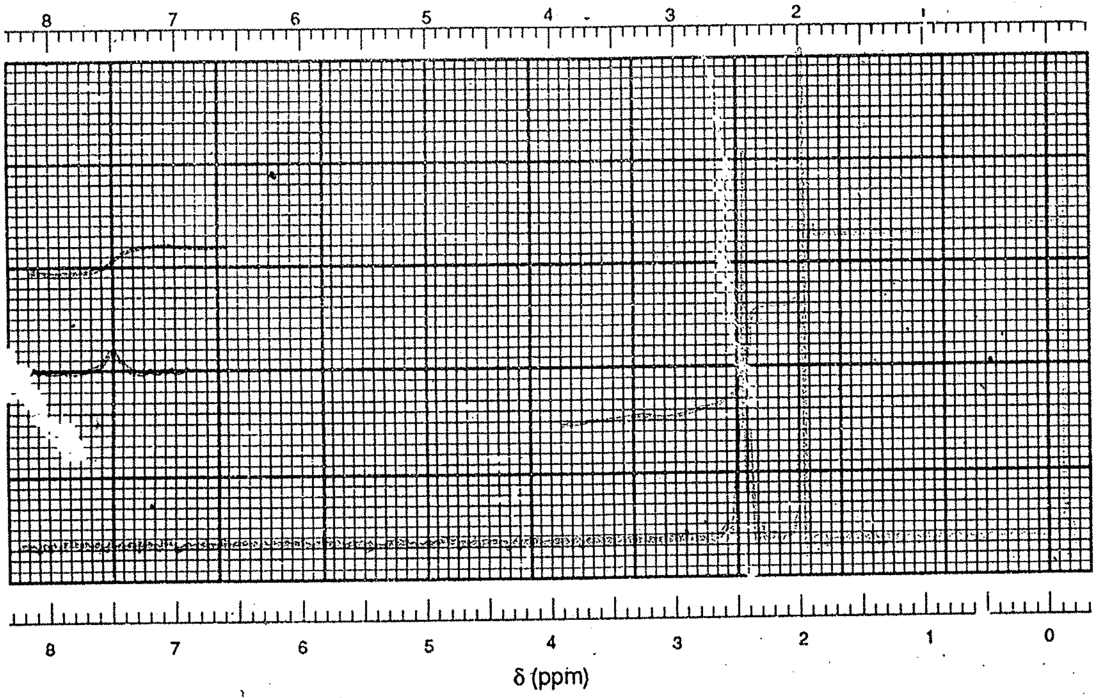


Fig. 13.18: ^{1}H-NMR spectrum of compound 6.

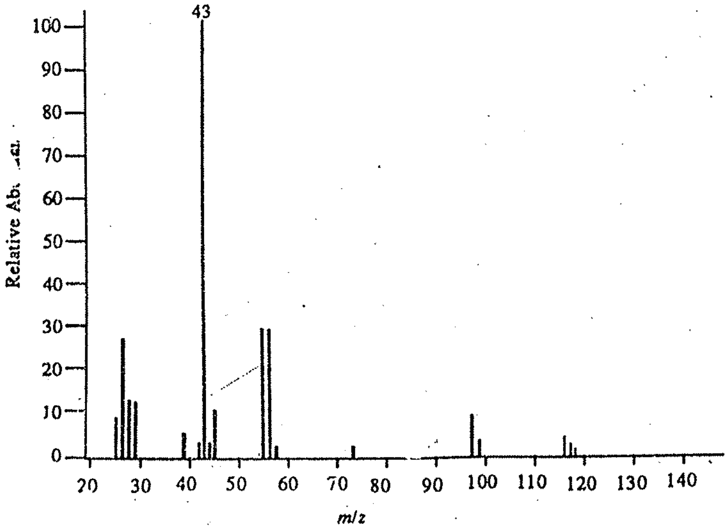


Fig. 13.19: Mass spectrum of compound 6.

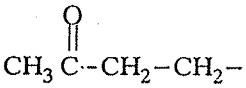
The index of hydrogen deficiency is 2. Thus, it may contain either two double bonds, or one double bond and one ring or two rings or a triple bond.

The IR spectrum (Fig. 13.17) shows a very broad absorption from 2300–3333 cm^{-1}

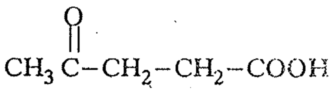
indicating the O–H stretching absorption of a carboxylic acid. The strong C=O band at 1715 cm^{-1} also supports this observation.

Its UV spectrum shows an absorption at λ_{max} 262 which indicates the presence of a keto group.

Let us now study its ^{1}H-NMR spectrum as shown in Fig. 13.18. It shows a signal at δ 11 due to –COOH proton. A singlet at δ 2.12 corresponds to three protons and another singlet at δ 2.60 due to four protons is observed. The signal at δ 2.12 could be due to a $-CH_3$ group attached to the keto group. The δ 2.60 four proton signal could be due to almost equivalent two CH_2 groups. Thus, we can say that we have



$CH_3\overset{O}{\overset{\|}{C}}-CH_2-CH_2-$ and –COOH groups. If we assemble them, we get the following structure:



$$CH_3\overset{O}{\overset{\|}{C}}-CH_2-CH_2-COOH$$

Let us see its mass spectrum given in Fig. 13.19.

It shows the small molecular ion peak at m/z 116. The base peak appears at m/z 43, which could be due to CH_3CO^+ fragment. Hence, it also supports the presence of a keto ($COCH_3$) group in the compound.

Problem 7

The following spectra were exhibited by a compound. What is its structure ?

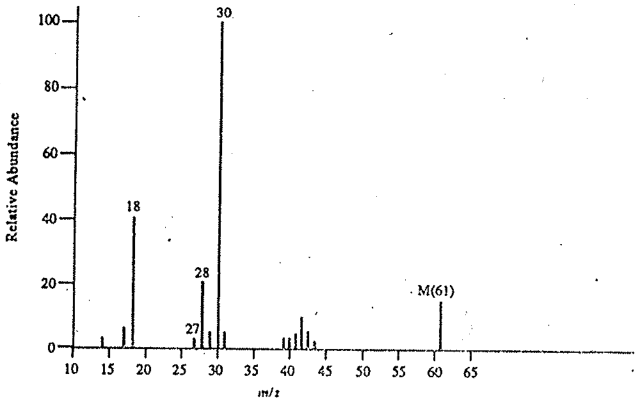


Fig. 13.20: Mass spectrum of compound 7.

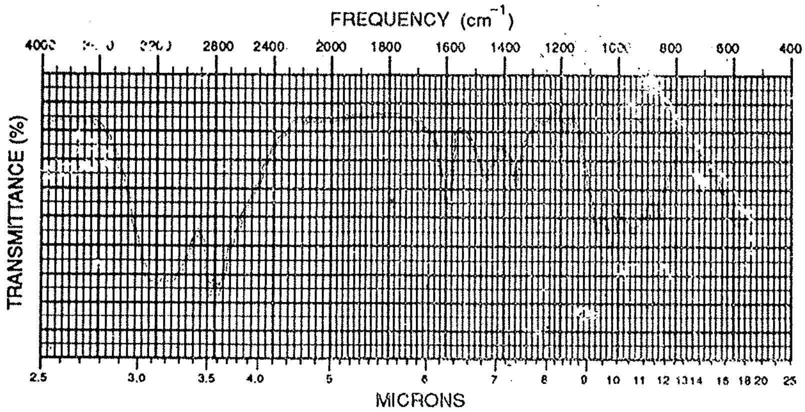


Fig. 13.21: IR spectrum of compound 7.

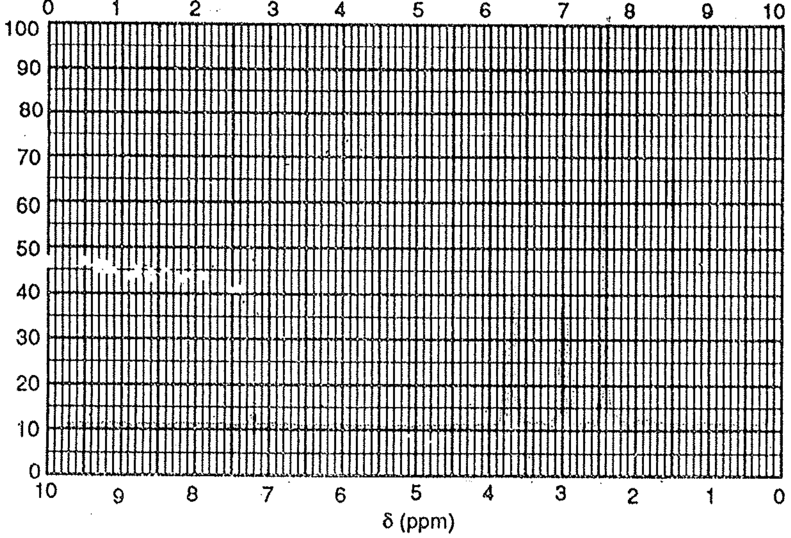


Fig. 13.22: ^{1}H-NMR spectrum of compound 7.

Let us first analyse the mass spectrum. The mass spectrum shows the molecular ion peak at *m/z* 61. Since it is an odd numbered peak, you can predict that a N atom is present in the molecule. The base peak appears at *m/z* = 30 which is very characteristic of primary amines due to the following fragmentation.

$$\left[R - CH_2 - NH_2\right]^{+\cdot} \longrightarrow R\cdot + CH_2 = \overset{+}{N}H_2$$
$$m/z = 30$$

Thus, the compound is a primary amine.

Let us confirm this from its IR spectrum. The IR spectrum shows two bands at 2850 and 2920 cm^{-1} confirming it to be a primary amine. The other broad band present in the region 3100– 3400 cm^{-1} could be due to hydrogen bonded hydroxyl group.

We can now say that it has $-NH_2$ and $-OH$ groups. So 61–(17 + 16) yields 28 mass units. If you analyse the NMR spectrum, you will see two triplets each due to two protons at δ 2.9 and δ 3.7. Thus the presence of $-CH_2 - CH_2-$ group is indicated. Another signal at δ 2.4 corresponding to 3 protons could be due -OH and $-NH_2$ protons. So we can write the structure of the compound as $HO - CH_2 - CH_2 - NH_2$.

13.5 SUMMARY

In this unit, the general approach to identify a given compound was discussed. The variety of information which can be obtained from various spectral data was highlighted. This information can then be pooled to arive at the possible structure of the given compound. This approach was illustrated using some simple organic compounds.

13.6 TERMINAL QUESTIONS

1. Calculate the number of double bond and/or ring equivalents in the compounds with the following molecular formulae:

   i) $C_{12}H_{12}N_2$

   ii) $C_6H_8O_3N_2$

2. A compound has molecular weight 130 and has the molecular formula $C_8H_{18}O$. It lacks any absorption in UV spectrum above 209 nm. In its IR spectrum, it shows bands at 2950– 2850, 1340 and 1075 cm^{-1}. It shows only one singlet in

^1H–NMR spectrum at δ 1.1. Find the structural formula of the compound.

3. A compound with molecular formula C_8H_8O gave a negative iodoform test. It exhibited the following spectral data.

   UV : λ_{max} 290nm, ε_{max} 18

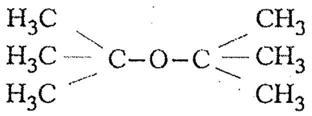
   IR : 3040, 2935, 2856, 2735, 1720, 1600 and 1570 and 1460 cm^{-1}.

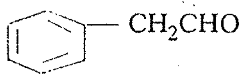
   NMR : (δ, $CDCl_3$) : 2.75 (*d*, 2H), 7.25 (*s*, 5H) and 9.72 (*t*, 1H).

4. The molecular weight of a compound is 112. It shows no UV absorption band above 200 nm. The IR spectrum is devoid of any functional group and the NMR spectrum shows a singlet at δ 1.52. Find the structure of the compound.

13.7 ANSWERS

1. (i) 7 (ii) 4

2. 

3. 

4. Cyclooctane

Further Reading

1. J.R.Dyer, Application of Absooption Spectroscopy of Organic Compounds, Eastern Economy Edition, Prentice-Hall of India Pvt.Ltd.

2. D.H.Williams and Ian Fleming, Spectroscopic Methods in Organic Chemistry. Tata Mc Graw Hill Publishing Co. Ltd. 4thEd

3. C.N Banwell, Fundamentals of Molecular Spectroscopy, 3rd Ed, Tata McGraw Hill Publishing Co. Ltd.