M.Sc. Final Year

Chemistry, MC06

APPLICATION OF SPECTROSCOPY, PHOTO CHEMISTRY AND SOLID STATE CHEMISTRY

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल

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SYLLABI-BOOK MAPPING TABLE

Application of Spectroscopy, Photo Chemistry and Solid State Chemistry

	Syllabi	Mapping in Book
Unit I	**Applications of Spectroscopy** (a) **Infrared Spectroscopy** (Instrumentation and sample handling). Symmetry and shapes of AB2, AB3, AB3, AB4, and AB6, mode of bonding of ambidentate ligands, ethylenediamine and diketonato complexes, application of resonance Raman spectroscopy particularly for the study of active sites of metalloproteins. Characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ethers, phenols and amines. (ketones. aldehydes, esters, amides, acides, acids, anhydrides, lactones, lactams and conjugated carbonyl compounds). Effect of hydrogen bonding and solvent effect on vibrational frequencies, overtones. Combination bands and Fermi resonance. FTIR IR or gaseous, solids and polymeric materials. (b) **Ultraviolet and Visible Spectroscopy:** Various electronic transitions (185-800 nm), Beer-Lambert law, effect of solvent on electronic transitions, ultraviolet bonds for carbonyl compounds, unsaturated carbonyl compounds, dienes, conjugated polyenes. Fieser-Woodward rules for conjugated dienes and carbonyl compounds, ultraviolet spectra of aromatic and heterocyclic compounds. Steric effect in biphenyls.	**Unit-1:** Applications of Spectroscopy: Infrared (IR), Ultraviolet (UV) and Visible **(Pages 3-44)**
Unit II	**Applications of Spectroscopy** (a) **Nuclear Magnetic Resonance Spectroscopy:** General introduction and definition, chemical shift, spin-spin interaction, shielding mechanism, mechanism of measurement, chemical shift values and correlation for protons bonded to carbon (aliphatic, olefinic, aldehydic and qromotic) and other nuclei (alcohols, phenols, enols, corboxylic acids, amines, amides & mercopto), chemical exchange, effect of deuteration, complex spin-spin interaction between two, three, four and five nuclei (first order spectra), virtual coupling. Stereochemistry, hindered rotation, Korplus curve-variation of coupling constant with dihedral angle. Simplification of complex spectra-nuclear magnetic double resonance, contact shift reagents, solvent effects. Fourier transform technique, Nuclear Overhauser Effect (NOE). Resonance of other nuclei-F.P. The contact and pseudo contact shifts, factors affecting nuclear relaxation, some applications including biochemical systems, an overview of NMR of metal nuclides with emphasis on ^{195}Pt and ^{119}Sn NMR. General considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, heteroromatic and carbonyl carbon), coupling constants. Two dimensional NMR spectroscopy - COSY, NOESY, DEPT, INEPT, APT and INADEQUATE techniques. (b) **Electron Spin Resonance Spectroscopy:** Hyperfine coupling, spin polarization for atoms and transition metal ions, spin orbit coupling and significance of g-tensors, application to transition metal complexes (having one unpaired electron) including biological systems and to inorganic free radicals such as PH_4, F_2 and $[BH_3]$ (c) **Mass Spectrometry:** Introduction, ion production - El, Cl, FD and FAB, factors affecting fragmentation, ion analysis, ion abundance. Mass spectral fragmentation of organic compounds, common functional groups, molecular ion peak, metastable peak, Mclafferty rearrangement. Nitrogen rule. High resolution moss spectrometery. Examples of mass spectral fragmentation of organic compounds with respect to their structure determination.	**Unit-2:** Applications of Spectroscopy: NMR, ESR and Mass Spectrocopy **(Pages 45-120)**

Unit III	**Applications of Spectroscopy** **(a) Applications of Spectroscopy** (i) **Mossbauer Spectroscopy:** Basic principles, spectral parameters and spectrum display. Application of the technique to the studies of (1) bounding and structures of Fe^{+2} and Fe^{+3} compounds including those of intermediate spin, (2) Sn^{+2} and Sn^{+4} compounds - nature of M-L bond, coordination number, structure and (3) detection of oxidation state and inequivalent MB atoms. (ii) **Optical Rotatory Dispersion (ORD) and Circular Dichroism (CD):** Definition, deduction of absolute configuration, octant rule or ketones. (b) **Photo Chemistry** (i) **Photochemical Reactions:** Interaction of electromagnetic radiation with matter, types of excitations, fate of excited molecule, quantum yield, transfer of excitation energy, actinometry. (ii) **Determination of Reaction Mechanism:** Classification, rate constants and life times of reactive energy states determination of rate constants of reactions. Effect of light intensity on the rate of photochemical reactions. Types of photochemical reactions - photodissociation, gass-phase photolysis.	**Unit-3:** Applications of Spectroscopy: Mossbauer Spectroscopy, Optical Rotatory Dispersion, and Circular Dichroism **(Pages 121-168)**
Unit IV	**Photochemistry** (i) **Photochemistry of Alkenes:** lnlramolecular reactions of the o!efinic bond-geometrical isomerism, cyclisation reactions, rearrangement of l, 4 - and l, 5 - dienes. (ii) **Photochemistry of Carbonyl Compounds:** Intramolecular reactions of carbonyl compounds - saturated,. cyclic and acyclic, β, γ- unsaturated and α, β - unsaturated compounds. Cyclohexadienones. Intermolecular cyloaddition reactions - dimerisation and oxetane formation. (iii) **Photochemistry of Aromatic Compounds:** lsomerisations, additions and substitution. (iv) **Miscellaneous Photochemical Reactions:** Photo-Fries reactions of anilides. Photo-Fries rearrangement. Barton reaction. Singlei molecular oxygen reactions. Photochemical formation of smog. Photodegradation of polymers. Potochemistry of vision.	**Unit-4:** Photochemistry **(Pages 169-212)**
Unit V	**Solid State Chemistry** (i) **Solid State Reactions:** General principles, experimental procedures, co-precipitation as a precursor lo solid stale reactions, kinetics of solid stale reactions. (ii) **Crystal Defects and Non-Stoichiometry:** Perfect ond imperfect crystals, intrinsic and octinisic defects - point defects, line and plane defects, vacancies-Schottky defects and Frenkel defects. Thermodynamics of Schottky ond Frenkel defect formation, colour centers, nonstoichiometry and defects. (iii) **Electronic Properties and Band Theory:** Metals, insulators and semiconductors, electronic structure of solids - band theory, bond structure of metals, insulators and semiconductors. Intrinsic and extrinsic semiconductors, doping semiconduclors, p-n juctions, super conductors. (iv) **Organic Solids:** Electrically conducting solids, organic charge transfer complex, organic metals, new superconductors.	**Unit-5:** Solid-State Chemistry **(Pages 213-258)**

CONTENTS

INTRODUCTION

NOTES

Spectroscopy is the study of the interaction between matter and electromagnetic radiation as a function of the wavelength or frequency of the radiation. Spectral measurement devices are referred to as spectrometers, spectrophotometers, spectrographs or spectral analyzers. Most spectroscopic analysis in the laboratory starts with a sample to be analyzed, then a light source is chosen from any desired range of the light spectrum, then the light goes through the sample to a dispersion array (diffraction grating instrument) and is captured by a photodiode.

Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm). Photochemical reactions require a light source that emits wavelengths corresponding to an electronic transition in the reactant.

Solid-state chemistry is the study of the synthesis, structure, and properties of solid phase materials, particularly, but not necessarily exclusively of, non-molecular solids. It therefore has a strong overlap with solid-state physics, mineralogy, crystallography, ceramics, metallurgy, thermodynamics, materials science and electronics with a focus on the synthesis of novel materials and their characterization.

This book, *Application of Spectroscopy, Photochemistry and Solid State Chemistry*, is designed to be a comprehensive and easily accessible book covering the basic concepts of chemistry. It will help readers to understand the basics of elementary, electromagnetic radiation, regions of the spectrum, IR spectroscopy, UV spectroscopy, vibrational frequencies, electronic spectrum, Raman spectrum, concept of stereochemistry, laws of photochemistry, nuclear magnetic resonance, electron spin resonance spectroscopy, mass spectroscopy, Mossbauer spectroscopy, optical rotatory dispersion, circular dichroism, determination of reaction mechanism, solid state chemistry, crystal defects, non-stoichiometry, band theory, and organic solids, etc.

The book is divided into five units that follow the Self-Instruction Mode (SIM) with each unit beginning with an Introduction to the unit, followed by an outline of the Objectives. The detailed content is then presented in a simple but structured manner interspersed with Check Your Progress to test the student's understanding of the topic. A Summary along with a list of Key Terms and a set of Self-Assessment Questions and Exercises is also provided at the end of each unit for understanding, revision and recapitulation. The topics are logically organized and explained with related theorems and examples, analysis and formulations to provide a background for logical thinking and analysis with good knowledge of physical chemistry. The examples have been carefully designed so that the students can gradually build up their knowledge and understanding.

UNIT 1 APPLICATIONS OF SPECTROSCOPY: INFRARED (IR), ULTRAVIOLET (UV) AND VISIBLE

Structure

1.0 INTRODUCTION

Spectroscopy is an identification tool for studying the structures of various atoms and molecules. Spectroscopy is an analytical method for identifying the constituents in a material having unknown chemical composition. In short, spectroscopy is the study of the absorption and emission of light and other radiation by matter depending on the wavelength of the radiation.

Infra Red (IR) spectroscopy deals with the infrared region of the electromagnetic spectrum. Infrared Spectroscopy (IR) generally refers to the analysis of the interaction of a molecule with the infrared light. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer or spectrophotometer.

UV spectroscopy or UV–visible spectrophotometry refers to the absorption spectroscopy in part of the ultraviolet and the full, adjacent visible regions of the electromagnetic spectrum. UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules.

In this unit, you will study about the basics, principles, and various applications of the Infrared Spectroscopy, and Ultraviolet-Visible Spectroscopy.

1.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the basics of UV-Visible and IR spectroscopic techniques.
- Explain the applications of IR spectroscopy.
- Conceptualize the symmetry and shapes of various organic molecules.
- Describe the UV spectroscopy and its role in identifying organic compounds.
- Explain the concept of steric effect.

1.2 INFRA RED SPECTROSCOPY: INSTRUMENTATION AND SAMPLE HANDLING

A spectrometer is a scientific instrument used to separate and measure spectral components of a physical phenomenon. Spectrometer is a broad term often used to describe instruments that measure a continuous variable of a phenomenon where the spectral components are somehow mixed.

Principally, there are two basic types of atomic spectrometers - emission and absorbance. An emission instrument detects the wavelengths of light released by the ionized atoms. In the absorbance spectroscopy method, the light is absorbed with respect to the wavelength. The sample molecules are excited to a higher energy state upon absorbing the incident light. The excitation is directly proportional to the wavelength of light.

Infrared Spectroscopy

Infrared Spectroscopy measures the vibrations of inter atomic bonds of a sample at different frequencies when the sample is exposed to infrared light. Infrared spectrometers can also be used to measure the number of absorbing molecules.

Experimental Recording of IR Spectra

The modern double beam infrared spectrophotometer is employed for recording IR spectra of a compound. It has four major components (*i*) Radiation Source (*ii*) Sample Handling (*iii*) Monochromator (*iv*) Detector

(i) **Radiation Source:** Infrared radiation source is often a Nernst filament which is fabricated from a binder and oxides of cerium, zirconium and thorium or globar which is a small rod of silicon carbide. The source is heated electrically to 1000–1800ºC. The radiation from the source is divided into two beams by mirrors M_1 and M_2. These are called sample beam and reference beam.

(ii) **Sample Handling:** Infrared spectra may be recorded of sample in gases, liquids of solids state. The spectra of gases or low boiling liquids may be recorded by expansion of the sample into an evacuated cells. Gas cells as of length varying from few centimeters to 40 meters.

Liquids may be examined neat or in solution. This is pressed between flat plates of 0.001 mm or less in thickness. Solutions are handled in cells of 0.1–1 mm thickness. The solvent selected must be dry and transparent in the IR region. Carbon tetrachloride and carbon disulphide are used as solvents. Solids are usually examined as a mull. Mules are prepared by throughly grinding 2–5 mg of a solid with 1–2 ml of mulling oil in an agate mortar. Nujol, a high boiling petroleum oil is used as a mulling agent. Fluorolube (a completely halogenated polymer containing F and Cl) is a common mulling agent.

The pressed-disc technique depends upon the fact that dry powdered potassium bromide can be pressed under pressure in vaccuo to form a transparent disc. 0.5–1.0 mg of the sample is intimately mixed with 100 mg of dry KBr. This is mixed and pressed with special dies under a pressure of 10,000 pounds per square inch.

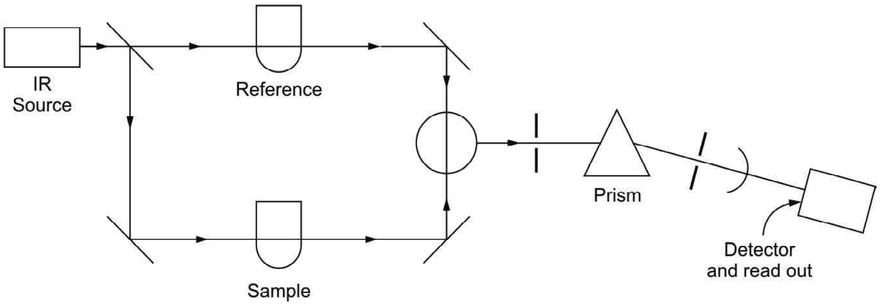


Fig. 1.1 *Double Beam IR Spectrometer*

(iii) **Monochromator:** The combined beam passes through the monochromator entrance slit to the mirror which reflects it to the diffraction grating. Maximum resolution is obtained by using grating only in the range of greatest dispersing effectiveness, Figure. 1.1 shows a double beam IR spectrometer.

(iv) **Detectors:** The most common type of detectors used in IR spectroscopy are bolometers, thermocouples and thermistors. The bolometer usually consists of a thin metal conductor such as platinum wire. When IR radiation falls on the conductor it becomes war mer and produces a change in its electrical resistance. The change in resistance is a measure of amount of radiation falling on it.

A thermocouple is made by joining two wires of different metals. One of these is called the hot junction while the other is called the cold junction. Potential is developed when the radiation falls on it.

Thermistors are made of a fused mixture of metal oxides. As their temperature increases their electrical resistance decreases. Thermistors typically changes resistance about 5 percent per°C. Response time of thermistors is rather slow.

Semiconductor detectors show a rapid response to the IR signal. These are otherwise insulators but become conductors when radiation does fall on them. In recent years Fourier-Transform instruments have become available. FT IR allows analysis of very small samples.

Interpretation of Spectra

There are no rigid rules for interpreting an IR spectrum. However certain requirements must be met before an attempt is made to interpret spectrum.

(i) The spectrum must be well resolved and of good intensity.

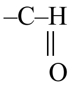
(ii) The sample must be extremely pure whose pure whose spectrum is recorded.

(iii) The spectrum be calibrated properly using a polystyrene film.

(iv) The method of sample handling must be specified and the solvent, concentration and cell thickness must be specified.

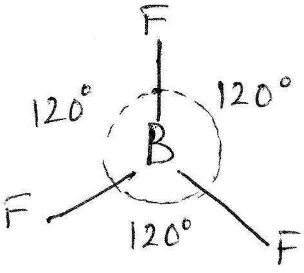
It must be clearly understood that the IR spectra of molecule is highly complex, it is therefore not possible to analyse all the bands. Only a few bands are analysed to get information about the different groups present in the molecule. Final confirmation is however done by comparing the spectra with the probable compound by matching band by band. This technique is called the finger print method. The whole region of IR spectra has been divided into eight most well defined areas.

***Table 1.1** Different regions of IR Spectra*

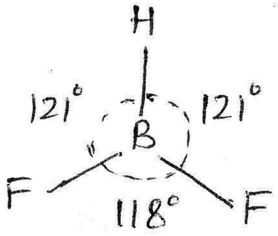
Wavelength (micrometers)	Wave Number $\bar{v}$ m^{-1}	Bond Causing Absorption
1. 2.7–3.3	3750–3000	O–H, N– H stretching
2. 3.0–3.4	3300–2900	–C=CH, C=C, Ar – H (C–H stretching)
3. 3.3–3.7	3000–2700	$-CH_3$, $-CH_2-$, –C–H  $-\underset{\underset{O}{\|}}{C}-H$ (C–H stretching)
4. 4.2–4.9	2400–2100	C =C, C=N (stretching)
5. 5.3–6.1	1900–1650	C = 0 (acids, aldehydes, ketones, amides, esters, anhydride) stretching
6. 5.9–6.2	1675–1500	C=C (aliphatic aromatic)
7. 6.8–7.7	1475–1300	– C – H (bending)
8. 10.0–15.4	1000–650	C = C, Ar – H (bending) (out of plane)

1.2.1 Symmetry and Shapes of AB2, AB3, AB4 and AB6

In the context of chemistry, symmetry is important both at the molecular level as well as in crystalline systems. The understanding of symmetry is important for explaining the molecular spectroscopy and calculation of molecular properties such as dipole moment and optical activity. For qualitative discussions, it is sufficient to refer to the shape of the molecule using the terms tetrahedral, octahedral or square planar. However, these descriptions cannot be always precise, e.g., consider the structures of BF_3 (X) and BF_2HC(Y), both of which are planar. The molecule of BF_3 is correctly



X



Y

described as being planar, as since its symmetry properties are fully consistent with this description; all the F-B-F bond angles are 120° and the B-F bond distances are all identical (131 pm). Whereas, the molecule of BF_2H. boron centre is in pseudo-trigonal planar environment, but the molecular symmetry properties are not the same as in BF_3. The F-B-F bond angle in BF_2H is smaller than the two H-B-F angles, and the bond length is shorter (119pm) than the B-F bonds (131 pm).

Description as the symmetrical means that a species possess a number of indistinguishable configurations, when the structure X is rotated in the plane of paper through 120°, the resulting structure is indistinguishable from the first; another 120°, rotation results in a third indistinguishable molecular orientation. This is not true if we carry out the similar rotations for any (BF_2H).

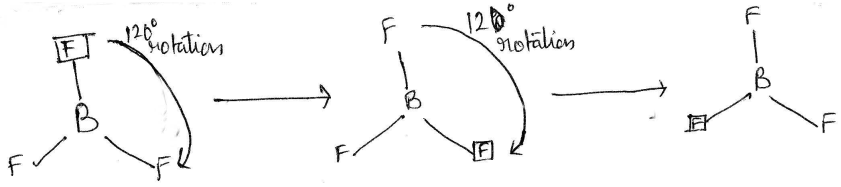


Fig 1.1 *Rotation of trigonal Planar BF_3 macule through 120°*

Symmetry Operations and Symmetry Elements

When 120° rotation shown in figure. 1.2 to BF_3 molecule is applied, we got a representation of the molecule that was indistinguishable from the first. Each rotation is an example of a symmetry operation. A symmetry rotation is an operation performed on an object which leaves it in a configuration that is indistinguishable from, and superimposable on the original configuration.

In simple terms, we can say that symmetry operation is the movement of an abject such that it leaves the object looking the same. A symmetry operation brings the molecule into the equivalent on identical configuration. This can be easily understood by using a cardboard shaped like an equilateral triangle (fig. 1.2a). Label the vertices of the triangle as 1, 2 and 3. Rotation of the triangular cardboards through 120° (2π/3) and 240° (4π/3) in the anticlockwise direction gives rise to equivalent configuration, *i.e.,* each configuration is indistinguishable from the original configuration (fig 1.2c) whereas, the rotation through 360° (2π) results in an identical configuration (Fig 1.2d). 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 in space are similar to those in the original configuration, i.e*.,* as before applying symmetry operation. (Compare Figs. 1.2a and d)

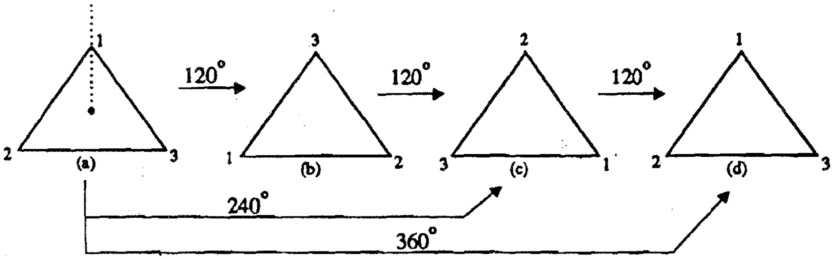


Fig 1.2 *(a) The configuration before rotation; the dolled line shows the axis of rotation indirection perpendicular to the plane of the molecule.*
(b) And (c) equivalent configurations (after anticlockwise rotation through 120° (2/π 3) and240° (4 π /3).
(d) Identical configuration (after rotation through 360° (2 π).

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.1.3a and b. Reflection through this plane once results in equivalent configuration, Fig. 1.3c. Another reflection through this plane results in an identical configuration, Fig.1.3

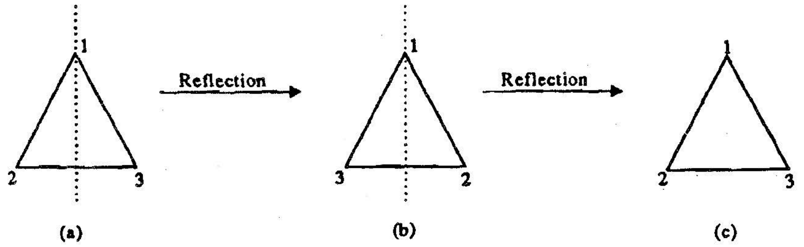


Fig 1.3 *(a) The configuration before Reflection.*
(b) The equivalent configuration resulting from Reflection through a perpendicular place (shown as a dotted line passing through the vertex 1)
(c) The Identical configuration resulting from another reflection through the same plane.

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 1.2. Corresponding to each symmetry operation, there is a symmetry element. The symmetry element is a line on a plane through which the symmetry operation is performed. Table 1.1lists the various symmetry elements and symmetry operations.

Table 1.2 *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 2π/*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)	Rogation about an axis by an angle 360°/*n*or2π/*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

Rotation about an Axis of Symmetry (C_n)

The *n*-fold axis of symmetry is a line about which a molecule is to be rotated through 360°/*n* to obtain an equivalent configuration. The *n*-fold axis of symmetry is denoted by the symbol *Cn*, where *n* is called to order of an axis defined as,

$$\underset{\text{order of axis}}{n} = \frac{360^\circ}{\text{Minimum angle of rotation}(\alpha)\text{ for obtaining equivalent configuration}} \qquad 1.1$$

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

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

i.e., H_2O molecule has a twofold axis of rotation (C_2 axis). C_2 axis of H_2O is illustrated in Fig. 1.4 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.

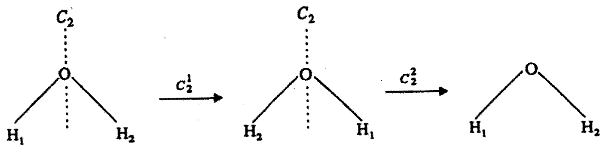


Fig 1.4 *Twofold axis* C_2 *in water molecule; the effect of one* C_2 *rotation* (C_2^1) *is shown by interchange* H_1 *and* H_2 *atoms. Application of* C_2, *twice* (C_2^2) *brings the molecule to identical configuration as indicated by the position of* H_1 *on the left side and* H_2 *on the right side.*

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

$$C_n^n = E \qquad (1.2)$$

Where, E refers to identity operation. Identity operations means doing nothing to the molecule and after performing the identity operation, the molecule regains identical configuration. A rotation through 360° (C_n^n) is an example of identity operation. The C_n^n means n times rotation about C_n axis.

In H_2O molecule, according to eqn.12, rotation through C_2 axis twice leads to identical configuration.

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

Similarly, 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 eqn.1.1

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

The C_3 of NH_3 is shown in Figure 1.5

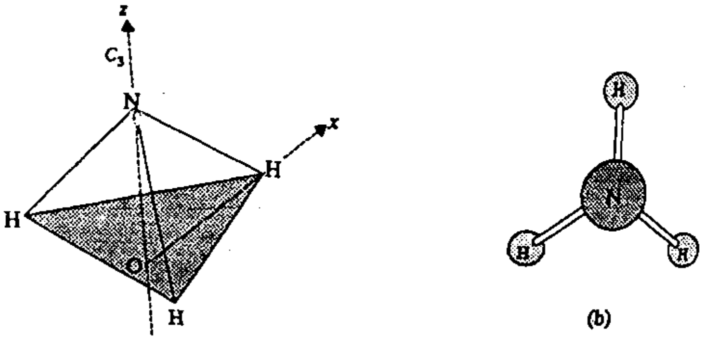


Fig 1.5 *(a) The shape of NH_3 molecule–trigonal pyramidal; point O lies in the xy plane (shown as shaded area) and on the z axis which is C_3 axis passing through nitrogen atom. The three hydrogen atoms form an equilateral triangle in the xy plane. (b) The top view of NH_3 molecule which is used in drawing the figures given at the margin to denote C^1_3, C^2_3 and C^3_3 operations.*

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 $C_3^1 \ C_3^2$ and C_3^3 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 times. Results of C_3^1, C_3^2 and C_3^3, operations in NH_3 are shown in figure 1.6.

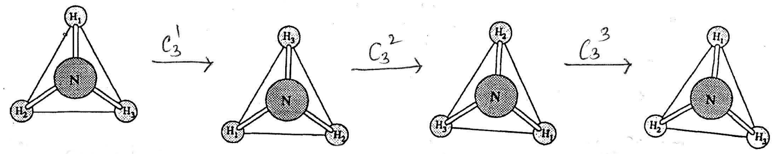


Fig 1.6 *the rotations in C_3^1, C_3^2 and C_3^3 in NH_3 molecule.*

In other words, a threefold axis of symmetry gives rise to three operations, C_3^1, C_3^2 and C_3^3

Also, $C_3^1 C_3^1 = C_3^2$ ...(1.3)

i.e., rotation through 240° is equivalent to rotation through 120° twice.

Further, $C_3^2 C_3^1 = C_3^3 = E$ ...(1.4)

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 (Figures. 1.7 a-b). Thus, the three C_2, axes are perpendicular to C_3, axis in BF_3.

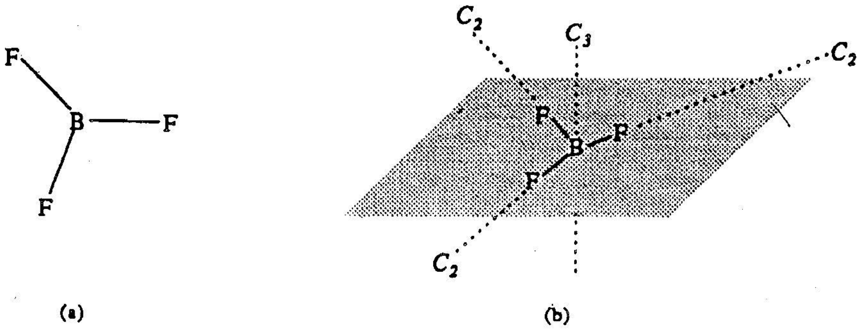


Figure 1.7:(a) The shape of BF_3, molecule - triangular planar
(b) Threefold axis of symmetry in BF_3; It is perpendicular to the molecular place. The molecular plane is shown by the shaded are. Each B - F bond t o twofold axis of symmetry. All the three C_2 axes are in the molecular plane.

Consider the case of because which has are C_6 axis (perpendicular to the molecular plane) and six C_2 axis (figure 1.8) 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 side opposite corners of the hexagon (i.e., along the C-H bonds). Hence in benzene, the six C_2 axes are perpendicular to C_6 axis.

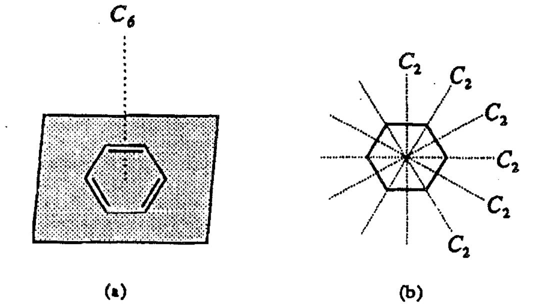


Fig 1.8 *(a) C_6, la benzene; It is perpendicular tube molecular plane (shown as shaded area)*
(b) The three C_2, axes along opposite C-H bonds and three C_2, axes in between parallel C-C bonds.

Reflection in a plane of symmetry (σ)

A plane bisects the object under consideration so that are 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. Water (H_2O) has two vertical planes of symmetry $(\sigma v - \sigma' v)$ as shown in figure 1.9 While NH_3 has three vertical plane of symmetry $(\sigma v, \sigma' v \text{ and } \sigma'' v)$ check symbols, (figure 1.10).

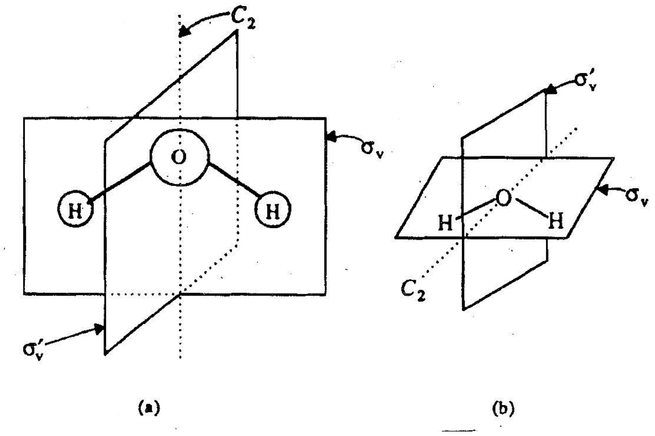


Fig 1.9 (a) *Two vertical planes of symmetry $(\sigma v - \sigma' v)$ in water.*
(b) a plane is differently shown so that it is Easter to visualise the two planes.

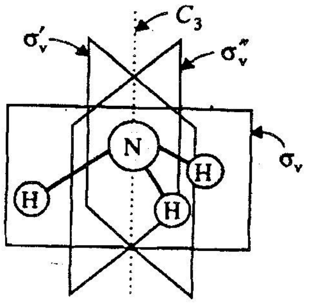


Fig 1.10 *The three vertical planes of symmetry in NH_3 $(\sigma v, \sigma' v \text{ and } \sigma'' v)$; each vertical plane of symmetry encloses one N-H bond also.*

When the plane of symmetry is perpendicular to the principal axis, it is called the horizontal plane, and, is devoted by σ_n. For example the plane containing all the six carbon atoms and six hydrogen atoms in benzene is the horizontal plane as it is perpendicular to the (C_6) principal axis.

Again, considers the cases of NH_3 and BF_3. Both of these molecules have three vertical planes of symmetry, Additionally, BF_3 has a horizontal plane of symmetry but not NH_3 (which is pyramidal).

Another type of plane of symmetry is a dihedral plane and is devoted by σ_d. A dihedral plane must be:

(i) **Vertical** (i.e., it must contain the principal axis) and

(ii) **Bisects** the angle between two c_2 axes which are themselves perpendicular to the principal axis.

For example, the staggered form of ethane (figure 1.11a) 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 plane is is shown in Figure 1.11b.

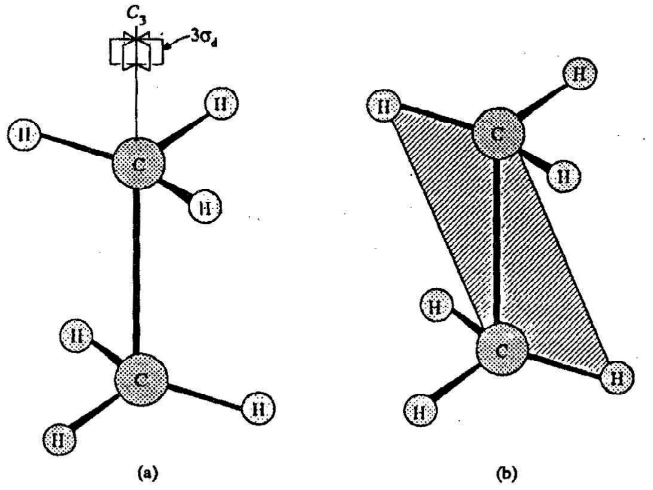


Fig 1.11 *(a) The staggered conformation of ethane. It has three* σ_d *planes and each* σ_d *contains C-C bond and a pair of C-H bonds.*
(b) One of the dihedral planes shown by the shaded portion.

Improper Relational Axis (S_n)

This is also known as rotation - reflection axis. This element is generated by rotating the molecule by an angle and then taking the reflection in a plane perpendicular to the rotational axis. If there is C_n axis deign Z-axis then,

$$S_{n(x)} = C_{n(x)} \cdot \sigma_{xy} \text{ check equation}$$

σ_{xy} is a plane perpendicular to the $Cn(x)$-axis.

There are many molecules where C_m and a plane (σ) perpendicular to it exist separately, and S_n axis present in all such molecules for example, BX_3 molecule has C_3 axis which is perpendicular to its molecular, plane (σ_n). This combination produces S_3 axis. Counter ethane molecules in its eclipsed form as shown in Figure 1.12.

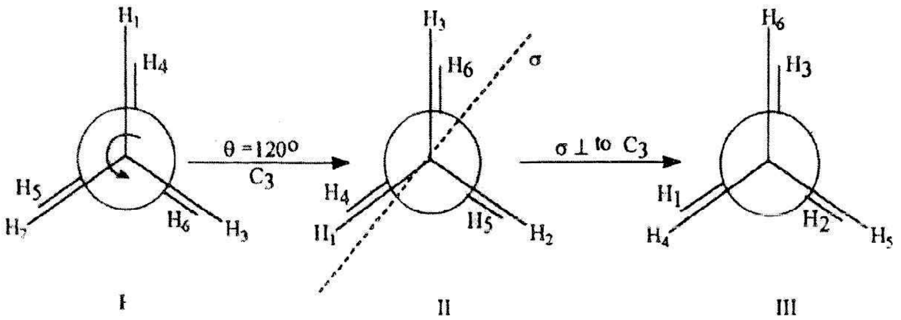


Fig 1.12 *Rotation-reflection operation on the eclipsed form of ethane molecule. The -plane in configuration II passes through the mid-point of C-C axis and is perpendicular to it.*

From the Figure 2.13, it is clear that both the rotational and reflection operations are genuine and the corresponding elements C_3 ($\theta = 120°$) and σ perpendicular to C_3 exist in the eclipsed conformation of ethane molecule. Therefore, a combination of them is also necessarily an operation corresponding to a product but distinct symmetry element. This situation exists in most of the regular eclipsed conformers of the molecules.

Now let us consider same examples of molecules which contain neither the rotational axis (C_n) nor the σ-plane perpendicular to it. For example, ethane molecule in staggered form (figure 1:13).

Now let us consider same examples of molecules which contain neither the rotational axis (C_n) nor the σ-plane perpendicular to it. For example, ethane molecule in staggered form (figure 1:13).

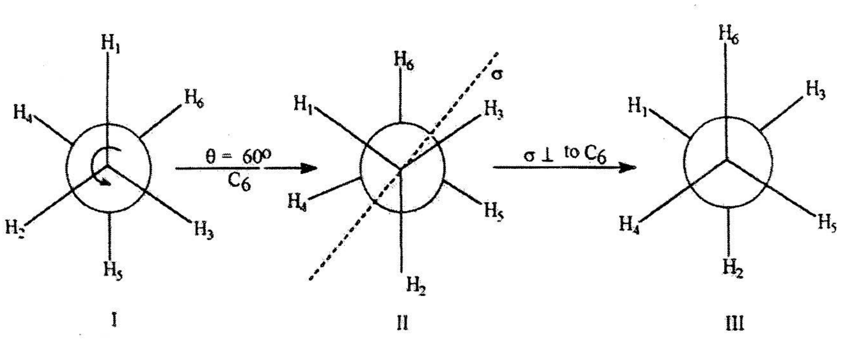
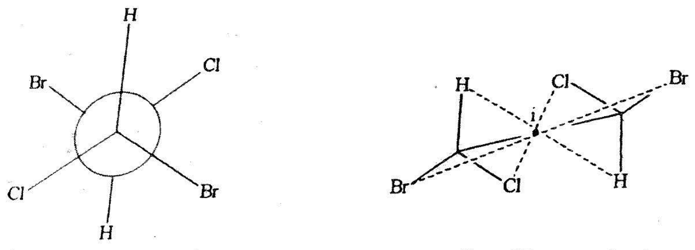


Fig 1.13 *Illustration for the existence of S_6-axis, though C_6 and s perpendicular to C_6 donot exist in ethane (staggered).*

Configuration I and II are not equivalent i.e., $\theta = 60°$ and the consequent C_6-rotational operation is not a valid symmetry operation by itself. Similarly, II and III are not equivalent, thus showing that operation perpendicular to the so called C_6, rotational axis is also not a genuine symmetry operation. But be configurations I and III are equivalent, so that C_6, followed by σ perpendicular to C_6, is a genuine, though combined, operation. This product operation results in an element called S_6, axis.

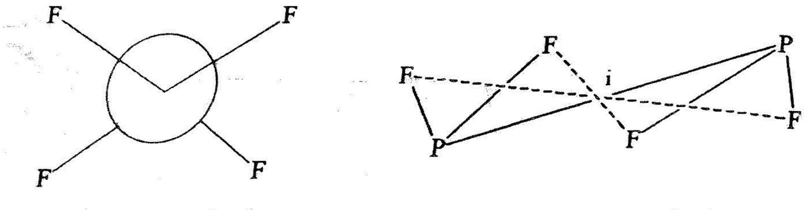
Inversion Centre or Centre of Symmetry (μ)

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 an equivalent point the centre of the molecule which generates in nerve is called the centre of symmetry on the inversion centre (i). All homo nuclear diatonic molecules (e.g., H_2, N_2, etc.) possess the centre of symmetry, while the molecules like H_2O, NH_3, BF_3 and CH_4 do not possess the centre of symmetry sure examples shown in Figure 1.14 will illustrate this element.



Newman projection Saw-Horse projection

(a) 1,2-dichloro-1,2-dibromoethane (all trans and staggered)



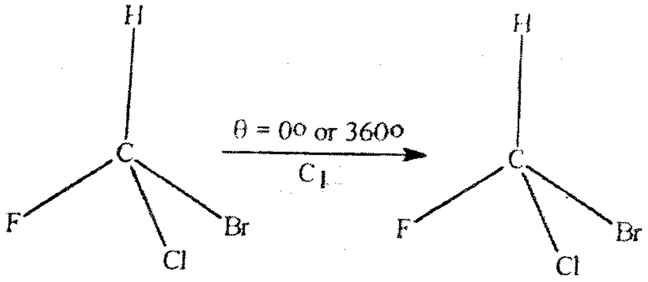
Newman projection Saw-Horse projection

(b) P_2F_4 has S_2, hence i

Fig. 1.14 *Illustration for the presence of i in some special molecules. (a) CHClBr-CHClBr has only i and (b)* P_2,F_4, *has i amongst others*

Identity Element (E)

This element is obtained by an operation called 'identity operation'. This is a 'doing-nothing' operation. After this operation, the molecule remains as such. This situation can be visualized by two ways. Either (i) we do not do anything on to molecule or (ii) we rotate the molecule by 360° ($\theta = 360°$). Consider the following molecule.



An element generated by this 'leave-it-alone' operation is trivial and is as important as the other symmetry elements. Every molecule has this clement of symmetry and it co-exists with the identity of the molecule, hence the name 'identity element' This is denoted by a special symbol E (the first letter of the word *Einheit* from German)

Dipole Movement

We know that dipole moment is a vector quantity and has both direction and magnitude. The symmetry operation allowed for a molecule should not affect the direction and on the magnitude of the dipole moment vector. In other words the dipole moment vector should be invent and must be contained in each of the symmetry elements of the molecule. As a result, only the molecules belonging to the groups C_n, C_{nv} and C_s may have dipole movement. This can be understood early H_2O molecule. The direction and of the remittent dipole moment vector in H_2O (indicated by ± check symbol sign) is as shown in figure 1.15a

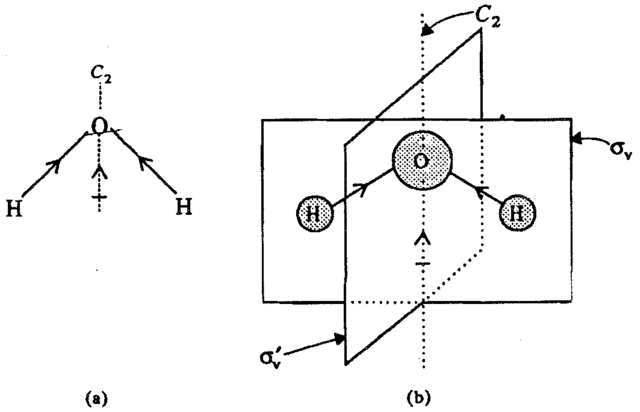


Fig. 1.15 Illustration of the fact that each of the symmetry elements of water contains the dipole moment vector. It is worth recollecting that H_2O has E, C_2, and $2s_v$, as symmetry elements.

(a) H'→—O stands for O-H bond moment and ± (check symbol) 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 (check symbols) and planes contains the moment vector.

(b) Is drawn to show that, σ_v, σ'_v C_2 contain the dipole moment vector.

As shown in figure 1.15b, the symmetry el--ements, C_2 axis and two $_v$ planes, also contain the relevant dipole moment vector in H_2O molecule.

In molecules with the points groups such as C_{nn}, D_n, D_{nh}, etc.; there are symmetry operations that correspond to turning the molecule upside down. This would reverse the direction of dipole movement vector which is not allowed so such molecules cannot have dipole moment.

Optical Activity

A molecule is optically active only if it could exist as mirror image isomers. For example, lactic acid is an optically active molecule (figure.1.16)

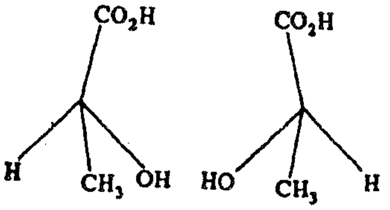


Fig1.16 Lactic acid the left- right-banded forms (mirror Images).

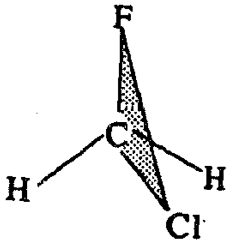


Fig 1.17 Plane CH_2FCL encloses C, F and CL.

From symmetry point of view, a molecule is optically active only if it cannot be superimposed on its mirror image through important rotation. Since a rotation about an axis as followed by a reflection in a perpendicular plane (i.e., improper rotation) converts a right-handed object to a left-banded object, the presence of S, 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 is 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_n 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.

Even if a molecule possesses σ, then also it is optically inactive as σ is equal to 5. Thus, flurochloro methane (figure 1.17) which has σ is not optically active. So it can be concluded that, 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.) S_1), *i* (i.e., S_2) or any other S_n are optically inches.

Spectra

The molecules having permanent dipole moment can give rise to pure rotational (or microwave) spectra. Thus only molecule cubes 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($D_{\infty n}$) and C Cl_4 (T_d). The former two possess permanent dipole moment but not the latter two. The vibrational spectra could be understood using symmetry the aspects of a particular vibration of a molecules assignment of infrared spectral frequencies to the specific vibrations causing the absorption can be made using group theory.

1.2.2 Mode of Bonding of Ambidentate Ligands

Coordination or complex compounds contain a central atom or ion. Usually a metal, which is chemically bonded to various groups is called *acceptor* and the attached groups are known as *donor* groups or *Ligands*. For example, in the complex on $[Fe (CN)6]^{4-}$, Fe^{2+} ion is the central metal ion or acceptor white CN^- ions are Ligands.

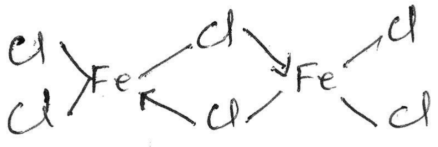
A ligand is defined as an atom, ion or molecule which is capable of donating a pair of elections to the metal atom. In the ligands, the particular atom which actually donates the election pain is called the donor atom. For example, as in Ku $[Fe(CN)_6]$, the six CN^- ions are ligands and nitrogen in CN^- is the donor atom.

The ligands are arranged around the central ion inside the first sphere of attraction in preferred geometries. The common geometries found in complexes one linear, equilateral, triangular, tetrahedral, square planar, tribunal pyramidal, square pyramidal and octahedral

Ligands can be classified into as monodentate and polydentate legends depending upon the number of donar atoms present.

A. Monodentate Ligands: If a ligand contains only one donor atom then it is capable of forming one coordinate bend with the central metal atom, it is known as *monodentate* ligand. For example, F^-, CL^-, Br^- , I^-, CN^-, SCN^-, NO_2^- NH_3, H_2O, pyridine $(C_2H_5)_3N$, acetone, etc.

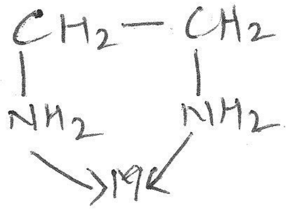
Monodantate ligand is generally capable of forming one coordinate bond to the metal atom. However, a monodentate legend may also coordinate simultaneously with two or more metal atoms and is therefore called a bridging ligand and the romlting compound is termed as a bridge complex. For example, Fe_2cl_2, OH^-, Cl^- , F^-, NH_2^-, O_2^-, so_{u2}^-, Co etc.



B. Polydentate Ligands: When a ligand has to or more donor atoms which may simultaneously coordinate with the metal atom, it is tenured' as polydentate ligand. Depending upon the presence of number of donor sites, these ligands can be further referred to as bidentate (two donar atoms), tridentate (three donor atoms, tetra dentate (four donor atoms), and so on.

Bonding of Ethylene-Diamine Ligand: Ethylene-diamine (en) is an organic compound with the formula $C_2 H_4 (NH_2)_2$. It is a bidentate ligand having two neutral donor N-atoms which can donate their lone pain of electrons.

Structure and bonding in some of the complexes of ethylene-diamine is shown below:



Modes of Bonding in Bidentate Ligands

1.2.3 Ethylenediamine and Diketonate Complexes

Ethylenediamine (abbreviated as en when a ligand) is the organic compound with the formula $C_2H_4(NH_2)_2$. This colourless liquid with an ammonia-like odour is a basic amine. It is a widely used building block in chemical synthesis, with approximately 500,000 tonnes produced in 1998.[6] Ethylenediamine readily reacts with moisture in humid air to produce a corrosive, toxic and irritating mist, to which even short exposures can cause serious damage to health. Ethylenediamine is the first member of the so-called polyethylene amines.

Aromatic difluoroboron â-diketonate complexes (BF2bdks) are classic fluorescent molecules that have been explored as photochemical reagents, two-photon dyes, and oxygen sensors. The potential of metal â-diketonate complexes for the catalysis of the chemical fixation of CO_2 into cyclic carbonates at 1 atm CO_2 and near room temperature was demonstrated. Their potential for the capture and simultaneous conversion of CO_2 in a dilute CO_2 stream was also determined. The catalysts were easily synthesized and commercially available. Therefore, this CO_2 transformation was less energy- and material-consuming, which made this reaction closer to true “green” chemistry.

1.2.4 Applications of Resonance Raman Spectroscopy (Study of Active Sites of Metalloproteins)

Resonance Raman spectroscopy is an advanced technique used to study vibrational bands in the group frequency region and the information obtained is similar to that obtained by furrier transform infrared (FTIR) and Raman studies. The enhancement of RRS over spontaneous Raman spectroscopy is about 10^6- 10^8 fold. RRS employs a laser light having frequency close to the energy required for the electronic transition of a compound. The resonance in frequency of the incident light and the analyte enhances the intensity of the Raman scattering. The comparison between IR, spontaneous Raman and resonance Raman spectroscopic methods is shown in figure. 1.18.

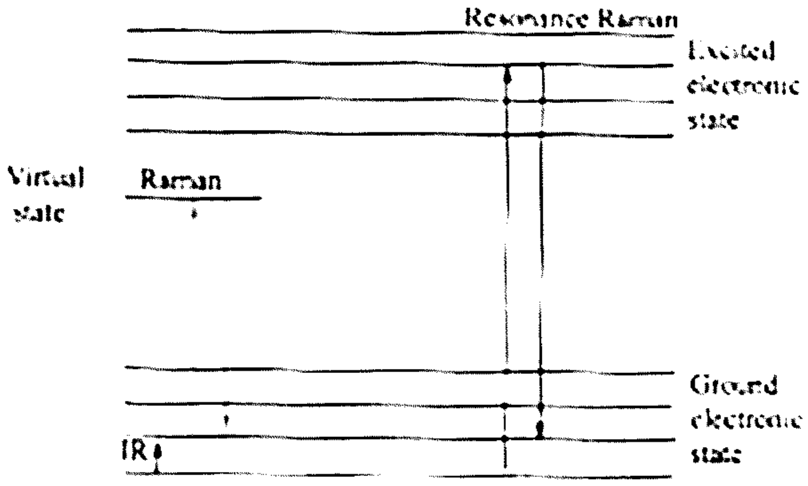


Fig. 1. 18 *Schematic representation of infrared, spontaneous Raman and resonance Raman spectroscopy.*

The resonance effect in RRs arises from the coupling of vibrational transition of the molecule with the motion of elections associated with the electronic excitation.

Some of the applications of RRS are enumerated below:

1. **Vibrational Frequencies in Exited States:** Ohta and Ito showed that measurement of the intensities of Raman lines taken at different excitation wavelengths can be used to assign excited state frequencies of non-totally symmetric modes. Ohta and Ito were able to show qualitatively that the strongest band observed in the vibronic spectrum should undergo the greatest frequency change between the excited and ground states. Since then *n* ’! π^* absorption spectrum of quinoxaline is dominated by a 425 cm^{-1} band, they concluded that the reported 62cm^{-}1 shift of frequency (425 487 cm^{-1}) was too small. Starting from the vibronic theory of the Raman Effect as set forth by Albrecht

Table 1.3 *Vibrational Assignments for Quinoxaline*

B, Vibrational Assignments for Quinoxaline (cm^{-1})		
Ground State	First Excited State^{a}	First Excited State^{b}
867	600	425
796	… *c*	600
718	… *c*	…*c*
487	425	… *c*
398	310	310

^{a} Jordan et al. (see Ref. (21).

^{b} Ohta and Ito (see Ref. (7).

^{c} Values not reported.

Ohta and Ito showed that the intensity enhancements of the non-totally symmetric vibrations were related to the differences of their frequencies in the excited and ground states through the $h_{es}{}^{a}$ term.

$$v^2 - v'^2 = \frac{1}{4\pi^2 c^2}\frac{2\left|h_{es}{}^{b_1}\right|^2}{E_e - E_s}$$

The primed term refers to the excited state frequency. Measurements of the relative intensities showed that the ratios of the coupling terms (in this case: $(^1\beta_1|\partial H|\partial Q|^1A_1))$ for the 867,796,487 and 398 cm^{-2} lines should be 4.2:1.7:0:1. On this basis they proposed the assignments given in column 3 of the table. In support of their conclusion they pointed out that the 867 cm^{-1} mode is due to an out-of-plane C-H bending motion which is similar to that motion found in pyrazine, whose frequency decreases from 925 to 385 cm^{-1} as a result of vibronic coupling

2. **Determination of Molecular Geometry in an Excited State:** Recording to Thirakawa and Tsubor, if a Raman line becomes stronger when the exiting frequency is brought into resonance with an electronic band, this means that the equilibrium conformation of the molecule as distorted along the normal. Coordinated of the given Ramey line in the transition from the ground to excited electronic state for example in case of gaseous NH_3 where on changing form an exciting line of 514.5 nm to one of 351.1 nm the intensity of the umbrella vibration (v_2, 930cm^{-1}) is enhanced ten times more than that of the symmetric stretch. This is exactly what is expected since the first excited electronic state of NH3, which lies at 216.8 nm above the ground state, is known to be planar (23).

3. **Overtones in Resonance Raman Spectra:** In a normal Raman spectrum, generally overtones and combination of bands are absent. When however the exciting line coincides with an electronic absorption band, simple molecules, such as I_2 and T_1I_4, frequently exhibit long, well defined progressions of overtones correspond rip to totally symmetric modes there is a useful academic application possible using these long overtone progressions, that being the calculation of harmonic frequencies and anti-harmonicas constants.

4. **Application of RRS in Biological Systems:** The greatest interest of RRS is in the study of biologically significant molecules, especially the metalloproteinase. The significance of RRS lies in the fact that the nature of the effect is such that only moles associated with the chromophoric graph of a molecule are enhanced. The consequences of this are:
   - (i) Vibrational modes of chromophoric groups in biological molecules, which are often the sites of their biological activities, will be strongly enhanced.
   - (ii) The remainder of the vibrational modes will not be enhanced and therefore cannot complicate the spectra.
   - (iii) Due to the increased sensitivity of the effect, spectra can be obtained under physiologically relevant conditions.

Harem related systems have received the most attention from spectroscopists. For example, the spin and oxidation states of Fe atoms in hemoglobin and cytochrome-c can be determined rather simply from the frequency shifts of RR enhanced modes (28). The appearance of a band showing inverse polarization (for a discussion of inverse polarization see ref. (6)) at~1580 cm^{-1} is indicative of low-spin Fe in both the Fe (II) and Fe (III) states (28). This band shifts to ~1553 cm^{-1} in high-spin complexes. In cytochrome-*c* and other home proteins, a band at ~1360 cm^{-1} indicates Fe(II); while if the Fe is oxidized to Fe(III) the band shifts to 1376 cm^{-1} More extensive tables of frequency correlations for hemes are available in the literature (5.6. 29).

Descent in symmetry of molecules with substitution

Symmetry of molecules discussed so far been assigned into a point group under ideal condition. But gradual substitution of the existing groups in the molecules leads to less symmetrical structures of the molecules.

1.2.5 Charecteristic Vibrational Frequencies of Various Compounds

The infrared spectrum of an organic compound contains a large number of bands due to the stretching and bending vibrational modes of each bond. Thus, it is quite difficult to assign each and every band to a particular mode of vibration. Organic chemists generally do not try to identify all the absorption bands in an IR spectrum. They just look at some characteristic bands that you will be dealing in the present module. These characteristic peaks tell about the presence of some particular functional groups present in the molecule. Now as more energy is needed to stretch a bond than to bend it, absorption bands for stretching vibrations are found in the high frequency region that is functional group region whereas absorption bands for bending vibrations are typically found in the fingerprint region.

Stretching vibrations, therefore, are the most useful vibrations in determining the functionality present in a molecule. The IR stretching frequencies associated with different types of bonds are discussed separately. Thus, the vibrational frequencies provide important structural information about a compound and since two same types of bonds in two different compounds would vibrate at different frequencies and so no two compounds can have exactly same infrared spectrum especially in the finger print region except enantiomers. This makes IR spectroscopy a simple and versatile tool for identification of samples. Here we describe the various vibrational modes and their characteristic absorption frequencies.

***Table 1.4** Vibrational Frequincies of Various Compounds*

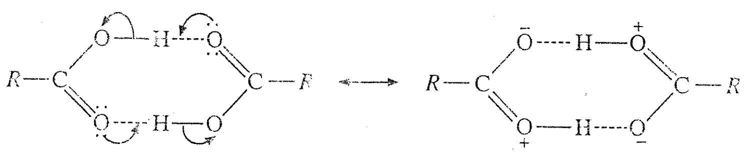
Formula	Bond	Characteristic IR Frequency range (cm^{-1})
alcohol	O-H stretching	3200 – 3600 (broad)
carbonyl	C=O stretching	1650 – 1750 (strong)
aldehyde	C-H stretching	~ 2800 and ~ 2700 (medium)
carboxylic acid	C=O stretching	1700 – 1725 (strong)
	O-H stretching	2500 – 3300 (broad)
alkene	C=C stretching	1620 – 1680 (weak)
	vinyl =C-H stretching	3020 – 3080
benzene	C=C stretching	~ 1600 and 1500 – 1430 (strong to weak)
alkyne	C≡C stretching	2100 – 2250 (weak)
	terminal ≡C-H stretching	3250 – 3350
alkane	C-H stretching	2850-2950
amine	N-H stretching	3300-3500 (medium)

1.2.6 Effect of Hydrogen Bonding and Solvent Effect on Vibrational Frequencies

Hydrogen bonding lowers the stretching frequencies of both the groups involved in it, and also changes the shape and intensity of absorption bonds. Usually, absorption bonds become more intense and broad on H-bonding. The stronger the hydrogen bond, lower is the O-H stretching frequency.

Non-hydrogen-bonded (free) O–H group of alcohols and phenols show sharp and strong absorption bands in the region 3590-3050 cm^{-1}. Sharp, non-hydrogen-bonded 0–H bands are observed only in the vapour phase, in very dilute solution, in non-polar solvents or when hydrogen bonding is prevented by steric hindrance. Pure samples and concentrated solutions of alcohols and phenols show broad O–H stretching bands in the region about 3200-3600 cm^{-1} due to intermolecular hydrogen bonding. The N–H stretching frequencies of amines are also affected by hydrogen bonding in the same way as that of the hydroxyl group but frequency shifts for amines are lesser than that for hydroxyl compounds. This is because nitrogen is less electronegative than oxygen and so the hydrogen bonding in amines is weaker than that in hydroxy compounds. For example. Non-hydrogen bonded primary amines exhibit two bands, one near 3400 cm^{-1} and the other near 3500 cm^{-1} due to symmetrical and asymmetrical N–H stretching modes, respectively. In pure amines, these bands respectively appear in the range 3250-3330 cm^{-1} and 3330-3400 cm^{-1} due to intermolecular hydrogen bonding.

In liquid or solid state, and in concentrated solutions, carboxylic acids exist as dimmers due to strong intermolecular hydrogen bonding.

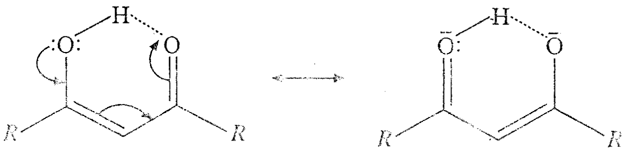


The strong hydrogen bonding between C=0 and OH groups lower their stretching frequency. Because of more polar O–H bond, carboxylic acids from stronger H-bond than alcohols. Carboxylic acid dimers show very broad, intense O-H stretching absorption in the region 2500-3000 cm^{-1}, whereas non-hydrogen bonded carboxylic acids show the O–H absorption near 3550 cm^{-1} H-bond weakens the C=O bond. Thus, C=O stretching bonds of monomers of saturated carboxylic acids appear at 1760 cm^{-1}.

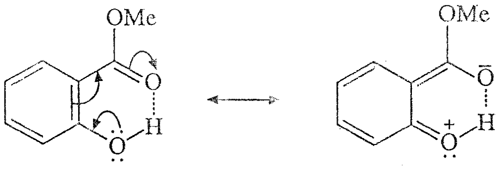
Distinction Between Inter-and Intramolecular H-Bonding

The intermolecular H-bonding is concentration dependent. On dilution with non-polar solvents, intermolecular H-Bonds are broken. Hence, there is decrease in intensity or disappearance of H-bonded O–H stretching bond and increase in intensity or appearance of free O–H stretching absorption. Thus, in very dilute solution solutions (in non-polar solvents, conc. < 0.01 m), the OH–stretching frequency is shifted to a higher frequency in case of intermolecular hydrogen bonding.

Intramolecular hydrogen bonding is within the same molecule, hence it is not affected by change in intermolecular distances. Thus, intramolecular hydrogen bonds are unaffected by dilution, and so the absorption band is also unaffected. Intramolecular hydrogen bonding (chelation) is very strong in enols and compounds like methyl salicylate etc., due to resonance stabilization of the chelate ring. For example, in enols, the O–H group involved in chelation shows broad absorption band in the range 2500-3200 cm^{-1}, whereas, the C=O stretching band in enolic form occurs at 1630 cm^{-1} and that in the keto form at 1725 cm^{-1}. From the relative intensities of the two bands, it is possible to determine the ratio of the keto and the enol forms.



enol of $RCOCH_2COR$



Methyl salicylate

Due to interactions of π electrons of Lewis bases (such as alkenes and benzene) with acidic hydrogen, lengthening and hence, weakening of the O–H bonds has also been observed. For example, the O–H stretching frequency of phenols is lowered by 40-100 cm^{-1} when the spectrum is recorded in benzene solution as compared to that recorded in CCl_4 solution.

1.2.7 Overtones

The IR spectrum besides containing fundamental absorptions, becomes complicated due to the presence of weak overtone, combination, and difference bands. Overtone bands may arise if a molecule is excited, e.g., from its first vibrational energy to the third vibrational energy level. The energy required is almost twice of that required for the excitation to second vibration energy level. In this way if there two fundamental bands at x and y in, then the overtone bands can be expected, e.g., at 2x, 2y, 3x and 3y cm^{-1}. The intensity of the overtone decreases as the order of the overtone increases, e.g., the second overtone (3x or 3y) is less intense than the first overtone (2x or 3y) So, second and third overtones are rarely observed, whereas first overt ones observed only for strong bands.

1.2.8 Combination Bands and Fermi Resonance

Combination bands are observed when more than two or more fundamental vibrations are excited simultaneously. One reason a combination band might occur is if a fundamental vibration does not occur because of symmetry. This is comparable to vibronic coupling in electronic transitions in which a fundamental mode can be excited and allowed as a “doubly excited state.” Combination implies addition of two frequencies, but it also possible to have a difference band where the frequencies are subtracted.

To determine if two states can be excited simultaneous the transition moment integral must be evaluated with the appropriate excited state wavefunction. For example, in the transition,

$$\psi^1\ (0)\ \psi^2\ (0)\ \psi^3\ (0) \rightarrow \psi^1\ (2)\ \psi^2\ (0)\ \psi^3\ (1)$$

the symmetry of the excited state will be the direct product of the irreducible representation for ψ1(2) and ψ3(1).

For example, in the point group C4v, v1 has symmetry e and v3 has symmetry a2. By performing the calculations listed above, it is determined that ψ1(2) has (a1 + b1 + b2) symmetry:

$$\Gamma[\psi_{es}] = \Gamma[\psi_1(2)] \otimes \Gamma[\psi_3(1)] = (a_1 + b_1 + b_2) \times a_2 = a_2 + b_2 + b_1$$

A practical use for understanding overtones and combination bands is applied to organic solvents used in spectroscopy. Most organic liquids have strong overtone and combination bands in the mid-infrared region, therefore, acetone, DMSO, or acetonitrile should only be used in very narrow spectral regions. Solvents such at CCl4, CS2 and CDCl3 can be used above 1200 cm-1.

Fermi Resonance

Fermi resonance results in the splitting of two vibrational bands that have nearly the same energy and symmetry in both IR and Raman spectroscopies. The two bands are usually a fundamental vibration and either an overtone or combination band. The wavefunctions for the two resonant vibrations mix according to the harmonic oscillator approximation, and the result is a shift in frequency and a change in intensity in the spectrum. As a result, two strong bands are observed in the spectrum, instead of the expected strong and weak bands. It is not possible to determine the contribution from each vibration because of the resulting mixed wave function.

If the symmetry requirements are fulfilled and the energies of the two states are similar, mixing occurs, and the resulting modes can be described by a linear combination of the two interacting modes. The effect of this interaction is to increase the splitting between the engery levels. The splitting will be larger if the original energy difference is small and the coupling energy is large. The mixing of the two states also equalized the intensities of the vibrations which allows a weak overtone or combination band to show significant intensity from the fundamental with which it has Fermi resonance with.

1.2.9 FTIR for Gaseous, Solids and Polymeric Material

Fourier Transform infra-red (FTIR) spectroscopy is a simple mathematical technique to resolve complex wave into its frequency components. The connectional IR spectrometers are not of much use for the far IR region (20-400 cm^{-1}) as the sources are weak and detector insensitive. FTIR has made this energy limited region more accessible. It has made the middle infrared (400-4000 cm^{-1}) also more useful.

Principle

The conventional spectroscopy, called the frequency domain spectroscopy, records the radiant power G (ω) as a function of frequency ω. In the time domain spectroscopy, the changes in radiant power f(t) is recorded as a function of time t. In a Fourier transform spectrometer, a time domain plot is converted into a frequency domain spectrum. In mathematics, the Fourier transform of the function f(t) is defined by

$$G(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt \tag{1}$$

Then the inverse relation is

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(\omega) e^{i\omega x} d\omega \tag{2}$$

Equations (1) and (2) are said to form a Fourier transform pair.

To illustrate the use of Fourier transform, consider the superposition of two sine waves. Figures 1.19 (a) and (b) of the same amplitude but of slightly different frequencies. Figure 1.19 (c) represents the superposed wave. The Fourier transform of the individual sine waves and the superposed wave train gives the frequencies in the frequency domain and arc represented in Figures 1.19 (d), (e) and (f).

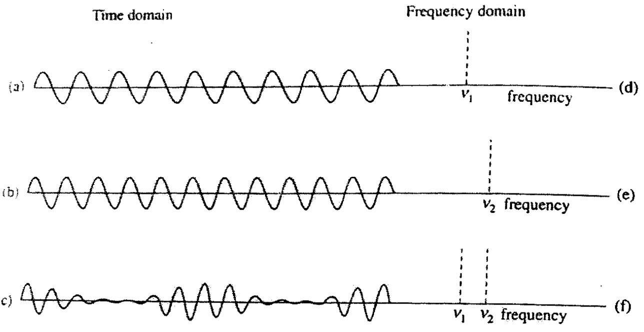


Fig. 1.19 *(a) A Sine wave: (b) Sine wave of slightly differing frequency: (c) sum of the sine waves in (a) and (b); (d)-(f): the frequency domain spectra of the Waves.*

In the same way, complicated time domain spectra could be transformed into frequency domain spectra. The actual calculation of the Fourier transform of such systems is done by means of high speed computers.

Application of FTIR in Polymers

Polybutadiene or thermoplastic elastomers like styrene-butadiene-styrene co-polymers are widely used in diverse industries. The presence of double bonds in their structure promotes degradation by heat or light. The hydrogenation of these materials is an effective method to improve their performance. In this context, the determination of microstructure before and after hydrogenation, is important since chemical and mechanical resistances are related to it. Microstructure can be evaluated with time of hydrogenation by FTIR for styrene-butadiene copolymers and also other polymers.

There is a good agreement in the microstructure calculated by FTIR and H' NMR, so FTIR can be used with confidence in order to evaluate composition and microstructure of styrene butadiene copolymers.

Check Your Progress

1. Define IR spectroscopy.
2. What is the source of radiation in IR spectroscopy?
3. What are the most common detectors used in IR spectroscopy?
4. Define inversion.
5. When a molecule is said to be optically active?
6. What are monodenate ligands?
7. What are polydenate ligands?
8. State the effect of hydrogen on vibration frequencies of compounds.
9. What are combination bands?
10. Define fermi resonance.

1.3 UV-VISIBLE SPECTROSCOPY

In the ultraviolet and visible region, the absorption of energy occurs mainly due to electronic transitions. These electronic transitions require relatively larger amount of energy, *i.e.*, approximately 30–300 kcal/mole corresponding to radiation of the wavelength between 100–800 nm . The wavelength region from 100 to 400 nm is the ultraviolet region while that from 400–800 nm is the visible region. Since oxygen (present in air) absorbs strongly below 210 nm, the region between 100 to 200 nm is generally called vacuum ultraviolet or far ultraviolet and is not of much use in the study of ultraviolet spectra.

Simultaneous to electronic transition there are changes in vibrational and rotational energies of the molecule but these can only be observed if the sample is in the gaseous state. Since most of the spectra measurement in chemistry are made in solution, vibrational and rotational changes are lost and only broad absorption peaks as a result of electronic transitions are observed.

For a given excitation a molecule absorbs only one discrete quantum of energy. Hence absorption spectrum should be a line spectrum but a group of molecules of any sample exists in a number of closely spaced energy levels differing only in relatively small amount of energy to absorb energy over a small range showing band absorption.

Table 1.5 *The Spectrum of Electromagnetic Radiations and congressional between these Pigeons and Types Molecular Excitation*

1.	Wavelength λ	10^{-1} mμ	10 mμ	100 mμ	200 mμ	400 mμ	800 mμ	50 μ	30 cm	10^3 cm	10^4 cm
2.	Region of spectrum	X-ray		Vacuum Ultra-violet (UV)	Near UV	Visible	Infrared	Microwave			Radio-wave
3.	Type of excitation	Sub valence electrons		Valence electrons			Molecular vibrations	Molecular rotations		Nuclear magnetic resonance	
4.	Wave number (cm^{-1})			10^5	5×10^4	2.5×10^4	1.25×10^4	200	3.3×10^{-2}	10^{-2}	10^{-4}

Instrumentation

A spectrophotometer used for obtaining ultraviolet and visible absorption spectrum essentially consists of the following components.

(*i*) **Source of Radiation**. For ultraviolet light a hydrogen lamp is used while a tungsten lamp is used for obtaining visible radiations.

(*ii*) **Monochromator**. A prism is used for resolving polychromatic radiations into narrow bands of radiations which then passes through a slit and split into two beams: one passing through sample cell and another through blank cell containing only solvent.

(*iii*) **Sample Cell**. As glass absorbs ultraviolet radiations quartz or fused silica cells of about 1 cm length are used to hold the sample.

(*iv*) **Photocell and Recorder**. These are used to monitor and record the absorbance.

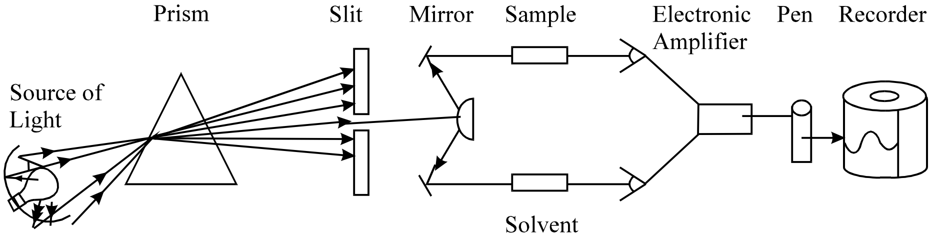


Fig. 1.20 *Schematic Representation of a Double Beam Spectrophotometer for Recording Absorption Spectra*

Procedure: A very dilute solution of substance in suitable solvent is taken in the sample cell. The concentration is adjusted so as to give appropriate absorption. The incident beam of monochromatic radiation is split with the help of mirrors which then passes through the sample tube containing substance as well as through pure solvent. The recorder then plots the log of molar extinction coefficient against wave length of absorbance.

It is customary to note the wavelength of maximum absorption (λ_{max}) and molar extinction coefficient (ε) for a particular absorption.

Some Common Terms used in UV and Visible Spectroscopy

(*i*) **Chromophore**. An isolated functional group not in conjugation with any other group is said to be a chromophore if it absorbs in ultraviolet or visible region. All coloured substances must have at least one chromophoric group though the mere presence of chromophore is not sufficient to make it coloured.

Groups having pi bonds and lone pairs are responsible for $n \to \sigma^*$, $\pi \to \pi^*$ and $n \to \pi^*$ transitions which happen to lie in the common or proper ultraviolet region, *i.e.*, 200–400 nm.

A list of some important chromophores along with their absorption maxima and molar extinction coefficient is given in Table 1.6.

NOTES

Table 1.6 *Some Important Chromophore with that absorption maxima*

Chromophore	*Compound*	λ_{max} *(nm)*	ε	*Solvent*
$>C=C<$	Ethylene	171	15,530	Vapour
$-C\equiv C-$	Acetylene	178	10,000	Vapour
$>C=O$	Acetaldehyde	160	20,000	Vapour
		180	10,000	Vapour
		290	17	Vapour
	Acetone	166	16,000	Vapour
		180	10,000	Hexane
		280	20	Hexane
$-C\equiv N$	Acetonitrile	167	Weak	Vapour
$-N=N-$	Azomethane	338	4	Ethanol
$-NO_2$	Nitromethane	201	5,000	Ethanol
		274	17	Ethanol

(*ii*) **Auxochrome**. Auxochromes are functional groups that do not in themselves show any absorption above 200 nm but which when attached to a given chromophoric system, generaly cause a shift of the absorption maxima to a longer wavelength and increase in the intensity of absorption poak.

Most of the auxochromes have nonbonding electrons such as $-\ddot{O}H$, $-\ddot{N}H_2$, $-\ddot{O}CH_3$, and $-\ddot{S}H$ and may cause *bathochromic* or *hypsochromic* effect on the absorption of a chromophore.

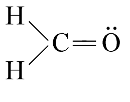
(*iii*) **Bathochromic Effect (Red Shift)**. Auxochromes when attached to a given chromophore not having nonbonding electrons shift the absorption maxima to a higher wavelength. This shift of λ_{max} to longer wavelength is called **bathochromic effect** or **red shift**.

$$CH_2=CH_2 \qquad\qquad CH_2=CH-\ddot{O}CH_3$$

$$\lambda_{max}=170 \text{ nm} \qquad\qquad \lambda_{max}=185 \text{ nm}$$

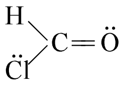
Here auxochrome $-OCH_3$ has increased $\pi \rightarrow \pi^*$ transition from 170 nm to 185 nm.

(*iv*) **Hypsochromic Effect (Blue Shift)**. Auxochrome when attached to a chromophore having both multiple bond and nonbonding electrons, results in shifting of the absorption maxima to lower wavelength. This shift of λ_{max} to shorter wavelength is termed **hypsochromic effect** or **blue shift**.



$H_2C=\ddot{O}$

$\lambda_{max}=295$ nm



$H(\ddot{Cl})C=\ddot{O}$

$\lambda_{max}=230$ nm

Auxochrome $-Cl$ has decreased $\pi \rightarrow \pi^*$ transition from 295 nm to 230 nm.

(*v*) **Hyperchromic Effect**. An increase in the intensity of absorption as shown by higher ε_{max} value is known as **hyperchromic effect**. It is generally observed along with bathochromic shift.

(*vi*) **Hypochromic Effect.** A decrease in the intensity of absorption as manifested in lower ε_{max} value is called **hypochromic effect**. It is observed in case of hypsochromic shift.

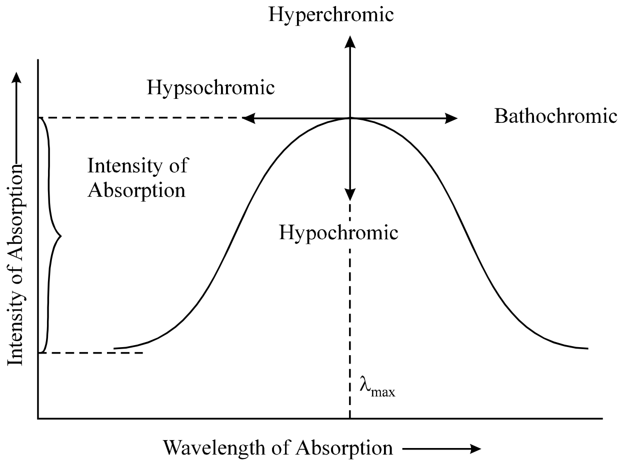


Fig. 1.21 *Shifts in Absorption Positions and Intensities*

1.3.1 Various Electronic Transitions (185-800 nm)

The energy corresponding to ultraviolet and visible radiations may bring about the following electronic excitations:

(*i*) sigma bonding electrons to vacant sigma antibonding orbitals ($\sigma \rightarrow \sigma^*$)

(*ii*) pi bonding electrons to vacant pi antibonding orbitals ($\pi \rightarrow \pi^*$)

(*iii*) Nonbonding electrons to vacant sigma antibonding orbitals ($n \rightarrow \sigma^*$)

and (*iv*) Nonbonding electrons to vacant pi antibonding orbitals ($n \rightarrow \pi^*$).

The energy required for these transitions is in the order $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$.

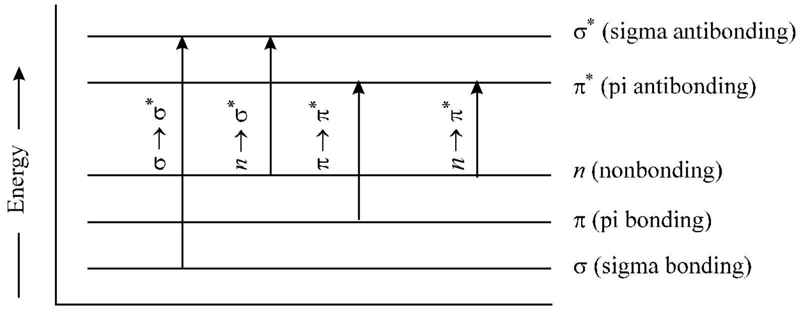


Fig. 1.22 *Energy Levels and Electronic Transitions Possible in a Molecule*

(*i*) $\sigma \rightarrow \sigma^*$ **Transitions**. The energy required for these transitions is high and lies in the vacuum ultraviolet region (below 210 nm). Consequently compounds in which all valence shell electrons are involved in single bond formation such as saturated hydrocarbons do not show any absorption in ordinary ultraviolet region (*i.e.* 200–400 nm).

Methane shows an absorption band at 125 nm corresponding to $\sigma \rightarrow \sigma^*$ transition.

(*ii*) **$n \rightarrow \sigma^*$ Transitions**. The energy required to promote a nonbonding (unshared) electron to vacant sigma antibonding orbital is much less than that required for $\sigma \rightarrow \sigma^*$. Hence molecules having lone pair or nonbonding electrons tend to absorb higher wavelength as compared to compounds having only sigma electrons.

Thus $n \rightarrow \sigma^*$ transitions in

$CH_3\ddot{O}H$ occurs at 183 nm

$CH_3\ddot{N}H_2$ occurs at 215 nm

$CH_3\ddot{I}$ occurs at 258 nm

$(CH_3)_3\ddot{N}$ occurs at 227 nm

Polar solvents shift these $n \rightarrow \sigma^*$ transitions towards shorter wavelength (higher energy) because of some interaction of nonbonding electrons with the solvent. The spectrum of tri-methylamine in aqueous acid shows no absorption due to $n \rightarrow \sigma^*$ transition (at 227 nm) because in acid solution tri-methylamine gets protonated and there are no free nonbonding electrons.

(*iii*) **$\pi \rightarrow \pi^*$ Transitions**. The excitation of bonding pi electrons to vacant antibonding pi orbitals requires still lesser energy as compared to $n \rightarrow \sigma^*$ excitation. Hence these absorptions generally occur in common ultraviolet region.

$\pi \rightarrow \pi^*$ transitions in some common compounds are given below:

Ethylene ($CH_2{=}CH_2$)	170 nm
Acetone ($CH_3CO.CH_3$)	180 nm
Acetylene ($CH{\equiv}CH$)	178 nm

Conjugation of π bonds shifts the wavelength of maximum absorption to longer wavelength. Thus 1,3 butadiene has a λ_{max} at 217 nm.

Polar solvents further shift the wavelength of absorption to longer regions in conjugated systems.

(*iv*) **$n \rightarrow \pi^*$ Transitions**. Such transitions are possible only in compounds having both the nonbonding (*n*) electrons as well as multiple bonds (π electrons) as they involve excitation of nonbonding electron to vacant antibonding pi orbital. These are generally the lowest energy transitions and occur at higher wavelengths.

$n \rightarrow \pi^*$ transitions in some common compounds are given below:

Acetone (CH_3COCH_3)	280 nm
Acetaldehyde (CH_3CHO)	292 nm
Benzaldehyde (C_6H_5CHO)	328 nm
Nitroethane ($C_2H_5NO_2$)	271 nm

Here also the conjugation shifts the absorption to a higher wavelength. Thus $CH_2{=}CH{-}CH{=}O$ absorbs at 320 nm but the polar solvents shift these $n \rightarrow \pi^*$

transitions to lower wavelength due to interaction between nonbonding electrons with polar solvents.

Thus $n \rightarrow \pi^*$ transition of acetone in hexane occurs at 280 nm, in ethanol at 270 nm and in water at 264 nm.

Molecules having σ, π and n electrons may undergo all types of possible transitions giving a number of absorption bands. The table below gives some examples.

Table 1.7 *Various Transitions of Molecules having σ, π, n electrons*

Compound	λ_{max}	ε_{max}
CH_3COCH_3	$n \rightarrow \sigma^*$	
	166 nm	16,000
	$\pi \rightarrow \pi^*$	
	180 nm	10,000
	$n \rightarrow \pi^*$	
	280 nm	20
CH_3CHO	$n \rightarrow \sigma^*$	
	160 nm	20,000
	$\pi \rightarrow \pi^*$	
	194 nm	10,000
	$n \rightarrow \pi^*$	
	292 nm	17
C_6H_5CHO	$\pi \rightarrow \pi^*$	
	244 nm	15,000
	$\pi \rightarrow \pi^*$	
	280 nm	1,500
	$n \rightarrow \pi^*$	
	328 nm	20
$C_2H_5NO_2$	$\pi \rightarrow \pi^*$	
	201 nm	5,000
	$n \rightarrow \pi^*$	
	271 nm	19

The exact electronic structure of excited state is not well understood but there is some kind of redistribution of electrons—not necessarily in accordance with present valence rules. Absorbed energy is generally re-emitted as light.

1.3.2 Beer-Lambert Law

Lambert's Law: The intensity of transmitted light passing through a homogeneous medium decreases geometrically as the thickness of the layer increases arithmetically.

Beer's Law: Each molecule of solute absorbs the same fraction of light incident upon it, regardless of concentration, in a nonabsorbing medium.

The above two laws can be expressed as

$$\frac{I}{I_0} = e^{-kcl} \qquad \text{and} \qquad 2.303 \log \frac{I_0}{I} = kcl = A$$

Where I = Intensity of Transmitted Light

I_0 = Intensity of Incident Light

k = Absorptivity or Extinction Coefficient

c = Concentration in g mole/litre

l = Length of Path in cm

A = Absorbance

and ε (Molar Extinction Coefficient) = $\frac{A}{cl}$

The plot of molar extinction coefficient against wavelength of absorption constitutes the absorption band.

1.3.3 Effect of Solvent on Electronic Transitions

For UV-spectroscopic study, the solvent is so chosen that it does not absorb radiations in the region under investigation and is less polar so that the interaction with solute molecule is minimum. Therefore, solvents such as hexane, cyclohexane, diethyl ether which are transparent above 210 nm and as well as non-polar are used for UV-spectroscopy.

Solvents which are transparent above 210 nm but are polar, such as water, ethanol, methanol, etc., are used but are less preferred compared to other nonpolar solvents as above.

Solvents such as benzene, chloroform and carbon tetrachloride because of their strong absorption, in the range of 240–280 nm, are not used.

The position and intensity of absorption maximum is shifted for a particular chromophore by changing the polarity of the solvent. In case of dienes and conjugated hydrocarbons, the band shift remains almost unaffected with change in polarity. However, in case of a, b unsaturated carbonyl compounds the polarity of solvent has great effect. In such compounds two types of shifts are observed:

(*i*) **$n \rightarrow \pi^*$ transition (less intense):** In this case, with increase in polarity of solvent the absorption band shifts to shorter wavelength. In $n \rightarrow \pi^*$ transition, the ground state is more polar compared to excited state and hence the solvent molecule stabilises the non-bonding electron in the ground state due to hydrogen bonding. In the excited state, the hydrogen bonding with carbonyl group takes place to lesser extent compared to the ground state. Thus, in case of acetone the absorption maximum is at 280 nm in hexane as compared to 264 nm in water.

(*ii*) **$\pi \rightarrow \pi^*$ transition (intense):** In this case, the absorption band moves to longer wavelength with an increased polarity of the solvent. The dipole-dipole interactions with solvent molecules lower the energy of the excited state compared to ground state. Here, the group is more polar in the excited state and thus the π^* orbital in the excited state gets stabilised by hydrogen bonding with solvents such as water, methanol, ethanol etc. and absorption shows a red shift.

$n \rightarrow \sigma^*$ transitions are also very sensitive to hydrogen bonding. For example, alcohols, amines etc., form hydrogen bonding with solvent molecules due to the presence of nonbonding electrons in the hetero atom (—$\underset{\cdot\cdot}{\dot{O}}$—, =$\dot{N}$—) and thus transitions require greater energy and a blue shift results.

1.3.4 UV Bands for Carbonyl Compounds, Unsaturated Carbonyl Compounds, Dienes and Conjugated Polyenes

The molecular spectroscopy is the study of the interaction of electromagnetic waves and matter. The scattering of sun’s rays by raindrops to produce a rainbow and appearance of a colorful spectrum when a narrow beam of sunlight is passed through a triangular glass prism are the simple examples where white light is separated into the visible spectrum of primary colors. This visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these apparently different forms of electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength.

Carbonyl Compounds

Carbonyl compounds have two principal UV radiations, the allowed π ’! π* transitions and the forbidden n ’! π* transitions. In amides, acids, esters or acid halides, the substituents viz. NR2, OH, OR, or –X on carbonyl group show pronounced hypsochromic effect on the n ’! π* transitions. The hypsochromic effect is due to inductive effect of nitrogen, oxygen or halogen atoms. The heteroatom withdraws electrons from carbonyl carbon and makes carbonyl oxygen lone pair of electrons more stabilized due to its involvement in increasing C=O bond order. As a result, the n ’! π* transition of these compounds is shifted to 200-215 nm range relative to 270 nm in aldehydes and ketones. Conjugation of the carbonyl group with double bond shifts both n ’! π* and π ’! π* transitions to longer wavelengths. The effect on π ’! π* band is more pronounced. Woodward formulated rules to predict the position of an absorption maximum in an unknown enone. These rules have been summarized in

Dienes

The presence of conjugate double bond decreases the energy difference between HOMO and LUMO of resulting diene. The figure 6 shows the change in energy of MO on conjugation. As a result, the radiations of longer wavelength are absorbed. The conjugation not only results in bathochromic shift (longer wavelength) but also increases the intensity of absorption. As the number of conjugated double bonds is increased, the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is progressively lowered. Therefore, the increase in size of the conjugated system gradually shifts the absorption maximum (λmax) to longer wavelength and also increases the absorption. For example, ethylene absorbs at 10 175 nm (ε = 1000) and the conjugation in butadiene gives a strong absorption at longer wavelength at 230 nm and with higher intensity (ε = >1000).

Conjugated Polyenes

The energy for transition is lowered with conjugation of double bonds. If there are enough double bonds in conjugation, absorption may ultimately occurs in the visible region and the compound may become coloured. In case of conjugated polyene system with more than five double bonds in conjugation the absorption occurs in the visible region around or above 400 nm. The presence of alkyl group on the double bond also causes red shift. For each alkyl substitution there is 5 nm shift in absorption and for each double bond extending conjugation in π-electron system the shift is 30 nm. The molar absorptivity (ε_{max}) also roughly doubles with each new conjugated double bond.

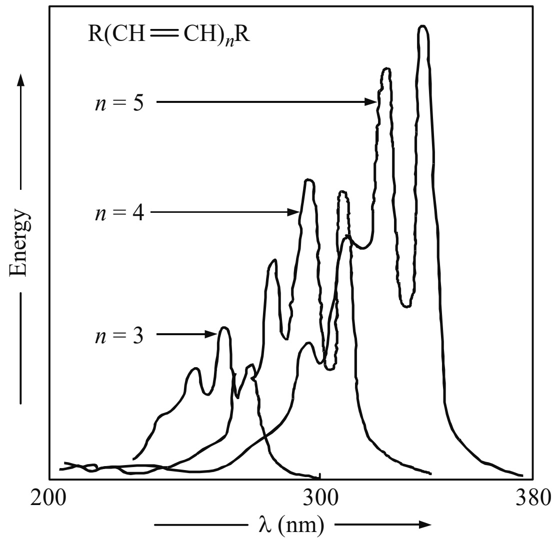


Fig. 1.23 *UV-VIS absorption spectra of linear conjugated polyene*

1.3.5 Fieser-Woodward Rules for Conjugated Dienes and Carbonyl Compounds

Based on the analysis of the data available on λ_{max} of various compounds, Woodward and Fieser formulated some empirical rules for the calculation of λ_{max} of a conjugated diene of known structure.

(*i*) **Dienes**. The basic value for an unsubstituted conjugated diene λ_{max} = 214 nm

(*a*) If both conjugated double bonds are in the same ring, then λ_{max} = 253 nm

(*b*) For each alkyl substituent or ring residue, add 5 nm

(*c*) For an exocyclic double bond, add 5 nm

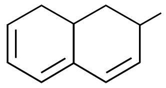
(*d*) For each double bond extending conjugation, add 30 nm

(*e*) For auxochromes given below, add as metnioned

—Cl, —Br, —I	5 nm
—OR	6 nm
—NR_2	60 nm
—SR	30 nm

Example

(*a*) Homoannular Conjugated Diene



Basic value (conjugated in same ring) = 253 nm

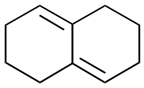
3 ring residue (3 × 5 = 15) = 15 nm

1 Exocyclic double bond conjugated = 30 nm

Total calculated λ_{max} = 298 nm

Observed λ_{max} = 298 nm

(*b*) Heteroannular conjugated



Basic value for diene = 214 nm

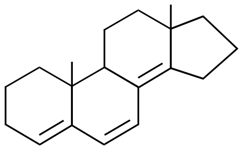
3 ring residue = 15 nm

1 Exocyclic double bond = 5 nm

Total calculated λ_{max} = 234 nm

Observed λ_{max} = 235 nm

(*c*) Miscellaneous



Basic value for diene = 214 nm

Exocyclic double bond 3 × 5 = 15 nm

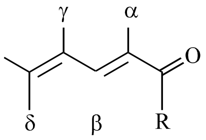
Substituent 5 × 5 = 25 nm

Double bond in conjugation = 30 nm

Total calculated λ_{max} = 284 nm

Observed λ_{max} = 284 nm

(*ii*) **Enones (α, β-Unsaturated Carbonyl Compounds)**



Basic values assigned for

(*a*) Parent α,β-unsaturated acyclic or six membered ketone λ_{max} = 215 nm

(*b*) Parent α,β-unsaturated five membered ring ketone λ_{max} = 202 nm

(*c*) Parent α,β-unsaturated aldehyde (R═H) λ_{max} = 207 nm

Increments for

(*d*) Double bond extending conjugation = 30 nm

(*e*) Double bond extending conjugation in homoannular diene = 39 nm

(*f*) For each alkyl substituent at α-position = 10 nm

at β- position = 12 nm

at γ-position or higher = 18 nm

(*g*) For each Auxochrome

—OH at α-position = 35 nm

at β-position = 30 nm

at γ-or higher position = 50 nm

—OMe at α-position = 35 nm

at β-position = 30 nm

at γ-position = 17 nm

at δ-position = 31 nm

—OAc	at α, β- or γ-position	= 6 nm
—Cl	at α-position	= 15 nm
	at β-position	= 12 nm
—Br	at α-position	= 25 nm
	at β-position	= 30 nm
—NR_2	at β-position	= 95 nm

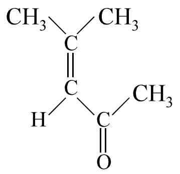
(*h*) For exocyclic nature of double bond = 5 nm

(*i*) Solvent correction

Chloroform	= + 1 nm
Ether	= + 7 nm
Water	= – 8 nm
Hexane or cyclohexane	= + 11 nm

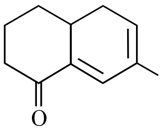
Examples

(*a*) α,β-Unsaturated Ketone Acyclic



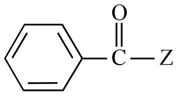
Basic value	= 215 nm
2β-substituents alkyl (2 × 12)	= 24 nm
In chloroform solvent	= 1 nm
Total calculated λ_{max}	= 240 nm
Observed λ_{max}	= 237 nm

(*b*) α,β-Unsaturated Cyclic Ketone



Basic value	= 215 nm
One α-alkyl group	= 10 nm
γ- alkyl group	= 18 nm
Exocyclic double bond	= 5 nm
Double bond extending conjugation	= 30 nm
Homoannular diene	= 39 nm
In ethanol solvent	= 0 nm
Total calculated λ_{max}	= 317 nm
Observed λ_{max}	= 315 nm

(*iii*) **Aromatic Carbonyls**



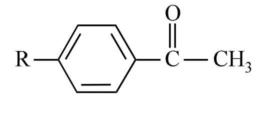
Basic values assigned for

(*a*) Z = H	= 250 nm
(*b*) **Z** = R— or ring residue	= 246 nm
(*c*) **Z** = —OH or —OR	= 230 nm

Increments for substituents in the ring

(*d*) Alkyl	at *o*- or *m*-position	= 3 nm
	at *p*-position	= 7 nm
(*e*) —OH or —OR	at *o*- or *m*-position	= 7 nm
	at *p*-position	= 25 nm
(*f*) —Cl	at *o*- or *m*-position	= 0 nm
	at *p*-position	= 10 nm
(*g*) —NR_2	at *o*- or *m*-position	= 20 nm
	at *p*-position	= 85 nm

Example



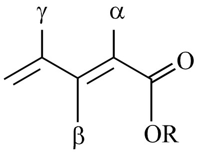
Basic value = 246 nm

Alkyl at *p*-position = 7 nm

Total calculated λ_{max} = 253 nm

Observed λ_{max} = 251 nm

(*iv*) α,β-Unsaturated Acids and Esters



Basic values assigned for

(*a*) β-Monosubstituted = 208 nm

(*b*) α,β-Disubstituted = 217 nm

(*c*) α,β,γ-Trisubstituted = 225 nm

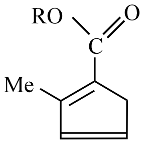
Increments for

(*d*) Double bond extending conjugation = 30 nm

(*e*) Exocyclic double bond = 5 nm

(*f*) Endocyclic double bond in ring = 5 nm

Example



Basic value = 208 nm

Extended conjugation = 30 nm

Endocyclic double bond = 5 nm

Total calculated λ_{max} = 243 nm

Observed λ_{max} = 241 nm

1.3.6 UV Spectra of Aromatic and Hetrocyclic Compounds

In case of aromatic compound such as benzene the strong absorption band is obtained near 180 nm (ε_{max} ~ 62,000), weak absorption at 200 nm (ε_{max} ~ 7,500) and a group of much weaker bands in the region between 250 nm to 300 nm (ε_{max} ~ 200). In the absorption maximum for added conjugation as in napthalene, anthracene, tetracene and pentacene, the absorption moves to longer wavelength, i.e., absorption shifts from UV region to visible region.

The molar extinction coefficient is also found to increase with added conjugations.

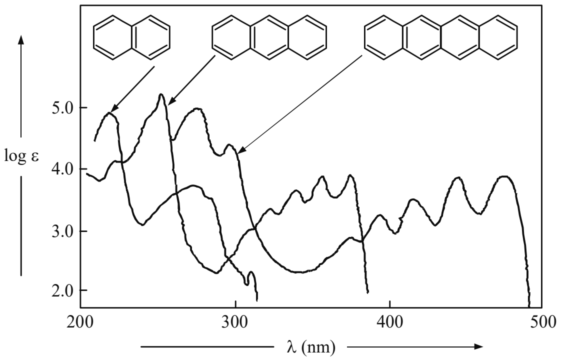


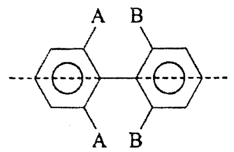
Fig. 1.24 *UV-VIS spectra of aromatic linear condensed system*

1.3.7 Steric Effect in Biphenyls

Isolable stereoisomers resulting from restricted rotation about simple bonds are called atropisomers. Suitably substituted biphenyls exhibit enatiomerism due to the presence of chiral axis, and three atropisomers because they exhibit enantiomerism due to restricted rotation about the single bond between the two phenyl rings. There is restricted rotation about the bond linking the two phenyl rings due to steric hindrance between the bulky ortho substituents. Because of this steric effect (hindrance) the two phenyl rings lie in different planes which are perpendicular, thus the molecule become chiral and exhibits enantiomerism.

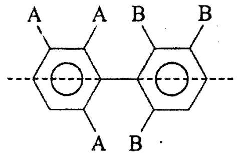
Biphenyls show enantiomerism when the following two conditions are satisfied:

(i) Each ring must be unsymmetrically substituted. Thus I is not resolvable, but II and III are resolvable.

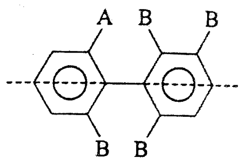


I

Both rings have a plane of symmetry, hence non-resolvable



II

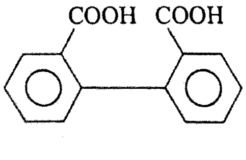


III

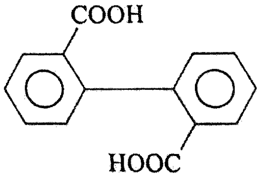
In II and III both rings have no plane of symmetry, hence, these are resolvable.

(ii) Both rings must be substituted in ortho positions (minimum number of substituents should be two, one substituent in each ring), and the substitutents must have a large size (e.g., Cl, Br, COOH, NO_2, SO_3H, CH_3 etc.).

If the substituents in ortho positions are smaller in size, the two phenyl rings become planner, i.e., free rotation occurs, thus cannot be optically active because would possess a plane or a centre of symmetry. For example, diphenic acid is not optically active because the molecule has a plan of symmetry in configuration IV and centre of symmetry in V.

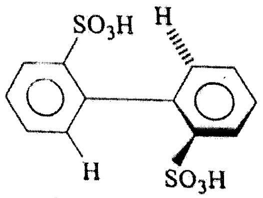


IV



~~VI~~ V

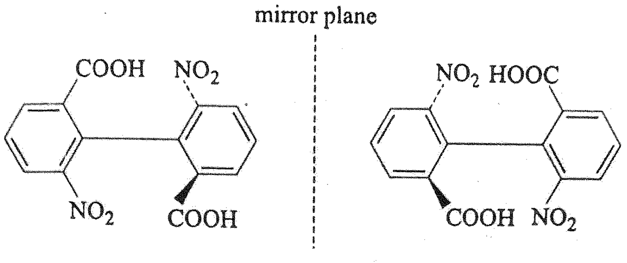
The SO_3H group is large enough to cause restricted rotation and non of the rings has plane or centre of symmetry, hence, biphenyl-2,2'-disulphonic acid could be resolved although only two SO_3H groups are present in the o- and o'-positions:



Resolvable into its enantiomers

Resolvable into its enantiomers

6, 6'-Dinitrobiphenyl-2,2'-dicarboxylic acid VI which can be resolved into its enantiomers and each isomer is stable indefinitely. This is because the nitro and carboxylic groups are so bulky that they cannot pass by each other, and there is no a plane or centre of symmetry in the molecule.

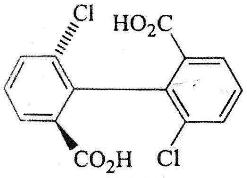


VI

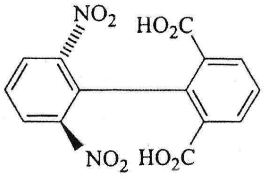
Biphenyl atropisomers

Biphenyl atropisomers

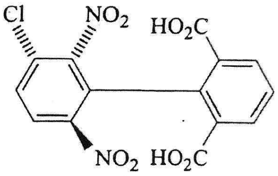
The compound VII is chiral but compounds VIII an IX are achiral. In compound IX both the rings have plane of symmetry, whereas in compound X the ring containing carboxylic groups has plane of symmetry, thus VIII and IX are achiral (optically inactive). It should be noted that the lack of symmetry cannot be generated by the groups in the para position.



VII
chiral

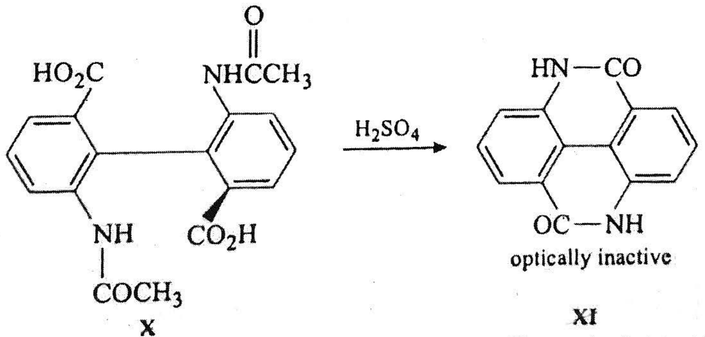


VIII
achiral



IX
achiral

There is a definite chemical evidence to show that the non-coplanarity of the two phenyl rings in biphenyls is essential for their optical activity. The method involves the conversion of a non-coplanar optically active compound X into a dilactam XI which is optically inactive because it is planar.



X
the optically active compound,
the rings cannot be coplanar

XI
the dilactam is planar and
it has a centre of symmetry

Check Your Progress

1. What is a source of radiation in UV spectroscopy?
2. What monochromator is used in UV spectroscopy?
3. Define chromophore.
4. Define auxochrome.
5. State the Beer's Law of UV spectroscopy.
6. State Lambert's Law.

1.4 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Infrared Spectroscopy measures the vibrations of inter atomic bonds of a sample at different frequencies when the sample is exposed to infrared light.
2. Infrared radiation source is often a Nernst filament which is fabricated from a binder and oxides of cerium, zirconium and thorium or globar which is a small rod of silicon carbide.
3. The most common type of detectors used in IR spectroscopy are bolometers, thermocouples and thermistors.
4. 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 an equivalent point the centre of the molecule which generates in nerve is called the centre of symmetry on the inversion centre (i).
5. A molecule is optically active only if it could exist as mirror image isomers.
6. If a ligand contains only one donor atom, then it is capable of forming one coordinate bend with the central metal atom, it is known as *monodentate* ligand.
7. When a ligand has to or more donor atoms which may simultaneously coordinate with the metal atom, it is tenured' as polydentate ligand.
8. Hydrogen bonding lowers the stretching frequencies of both the groups involved in it, and also changes the shape and intensity of absorption bonds.
9. Combination bands are observed when more than two or more fundamental vibrations are excited simultaneously.
10. Fermi resonance results in the splitting of two vibrational bands that have nearly the same energy and symmetry in both IR and Raman spectroscopies.
11. For UV Spectroscopy a hydrogen lamp is used is a source.
12. A prism is used for resolving polychromatic radiations into narrow bands of radiations which then passes through a slit and split into two beams: one passing through sample cell and another through blank cell containing only solvent.
13. A chromophore is an isolated functional group not in conjugation with any other group is said to be a chromophore if it absorbs in ultraviolet or visible region.
14. Auxochromes are functional groups that do not in themselves show any absorption above 200 nm but which when attached to a given chromophoric

system, generally cause a shift of the absorption maxima to a longer wavelength and increase in the intensity of absorption peak.

15. **Beer's Law:** Each molecule of solute absorbs the same fraction of light incident upon it, regardless of concentration, in a non-absorbing medium.
16. **Lambert's Law:** The intensity of transmitted light passing through a homogeneous medium decrease geometrically as the thickness of the layer increases arithmetically.

1.5 SUMMARY

- Spectrometer is a broad term often used to describe instruments that measure a continuous variable of a phenomenon where the spectral components are somehow mixed.
- Infrared Spectroscopy measures the vibrations of inter atomic bonds of a sample at different frequencies when the sample is exposed to infrared light.
- Infrared spectrometers can also be used to measure the number of absorbing molecules.
- Infrared radiation source is often a Nernst filament which is fabricated from a binder and oxides of cerium, zirconium and thorium or globar which is a small rod of silicon carbide.
- In the context of chemistry, symmetry is important both at the molecular level as well as in crystalline systems.
- The symmetry element is a line on a plane through which the symmetry operation is performed.
- 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 an equivalent point the centre of the molecule which generates in nerve is called the centre of symmetry on the inversion centre (i).
- A molecule is optically active only if it could exist as mission image isomers.
- A ligand is defined as an atom, ion or molecule which is capable of donating a pair of elections to the metal atom.
- Ethylenediamine (abbreviated as en when a ligand) is the organic compound with the formula $C_2H_4(NH_2)_2$.
- Aromatic difluoroboron â-diketonate complexes (BF2bdks) are classic fluorescent molecules that have been explored as photochemical reagents, two-photon dyes, and oxygen sensors.
- Resonance Raman spectroscopy is an advanced technique used to study vibrational bands in the group frequency region and the information obtained is similar to that obtained by furrier transform infrared (FTIR) and Raman studies.
- The infrared spectrum of an organic compound contains a large number of bands due to the stretching and bending vibrational modes of each bond.
- The infrared spectrum of an organic compound contains a large number of bands due to the stretching and bending vibrational modes of each bond.

- Combination bands are observed when more than two or more fundamental vibrations are excited simultaneously.
- Fermi resonance results in the splitting of two vibrational bands that have nearly the same energy and symmetry in both IR and Raman spectroscopies.
- Fourier Transform infra-red (FTIR) spectroscopy is a simple mathematical technique to resolve complex wave into its frequency components.
- In the ultraviolet and visible region, the absorption of energy occurs mainly due to electronic transitions.
- Isolable stereoisomers resulting from restricted rotation about simple bonds are called atropisomers.

1.6 KEY TERMS

- **Spectrometer:** A spectrometer is a scientific instrument used to separate and measure spectral components of a physical phenomenon.
- **IR Spectroscopy:** Infrared Spectroscopy measures the vibrations of inter atomic bonds of a sample at different frequencies when the sample is exposed to infrared light.
- **Inversion:** 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 an equivalent point the centre of the molecule which generates in nerve is called the centre of symmetry on the inversion centre (i).
- **Monodentate Ligands:** If a ligand contains only one donor atom, then it is capable of forming one coordinate bend with the central metal atom, it is known as *monodentate* ligand.
- **Polydentate Ligands:** When a ligand has to or more donor atoms which may simultaneously coordinate with the metal atom, it is tenured' as polydentate ligand.
- **Resonance Raman Spectroscopy:** Resonance Raman spectroscopy is an advanced technique used to study vibrational bands in the group frequency region and the information obtained is similar to that obtained by furrier transform infrared (FTIR) and Raman studies.
- **Overtones:** Overtone bands may arise if a molecule is excited, e.g., from its first vibrational energy to the third vibrational energy level.
- **Combination Bands:** Combination bands are observed when more than two or more fundamental vibrations are excited simultaneously.
- **Monochromator**: A prism is used for resolving polychromatic radiations into narrow bands of radiations which then passes through a slit and split into two beams.
- **Chromophore**: An isolated functional group not in conjugation with any other group is said to be a chromophore if it absorbs in ultraviolet or visible region.

- **Auxochrome:** Auxochromes are functional groups that do not in themselves show any absorption above 200 nm but which when attached to a given chromophoric system, generally cause a shift of the absorption maxima to a longer wavelength and increase in the intensity of absorption peak.

1.7 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answers Questions

1. What do you understand by symmetry operations?
2. Define symmetry elements.
3. What is plane of symmetry?
4. Define improper relational axis.
5. What is identity element?
6. Define dipole movement.
7. What do you understand by ambidenate ligands?
8. What do you understand by diketonate complexes?

Long-Answers Questions

1. What do you understand by symmetry? Discuss the shapes of various molecules.
2. Explain the mode of bonding in ambidenate ligands.
3. Describe the applications of Resonance Raman Spectroscopy in detail.
4. Describe IR spectroscopy and its various components in detail.
5. Discuss the basics of UV spectroscopy briefly.
6. Discuss the applications of FTIR in detail.
7. Describe in detail the steric effects in biphenyls.

1.8 FURTHER READING

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UNIT 2 APPLICATIONS OF SPECTROSCOPY: NMR, ESR AND MASS SPECTROCOPY

NOTES

Structure

NOTES

2.0 INTRODUCTION

Nuclear magnetic resonance spectroscopy, commonly referred to as NMR, has become the preeminent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. Although larger amounts of sample are needed than for mass spectroscopy, NMR is non-destructive, and with modern instruments good data may be obtained from samples weighing less than a milligram.

NMR can detect very fine structural components, works for organic and inorganic, qualitative and quantitative, versatile, and reliable. ESR is a microwave technique based on splitting electronic energy fields in a magnetic field. It is used to determine structures of samples containing unpaired electrons. Electron Paramagnetic Resonance (EPR) or Electron Spin Resonance (ESR) spectroscopy is a technique for studying chemical species that have one or more unpaired electrons, such as organic and inorganic free radicals or inorganic complexes possessing a transition metal ion.

Stereochemistry, a sub-discipline of chemistry, involves the study of the relative spatial arrangement of atoms that form the structure of molecules and their manipulation.

Electron Paramagnetic Resonance (EPR) or Electron Spin Resonance (ESR) spectroscopy is a method for studying materials with unpaired electrons. The basic concepts of EPR are analogous to those of Nuclear Magnetic Resonance (NMR), but the spins excited are those of the electrons instead of the atomic nuclei.

Mass Spectrometry (MS) is an analytical technique that is used to measure the mass-to-charge ratio of ions. The results are presented as a mass spectrum, a plot of intensity as a function of the mass-to-charge ratio. Mass spectrometry is used in many different fields and is applied to pure samples as well as complex mixtures.

In this unit, you will study about the basics, principles, usage, and applications of various spectroscopic techniques like, Nuclear Magnetic Resonance (NMR) spectroscopy, Stereochemistry, Electron Spin Resonance (ESR) spectroscopy, and Mass Spectroscopy.

2.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the principle and applications of Nuclear Magnetic Resonance (NMR) spectroscopy.

- Explain the uses of various spectroscopic techniques in chemistry.
- Conceptualize the details of the stereochemistry.
- Define various scientific terms in spectroscopic techniques.
- Explain the basics of Electron Spin Resonance (ESR) spectroscopy and Mass Spectroscopy.

2.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear Magnetic Resonance Spectroscopy is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule.

The energy of radio frequency wave having frequency of 10^7 to 10^8 cycle per second is about 6.6×10^{-20} to 6.6×10^{-19} ergs. The energy is too small to rotate, vibrate or excite an atom or molecule but sufficient to affect the nuclear spin of atoms in a molecule. Thus, by absorption of radio frequency radiation direction of spin of nuclei of atoms in a molecule may change.

Without a magnetic field, the spin state of nuclei is degenerate, i.e. of same energy, and energy level transition is not possible. But when an external magnetic field is applied, the degeneracy is broken and the radio frequency radiation can cause transition between the energy levels.

The nuclear spin, is the resultant of angular momenta of all the nuclear particles, the protons and neutrons. The protons and neutrons by virtue of their spin on their own axis posses the angular momentum $\frac{1}{2}\left(\frac{h}{2\pi}\right)$. The nuclear spin is given by $\sqrt{I(I+1)}\frac{h}{2\pi}$ where I is the spin quantum number. The net spin of a nucleus depends on the number of particles. The rules of determining net spin of a nucleus are as follows:

1. A nucleus with odd mass number has a half integral spin $\left(\frac{1}{2}, \frac{3}{2}, \frac{5}{2} \text{ etc.}\right)$.
2. A nucleus with odd number of protons and odd number of neutrons has an integral spin. (1, 2, 3, etc.)
3. A nucleus with even number of protons and even number of neutrons has zero spin.

Thus ^{12}C, ^{16}O which have net spin zero will not respond to NMR. On the other hand, for ^{13}C which has odd mass number ($N = 7$ and $P = 6$) the spin is $\frac{1}{2}$ and respond to NMR and so is the case with ^{1}H and ^{11}B.

NMR techniques helps us to study the shape and structure of molecules. The most important application of NMR is in the study of hydrogen atoms in organic molecules.

Radio Frequency Absorption: The Cause and Effect

A nucleus is positively charged. Any electrical charge in motion sets up a magnetic field and hence a nucleus due to its motion (spinning) also generates a magnetic field and possesses magnetic moment. The magnetic moment, μ, is proportional to its spin angular momentum,

$$\begin{aligned}\mu &= \gamma \times \text{spin angular momentum}\\ &= \gamma \times \sqrt{I(I+1)}\,\frac{h}{2\pi}\end{aligned}$$

where h is Planck's constant and ν is called the gyromagnetic ratio, a fundamental nuclear constant.

Now, when a nucleus is placed in a homogeneous external field of strength say H_O, it will behave as a magnet and tend to orient itself in relation to the field. For a nucleus with spin quantum number I, the number of possible orientations is given by $(2I + 1)$.

Thus, a proton with spin quantum number 1/2 there is a possibility $\left(2 \times \frac{1}{2} + 1 = 2\right)$ of two orientations with respect to the axis of the external field.

The two orientations will be

(*i*) Alignment with the field, and

(*ii*) Alignment against the field.

In the absence of an external magnetic field, these orientation are of equal energy. When external magnetic field is applied, energy levels split corresponding to $m_I = -\frac{1}{2}$ (antiparallel to the direction of magnetic field) and to $m_I = +\frac{1}{2}$ (parallel to the direction of magnetic field). The energy for a particular level is given by

$$E = \pm \frac{\gamma h}{2\pi}\, mH_0 \quad (\text{‘}m\text{’ is the magnetic quantum number})$$

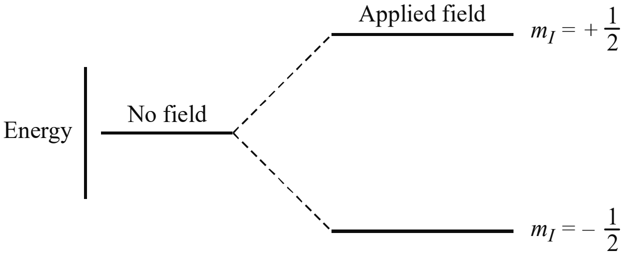

Fig. 2.1 *Energy level splitting of spin $\frac{1}{2}$ nucleus in an applied magnetic field*

Thus, energy with $m_I = -\frac{1}{2}$ and $+\frac{1}{2}$ respectively, is

$$E_1 = -\frac{1}{2}\left(\frac{\gamma h}{2\pi}\right)\mathrm{H}_0$$

and $$E_2 = +\frac{1}{2}\left(\frac{\gamma h}{2\pi}\right)\mathrm{H}_0$$

When the nucleus absorbs energy it is promoted from a lower energy state E_1 to higher energy state E_2, i.e., the nucleus precessing in the aligned orientation, passes into opposed orientation. From higher energy opposed orientation it can come back to the lower energy aligned orientation by losing energy. The transition from one energy state to the other is called flipping. The difference in energy $\Delta E(E_2 - E_1)$ changes the magnetic moment from parallel state $m_I = +\frac{1}{2}$ to antiparallel state $m_I = -\frac{1}{2}$.

$$\Delta E = E_2 - E_1 = h\nu$$

or $$\nu = \frac{E_2 - E_1}{h} = \frac{\frac{1}{2}(\gamma H/2\pi)H_0 + \frac{1}{2}(\gamma h/2\pi)H_0}{h}$$

or $$\nu = \frac{\gamma}{2\pi}H_0$$

where ν = Frequency in cycle per sec. or Hz,

H_0 = Strength of applied magnetic field in gauss,

γ = Nuclear constant or gyromagnetic ratio and is equal to 26750 for the proton.

It is therefore seen that the frequency absorbed or emitted by a nucleus in its transition from one energy level to the other is directly proportional to the applied magnetic field (H_0).

The stronger the applied field, greater will be the tendency of the nuclear magnet to remain lined up with it and higher will be the frequency needed to flip the proton to the higher energy state.

Now when the nuclei is irradiated with a beam of electromagnetic radiation of desired frequency, the lower energy nuclei will absorb it and move to higher energy state. The precessing proton will absorb energy from the radio-frequency region only if the precessing frequency is exactly equal to the frequency of radio frequency region, i.e., when the quantum energy ($h\nu$) of the radiation matches up the energy difference between the two energy states at the applied field strength H_0. When this occurs, the nucleus and the radio frequency beam are said to be in resonance. Hence, the term nuclear magnetic resonance (NMR).

In NMR techniques, mainly organic compounds are exposed to a powerful magnetic field. The different sets of protons will precess at different frequencies (protons might have different environment around it) and now if these precessing protons are irradiated with steadily changing frequencies at some frequency/frequencies resonance condition will be established leading to absorption. In NMR it is the absorption of energy which is detected. It is, however, more convenient to keep the radio frequency constant and change the magnetic field strength constantly. At some value of the field strength resonance condition will occur and energy of the radiation will be absorbed. The absorption will produce a signal. The signal at the detector is amplified and recorded as a band in the spectrum. Such a spectrum is called Nuclear Magnetic Resonance Spectrum.

2.2.1 Chemical Shift: Values and Correlation for Protons Bonded to Carbon and Other Nuclei

It might be expected that different protons in a molecule will absorb the same frequency (as H_0, μ and *h* all are constant) and if it were so the PMR spectra of a compound will be of little use to organic chemists. The protons in molecules are surrounded by electrons which shield them from the applied magnetic field H° to different extent. Hence the magnetic field experienced by different protons in different environments in a molecule is somewhat lower or

$$H_{\text{effective}} = (1-\sigma)H^\circ$$

where σ is known as *shielding constant*. The protons in different environment in same molecule are shielded by the circulation of surrounding electrons to different extent. Thus the electron withdrawing groups or atoms *e.g.* —F, —Cl, —NO_2, —OH, —COOR etc. adjacent to the proton reduce the density of electron cloud and the shielding constant (σ) and the resonance therefore, occurs at a lower magnetic field while the electron releasing groups *e.g.* —R etc. have the reverse effect. This separation of resonance frequencies of protons in different structural environments from some arbitrary standard is termed as *chemical shift.*

The shielding effect is proportional to the magnitude of the applied magnetic strength and therefore the magnitude of chemical shifts is also dependent on the strength of applied magnetic field. Different kind of protons in organic compounds absorb at frequencies spread over 700 cycles per second at a magnetic field of 14,000 gauss. The absorption of protons at this magnetic field is at a frequency of about 60×10^6 cycles per sec. which makes it difficult to measure the position of absorption of protons with accuracy. Therefore absolute absorption frequencies cannot be observed directly and relative proton resonance frequencies are determined. It is also desirable that chemical shift values be expressed in some form independent of field strength and hence these are recorded as fraction of the field strength or frequency.

$$\delta = \frac{(H_r - H_s)}{H_r} = \frac{\Delta\nu \times 10^6}{\text{Oscillator frequency in c.p.s.}}$$

where H_r and H_s are field strengths corresponding to resonance for proton in reference compound (H_r) and sample (H_s) respectively and Δν is the difference in absorption frequencies of sample and reference. The delta (δ) values so obtained are dimensionless and are expressed as ppm (parts per million).

Alternatively, TetraMethyl Silane (TMS) is taken as a reference because it is chemically inert, volatile, miscible with most solvents and gives only one resonance

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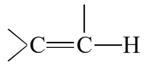
absorption at higher frequency than most common organic protons. When TMS is used as a reference the chemical shift values are expressed in tau (τ) where $\tau = 10 - \delta$ and it is also expressed in ppm. Thus, PMR values can be expressed either as δ (reference compound must be mentioned) or τ (TMS is assumed as reference).

Chemical shift value for protons in different environment are tabulated below:

Table 2.1 *Typical chemical shift values for protons*

Type of proton		δ ***ppm***	τ ***ppm***
Alkanes			
	$R{-}CH_3$	0.86	9.14
	$\begin{matrix}R\\R\end{matrix}\!\!>CH_2$	1.3	8.7
	R_3CH	1.45	8.55
Adjacent to sp² carbon			
	$>C{=}CH{-}CH_3$	1.6–2.7	8.4–7.3
	 $>C{=}\overset{\vert}{C}{-}H$	4.5–6.5	5.5–3.5
Terminal alkynes $R{-}C{\equiv}CH$		2.5	7.5
Aromatic		6.5–8.5	3.5–1.5
Adjacent to electronegative atom			
	$R{-}CH_2{-}Cl$	3.7	6.3
	$R{-}CH_2{-}Br$	3.5	6.5
	$R{-}CH_2{-}I$	3.0	7.0
	$R{-}OH$	5.0	5.0
Aldehydes	CH_3CHO		
	Alkyl proton	2.17	7.83
	Aldehydic proton	9.5	0.5
Acids	RCOOH	9.7	0.3
Esters	CH_3COOR	2.0	8.0
Amines	$R{-}NH_2$	1.8	8.2

Chemical shift values are also dependent on the nature of solvent, temperature and concentration.

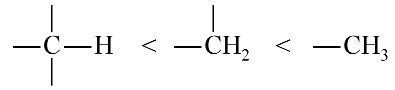
The area under the absorption peak curve in PMR spectrum is proportional to the number of protons of a given type which may be calculated either graphically or with the help of electronic integrator.

Some generalizations may be made regarding the chemical shift values of protons:

(*i*) All hydrogens with identical environment have the same chemical shift even though they may be on different carbon atoms in the molecule.

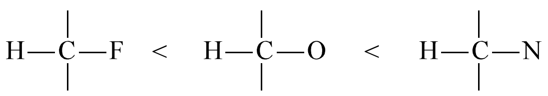
(*ii*) The hydrogens of methylene group may not be equivalent in (*a*) rigid cyclic system (remember *axial* and *equatorial* hydrogen in cyclo-hexane), and (*b*) hindered rotation.

(*iii*) In identical circumstances greater the number of hydrogen on one carbon, greater is the shielding and thus greater τ value.



$$-\overset{|}{\underset{|}{C}}-H \;<\; -\overset{|}{C}H_2 \;<\; -CH_3$$

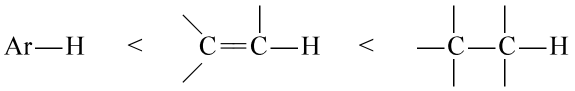
(*iv*) When an electronegative atom is attached to carbon of C—H bond, it causes deshielding, greater the electronegativity, greater is the deshielding and lower the τ values.



$$H-\overset{|}{\underset{|}{C}}-F \;<\; H-\overset{|}{\underset{|}{C}}-O \;<\; H-\overset{|}{\underset{|}{C}}-N$$

(*v*) The greater the ring size in alicyclic compounds lower is shielding and lower τ values.

(*vi*) Unsaturation generally lowers τ values



$$Ar-H \;<\; >C=\overset{|}{C}-H \;<\; -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H$$

(*vii*) Protons on heteroatoms (*e.g.* H—O, H—N etc.) show variable chemical shifts.

2.2.2 Spin Spin Interaction

Consider the PMR spectrum of ethyl bromide. It exhibits two peaks, one corresponding to three protons of methyl group and the other corresponding to two protons of methylene group (Fig. 2.2). Now observe the high resolution PMR spectrum of pure ethyl bromide (Fig. 2.3). It can be seen that PMR signal for —CH_3 group has split into a triplet while that for —CH_2— group has split into a quartet. In contrast to the chemical shift the line spacing for these splittings are independent of the applied magnetic field or radio frequency.

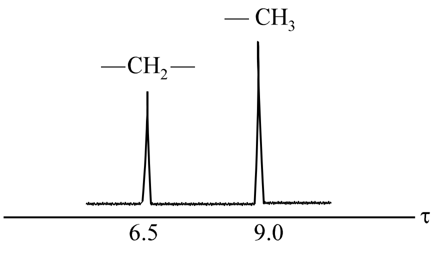


Fig. 2.3 *PMR spectrum of ethyl bromide.*

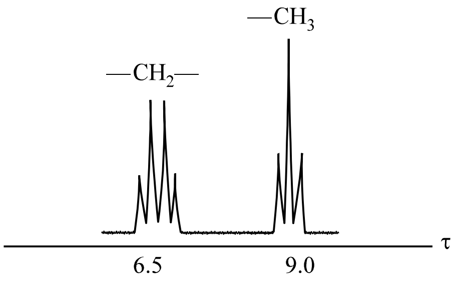


Fig. 2.4 *High resolution PMR spectrum of pure ethyl bromide.*

In the case of ethyl bromide it can be seen that the multiplicity of lines is (n + 1) where 'n' is number of protons on adjacent carbon atom. Thus, it is clear that protons on adjacent atoms are able to split the chemical shift absorption peaks by modifying the effective magnetic field at a proton or group of protons, so that it is not the same as the applied field. One adjacent proton may have two orientations ↑ and ↓ leading to a symmetrical doublet, two adjacent protons may have three orientations shown below:

↑↑
↑↓ ↓↑
↓↓

Leading to a 1 : 2 : 1 triplet, three adjacent protons may lead to a 1 : 3 : 3 : 1 quartet due to four orientations and so on.

↑↑↑
↑↑↓ ↑↓↑ ↓↑↑
↓↓↑ ↓↑↓ ↑↓↓
↓↓↓

The distance between multiple peaks in spin-spin splitting is a measure of the extent of effectiveness of spin-spin coupling and is known as *coupling constant* 'J'. The magnitude of 'J' is expressed in cycles per second and is independent of applied field strength but depends on number and kind of intervening chemical bonds and on the spatial relationship between the groups. It is important to note that spin-spin splitting is not observed in case of identical protons. Thus there is no spin-spin splitting of proton signals in $Cl.CH_2.CH_2.Cl$ or $Cl.CH{=}CH.Cl$ or cyclobutane etc.

2.2.3 Shielding Mechanism

The chemical shift values of different nuclei in a molecule arise due to differences in the local magnetic field felt by nuclei in different parts of the molecule. Due to the effects like inductive effect, resonance effect, anisotropic effect and ring currents effects the electron density surrounding the differential nuclei in a molecule may result in shielding or deshielding of these nuclei.

When a bond and its electron density are subjected to an external magnetic field, there is an induced magnetic field which is anisotropic (anisotropy is the property of being directionally dependent). Chemical shift anisotropy is generally caused by the pi electrons which is predictable in most simple organic compounds and loads to shielding or deshielding.

Electronegativities of carbon atoms in some common hydrocarbons is in the order $C_2H_2 > C_2H_4 > C_2H_6$. Therefore the expected chemical shifts for the protons in these molecules should also be in the same order but experimentally found order is $C_6H_6(\delta \sim 8$ p.p.m.$) > C_2H_4(\delta \sim 5$ p.p.m.$) > C_2H_2$ $(\delta \sim 2.5$ p.p.m.$) >$ C_2H_6 $(\delta \sim 0.9$ p.p.m.).

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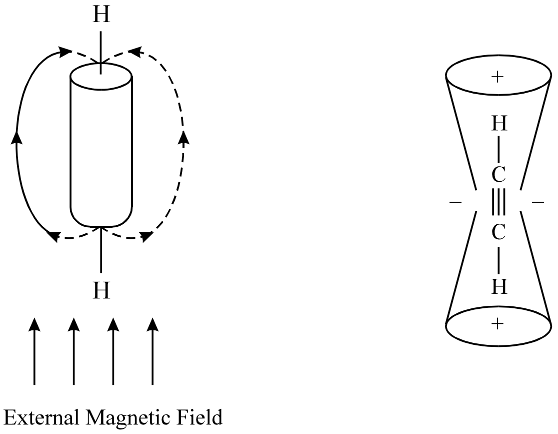

Fig. 2.4 *Showing shielded and deshielded areas in acetylene.*

To explain this anomalous behaviour it has been assumed that some kind of shielding- deshielding effect is operative in acetylene and aromatic rings which is much smaller in ethylene. Suppose acetylene is orientated in such a manner that its molecular axis is parallel to applied field, then the induced circulation of electrons in π orbitals produces an induced magnetic field in a direction opposite to that of applied field, resulting in *shielding* of protons in line with triple bond from applied magnetic field. This results in decreased chemical shift and higher τ values. At the same time protons which happen to lie above or below the shielded area are *deshielded*. The net result of this induced magnetic field is that there are areas within which shielding is experienced (shown with +ve sign in figure below) and outside these areas deshielding is experienced (shown by –ve sign) by the protons.

In case of double bond of ethylene or carbonyl compounds shielding and deshielding is much weaker and induced currents are produced only when molecular axis is perpendicular to applied magnetic field.

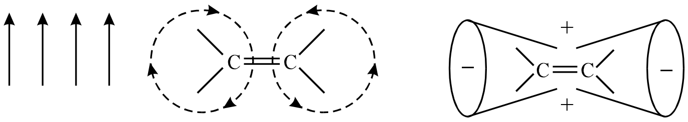

Fig. 2.5 *Shielding and deshielding in ethylene.*

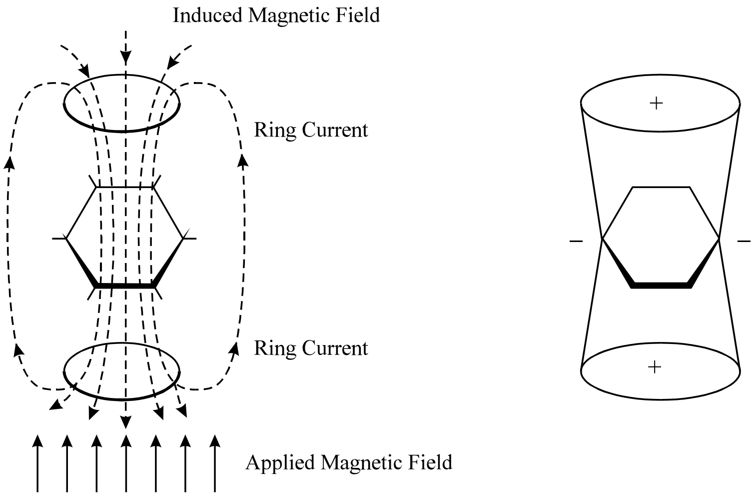

Fig. 2.6 *Shielding and deshielding in aromatic systems.*

In case of aromatic systems, normally the delocalised π electrons can circulate in either direction but when orientated perpendicular to applied magnetic field circulation of π electrons occur only in one direction producing ring currents which induces a magnetic field perpendicular to molecular plane. This induces magnetic field is aligned to external magnetic field outside the ring causing deshielding but opposed to it above and below the area of the ring causing shielding (Figure 2.6) The protons attached to benzene are in the plane of ring and in the deshielded area and hence their chemical shifts occur at much lower field (τ for aromatic proton of benzene is 2.73).

2.2.4 Mechanism of Measurement

The experimental method for the determination of nuclear magnetic resonance was developed independently by F M Purcell and Bloch in 1946. A simplified diagram of a nuclear magnetic resonance spectrometer is shown in Fig. 25.13. A magnetic field B varying from 0 to 10.000 gauss is applied and this field produces an equidistant splitting of the nuclear energy levels. Transitions between the energy levels are stimulated by radiation from the radio frequency transmitter which sends out electromagnetic radiation from the transmitter coil. The transitions are detected in the indicator. Usually, a cathode ray oscillograph is used as indicator.

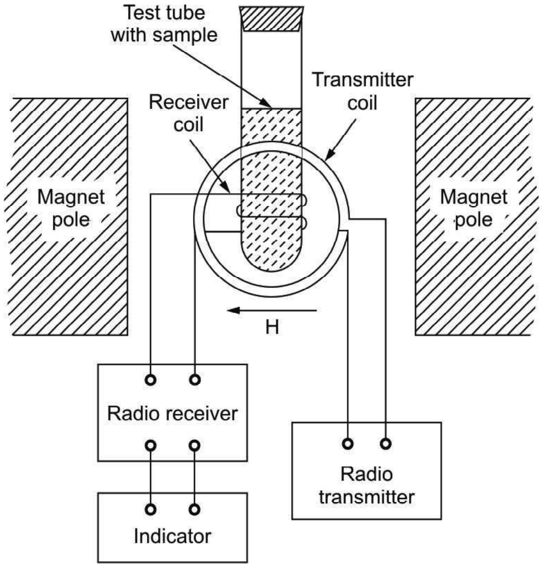

Fig. 2.7 *Schematic Representation of an NMR Spectrometer*

The resonance condition is achieved by superimposing a small variable magnetic field. The low resolution NMR spectrum of ethyl alcohol or ethanol is shown in Figure 2.7. This absorption spectrum is historically significant because it was the first compound which was studied by Packard in 1951. He was able to detect three different values for the precessional frequencies of the protons. He thus, demonstrated that these corresponded to three different chemical environments for the protons an ethanol (CH_3, CH_2 and OH).

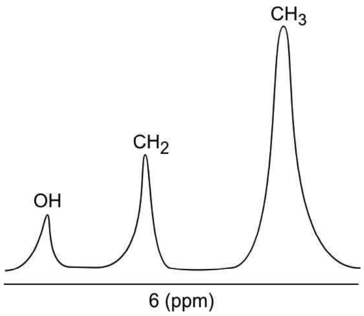

Fig. 2.8 NMR Spectrum of ethanol

The NMR spectra helps us to know the types of hydrogen atoms in the molecule, which is given by the number of peaks in the NMR spectra. Secondly the number of hydrogen atoms of each type can be determined by finding the ratio of the relative area under each peak. The area under the peaks in ethanol molecule is in the ratio of 1: 2: 3.

Spin-spin Splitting: When the NMR spectrum of ethanol is recorded at high resolution, the CH_2 peak is split into four lines and that for CH_3 into three lines. This splitting is not a chemical shift is proved by the fact the observed splitting does not depend on the strength of the applied field. The effect is caused by the interaction of the nuclear spins of one set of equivalent protons with those of another set. This is called spin-spin coupling. Further the splitting of an NMR line due to interaction of the spins is measured by the spin-spin coupling constant *J*.

Let us consider a proton A which has another Proton *X* in its neighbourhood. Now the proton *X* can have either its nuclear magnet aligned with proton A or opposed to it. Thus, the proton *X* can either increase the net magnetic field experienced by A (*X* aligned) or decrease it (*X* opposed). The two spin orientations of *X* create two different magnetic fields around proton A. Therefore, the proton A comes to resonance not once but twice thus producing doublet as shown in Figure 2.9.

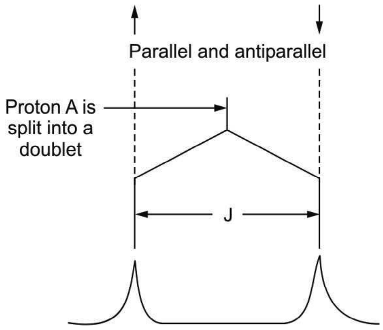

Fig. 2.9 Spin compling be hower neighbour proton x

Similarly a proton A sees two neighbouring protons *X* and *X*′ the A can see three different possible combinations of spins (*i*) the nuclear spins *X* and *X*¢ both be parallel to A (↑↑); (*ii*) both can be anti-parallel to A (↓↓) (*iii*) one can be parallel and another anti-parallel and this can arise in two ways–*X* parallel with *X*′ anti-parallel (↑↓) or *X* antiparallel and *X*′ parallel (↓↑). Three distinct situations are thus created. The probability of the first two states arising is equal while the third state since it can occur in two ways has twice the probability to occur than the first two. This is shown in Figure 2.10.

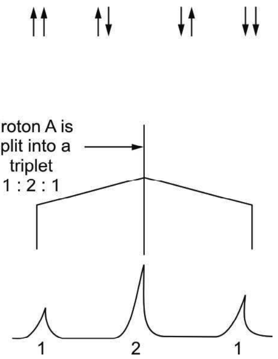

Fig. 2.10 *Spin Coupling between Proton and Two Neighbour Protons X and X′*

In general if there are n number of equivalent protons interacting with the neighbouring proton the absorption will be split into $n + 1$ lines and their relative intensities will be proportional to the coefficients of the binomial expansion of $(1 + x)^m$ where $m = n - 1$. Alternatively these coefficients can also be calculated using Pascal's triangle.

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1

Pascal's triangle

A high resolution NMR spectrum of ethanol is more complicated than the ordinary low resolution spectrum. With higher resolution the lines in the spectrum are split into multiplets. The absorption line due to methyl (CH_3) protonts is split into three components (1 : 2 : 1) because the neighbouring methylene group (CH_2) contains two protons each with spin $\frac{1}{2}$. We can think of the first methylene proton splitting the methyl proton resonance into a doublet as shown in Figure 2.12.

Then the second methylene proton splits the doublet into a triplet with the center line twice as intense as the other two. The two methylene protons produce the same spin-spin splitting because there is rapid rotation of around the C–C bond.

The absorption line due to methylene protons is split into four components by three protons of the neighbouring CH_3 group. The relative intensities will be 1 : 3 : 3 : 1.

In the high resolution spectrum recorded in presence of trace amounts of acid the proton in the hydroxyl group does not cause splitting because it undergoes chemical change so rapidly with protons in other molecules that it does not produce splitting effect.

Fig. 2.11 *High resolution NMR spectra ethanol*

2.2.5 Chemical Exchange

Consider the high resolution PMR spectrum of ethanol. The resonance absorption peak of hydroxylic proton does not exhibit multiplicity theoretically it should be split into a triplet due to spin-spin coupling with adjacent methylene protons.

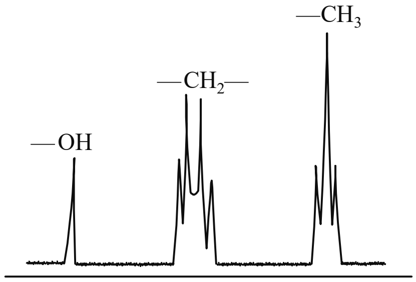

Fig. 2.12 *High resolution PMR spectrum of ethanol.*

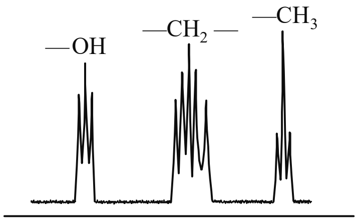

Fig. 2.13 *High resolution PMR spectrum of highly purified ethanol.*

On the other hand if the high resolution PMR spectrum of highly purified ethanol is studied the expected multiplicity of hydroxyl proton absorption peak is observed along with increase in multiplicity of the absorption peak of methylene group.

The phenomenon is explained by suggesting that in the presence of impurities there is a rapid ***chemical exchange*** of hydroxylic protons between different ethanol molecules. The term *chemical exchange* is used to explain the fact that during a certain period of time, a single hydroxyl proton may be attached to a number of different ethanol molecules. If this happens there is no coupling between the hydroxylic proton and methylene protons or in other words rapid chemical exchange causes spin decoupling.

On the other hand the rate of chemical exchange of proton is relatively low in highly purified ethanol and expected multiplicity of absorption signals is observed. The rate of chemical exchange increases with increase in temperature.

2.2.6 Effect of Deuteration

It has been found that if a few drops of deuterium oxide are added in the sample, the D_2O exchanges with the labile protons such as –OH, –NH, –SH and also with the reactive methylene protons flanked by the carbonyl groups. The mechanism involves the same course as is seen in proton exchange reactions.

When a little D_2O is added to ROH, then due to rapid exchange, ROH becomes ROD.

$$ROH + D_2O \rightleftharpoons R-OD + H-OD$$

Thus, the signal for –OH proton normally observed in ROH will be missing in the PMR spectrum and instead, a signal for proton in H-OD appear. Similarly, if a little D_2O is added to RCOOH, then due to rapid exchange, it becomes RCOOD.

$$RCOOH + D_2O \rightleftharpoons RCOOD + H\text{–}OD$$

Clearly, the signal for the proton in RCOOH (in the PMR spectrum) which appears (in the absence of D_2O) at a negative tau value will be missing or diminished and a signal for proton corresponding to H–OD appears instead. This technique which is employed for detecting the presence of OH, NH groups etc. is called deuteration. For the deuterium exchange technique, two spectra are run.

(i) One with the sample dissolved in a solvent other than D_2O.

(ii) Second spectrum with the sample dissolved in the same solvent and containing a few drops of D_2O.

No comparing the two spectra, if the peak areas are seen to diminish then the sample may contain –OH, –NH, –SH group in which deuterium exchange is possible.

2.2.7 Complex Spin-Spin Interaction between Two, Three, Four, and Five Nuclei (First Order Spectra)

Nuclear Magnetic Resonance (NMR) interpretation plays a pivotal role in molecular identifications. As interpreting NMR spectra, the structure of an unknown compound, as well as known structures, can be determined by several factors such as chemical shift, spin multiplicity, coupling constants, and integration. This module focuses on the most important ^{1}H and ^{13}C NMR spectra to find out structure even though there are various kinds of NMR spectra such as ^{14}N, ^{19}F, and ^{31}P. NMR spectrum shows that x- axis is chemical shift in ppm. It also contains integral areas, splitting pattern, and coupling constant.

Spin-Spin splitting means that an absorbing peak is split by more than one “neighbour” proton. Splitting signals are separated to J Hz, where is called the coupling constant. The spitting is a very essential part to obtain exact information about the number of the neighboring protons. The maximum of distance for splitting is three bonds. Chemical equivalent protons do not result in spin-spin splitting. When a proton splits, the proton’s chemical shift is determined in the center of the splitting lines.

Spin multiplicity plays a role in determining the number of neighboring protons. Here is a multiplicity rules: In case of $\mathbf{A_m B_n}$ system, the multiplicity rule is that Nuclei of B element produce a splitting the A signal into nB+1 lines. The general formula which applies to all nuclei is 2nI+1, where I is the spin quantum number of the coupled element. The relative intensities of the each lines are given by the coefficients of the Pascal’s triangle.

First-Order Splitting Pattern

The chemical shift difference in hertz between coupled protons in hertz is much larger than the J coupling constant:

$$\frac{\Delta\nu}{J} \geq 8$$

Where, Δv is the difference of chemical shift. In other word, the proton is only coupled to other protons that are far away in chemical shift. The spectrum is called first-order spectrum. The splitting pattern depends on the magnetic field. The second-order splitting at the lower field can be resolved into first-order splitting pattern at the high field. The first-order splitting pattern is allowed to multiplicity rule (N+1) and Pascal's triangle to determine splitting pattern and intensity distribution.

High-Order Splitting Pattern

High-order splitting pattern takes place when chemical shift difference in hertz is much less or the same that order of magnitude as the j coupling.

$$\frac{\Delta v}{J} \leq 10$$

The second order pattern is observed as leaning of a classical pattern: the inner peaks are taller and the outer peaks are shorter in case of AB system. This is called the roof effect.

Vicinal Proton-Proton Coupling (3JHH)

Vicinal coupling occurs though three bonds. The Vicinal coupling is the most useful information of dihedral angle, leading to stereochemistry and conformation of molecules. Vicinal coupling constant always has the positive value and is affected by the dihedral angle (?; HCCH), the valence angle (?; HCC), the bond length of carbon-carbon, and the effects of electronegative atoms. Vicinal coupling constant depending on the dihedral angle is given by the Karplus equation.

Spin-Spin Splitting

Comparing the ^{1}H NMR, there is a big difference thing in the ^{13}C NMR. The ^{13}C-^{13}C spin-spin splitting rarely exit between adjacent carbons because 13C is naturally lower abundant (1.1%) **^{13}C-^{1}H Spin Coupling:** ^{13}C-^{1}H Spin coupling provides useful information about the number of protons attached a carbon atom. In case of one bond coupling ($^1J_{CH}$), -CH, -CH$_2$, and CH$_3$ have respectively doublet, triplet, and quartets for the ^{13}C resonances in the spectrum. However, ^{13}C-^{1}H Spin coupling has a disadvantage for ^{13}C spectrum interpretation. ^{13}C-^{1}H Spin coupling is hard to analyze and reveal structure due to a forest of overlapping peaks that result from 100% abundance of ^{1}H.

Decoupling: Decoupling is the process of removing ^{13}C-^{1}H coupling interaction to simplify a spectrum and identify which pair of nuclei is involved in the J coupling. The decoupling ^{13}C spectra shows only one peak (singlet) for each unique carbon in the molecule. Decoupling is performed by irradiating at the frequency of one proton with continuous low-power RF.

2.2.8 Virtual Coupling

The term virtual coupling refers to an NMR phenomenon in which first order multiplets contain false coupling in formation. In extreme cases, proton that are not actually coupled will show splitting. The magnitude of coupling constants obtained by first-order analysis is incorrect. All virtual coupling effects arises when protons, well isolated from other protons in chemical shift are coupled to a group of other protons which are strongly coupled to each other i.e., these protons are both close in chemical shift and coupled to each other with $J > \Delta\nu$.

The phenomenon of virtual coupling can be explained as, when two or more protons are strongly coupled, then any protons coupled to them will give multiplets with false coupling information and an unexpectedly complex multiplet structure. Furthermore, the strongly coupled protons themselves will contain misleading multiplet structure.

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The simplest systems to show virtual coupling effects are ABX patterns, where the X-multiplet will give incorrect values for J_{AX} and J_{BX} when it is analyzed as a doublet of doublets of v_{AB} is similar to or smaller than J_{AB}. What is particularly insidious about this effect is that analysis of the AB part by a first-order method (treatment of each part as a distorted doublet of doublets). If H_A and H_B are strongly coupled then H_X will not be a simple doublet, even if $J_{A-X} = 0$

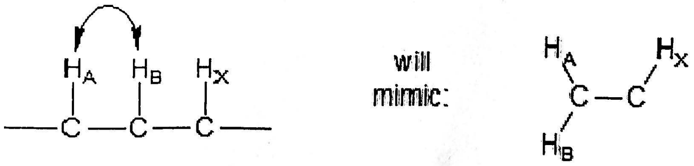


Fig. 2.14 *If $v_{A-B} = 0$ then H_X will be a triplet, even if $J_{A-X} = 0$*
It will appear that H_X is coupled equally to H_A and H_B
Strongly–Coupled $J_{A-B} > v_{A-B}$

A typical example of virtual coupling is provided by the epoxide below. H_A and H_B are more or less first order when the spectrum is taken in $CDCl_3$ because H_A and H_B have a significant chemical shift (although typical second order effects are starting to appear). However, in acetrone-d_6, H_A and H_B are essentially superimposed, and H_C appears as a triplet, as if H_A and H_B were equally coupled to H_C, leading to a very different structure assignment. The small coupling visible for H_B and H_C in $CDCl_3$ is probably not entirely real– it is the beginning of the "virtual coupling" effect which eventually leads to a triplet for H_C.

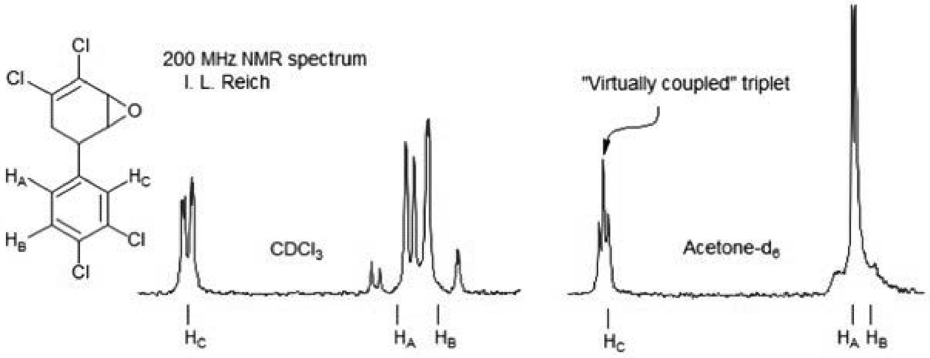


Fig. 2.15 *Virtual Coupling*

Check Your Progress

1. Define Nuclear Magnetic Resonance Spectroscopy.
2. What do you understand by shielding constant?
3. Define chemical shift.
4. Define chemical exchange.
5. What do you understand by decoupling?
6. Define virtual coupling.

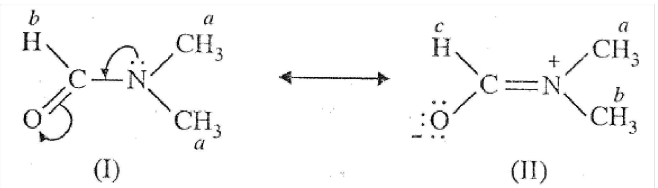
2.3 STERIOCHEMISTRY

Stereochemistry is a branch of chemistry that deals with the study of the relative spatial arrangement of atoms that form the structure of molecules and their manipulation. The study of stereochemistry focuses on stereoisomers, which by definition have the same molecular formula and sequence of bonded atoms (constitution), but differ in the three-dimensional orientations of their atoms in space. For this reason, it is also known as 3D chemistry—the prefix "stereo-" means "three-dimensionality".

2.3.1 Hindered Rotation

The isomers which arise due to rotation bond are called conformational isomers or conformers. The presence of conformation in a solution cannot be detected by the NMR spectroscopy. But at temperatures much below room temperature, the rate of inter-conversion of rotational isomers is usually diminished and NMR absorption resulting from each may be observed.

The presence of double bond (a sigma and a π bond) in a compound restricts rotation and results in the formation of cis and trans isomers. Cis and trans isomers are the distinct compounds with different properties and different NMR spectra. In a compound, where a double bond may originate in its equivalent resonating structure, the rate of rotation about the given bond becomes intermediate between free rotation about unhindered single bond in one structure and hindered rotation about the double bond in the other structure. Consider the spectrum of N, N-dimethyl formamide at room temperature.



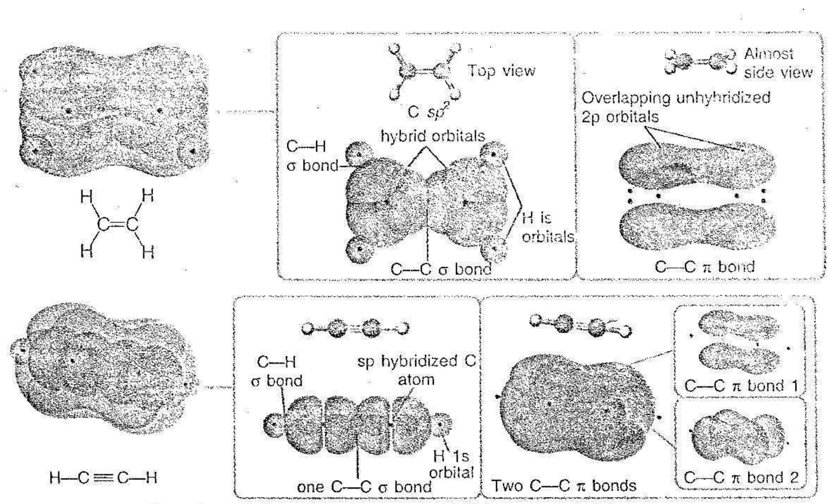


Fig 2.16 Restricted Rotation in case of Ethane and Ethyne

Thus, the NMR spectrum for such a compound usually consists of a superimposition of spectra resulting from two or more rotational isomers present at equilibrium. Some amides, oximes, nitroso amines etc. show restricted rotation. The spectrum for N, N-dimethyl formamide shows two non-equivalent methyl groups which absorb at different field strengths. The two signals observed (doublets) for methyl groups are as a result of coupling with the formyl proton. For each doublet, we observe a different value of coupling constant. Proton absorption for one methyl doublet is at 7.21τ and that for the other methyl doublet is at 7.06τ. The value of coupling constant for methyl signal appearing at 7.21τ is found to be higher. Clearly, its position is predicted as trans with respect to the formyl proton. At elevated temperatures, the rapid rotation between C—N makes both the methyls magnetically equivalent and only one signal is observed for both the methyl groups.

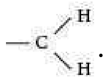
2.3.2 Karplus Curve- Variation of Coupling Constant with Dihedral Angle

The distance between the centers of two adjacent peaks in a multiplet is called coupling constant or spin-spin coupling constant, or spin-spin coupling constant, denoted by J. The value of coupling constant in independent of the external field. It is measured in Hertz (Hz) or in CPS (Cycles Per Second).

If we work the spectrum of a particular compound at different radio-frequencies, the separation of signals due to different chemical shifts change but the separation of two adjacent peaks in a multiplet remains always constant. It other words, we say that the value of J (separation of adjacent peaks in the multiplet) remains the same whatever the applied field is. From the value of coupling constant, one can distinguish between the two singlets and one doublet and also a quartet from two doublets. It can be done by simply recording the spectrum at two different radio-frequencies. If the separation (in Hz) between the lines (value of J) does not change, then the signal is a double. On the other hand, if the separation between the lines increases with increasing frequency, then the signal in fact, will be two singlets. The value of 'J' generally lies between 0 and 20 Hz.

The value of J, coupling constant depends partly on the number of covalent bonds through which the proton may interact and also upon the structural relationships between the coupled protons. The important factors which affect the magnitude of coupling constants in various types of coupling are discussed as follows:

1. **Geminal Coupling:** Protons attached to the same carbon atoms and having different chemical environments are called geminal protons. The value of J depends upon the bond angle,



. J can have any sign.

Geminal protons are separated by two bonds. If these protons are in different environments, then the coupling is very strong. When the bond angles is 105^0, J is approximately – 25 cps. J becomes merely -12cps when the bond angle increases to 109^0. With the bond angle widened to 125^0, the value of J increases to zero. If the bond angle is wider than 125^0, we observe small positive values for the coupling constants. A plot showing the relationship between the values of J versus the bond angle is shown as under:

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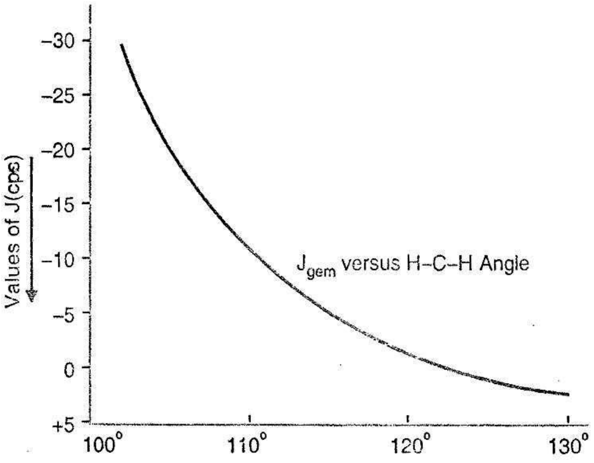


Fig 2.17 *Geminal Coupling Constants.*

A few characteristics of germinal coupling constant (J_{gem}) may be noted:

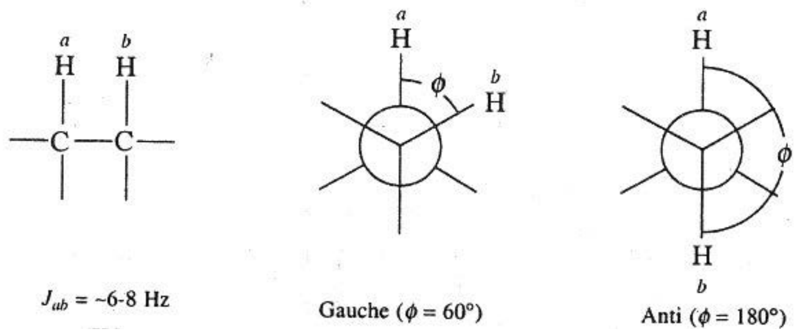
(i) The value of coupling constant increases with the increase in bond angle (increases in s-character) J_{gem} is -12.4 cps for methane whereas, it is +2.5 cps for ethylene.

(ii) The increase in electro negativity of the atom or group, which withdraws sigma electrons, increases the value of coupling constant. For example, the value of coupling constant for methyl chloride is -10.8 cps, whereas it is -9.4 cps for methyl fluoride.

(iii) The value of J decreases if an electronegative substituent withdraws from the π bonds. For example, J_{gem} is +2.3 cps for ethane whereas it is -3.3 cps for vinyl fluoride. The values of germinal coupling constants for some compounds are as follows:

Compound	J_{gem}
Methane	-12.4 cps
Methyl Chloride	-10.8 cps
Methyl Fluoride	-9.4 cps
Ethene	+2.5 cps
Formaldehyde	+41.0 cps

2. Vicinal Coupling: Protons attached to the adjacent atoms are called vicinal protons (I). These are separated by three bonds. Vicinal coupling constants J_{vic} which depend on the dihedral angle (angle of rotation) ϕ are largest when the angle ϕ is 0 or 180^0, and has small negative value near 90^0. For axial protons in cylohexanes,



I II III

Fig 2.18 Vicinal Coupling

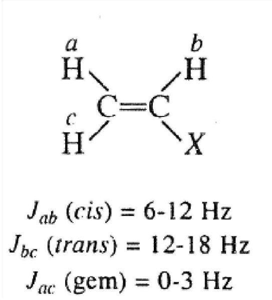
Where dihedral angle is about 180^0 (III), the J_{vic} is approximately 8 Hz, whereas, for axial-equatorial and equatorial protons, where dihedral is about 60^0 (II), the J_{vic} is about 2 Hz. The relationship between J_{vic} and dihedral angle ϕ is given approximately by theoretically derived Karplus equations as:

$J_{vic} = 10 \cos^2 \phi$, for values of ϕ between 0 and 90^0

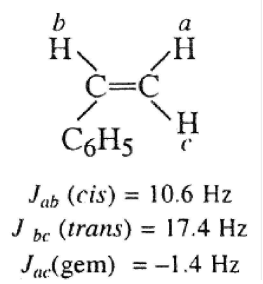
$J_{vic} = 15 \cos^2$, for values of between 90 and 180^0

Karplus relationships are very useful for determining the stereochemistry of organic compounds.

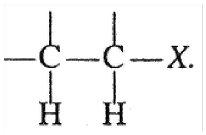
For isomeric olefins, J_{trans} is always greater than J_{cis}, and it is usually observed that $J_{cis} = -\frac{2}{3} J_{trans}$. Thus, it is possible to determine the configuration of geometrical isomers of a di-substituted olefin. For mono-substituted olefins (IV), $J_{trans} > J_{cis} > J_{gem}$. As an example, experimental data for styrene (V) are given as follows:



(IV)



(V)

The J_{vic} decreases with increasing electro negativity of X in a freely rotating system 

$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{H}{\overset{|}{\underset{|}{C}}}-X.$$

A plot for the values of J_r versus dihedral angle for vicinal protons is shown as under.

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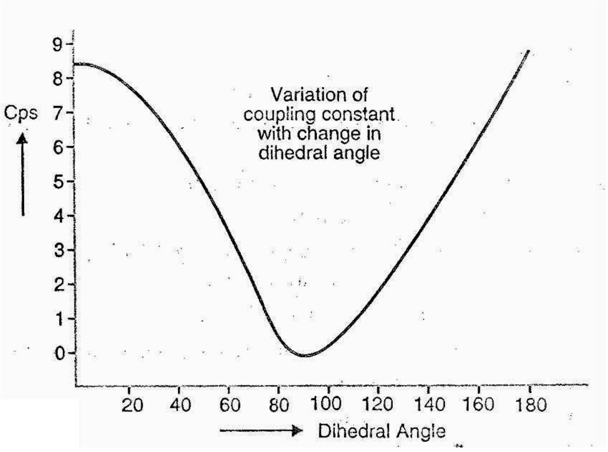
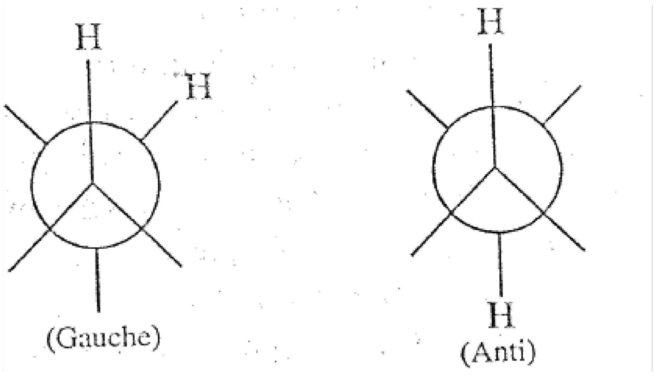


Fig.2.19 Variation of coupling constant with dihedral angle

When the dihedral angle is 0^0 or 180^0, we observe largest values for the coupling constants. The value of 'J' is slightly negative when the dihedral angle is 90^0.

Consider the gauche and the anti-conformations of a compound.



In a signal (multiplet) for gauche proton, the value of J varies from 2 to 4 cps and that for anti-protons, the coupling constant varies from 5 to 12 cps.

In the case of cyclo-pentanes, where the dihedral angle in cis protons is zero, the value of J is expected to be 8 cps whereas, it is nearly zero when the dihedral angle in trans is 90^0. It has been observed that in cyclo-hexanes, the absorption due to axial and equatorial protons are different. For axial-axial interactions, when the dihedral angle is nearly 180^0, the coupling constant is approximately 8 cps whereas for axial-axial and equatorial - equatorial interactions when the dihedral angle is 60^0, the coupling constant is nearly 2 cps. Thus, from the value of the coupling constant, it is possible to determine the configuration of a particular system.

2.3.3 Simplification of Complex Spectra- Nuclear Magnetic Double Resonance

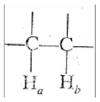
The complete analysis of a NMR spectrum becomes difficult when signals overlap and thus, useful information is buried due to complexity of the spectrum. For example, if several closely related methylene groups are present in a molecule, their signals may overlap and may not be clearly recognized. Sometimes, an intense, broad and unresolved signal due to several methylene groups is observed at about δ 1-2 which is called as the methylene envelope. When there is not much difference between the chemical shifts and coupling constants, more complex (second order) spectra are obtained.

High Field Strengths

We have noted that the chemical shift in Hz is directly proportional to the applied magnetic field, whereas the value of coupling constant in Hz remains constant in different applied magnetic fields. On increasing the field strength the chemical shift separation Δv (Hz) increases, but the value of J (Hz) remains constant. Thus, the multiplets which are overlapped at lower field are expected to separate out at high field strengths. In this way, the NMR spectrometers operating at high magnetic fields (i.e., at high radio frequencies) give better resolution and relatively easily interpretable spectra.

Nuclear Magnetic Double Resonance (Spin Decoupling)

This technique involves the irradiation of a proton or a group of equivalent protons with sufficiently intense radio-frequency energy to eliminate completely the observed coupling to the neighboring protons. A signal for a particular proton or a set of equivalent protons in split up into a multiplet under the influence of the neighboring proton/protons under different environments. Consider the case of a compound



in which H_a ad H_b are in different environments. Clearly, in its NMR spectrum, two doublets corresponding to each proton should be observed at different field strengths.

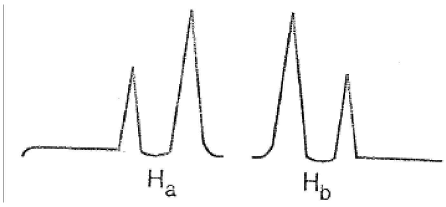


Fig 2.20 Two doublets

It has been observed that if we irradiate H_a with correct frequency energy (intense) so that the rate of its transitions between the two energy states (spin states) becomes much larger, then the life time of this nucleus in any one spin state will be too short to resolve coupling with H_b. In such a case, H_b proton will be one time average view of H_a and hence H_a will come to resonance only once and H_b will appear as a singlet (not doublet).

In the same way, if we irradiate H_b with sufficiently intense radio frequency energy, then due to its rapid transition between the two spin states, H_a will have one time average view of H_b and hence, H_b will come to resonance only once and H_a will also appear as a singlet.

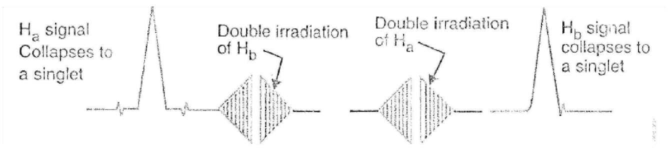
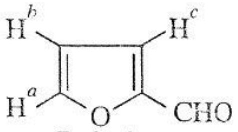


***Fig 2.21** Spin Decoupling*

It may be noted that the time (*dt*) needed to resolve the two lines of a doublet is related to the separation between the lines, i.e., coupling constant J. Thus, the formation of doublet in the above example is possible if each spin state of H^a has a life time greater than *dt*. With double irradiation, the said life time becomes still less and thus, due to the increase in the rate of transition, coupling is not possible and thus, singlets result.

In this technique, we make simultaneous use of two radio frequency sources. In addition to the normal NMR instrument, a second tunable radio frequency source is needed to irradiate H_a at the necessary frequency and the recording of the spectrum is done in the same way. It is called double resonance or double irradiation. Since the multiplet collapses to a singlet in the process, it is also spin decoupling.

Double resonance technique is a powerful tool for simplifying a spectrum and is of great value to organic chemists working with complex molecules. It helps in the identification of coupled protons in spectra that are too complex for detailed analysis. We know that the NMR spectrum of Furfural (furan 2-aldehyde) is quite complex.



Furfural

Proton H_a couples with H_b which splits H_a into a doublet but H_a also couples with H_c so that each line of H_a is further split into two giving four lines in all for H_a proton. Similarly, four lines result for each of H_b and H_c. Thus, a spectrum consisting of 12 lines (three multiplets) results for three protons. Each multiplet is found to show two different value of J (see Fig 2.6)

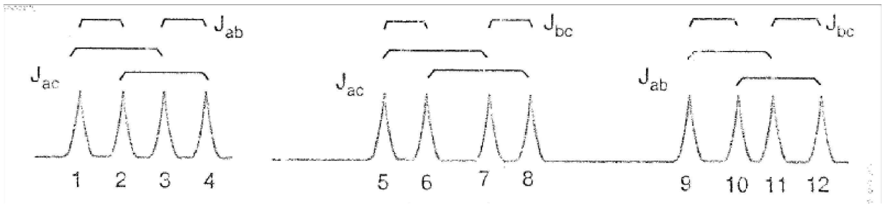


***Fig. 2.22** Spectrum Consisting Tree Multiplets*

The effect of strong decoupling eliminates the coupling of H_a with H_b and H_c. This results in the collapse of each of the four line multiplet (for H_b and H_c) into the doublet. In the 12 line spectrum, we find that J_{bc} value is very small as compared to J_{ac} and J_{ab}.

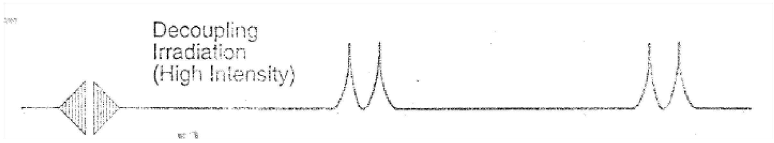


Fig. 2.23 *Double Irradiation*

Now if spin tickling (low intensity irradiation) is carried out by weakly irradiating one line of spectrum due to the proton H_a, we observe that the line 7, 8 of H_c signal and the lines 11, 12 of H_b are further split* (see Fig. 2.24)

Here the lines 5 and 6 are associated with one particular spin orientation of H_a while the lines 7 and 8 are associated with the opposite spin orientation of H_a. Also we say that the lines 5 and 7 are associated with one spin orientation of H_b while the line 6 and 8 are associated with opposite spin orientation of H_a while the lines 11 and 12 from its opposite spin orientation. Also the lines 9 and 11 are the result of one spin orientation of H_c while the lines 10 and 12 due to its opposite spin orientation.

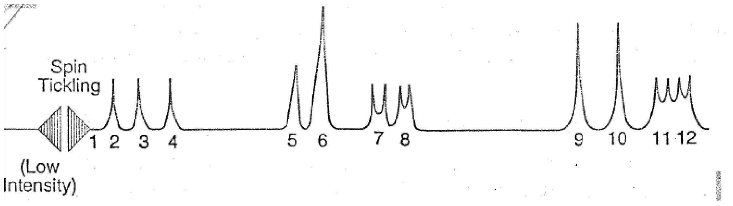
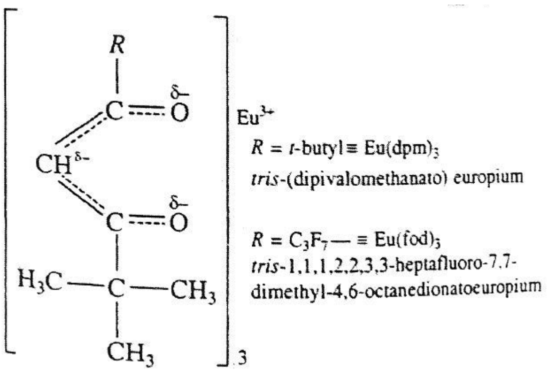


Fig. 2.24 *Spin Tickling*

Since spin tickling on line 1 in the spectrum of H_a has been shown to disturb the lines 7,8 and 11, 12 hence we say that all these lines arise from the same spin orientation of H_a. Thus, it this technique is of great value in determining the absolute sign for the J value.

2.3.4 Contact Shift Reagent

Shift reagents were first introduced by Hinckely in 1969. Shift reagents provide a useful method for spreading out normally overlapped PMR absorption patterns without increasing the strength of the applied magnetic field. The shift reagents are usually enolic β– dicarbonyl complexes of a rare earth (lanthanide) metal and these complexes are mild Lewis acids. Following are the structures of more commonly used shift reagents Eu(dpm)$_3$, and Eu(fod)$_3$:



The use of such shits reagents is illustrated in Fig 2.25 in which the PMR spectrum of l-hexanol is simplified by addition of Eu(dpm)$_3$. Fig 2.25(a) shows the PMR spectrum of l- hexanol in the absence of the shift reagent. In this spectrum, the only interpretable signal is that of the methylene groups (a triplet at δ3.8) adjacent to OH and the terminal methyl (a distorted triplet at δ 0.9). The protons of the remaining methylene groups are buried in the methylene envelope (between δ 1.2-1.8). Upon addition of the shift reagent Eu(dpm)$_3$ the signals of the methylene groups closer to the OH group are shifted downfield, resulting in a separate signal for each of the methylene groups. (Fig 2.25 (b)). Thus, the spectrum is simplified almost to the first order.

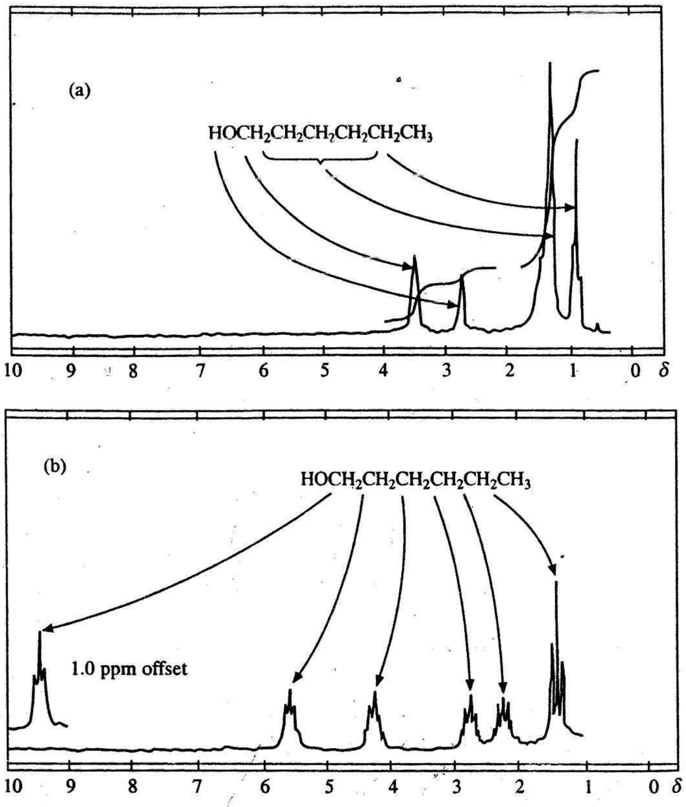
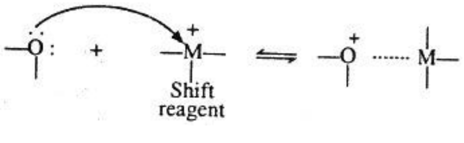


Fig 2.25 *PMR spectrum of l-hexanol at 100 MHz: (a) in the absence of the shift reagent and (b) after addition of the shift reagent Eu(dpm)$_3$*

The signal due to the hydroxylic proton is shifted to low field to be observed. In the shift reagents, the lanthanide ion can increase its coordination through bonding interaction with lone pair of electrons of the groups like OH, NH2, C=0, –O–, COOR, CN etc. present in the organic compound under study.



The metal ion of the shift reagent is a paramagnetic moiety which causes market changes in the observed chemical shifts of the protons present in the substrate. Hence, the name *shift reagent*. Europium complexes generally produce downfield shifts, whereas praseodymium complexes produce upfield shifts.

2.3.5 Solvent Effect

The basic Nuclear Magnetic Resonance (NMR) experiment involves the subjection of a macroscopic assembly of atoms or molecules to the influence of a strong static magnetic field and of a much weaker one derived from a radiofrequency signal. If the magnitude of either the former field or the frequency of the latter is maintained constant and the other varied, conditions may be achieved where the combined interactions of the two fields with magnetic nuclei in the sample lead to discrete changes in the energy of the nuclei. These energy changes can be detected by various means and a spectrum of nuclear resonance conditions may be recorded. At an early stage in the development of the technique it was discovered that the resonance condition for a particular nuclide was influenced by its chemical environment. Subsequently, it was established that a compound containing several nuclei of the same type could produce a spectrum exhibiting separate absorption bands which were chemically shifted, depending on the environments of the nuclei.

A substantial proportion of the use of NMR has been devoted to the determination of chemical shifts and spin-spin coupling constants (J) and their interpretation in terms of the functional group type of the nuclei involved, their dispositions, and their relative quantities.

However, the appearance of NMR spectra is not influenced by intramolecular factors alone, but by intermolecular effects also which can modify chemical shifts significantly and, to a lesser extent coupling constants.

2.3.6 Fourier Transform (FT) NMR Spectroscopy

The common method for obtaining NMR spectra is to irradiate the sample with a constant radio frequency while changing (sweeping) the applied magnetic field (field sweep). Alternatively, NMR spectrometers operate at a constant magnetic field while the radio frequency is varied (frequency sweep). Both the methods give the same NMR spectrum. This commonly used technique is called Continuous Wave (CW) NMR spectroscopy.

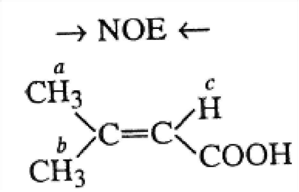
In a recent method for obtaining NMR spectra, the sample is irradiated with an intense pulse of all radio frequencies in the desired range (e.g., covering all ^{1}H frequencies) at once while keeping the magnetic field constant. All the nuclei under study absorb at their individual frequencies and are flipped to their higher energy spin states. This results in an interferogram (called Free Induction Decay, FID or time-domain spectrum) which cannot be interpreted directly. The time-domain spectrum is converted into ordinary frequency-domain spectrum (showing the intensity of absorption against frequency) by performing a mathematical operation known as Fourier transformation. This technique is called pulsed-Fourier Transform Nuclear Magnetic Resonance (FT-NMR) spectroscopy. It gives good spectra even very small quantities of samples (less than a milligram). The principal advantage of FT-NMR spectroscopy is a great increase in sensitivity per unit time of experiment. It is the increase in sensitivity brought about by the introduction of FT-NMR spectroscopy which has allowed the routine observation of ^{13}C NMR spectra.

2.3.7 Nuclear Overhauser Effect (NOE)

This effect is a change in the intensity of absorption of a nucleus on double irradiation of another nucleus. In this case, less intense radiation is used than that in spin tickling. Usually, an increase of a few per cent (theoretically up to 50%) in the intensity of absorption is observed between protons which are in close spatial proximity or not. It is useful in the study of stereochemical relationships within molecules. NOE is observable only over very short distance, generally 2-4 ú. Since NOE involves the interaction of magnetic nuclei through space, the number of intervening bonds between the concerned protons has no significance. NOE does not lead to spin-spin coupling. It must be clearly understood that spin-spin coupling and NOE are different phenomena and that coupling interaction takes place via the bonds separating the nuclei, whereas the NOE is transmitted through space and originates from the relaxation process.

NOE has its origin in the relaxation process. The double irradiation upsets the Boltzmann equilibrium by producing the saturation condition, i.e., we eliminate the population difference across some transitions by double irradiation. Thus, other parts attempt to maintain the Boltzmann equilibrium of the total system by spin relaxation resulting in the change of their intensity of absorption. A nucleus in higher energy spin state may undergo spin relaxation by transferring its energy to an adjacent nucleus with lower energy spin state. The efficiency of this spin relaxation is directly related to the distance between the two nuclei.

Let us take the example of 3-methyl-2 butenoic acid shown below. If the vinyl hydrogen (H) is irradiated, then the intensity of the signal due to the methyl group a, which is *cis* to , becomes greater than that due to the *trans* methyl group b. On irradiation of the *cis* methyl group a, shows an increase of 17% in the intensity of its absorption, whereas the irradiation of relatively distant *trans* methyl groups b does not affect the intensity of the absorption.



2.3.8 Resonance of Other Nuclei- FP

The nucleus of an isotope whose spin quantum number I is greater than zero shows absorption in the NMR spectroscopy. The NMR spectroscopy studied for the absorption of most abundant natural isotope of hydrogen, H^1 is called Proton Magnetic Resonance (PMR) spectroscopy. The numerical value of 1 is related to the mass number and the atomic number of the concerned isotope. Such nuclei are said to be magnetic and assume only a discrete set of orientations. Some nuclei of this type are tabulated below:

Table 2.2 *Various Nuclei showing Discrete Set of Orientations*

Isotope	Spin quantum number I
H^1	$\frac{1}{2}$
H^2	1
B^{10}	3
C^{13}	$\frac{1}{2}$
N^{14}	1
F^{19}	$\frac{1}{2}$
P^{31}	$\frac{1}{2}$
Cl^{35}	$\frac{1}{2}$
Br^{79}	$\frac{3}{2}$
I^{127}	$\frac{5}{2}$

The nuclei of some isotopes viz. C^{12}, O^{16} etc., for which $1 = 0$ are non-magnetic and hence cannot cause such orientations. Thus, such nuclei are not capable of causing absorption in the NMR spectroscopy.

The spin quantum number 1 indicates the number of orientations (2I+1) that a nucleus may assume in a magnetic field. For NMR spectroscopy of other nuclei, no modification compared with H^1 NMR spectrometer is needed except for the appropriate radio-frequency source. In a magnetic field of 14092 gauss, the NMR frequency in mega cycles is different for different nuclei. Out of the halogens (F, Cl, Br, I), protons can couple only with fluorine atom present on the same or on the adjacent carbon atom. It is due to the fact that a very large electric quadruple moment of the halogen atoms (Cl, Br, I) effectively cause spin decoupling of adjacent protons. In F^{19} NMR spectroscopy, chemical shifts are usually measured in ppm relative to $CFCl_3$ taken as the internal standard. Coupling with H^1 and H^{19} is quite strong. Fluorine attached with benzene also couples with the nuclear protons. Consider the spectrum of CH_3CHFCl. Normally, in the H^1 NMR spectrum, $CH_3CH–$ should form a doublet (^3H) and a quartet (^1H). But due to the presence of fluorine atom, each line of doublet is further split into two and the signal is, therefore, a double doublet. Similarly, each line of a quartet (for –CH–) is further split into two due to coupling with fluorine atom and the signal is, therefore, a doublet of quartets.

Also, a signal for one fluorine nucleus appears as a doublet of quartet since it is under the influence of –CH– (attached with the same carbon atom) and $–CH_3$ protons under different environments. This absorption range in fluoro compounds is 200 ppm with large values of coupling constants. Thus, in the normal PMR spectrum (scale 0-10 ppm), the signal for fluorine absorption will be missing. Hence, for the above compound, only two signals are observed.

(i) A three proton double doublet at 7.2 τ. The methyl group appears as a double doublet (4 lines). In this signal $J_{H, H}$ is 6 cps while J_{HF} is 22 cps.

(ii) A one proton double quartet at 2.7. The values of coupling constants in this signal will be

$J_{H'H} = 6$ cps and J_{HF} 50 cps

It is clear that fluorine resonances are well separated and do not appear in the normal range from 0 – 10 ppm. Moreover, the values of coupling constants in the absorption for the fluorine nuclei are very high as compared to those observed in H^1 NMR signals. For example, germinal F-F coupling ranges from 40 – 370 cps while vicinal F–F couplings have values of J between 0 – 40 cps. Trans fluorine show coupling constant (J) between 106-150 cps while in *cis*, the value is between 0 – 58 cps. In the case of nitrogen (N^{14}), the electric quadruple can effectively provide the vectors necessary for excited protons to relax. Clearly, the splitting of the nitrogen nucleus by a proton is not resolved. NMR spectrum of other nuclei provide structural information just as PMR does. Generally, very broad bands are observed compared with proton spectrum. Double resonance techniques can be used to remove broadening of absorption.

2.3.9 Contact and Pseudo Contact Shift

Hyperfine shifts result from two mechanisms, contact shifts and pseudo-contact shifts. Both effects operate simultaneously but one or the other term can be dominant. Contact shifts result from spin delocalization through molecular orbitals of the molecule and from spin polarization. Pseudo-contact shifts result from magnetic anisotropy of the paramagnetic molecule. Pseudo-contact shifts follow a $1/r^3$ and an angular dependence. They are large for many lanthanide complexes due to their strong magnetic anisotrpy. NMR shift reagents such as EuFOD can interact in fast exchange with Lewis-basic organic compouds (such as alcohols) and are therefore able to shift the NMR signals of the diamagnetic compound in dependance of its concentration and spatial distance.

The effect of the contact shift arises from transfer of unpaired spin density to the observed nucleus. This coupling, also known by EPR spectroscopists as hyperfine coupling, is in the order of MHz, as compared with the usual inter-nuclear (J) coupling observed in conventional NMR spectra, which are in the order of a few Hz. This difference reflects the large magnetic moment of an electron (–1.00 μB), which is much greater than any nuclear magnetic moment.

The effect of the pseudo-contact shift arises from magnetic anisotropy of the paramagnetic center (reflected in g-anisotropy in the EPR spectrum). This anisotropy creates a magnetic field which supplements that of the instrument's magnet. The magnetic field exerts its effect with both angular and a $1/r^3$ geometric dependences.

2.3.10 Factors Affecting Nuclear Relaxation

Relaxation processes involve some non-radioactive transitions by which a nucleus in an upper transition state returns to the lower spin state. Three kinds of relaxation processes are:

(i) Spin-Spin Relaxation

(ii) Spin-Lattic Relaxation

(iii) Quadruple Relaxation

(i) **Spin-Spin Relaxation –** It is due to the mutual exchange of spins by two precessing nuclei which are in close proximity to each other. We know each precessing nucleus is associated with a magnetic vector component rotating in a plane perpendicular to the field. If this small rotating magnetic field is the same as is required to induce a transition in the neighboring proton, then mutual exchange of spin takes place. In other words, it involves the transfer of energy from one nucleus to the other. There is no net loss of energy. The spread of energy among the nuclei concerned results in line broadening which makes NMR spectra of solids comparatively more interesting.

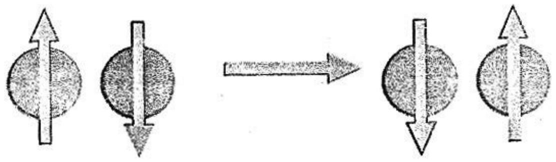


Fig. 2.26 *Spin-Spin Relaxation*

(ii) **Spin-Lattice Relaxation (Longitudinal Relaxation) –** It involves the transfer of energy from the nucleus in its higher energy state to the molecular lattice. The energy is transferred to the components of the lattice as the additional translational, vibrational and rotational energy. The total energy of the system remains the same. An efficient relaxation process involves a short time and results in the broadening of absorption peaks. Smaller the time of the excited state, greater is the line width. This mechanism is not effective in solids. This process keeps the excess of nuclei in the lower energy state which is a necessary condition for nuclear magnetic resonance phenomenon.

Fig. 2.27 *Spin-Lattice Relaxation*

(iii) **Quadruple Relaxation -** It is a prominent relaxation process for nuclei having. The nuclei (such as ^{14}N, ^{17}O, ^{11}B, etc.) due to anisotropic interaction between non-spherical, electrically quadruple nuclei and the electric field gradients at the nucleus caused by electric environments possess an asymmetric positive charge distribution on the nuclei. Hence, these nuclei exhibit electric quadruple moments and relax rapidly as display very broad signals. This process of deactivation of nuclei is called electric quadruple relaxation. In case of chlorine, bromine and iodine, this mechanism is very fast and theses nuclei became practically non-magnetic for the purpose of high resolution nuclear magnetic resonance spectroscopy. But for nitrogen

(N^{14}) and deuterium (H^2), quadruple relaxation is less effective and their resonance lines are observed more easily.

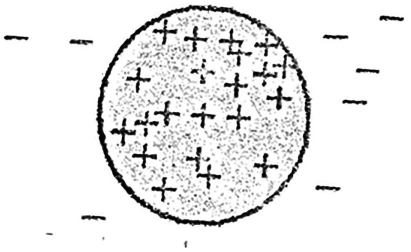


Fig. 2.28 *Quadroupole moment*

The broadcasting of a signal is directly proportional to the life time of the absorbing nuclei in the excited state. More efficient the relaxation process, broader is the resonance band. Thus, for maximum resolution:

(i) The spin-spin relaxation process is efficient in solids and viscous liquids. Clearly, for better resolution, use of solids viscous samples should be avoided otherwise broad signals result.

(ii) Paramagnetic impurities like oxygen and other magnetic ions and materials should be removed from the sample.

2.3.11 Some Applications Including Biochemical Systems

The value of NMR for molecular structural and quantitative analysis is attributable to its element-selective detection and sensitivity of nuclear spin properties to the intra- and inter-molecular environment, as well as to the robust and quantitative nature of NMR measurement. These advantages have made NMR an early choice for metabolite profiling efforts.

NMR methodologies afford some unique advantages such as detailed positional isotopomer analysis for enriched metabolites, de novo structure determination of unknown metabolites (both unenriched and enriched) without the need for standards, and in situ analysis of pathway dynamics from cells to whole organisms

1. **Identification and Determination of Metabolite Structures:** NMR has been employed since a long time to determine the chemical structures and conformations of molecules and is second only to single crystal X-ray diffraction in determination of absolute stereochemistry. Because of the rich structural information and multinuclear capability of NMR, it is practical to determine the structure of a purified small molecule *ab initio*.
2. **Metabolite Quantification:** It is practical to use a single standard for both quantification and internal chemical shift referencing without the need for authentic metabolite standards. Common choices of ^1H or ^{13}C NMR standards include DSS (2,2-Dimethyl-4-Silapentane-4-Sulfonic acid)/DSS-d_6 (to eliminate the CH_2 signals that can interfere with analysis of some metabolites).

2.3.12 An Overview of NMR of Metal Nuclides (^{195}Pt and ^{119}Sn)

^{195}Pt NMR Spectrum: Platinum (Pt) has one medium sensitivity NMR spin-1/2 nucleus, ^{195}Pt that yields narrow signals over a very wide chemical shift range. Because platinum has such a wide chemical shift range and ^{195}Pt gives narrow signals, the slightest effect can be resolved as in the spectrum.^{195}Platinum NMR is mostly used for studying platinum complexes, their structure, conformation and dynamics, and platinum binding in biological systems. Because platinum is widely used as an industrial catalyst and in medicine its chemistry and NMR has been widely studied.

^{119}Sn NMR Spectrum: Tin is unique in that it has no less than three NMR active spin ½ nuclei, ^{115}Sn, ^{117}Sn and ^{119}Sn, that yield narrow signals (figure 2.29) over a very wide chemical shift range. ^{119}Sn is very slightly the more sensitive than ^{117}Sn so ^{119}Sn is therefore usually the preferred nucleus. ^{115}Sn is much less sensitive than either ^{117}Sn or ^{119}Sn. Tin NMR is mostly used for the study of organotin compounds, but is also applicable to inorganic tin compounds.

^{119}Sn is slightly more sensitive than ^{117}Sn and much more sensitive than ^{115}Sn, so it is usually the preferred nucleus of tin. It is a spin ½ nucleus and yields sharp signals (figure 2.30)

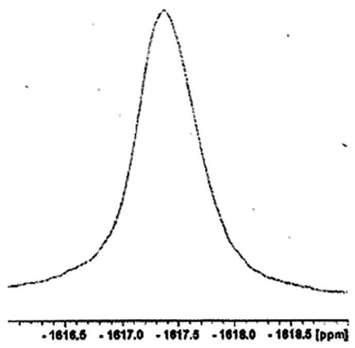


Fig 2.29 ^{195}Pt NMR Signal

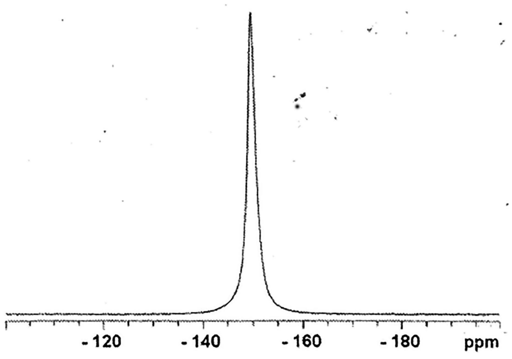


Fig 2.30 ^{119}Sn NMR Signal

2.3.13 General Considerations

Atomic nuclei of many atoms have a spin magnetic moment associated with the spinning of a charged nucleus on its axis. The mechanical spin or angular momentum of nuclei depends on the nuclear spin or *spin quantum number* I, which may have values of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$ etc. .... depending on the nucleus. Magnetic properties are observed in nuclei of odd mass number and nuclei of even mass number but odd atomic number. Thus nuclei like ^{12}C, ^{16}O, ^{32}S etc. with even mass number and even atomic number have no magnetic properties and are insensitive to NMR method. Nuclei with spin quantum number of $\frac{1}{2}$ *e.g.* ^{1}H, ^{19}F, ^{31}P are most useful for NMR studies. Nuclei with spin quantum number 1 (*e.g.* ^{2}H, ^{14}N) or $\frac{3}{2}$ (*e.g.* ^{11}B, ^{35}Cl) possess an electric quadruple moment in addition to spin magnetic moment and are studied by *Nuclear Quadruple Resonance* (NQR) method.

However, the main application of NMR spectroscopy in organic chemistry is confined to hydrogen nuclei or proton since they are present in almost all organic compounds and also because they are highly sensitive to the method. The study of hydrogen nuclei by nuclear magnetic resonance method is commonly referred to as *Proton Magnetic Resonance* (PMR) spectroscopy.

As explained earlier, the spinning nucleus gives rise to a magnetic field whose axis is coincident with the axis of spin. Such a nucleus behaves as a tiny magnet of magnetic moment μ. If such a nucleus is placed in an external magnetic field of H° gauss, then according to quantum mechanics, it may assume any of (2I + 1) orientations with respect to the direction of the applied magnetic field. Thus for proton ($I = \frac{1}{2}$), there is a possibility of two orientations only—aligned with the direction of external field (parallel orientation), $m = +\frac{1}{2}$ or aligned against the direction of external field (antiparallel orientation), $m = -\frac{1}{2}$ which correspond to energy levels of $+\mu H°$ and $-\mu H°$ respectively. The parallel orientation of the tiny nuclear magnet is more stable and favourable. Hence under ordinary conditions there is a slight excess of nuclei in lower spin state which are responsible for absorption of discrete amount of energy (ΔE) such that $\Delta E = 2\mu H° = h\nu$. For protons in a magnetic field of 14,000 gauss the frequency of such energy is in the radio frequency regions of about 60 mega cycles per second.

Concept of Resonance

In an applied external magnetic field the *precessional frequency** of the spinning nucleus must be exactly equal to the frequency of electromagnetic radiations (radio frequency) necessary to induce transition from one nuclear spin state to another. When the precessional frequency of spinning nucleus coincides with the frequency of rotating magnetic field, they are in *resonance* and then and only then the absorption or emission of energy by the nucleus can occur.

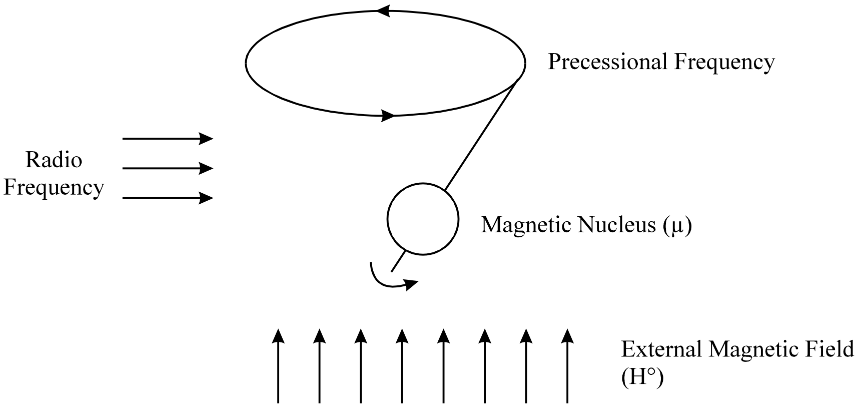


Fig. 2.31 *Schematic description of precessional frequency.*

In this respect NMR spectroscopy is different from UV, visible and infrared spectroscopy as here in NMR different energy states between which transition may occur are not pre-existent but created as a result of application of external magnetic field and resonance is essential for absorption or emission of energy.

The transition of nucleus from one spin state to another corresponds to change in angle that the axis of nuclear magnet makes with respect to applied magnetic field. The nucleus in higher energy state reverts back to lower energy state through spin-spin relaxations and spin-lattice relaxations.

It is also important to note that resonance frequencies for different types of nuclei differ considerably from each other and their NMR spectra do not overlap.

2.3.14 Chemical Shift (Aliphatic, Olefinic, Alkyne, Aromatic, Heteroaromatic, Carbonyl Compounds)

Chemical shift is associated with the Larmor frequency of a nuclear spin to its chemical environment. Tetramethylsilane [TMS; (CH3)4Si] is generally used for standard to determine chemical shift of compounds: δTMS=0ppm. In other words, frequencies for chemicals are measured for a 1H nucleus of a sample from the 1H or resonance of TMS. It is important to understand trend of chemical shift in terms of NMR interpretation. The proton NMR chemical shift is affect by nearness to electronegative atoms (O, N, halogen.) and unsaturated groups (C=C, C=O, aromatic). Electronegative groups move to the down field (left; increase in ppm). Unsaturated groups shift to downfield (left) when affecting nucleus is in the plane of the unsaturation, but reverse shift takes place in the regions above and below this plane. 1H chemical shift play a role in identifying many functional groups.

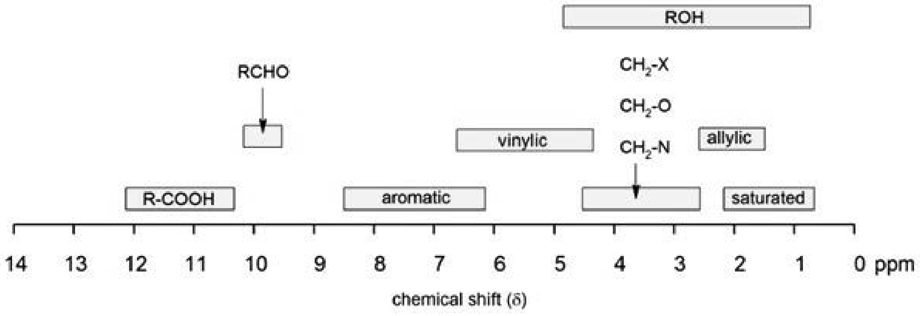


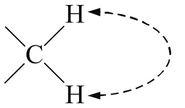
Fig. 2.32 *Chemical Shifts in various Functional Groups*

2.3.15 Coupling Constants

The distance between the peaks in a given multiplet (fine structures) is a measure of magnitude of splitting effect. This is known as coupling constant and is designated by the symbol *J*, which is expressed in cycle per second or Hertz (Hz). Whereas, chemical shift is dependent on applied field, the coupling constant is independent of the applied field but depends on the structure of a molecule.

In case of mutually coupled protons the magnitude of splitting of signal of one proton by the other is the same. The coupling constant is determined by the nature of the bond and the spatial relations between the protons.

(*a*) For protons attached to the same carbon atom (i.e., geminal protons), the value of *J* varies from 0–20 Hz depending on bond angle and overall structure of the molecule.



J = *0 – 20 Hz*

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(*b*) For protons attached to adjacent carbon atoms (i.e., vicinal protons), the value of *J* depends on the dihedral angle.

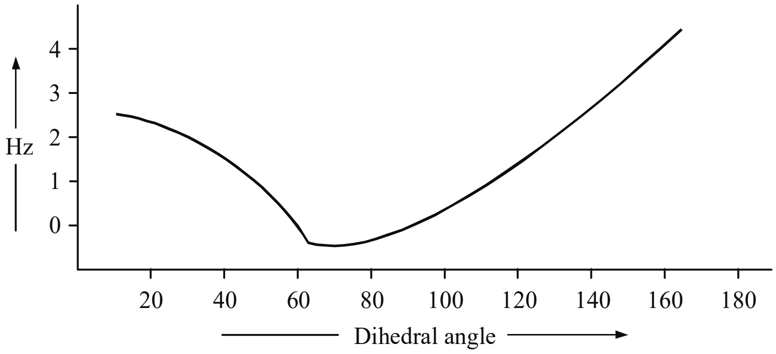
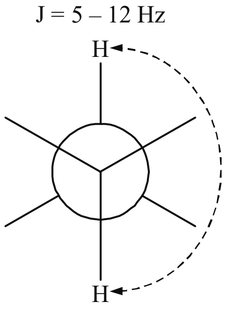


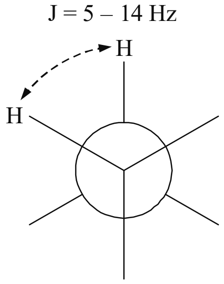
Fig. 2.33 *Variation of J with dihedral angle*

For 0º and 180º, coupling constants is higher. At 90º '*J*' is slightly negative.

In case of ethane (C_2H_6), which has freely rotating groups, protons with anti conformation have '*J*' value 5–12 Hz while protons with gauche conformation have *J* = 2 – 4 Hz.



Anti



Gauche

Coupling constants are a measure of the effectiveness of spin-spin coupling and are helpful in determining complex molecular structures.

2.4 TWO DIMENSIONAL SPECTROSCOPY (2D-NMR)

A conventional 'HNMR spectrum has a frequency axis and an intensity axis, 2-D spectra have two frequency axes and are intensity axis. The common 2-D spectra are 'H– 'H shift correlation in which both frequency axes show 'H chemical shifts. This is known as 'H–'H shift correlated spectroscopy which is known by the acronym COSY (Correlated Spectroscopy). COSY identifies pairs of protons which are coupled to each other. A portion of the COSY spectrum of a compound gives a look of a mountain range viewed from the air. These "mountain like" spectra (known as stack plots) are not the spectra which are used in practice to study a compound. However, the compound is identified using a contour plot, where slices of each mountain are represented by contour circles (I, figure 2.34) rather than stack plot (II, figure 2.34)

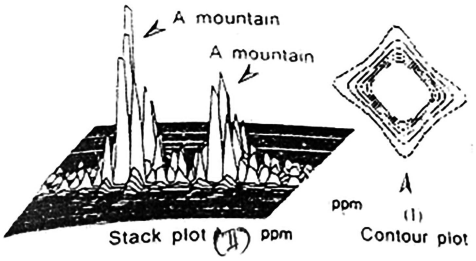


Fig 2.34 COSY spectrum of an organic compound will appear like a mountain range when viewed from air. These mountain like spectra (stack plots) are not used but instead a contour plot is used where each mountain is represented by large dot (I).

$^{13}C – ^{1}H$ atoms. Spectra showing $^{13}C – ^{13}C$ shift correlations are called 2-D^{13}C INADEQUATE; these spectra identify directly bonded carbons. Other 2-D spectra involve the Nuclear Overhauser effect (NOESY for very large molecules; ROESY for medium size molecules). They are employed to determine through space interactions for stereo chemical analysis.

COSY Correlation Spectroscopy (Cross-Peak Correlations)

The COSY spectrum of m-dinitrobenzene is shown in figure 2.35 as a contour plot. The COSY spectrum is the ‘H NMR spectrum run both along the x-axis and then at the y-axis and the signals are repeated yet again as spots on the diagonal (diagonal peaks as contours). In the COSY spectrum of m-dinitrobenzene (fig. 2.12) the diagonal (which is drawn as a solid line to help you) runs from upper right corner to lower left corner. The important peaks in the spectrum are off-diagonal peaks (cross peaks). If a proton couples with another proton i.e., if a correlation is established then a horizontal line drawn (drawn as dotted line to assist you) from a cross peak will intercept a contour on the diagonal and a vertical line (again drawn as a dotted line to assist you) from the same cross peak will intercept another contour on the diagonal. Notice that cross peaks are on both sides of the diagonal, and the cross peaks only on one side of the diagonal are interpreted e.g., the cross peak below the diagonal (Figure 2.35). The cross peaks above the diagonal give the same information). The following is the point wise discussion on the interpretation of the COSY spectrum of m-dinitrobenzene.

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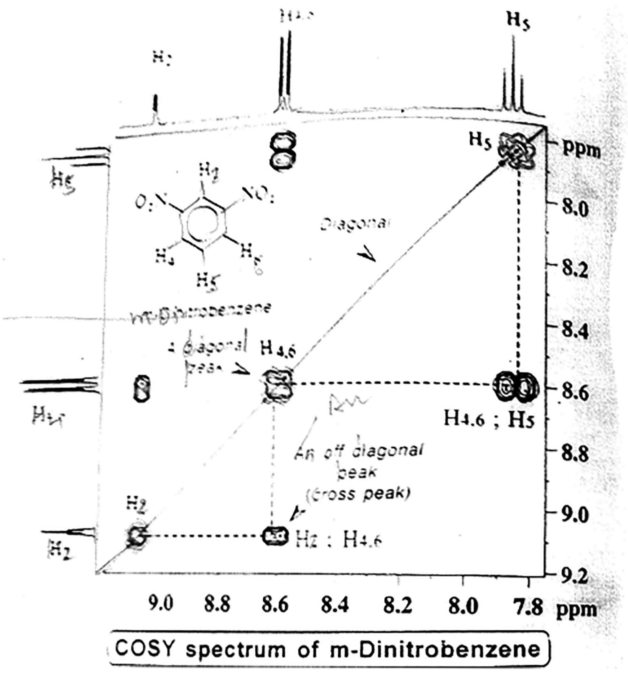


Fig. 2.35 *COSY spectrum of m-Dinitrobenzene*

(i) In the COSY spectrum, the conventional ordinary one-dimensional – ID H spectrum is shown along both the horizontal and vertical axes (for the interpretation of ordinary, i.e., conventional 1-D H NMR spectrum of m-dinitrobenzene).

(ii) Along the diagonal of the COSY spectrum is a view which corresponds to looking down on the conventional one-dimensional spectrum of m-dinitrobenzene as though each peak were a mountain.

(iii) The one-dimensional counterpart of a given peak on the diagonal lies directly below that peak on each axis.

(iv) The off-diagonal peaks which are termed as cross peaks provide useful information. The presence of a cross-peak normally indicates that the geminally or vicinally coupled. Long range couplings normally do not give significant cross-peaks. However, there may be exceptions when long range couplings are large.

(v) One starts at a given cross-peak and imagines two perpendicular lines (shown as dashed lines, these lines are parallel to each spectrum axis) which lead back to the diagonal. The peaks which are intersected on the diagonal by these lines are coupled to each other. Therefore, the peaks on the one-dimensional spectrum which are directly below the coupled diagonal peaks are coupled to each other.

(vi) To start interpreting a COSY spectrum, it is essential to make an initial assignment through the traditional considerations of chemical shifts and coupling constants. The peak, to a cross-peak and back to the diagonal for the assignment of a new peak [as already discussed above under (v)].

In the case of COSY spectrum of m-dinitrobenzene, the starting point could well be the signal from H_2 proton which is the most downfield and therefore, readily assigned. Thus, the signal from H_2 at the bottom left of the diagonal has a cross-peak labeled H_2, $H_{4,6}$ connecting it (dashed lines) to the signal from $H_{4,6}$. Thus the H_2 proton around 9.1 is coupled to the hydrogens whose signal appears around 8.6(i.e., H_4, H_6 protons). Similarly the signal from H_4, H_6 is further connected (dashed lines) by a cross-peak to the signal from H_5 to show the coupling between $H_{4,6}$ and H_5.

(vii) One may note that the cross-peaks are labeled with two frequencies and are symmetrically observed below the diagonal as well as above the diagonal relating J correlation among the various protons. Therefore, the cross-peaks in upper left or lower right side of the diagonal can be interpreted in terms of coupling correlation. Moreover, the intensities of the cross-peaks provide some indication about the order of the coupling constant.

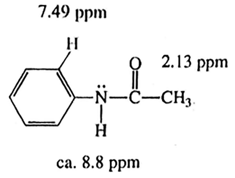
(viii) Since following this procedure H_2 cannot be connected to H_5 (no corresponding cross peaks), H_2 and H_5 are not (apparently) coupled (para coupling is indeed very small 0-1 Hz).

The NOESY Technique

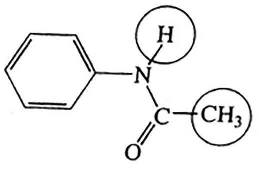
The NMR experiment that takes the advantage of Nuclear Overhauser Effect is Nuclear Overhauser Effect Spectroscopy, or NOESY. Any ‘H nuclei that may interact with one another through a dipolar relaxation process will appear as cross peaks in a NOESY spectrum. This type of interaction includes nuclei that are directly coupled to one another, but it also includes nuclei that are not directly coupled but are located near to one another through space. The result is a two dimensional spectrum that look like a COSY spectrum but includes, besides many of the COSY cross peaks, additional cross peaks that arise from interactions of nuclei that interact through space. In practice, the nuclei must be within 5 ú of each other for this spatial interaction to be absorbed.

NOESY spectroscopy has become especially useful in the study of large molecules, such as, proteins and poly nucleotides. Very large molecules tend to tumble more slowly in solution, which means that Nuclear Overhauser Effect interactions have more time to develop. Small molecules tumble more quickly in solution; the nuclei more past one another too quickly to allow a significant development of dipolar interactions. The result is that NOESY cross peaks may be too weak to be observed.

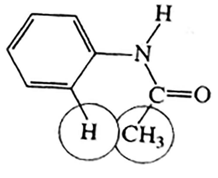
Because the cross peaks in NOESY spectra arise from spatial interactions, this type of spectroscopy is particularly well suited to the study of configurations and conformations of molecules. The example of acetanilide demonstrates the capabilities of the NOESY experiment. The structural formula is shown, with the proton NMR chemical shifts of the relevant protons indicated.



We have to decide which of the two possible conformations is the more important for this molecule. The two conformations are shown, with circles drawn around the protons that are close to each other spatially and would be expected to show Nuclear Overshauser Interactions.



A



B

For conformation A, the N—H hydrogen is close to the methyl C—H hydrogen. We would expect to see a cross peak in the NOESY spectrum that correlates the N—H peak at 8.8 ppm with the C—H peak at 2.13 ppm. For conformation B, the protons that are close to each other are the methyl C—H protons and the *ortho* proton of the aromatic ring. For this conformation, we would expect to see a cross peak that correlates the aromatic proton at 7.49 ppm with the methyl protons at 2.13 ppm. When the actual spectrum is determined, one finds a weak cross peak that links the 8.8-ppm peak with the 2.13 pp peak. This demonstrates clearly that the preferred conformation for acetanilide is A.

Certainly, when one considers solving the three-dimensional structure of a complex molecule such as a polypeptide, the challenge of assigning every peak and every cross peak becomes formidable. Nevertheless, the combination of COSY and NOESY methods finds wide application in the determination of the structures of biomolecules.

DEPT Technique

In a DEPT (Distortionless Enhanced Polarization Transfer) three spectra are obtained. One is a normal broad-band decoupled spectrum. The second spectrum (DEPT 90^0 spectrum) is obtained under special conditions in which only carbons bonded to a single hydrogen (CH's) appear. A third spectrum (DEPT 135^0 spectrum) is obtained under conditions in which CH's and CH_3's appear as normal signals, but CH_2's appear as negative absorptions, and no peaks for quaternary carbons. Example of limonene (Figure 2.36) illustrates this.

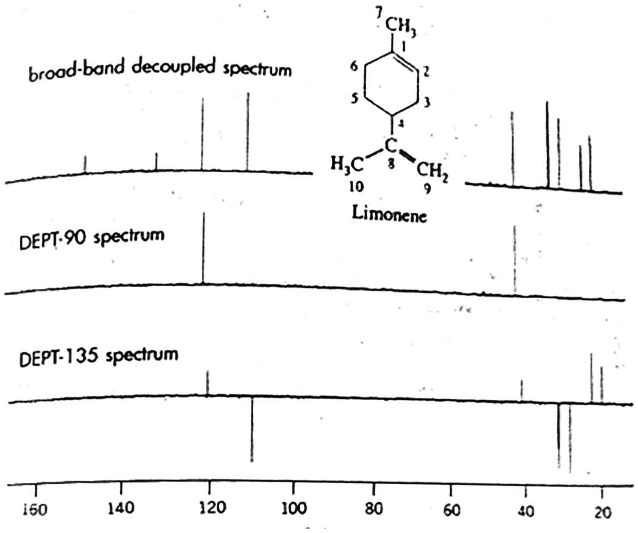


Fig 2.36

The spectrum 1 is the usual broad-band decoupled spectrum which displays the expected number of 10 lines for ten carbons and groups these into six alkyl carbon signals at high field (20-40 ppm) and four alkenyl carbon signals at low field (108-150 ppm). The spectrum 2 is DEPT-90 spectrum in which only two CH signals for carbons C-2 and C-4 appear. Spectrum in which only two CH signals for carbons C-2 and C-4 appear. Spectrum 3 is DEPT-135 spectrum which displays positives absorptions for two CH_3 groups (C-7 and C-10) and for two CH groups (C-2 and C-4). Moreover, it shows negative peaks for four CH_2 groups (C-3, C-5, C-6 and C-9) while no signals for C-1 and C-8.

INEPT (Insensitive Nuclei Enhancement by Polarization Transfer) Technique

This is a signal resolution enhancement method used in NMR spectroscopy. This method of signal enhancement was introduced by Ray Freeman in 1979. INEPT uses J-coupling for the polarization in contrast to Nuclear Overhauser Effect (NOE). Due to its usefulness in signal enhancement, pulse sequences used in heteronuclear NMR experiments often contain blocks of INEPT on INEPT-like sequences.

Signal Enhancement via the INEPT Technique

The INEPT signal enhancement has two sources:

- The spin population effect increases the signal by a factor of K = ratio of gyromagnetic rations y_1/y_s of the nuclei, where y_1 and y_s are the gyromagnetic ratio of the proton (the spins) and the low-sensitivity nuclei (the S spins) respectively.
- Nuclei with higher magnetogyric ratio generally relax more quickly. Since the rate at which the INEPT transfer that can be repeated is limited by the relaxation of these spins (rather than the low sensitivity spins), then the experiment can be repeated more frequently, increasing the signal-to-noise ratio.

As a result, INEPT can enhance the NMR signal by a factor larger than K, while the maximum enhancement via NOE is by a factor of 1 + K/2. Unlike NOE, no penalty is incurred by a negative gyromagnetic ratio in INEPT, it is therefore a useful method for enhancing the signal from nuclei with negative gyromagnetic ratio such as ^{15}N or ^{29}Si. The ^{15}N signal may be enhanced by a factor of 10 via INEPT.

The graphical representation of the INEPT NMR pulse sequence is shown in figure 2.37. The thin bar denotes a 90^0 pulse, while the thick bar denotes a 180^0 pulse.

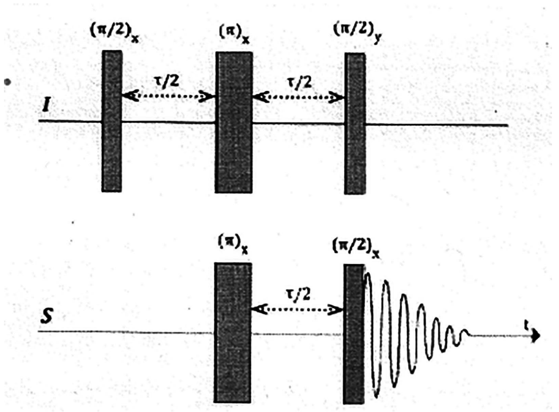


Fig 2.37 The INEDT NMR Pulse Sequence

NOTES

APT (Attached Proton Test) Technique

The attached proton test is a ^{13}C NMR experiment that is used as an aid to assignment by separating carbons unattached to protons and CH_2 signals from CH and CH_3 signals. The APT experiment yields methane (CH) and methyl (CH_3) signals positive and quaternary (C) and methylene (CH_2) signals negative. It is slightly less sensitive than DEPT but a single experiment shows all carbon signals at once unlike DEPT that suppresses quaternary carbons and requires up to three different acquisitions to yield full results.

The APT pulse sequence of ethylbenzene is shown in figure 2.38. The delay between the first two pulses is set to one over the carbon proton coupling constant. For CH_2 (which is the deciding factor for this experiment) this is usually about 125 Hz so the delay is 8 μs. between the last two pulses and between the last pulse and the acquisition 100 μs is usually sufficient.

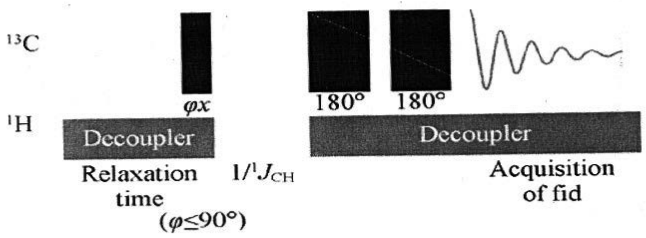


Fig 2.38 *APT Pulse Sequence of Ethylbenzene*

INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment)

The INADEQUATE technique is used to measure ^{13}C-^{13}C coupling constants and for determining carbon-carbon connectivity by determining coupling magnitudes which are common to two carbon atoms. However, in practice, application to determine connectivity problems is complicated not only by the inherently low sensitivity of detecting two dilute nuclei but also by the similarity of many ^{13}C — ^{13}C couplings. Thus all the one-bond carbon-carbon couplings in cyclooctanol fall in the narrow region 34.2—34.5 Hz, except for C-1 — C-2, which is 37.5 Hz. This latter problem is largely solved by translating the experiment into two dimensions.

In an INADEQUATE experiment one is detecting the signals from the minute number (about 1 in 10,000) of the total number of carbon atoms that are ^{13}C atoms directly bonded to other ^{13}C atoms. This experiment is indeed the most powerful and gives information regarding direct carbon connectivities and is thus helpful in establishing the carbon skeleton. Vicinal proton-proton couplings help to elucidate the components which make up the chain of carbon atoms. Difficulties will arise, e.g., when there is an intervening quaternary carbon, and with no protons on it to couple with the adjacent protons, the chain is interrupted.

The INADEQUATE experiment involves a pulse sequence—a double-quantum filtering which removes all single spin interactions which correspond to isolated ^{13}C atoms. It detects only transitions from systems with two spins (AB and AX systems). A gap caused due to the presence of a heteroatom C—X—C will prevent mapping the entire molecule.

Consider the INADEQUATE spectrum of 2-butanal (figure 2.39) in contour form along with the conventional ^{13}C NMR and consider the following points:

(i) Make a simple assignment from which the remainder of the structure can be mapped. In the case of 2-butanal it is the oxygen substituted C-2 which resonates at highest frequency (therefore left)

(ii) The cross-peaks labeled a and b represents the connectivities between C-2 and C-3 and between C-2 and C-1, respectively. The cross-peaks c identify the remaining connection between C-3 and C-4.

(iii) The dashed line bisects the mid-point between each of the pairs of cross-peaks, which is helpful in picking the cross-peaks out from noise.

(iv) Initially, a connectivity is established by making a horizontal correlation between cross peaks which are symmetrically placed with respect to the dashed line which is followed by vertical correlation at either end to other cross peaks. The termini of carbon chains are readily detected since these have only vertical correlations at one end. One thus find that the upfield cross-peaks b and c have no cross-peaks above or below them to show that these atoms are bonded only to one carbon atom each.

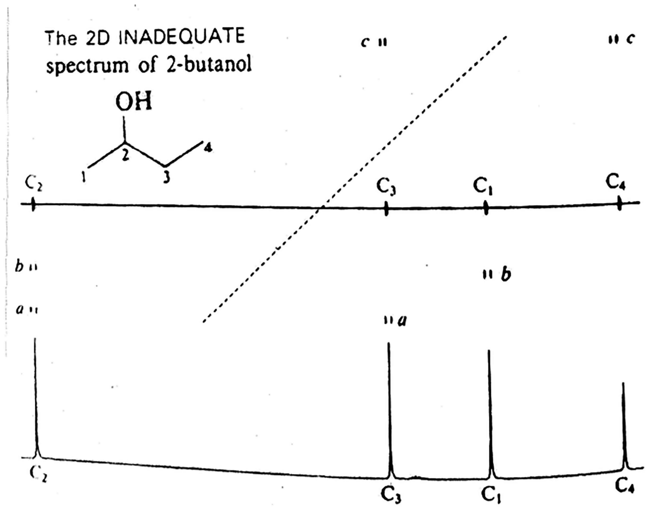


***Fig 2.39** The 2D INADEQUATE spectrum of 2-butanol*

Check Your Progress

7. What do you understand by stereochemistry?
8. Define geminal protons.
9. Define vicinal protons.
10. State the significance of Karplus curve.
11. State the significance of NOESY spectroscopy.
12. What do you understand by INEPT spectroscopy?
13. Define APT technique.
14. What is the significance of INADEQUATE technique?

2.5 ELECTRON SPIN RESONANCE SPECTROSCOPY

An electron possesses spin angular momentum and because of this momentum a spin magnetic moment. The spin may take two orientations denoted as α or β with respect to some selected direction.

$$E_{ms} = 2\mu_B, m_s B, \quad m_s = \pm \frac{1}{2}$$

where B is the applied magnetic field, μ_B is the Bohr magneton. It shows that the electron with a spin ($m_s = + 1/2$) rise while that of the β-spin electron talls as the magnetic field is raised. The energy of separation of the two spin states is shown in Figure 2.40.

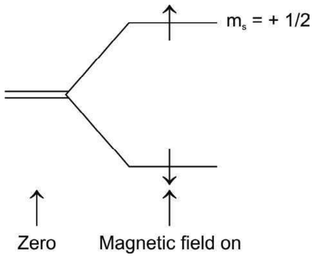


Fig. 2.40 *Electron Spin Energy Levels in a Magnetic Field*

$$\Delta E = E_{1/2} - E_{-1/2} = 2\mu_B B$$

The sample is bathed in a radiation of frequency v. The unpaired electron spins of the sample have energy levels that come into resonance with the radiation when the magnetic field has been adjusted so that

$$hv = 2\mu_B B$$

when this condition is satisfied the energy levels are in resonance with the surrounding radiation. The resonance condition is satisfied and strong energy absorption takes place. The electron spin resonance spectroscopy technique is also called electron paramagnetic resonance is the study of the properties of molecules containing unpaired electrons by observing the magnetic fields at which they produce resonance with the applied field of define frequency.

Experimental Arrangement: The block diagram of a simple esr spectrometer is shown is Figure 2.41. As in NMR spectrometer the frequency is kept constant and the magnetic field is swept through resonance. Microwave radiation from a klystron passes down a waveguide to a resonant cavity containing the sample. When there are transitions between electron spin levels containing the sample. When there are transitions between electron spin levels in the sample, energy is absorbed from the microwave radiation and less microwave energy is

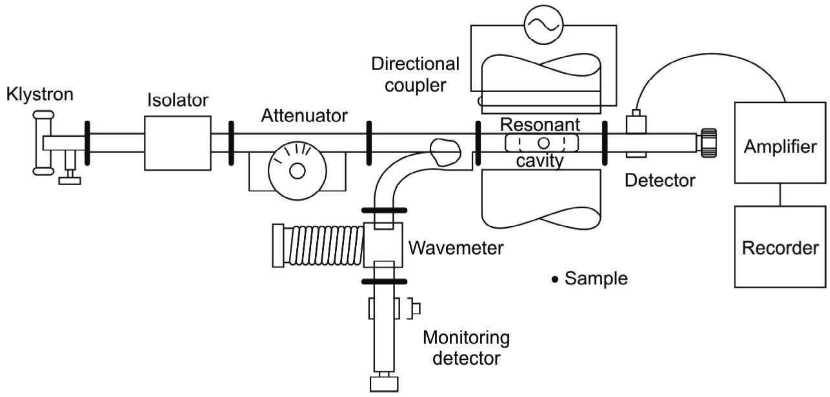


Fig. 2.41 *A Electron Spin Resonance Spectrometer*

received at the crystal detector. By using a field modulator and a phase sensitive detector the derivative of the absorption line is recorded on the oscilloscope or on a phase sensitive detector. The sample may be a gas liquid or solid but the gas phase involves complications. The only requirement is that the molecules of sample must possess unpaired spins. Therefore ESR may be used for studying free radicals formed during chemical reactions or on photolysis, from transition metal complexes and the molecules in the triplet state. However, it is insensitive to normal spin paired molecules. The molecules of different kinds come into resonance at different applied magnetic fields as shown in Figure 2.42.

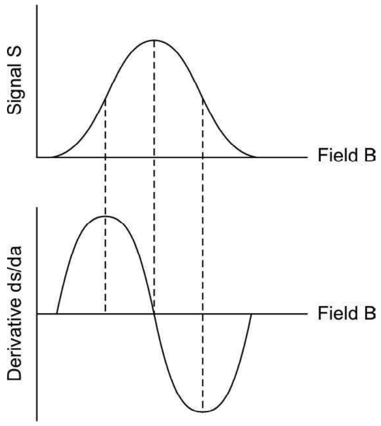


Fig. 2.42 *Rate of Change of Absorption vs Field Strength of ESR Signal*

ESR spectrum of hydrogen atom. The ESR spectrum of hydrogen atoms show two as shown in Figure 2.43.

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 $m_s = -\frac{1}{2}$.

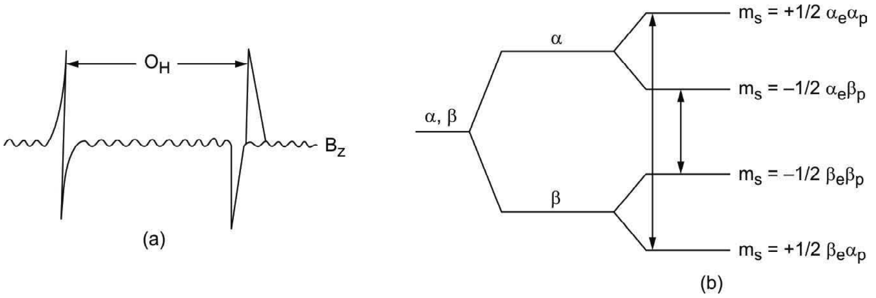


Fig. 2.43 *(a) ESR Spectrum of Hydrogen Atom (b) The Energy Levels Obtained as a Result of Nuclear Hyperfine Interaction*

If we consider the interaction between these levels with a single nuclei having $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$, we get four energy levels.

ESR spectrum of Deuterium has the nuclear spin quantum number $I = I$. Thus, there are three values of the component of angular momentum vector m_I as given below

$$m_I = I, (I-1) \ldots 0, \ldots, (I-1), -I$$
$$= +, 0, -I$$

The interaction of nuclear spin with the values of m_s of electron $\left(\pm\frac{1}{2}\right)$ yield six energy levels as shown in Figure 2.44.

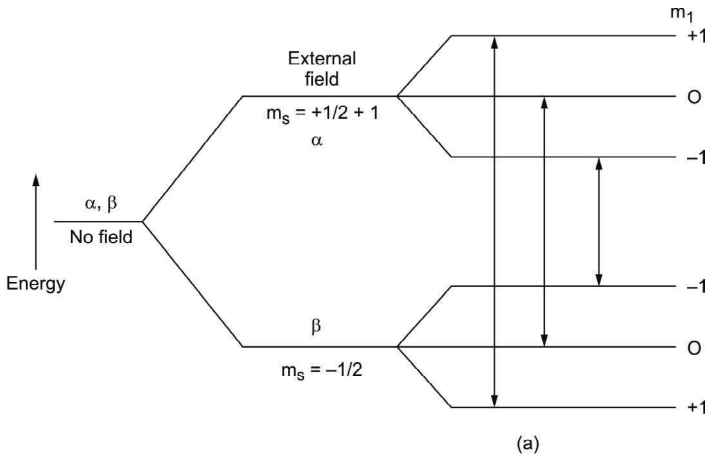


Fig. 2.44 *(a) Energy Levels of Denterium*

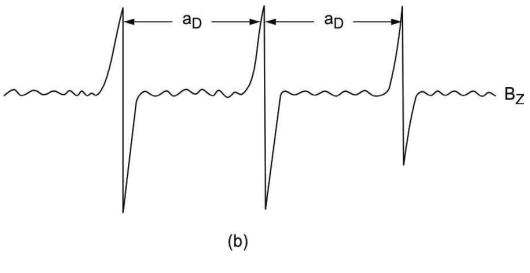


Fig. 2.44*(b) ESR Spectrum of Denterium*

Now let us discuss the ESR spectra of some species which contain more than one magnetic melei. The simple example can be considered as that of a single electron in presence of two protons. The two protons interact equally with the electron which results in six energy levels, using the selection rule $\Delta m_s \pm$ and $\Delta m_I = 0$ three transitions as shown in Figure 2.45 are possible. This is illustrate in the ESR spectrum.

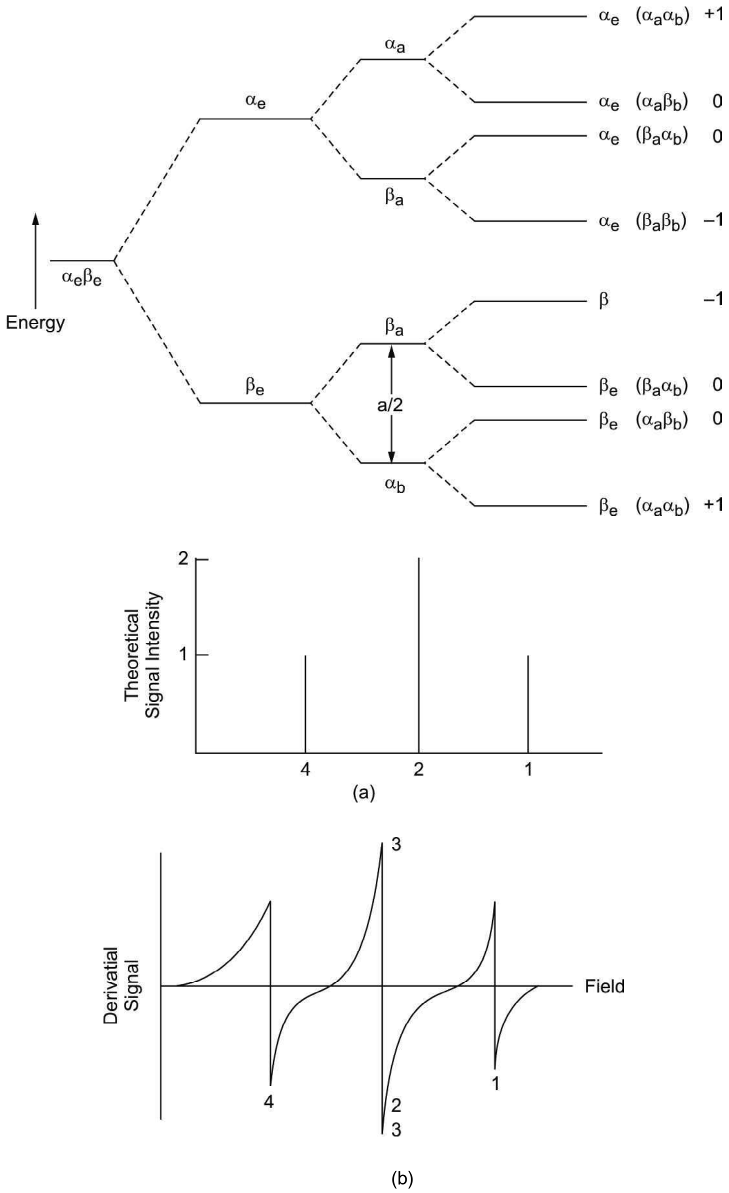


Fig. 2.45 (a) ESR Energy Level for the Interaction of One Electron with Two Protons (b) ESR Spectrum

ESR spectra of methyl radical (—CH_3). It contains three equivalent hydrogen atoms, $I = 3/2$, $m_I = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ in the direction of the applied magnetic field. Each of these m_I values will interact with $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ and will yield eight energy levels. The ESR spectrum of methyl radical is shown in Figure 2.46. The signals are not of equal intensity but are in the ratio of 1 : 3 : 3 : 1. The splitting pattern is shown Figure 2.47.

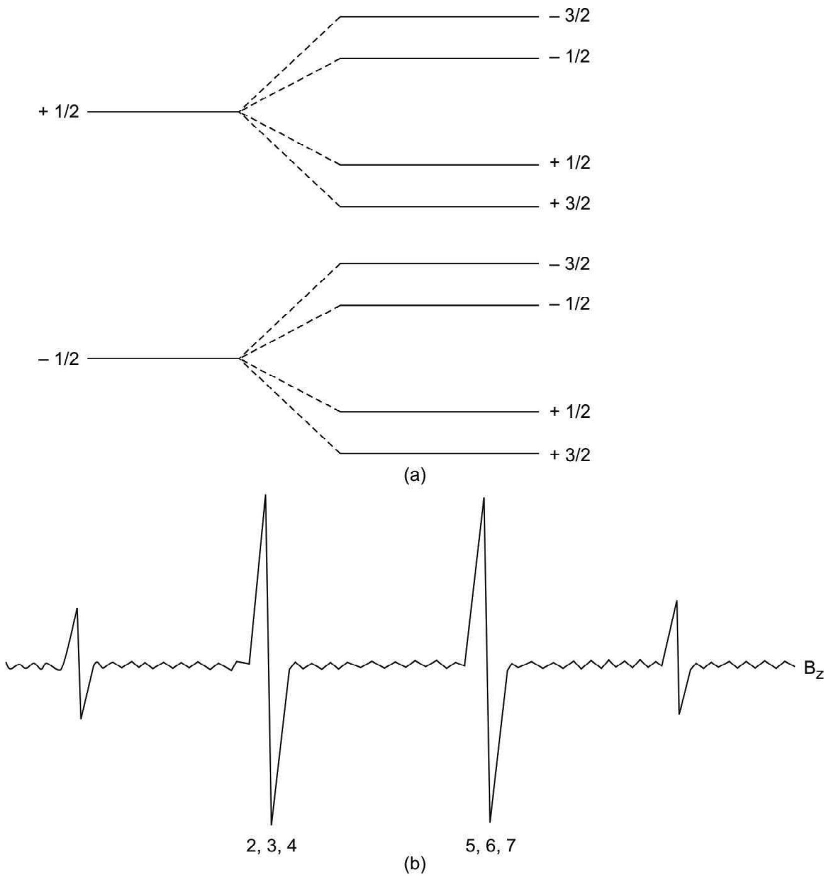


Fig. 2.46 *(a) Energy Levels the Allowed Transitions in Methyl Radical (b) ESR Spectra of the Methyl Radical*

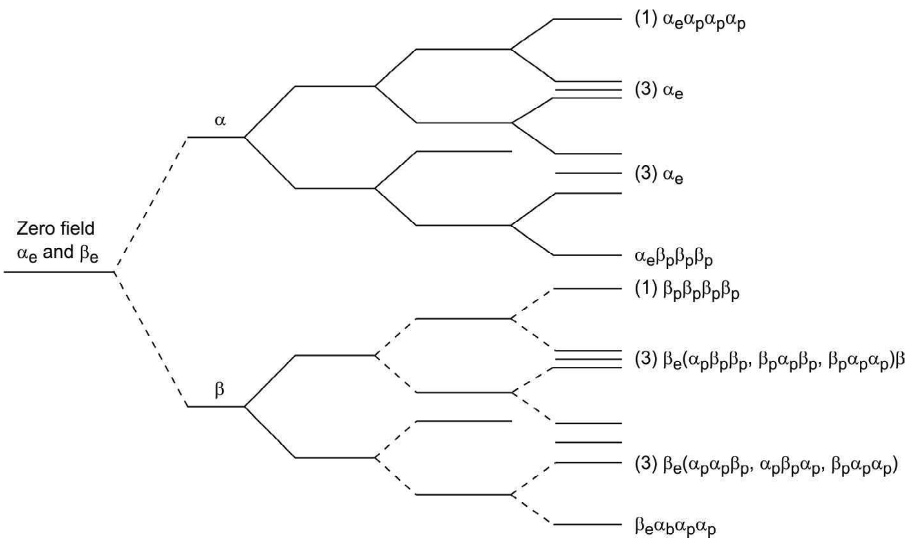


Fig. 2.47 *Splitting Caused by Three Equivalent Protons*

Pascal triangle can be used for determining the number of lines obtained after splitting, as tabulated below:

NOTES

Table 2.3 *Pascal's 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

Pascal's Triangle

The g_e value for a free electron is 2.00 232. The systems which are without directional properties, i.e., isotropic systems g is given by

$$g = g_e (1 - \sigma)$$

The anisotropic systems on the other hand will show different g values depending upon its direction of measurement. For such systems the g values are measured by applying the field along the three coordinate axes, i.e., g_{xx}, g_{yy} and g_{zz}. The g values can also be referred to as g_{11} (g parallel) or g_I (perpendicular) depending upon whether we are measuring g values parallel to the axis of symmetry or perpendicular to it.

The g values for organic radicals are almost isotropic and differ very little from g_e for the free electron. For example the g values for CH_3 and CH_3CH_2 radicals are 2.00255 and 2.0026.

Applications of ESR: ESR spectral provides very useful information in large number of studies.

1. **Study of Free Radicals:** Free radicals can be studied using esr even in small concentrations. It is a sort of finger print and helps to identify the radical present in a sample. The hyperfine splitting constant a is given by,

   $$a = Q\rho$$

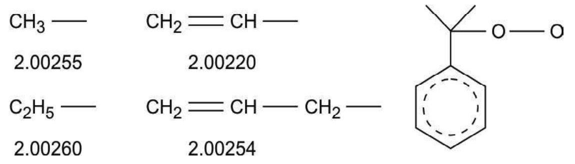
   Where Q is the hyperfine splitting constant for unit density and ρ is the electron density.
2. **Study of Transition metal Complexes:** The ESR spectrum helps in determining if the electron is localized on transition metal atom or on the ligand.

   ESR spectral study can also be used in the study of organonetallic compounds.

Molecules of different kinds come into resonance at different applied magnetic fields. In order to accommodate the differences between species the resonance condition can be written as,

$$hv = g\mu_B B \qquad ...(19)$$

where g, the value of the electron is an experimental parameter which depends on the molecule under study. For free electron $g_e = 2.0023$. For many radicals g value lies in the range 1.9 to 2.1. The reason for the deviation of g from 2 is that the electronic spin magnetic interacts with the local magnetic field which may be different form the applied field. The ESR spectra are a plot of the rate of change absorption against field strength as shown in Figure 3.10. The magnetic moment of an unpaired electron is 700 times ESR that of the proton so that the signal the sensitivity of an ESR detector is much higher than in NMR. The esr spectra can be recorded for radical concentrations as low as 10^{-4} mole dm^{-3} irrespective of the number of non-radical species present. The *g* valuesfor some organic radicals are shown below:



2.5.1 Hyperfine Coupling

The Hyperfine Splitting (HFS) or hyperfine coupling is a special feature of ESR caused by the interaction of electron spins with the magnetic nuclei in the sample. A magnetic nucleus with quantum number I will split a single ESR line (peak) into 2I+1 lines (peaks).

Magnetic hyperfine splitting, also known as Zeeman Effect, arises from the interaction between the nuclear magnetic dipole moment and the magnetic field at the nucleus. This interaction gives rise to six transitions, whereby the separation between the according peaks in the spectrum is proportional to the magnetic field at the nucleus. For materials consisting of fine particles, the effective magnetic field is not uniform because the number of magnetic neighbors of a given atom or ion varies depending on whether it is located in the bulk or in a surface layer.

The magnetic field separation between two neighboring peaks in the splitting due to the same nucleus is called the hfs-constant of that magnetic nucleus. The value of the hfs -constant depends on the nature of the nucleus and the density of electron spin distributed on the nucleus.

Since all hyperfine interactions occur simultaneously, the spectra can be described by the eigenvalues of a combined hyperfine Hamiltonian. In magnetically ordered compounds with a non-vanishing EFG, the shape of the spectrum depends on the relative strengths of the magnetic dipole and the electric quadrupole interaction.

2.5.2 Spin Polarization for Atoms and Transition Metal Ions

Spin polarization is the degree to which the spin, i.e., the intrinsic angular momentum of elementary particles, is aligned with a given direction. This property may pertain to the spin, hence to the magnetic moment, of conduction electrons in ferromagnetic metals, such as iron, giving rise to spin-polarized currents. It may refer to (static) spin waves, preferential correlation of spin orientation with ordered lattices (semiconductors or insulators).

It may also pertain to beams of particles, produced for particular aims, such as polarized neutron scattering. Spin polarization of electrons or of nuclei, often called simply magnetization, is also produced by the application of a magnetic field. Curie law is used to produce an induction signal in Electron spin resonance (ESR or EPR) and in Nuclear magnetic resonance (NMR).

Spin polarization is also important for spintronics, a branch of electronics. Magnetic semiconductors are being researched as possible spintronic materials.

The spin of free electrons is measured either by a LEED image from a clean wolfram-crystal (SPLEED) or by an electron microscope composed purely of electrostatic lenses and a gold foil as a sample. Back scattered electrons are decelerated by annular optics and focused onto a ring shaped electron multiplier at about 15°. The position on the ring is recorded. This whole device is called a Mott-detector. Depending on their spin the electrons have the chance to hit the ring at different positions. 1% of the electrons are scattered in the foil. Of these 1% are collected by the detector and then about 30% of the electrons hit the detector at the wrong position. Both devices work due to spin orbit coupling.

The circular polarization of electromagnetic fields is due to spin polarization of their constituent photons. In the most generic context, spin polarization is any alignment of the components of a non-scalar (vectorial, tensorial, spinor) field with its arguments, i.e., with the nonrelativistic three spatial or relativistic four spatiotemporal regions over which it is defined. In this sense, it also includes gravitational waves and any field theory that couples its constituents with the differential operators of vector analysis.

2.5.3 Spin Orbit Coupling and Significance of G Tensor

The spin-orbit coupling terms in the molecular electronic Hamiltonian have important, spectroscopically observable, effects. In states possessing an orbital degeneracy (e.g. II states of diatomic molecules) they produce a first-order splitting of the various multiplet levels; and in states which are degenerate in spin only the y give second-order effects embodied in a n effective g tensor. Owing to the complexity of the spin-orbit operators, such effects are usually discussed using simple approximate form s and semi-empirical wave-functions**.**

This phenomenon is detectable as a splitting of spectral lines, which can be thought of as a Zeeman effect product of two relativistic effects: the apparent magnetic field seen from the electron perspective and the magnetic moment of the electron associated with its intrinsic spin. A similar effect, due to the relationship between angular momentum and the strong nuclear force, occurs for protons and neutrons moving inside the nucleus, leading to a shift in their energy levels in the nucleus shell model. In the field of spintronics, spin–orbit effects for electrons in semiconductors and other materials are explored for technological applications.

G Tensors

The g-tensor arises from the interaction of the electronic spin with external magnetic field. This term plays a somewhat similar role to the shielding in NMR; induced electronic currents in the sample modify the g tensor from its vacuum value. g-tensor is a central quantity for the interpretation of electron paramagnetic resonance spectra.

2.5.4 Applications of Transition Metal Complexes (Including Biological System and Inorganic Free Radicals)

NOTES

Transition metal complexes or coordination complexes are molecules that contain groups arranged around a central metal ion. In a way, these are like "lego-molecules", easily assembled from smaller parts, and sometimes they are easily transformed into new molecules by switching out old parts for new ones. That rapid assembly and disassembly is part of what makes these compounds very useful in both industrial and biological catalysis.

Transition metal complexes have played a remarkable role in the development of homogeneous catalysis. The existence of many possibilities of combining a catalytically active metal with various chiral ligands cause metal catalysts to continue playing a dominant role in asymmetric catalysis.

Inorganic compounds particularly transition metals have played an important role in the development of new metal based drugs and in some cosmetic formulations. In this review a cursory look at the application of these metal complexes in the areas of pharmacy, microbiology and cosmetology has been expatiated to provide an insight of the contribution of inorganic chemistry towards drugs and cosmetic delivery.

Many transition metals with mixed amino acid complexes revealed their biological activity, which place them in several biochemical processes. The ternary complex models provide information about how biological systems achieve their specificity and stability, as well as strategies, to improve these features for biotechnological applications.

Additionally, the metal complexes could be considered as a precursor for thermal preparation of nanosized metal oxides. Thus, we will investigate calcinating the complexes under investigations to check the possibility of obtaining metal nano-oxides in a facile way for possible application as photocatalysts.

Check Your Progress

15. What do you understand by hyperfine coupling?
16. Define spin polarization.
17. What do you understand by spin orbit coupling?
18. Define g-tensors.

2.6 MASS SPECTROSCOPY

Mass spectrometry, in recent years has been applied extensively for the structure determination of organic molecules. This technique provides qualitative and quantitative information about the atomic and molecular composition of inorganic and organic materials. This technique was first used by J.J. Thompson in 1912, F.W. Aston in 1919. The mass spectrometer produces charged particles that consist of the parent ion and ionic fragments of the original molecule, and it sorts these ions according to their mass/change ratio. The mass spectrum is a record of the relative numbers of different kinds of ions and is characteristics of energy compound, including isomers. The main advantages of mass spectrometry as an analytical techniques are its increased sensitivity over most other analytical techniques and its specificity in identifying unknowns or confirming the presence of suspected compounds. Mass spectrometry is also extensively for the determination of molecular weights, for ascertaining isotopic ratios of some elements present in different compound and as an essential adjunct to the use of stable isotopes in tracer work and reaction mechanism studies. It is also possible to determine the ionization potential of a molecule and the bond dissociation energies using mass spectrometry.

2.6.1 Ion Production Methods

The important ionization methods for the production of ions are discussed as:

1. Electron Impact (EI) Method: In this method, the sample is bombarded in the vapour phase with a because of high energy electrons (70 eV).

(i) On collision of a molecule M with an electron e, the molecule M is highly energized and ejects an electron to give a radical cation $M^{\pm}$ which is known as the molecular or parent ion. This is the most probable process. The molecular ion (often denoted as M^+) has the same mass as the initial molecule M. Thus, its mass gives a direct measure of molecular weight of a compound

$$M + e \rightarrow \underset{\text{Molecular or parent ion}}{M^+} + 2e$$

(ii) The alternative and far less probable process (less probable by a factor of $\sim 10^{-2}$) involves the capture of an electron by a molecule to give a radical anion M^-.

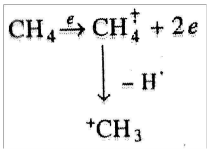
$$M + e \rightarrow M^-$$

(iii) A least probable process gives multiply charged ions

$$M + e \rightarrow M^{n+} + (n+1)e$$

Mass spectrometers are generally set up to detect only positive ions, but negative-ion mass spectrometry is also possible

2. Chemical Ionization (CI) Method: In this method the sample is introduced into the ionization chamber near the atmospheric pressure with a large excess of an intermediate substance (methane, iso-butane or NH_3) also called the carrier gas. Methane is generally used as the carrier gas which is first ionized by electron impact to primary ion.



$$CH_4 \xrightarrow{e} CH_4^{\dagger} + 2e \quad \xrightarrow{-H^{\cdot}} \quad {}^{+}CH_3$$

Primary ions react with excess of methane to give secondary ions

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

The sample (*R*H) is then ionize largely by collision with these secondary ions rather than electrons

$$CH_5^+ + RH \rightarrow RH_2^+ + CH_4$$

$$C_2H_5^+ + RH \rightarrow RH_2^+ + C_2H_4$$

These RH_2^+ (M+1) ions are often prominent and are called quasimolecular ions. They can lose H_2 to give prominent M – l ions. This method causes less fragmentation and so the mass spectra can be interpreted more easily. Further, this technique is very useful for locating the molecular ion peak for compounds which give either no molecular ion peak or a weak parent peak.

3. Field Desorption (FD) Method: This technique was developed by Bakey in 1969. In this method, ion formation is achieved by applying high electrical field gas phase from a material deposited on solid surface (a multi tipped emitter where a carbon or silicon whiskers grown on tungsten wire).

This method is generally used for thermally labile substances or non-volatile compounds. In this method, ionization takes place by quantum mechanical funneling mechanism, where there is a shifting of ions to the anode (emitter) from the sample molecule. It leads to the formation of positive ions (M^+) and cation attached species like $(M + Na)^+$. $(M + Na)^+$ get produced while desorption process because of the trace alkali metal ions present in the analyte. This ion source is good to identify small organic molecules, low molecular weight polymers and for petrochemical fractions.

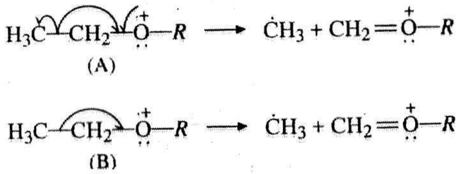
4. Fast Atom Bombardment (FAB): Developed by Michael Barber, 1980, in this technique beam of Ar and Xe is focused onto an analyte and non-volatile liquid matrix mixture. High molecular weight compounds like peptides with molecular weight up to 1000 Da can be analysed by this method. This is a soft ionization technique and generally matrices used in this process are glycerol, *Monothioglycerol*, 3NBA etc. In the process, organic compound get easily dissolve in solvent and do not evaporate in vacuum. In this process, Xe and Ar get ionized first, with a beam of high translational energy to give Xe or Ar radical cations; $Xe \xrightarrow{e-} Xe^{++} + 2e^-$. The acceleration (6-10 key) of the radical cations to produce radical cations with high transitional energy (Xe^{++}),these are then run through a chamber containing Xe atoms at 10-15 Torr pressure. By the process of electrolytic deflector, the lower energy lens get removed.

$(Xe)^{++} = Xe^{++}\ Xe$

$(Xe)^{++}\ Xe = (Xe)^+\ Xe^+$

2.6.2 Factors Affecting Fragmentation

Most of the fragmentation processes involve elimination of radicals from radical cations. Therefore, these may be regarded as hemolytic processes (one-electron shift) and are indicated by a single barbed fishbook ($\curvearrowright$). A heterolytic process (a two-electron shift) is indicated by an arrow ($\curvearrowright$). For example, a hemolytic fragmentation is represented as follows:



The homolysis of a bond could be indicated by showing two fishbooks shown in (A), but for brevity and clarity only one is drawn as in (B).

The following factors dominated the general modes of fragmentation:

(i) Weak bonds tend to be broken.

(ii) Stable fragments (ions, radicals and molecules) tend to be formed.

(iii) Ability of ions to assume cyclic transition states- rearrangement processes.

Favourable fragmentation process naturally occur more frequently and ions thus formed appear as strong peaks in the mass spectrum. General concepts of mechanistic organic chemistry are very useful in predicting and understanding favourable mass spectrometric fragmentation processes.

2.6.3 Ion Analysis and Ion Abundance (The Base Peak)

The mass spectral data are commonly presented in the form of bar graph (fig 1) in which the relative abundance (intensity) of ions is plotted against their m/e ratio. The relative abundance of any in is given as the percentage of the corresponding peak relative to the most intense peak (most abundant ion). Thus, the most intense peak also known as the base peak is assigned a value 100 and other peaks are reported as percentages of the base peak. Sometimes, the molecular ion peak or parent peak itself may be the base peak. A tabular representation of mass spectra is also used in which m/e values of the various ions and their relative abundances are reported (Table 2.4)

Table 2.4 *Tabular Representation of the Mass Spectrum of Methane*

m/e	Relative abundance (%)
1	3.4
2	0.2
12	2.8
13	8.0
14	16.0
15	86.0
16	100.0 (Base peak)
17	1.1

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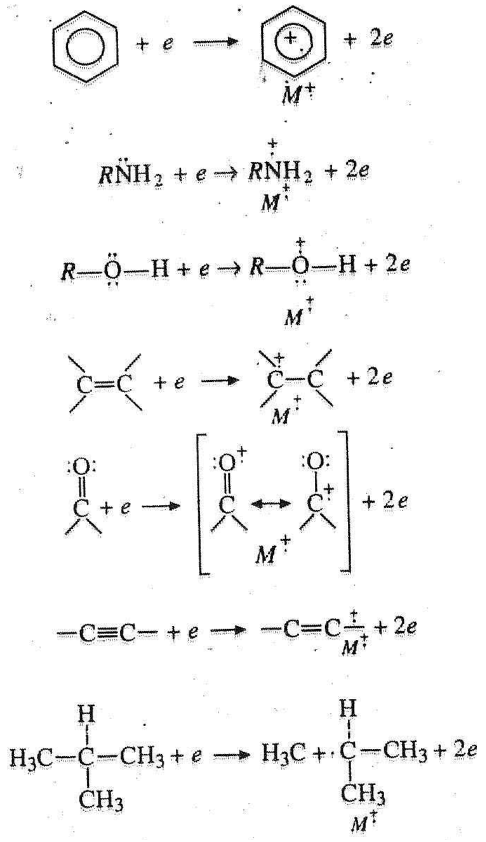
2.6.4 Mass Spectral Fragmentation of Organic Compounds

As discussed earlier, the bombardment with a beam of high energy electrons (70 eV) usually removes one electron from the molecule M to give the molecular or parent ion M^+ in vapour phase. The molecular ion gives the molecular mass of the sample because the mass of the electron lost from the molecule is negligible. The electron with the lowest ionization potential in the molecule is lost to give the molecular ion. The formation of molecular ions from some very common organic compounds are



The order of the energy required to remove an electron from the molecule to give the molecular ion is

lone pair < conjugated π < non-conjugated π < σ electron

In alkanes, the removal of an electron from C—C σ bonds is easier than that from C—H bonds.

The energy required for removing one electron from neutral organic molecules is about 10-12 eV. In practice, much higher energy ~70 eV (1 eV = 95 KJ mol^{-1}) is used which causes further fragmentation of the molecular ion resulting in *fragment* or the *daughter* ions. Generally, fragment ions are formed from the molecular ion in the following two ways:

$$M^+ \rightarrow \underset{\text{Even-electroncation}}{A^+} + \underset{\text{Radical}}{B^+}$$

$$M^+ \rightarrow \underset{\text{Radical cation}}{C^+} + \underset{\text{Neutral molecule}}{D^+}$$

Since only species bearing a positive charge are detected in the mass spectrometer, the mass spectrum will show signals due to M^+, A^+, C^+ and also due to fragment ions resulting from subsequent fragmentation of A^+ and C^+, but there will be no signal due to B^+ and D. Fragmentation of A^+ usually gives an even-electron ion E^+ and a neutral molecule G, whereas C^+ fragmentation in two ways similar to M^+. It should be noted that the mass spectrometer records signals due to radical cations and cations only. Any species may fragment in a variety of ways; so a mass spectrum consists of many signals.

2.6.5 Recognition of the Molecular Ion (Parent) Peak, Detection of Isotopes and Metastable Peak

The recognition of the molecular ion (M^+) peak (parent peak) in the mass spectrum is very important as it gives the molecular mass of the compound from which the molecular formula of the compound can be derived. The molecular ion peak is the peak of highest mass number except for the isotope peaks at mass numbers M^{+1}, M^{+2} etc. (M – mass of molecular ion).

The isotope (satellite) peaks appear because of the presence of certain number of molecules containing heavier isotopes than the common isotopes. Since the natural abundance of heavier isotopes is generally much more less than that of the lightest isotope, the intensities of isotope peaks are very low relative to the parent peak. Thus, M + 1 isotope peak appearing due to ^{13}C is about 1.1% of the molecular ion peak because the natural abundance of ^{12}C. For example, in the mass spectrum of methane, the M +1 isotope peak appears at m/e 17 and its abundance relative to the molecular ion peak is 1.1%. It should be noted that in this particular case the molecular ion peak itself is the base peak. The presence of ^{2}H(D) will make an additional but very small (0.016%) contribution to the M +1 peak because the natural abundance of deuterium is about 0.016% as compared to 99.984% natural abundance of ^{1}H.

Because of very low natural abundance of ^{13}C and ^{2}H the probability of finding two ^{13}C of ^{2}H in the same molecule is so low that M +2 peaks due to ^{13}C and ^{2}H are often negligible. Thus, for most of the organic compounds M+2 peaks are too small to be considered. However, for compounds containing chlorine, bromine or sulphur, the M +2 isotope peak is important. The M +2 isotope peak due to the presence of a chlorine or a bromine atom is about 33% or 50% of the molecular ion peak, respectively. Thus, in a chloro or bromo compound the ratio of intensity of M^+ and M +2 peaks will be 3:1 or 1:1, respectively. This is because of the 24.6% natural abundance of ^{37}Cl as compared to 75.4% of ^{35}Cl, and almost equal abundance of ^{79}Br and ^{81}Br (Table 8.2). Similarly, if one sulphur atom is present in a molecule, then according to the natural abundance (4.2%) of ^{34}S, the M +2 peak will be about 4.4% of the parent peak (the natural abundance of ^{32}S is 95.06%). Thus, the presence of CI, Br or S is easily detectable on the basis of the intensity of M +2 peak relative to the parent peak. Fluorine and iodine have no isotope, ie., they are isotopically pure. Natural abundances of isotopes of some common elements are given in Table 2.5.

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Table 2.5 *Natural Abundance of Isotopes of Some Common Elements*

Isotope	Natural abundance (%)	Isotope	Natural abundance (%)
^{1}H	99.984	^{19}F	100
^{2}H	0.016	^{31}P	100
^{12}C	98.9	^{32}S	95.06
^{13}C	1.1	^{33}S	0.74
^{14}N	99.64	^{34}S	4.2
^{15}N	0.36	^{35}Cl	75.4
^{16}O	99.76	^{37}Cl	24.6
^{17}O	0.04	^{79}Br	50.57
^{18}O	0.2	^{81}Br	49.43
		^{127}I	100

The intensity (height) of the molecular ion peak depends on following factors:

(i) Ionization potential: The lower the, ionization potential of a molecule, the stable is the molecular ion, and the more intense will be the molecular ion peak.

(ii) Structure of the compound: Since the stability of a chemical species is strongly affected by its structure, the intensity of the parent peak shows a great variability. Thus, in some cases the parent peak has the highest intensity, i.e., it is the base peak, whereas, in other cases it is not the base peak and may be even so small that a lot of effort is made to locate it.

(iii) The parent peak will be of low intensity if the molecule contains bonds that can be cleared easily.

(iv) In general, aromatic compounds, conjugated olefins, saturated cyclic compounds, certain sulphur compounds, and short, straight-chain, hydrocarbons give an intense molecular ion peak. Straight chain aldehydes, ketones, esters, acids, amides, ethers and halides give a recognizable parent peak. Aliphatic alcohols, amines, nitrites, nitrates, nitro compounds, and highly branched compounds give a parent peak which is frequently not detectable.

(v) When identification of molecular ion peak is difficult because it is very weak or does not appear, in such cases spectrum should be run at maximum sensitivity using larger quantity of sample.

(vi) If the molecular ion peak is present but it is one of the several peaks, then the energy of the bombarding electron beam should be decreased. This reduces the intensity of all peaks, but increases the intensity of the molecular ion peak relative to other peaks.

Confirmation of the Recognized Molecular Ion Peak

The confirmation of the molecular ion peak is ascertained by following methods:

1. Ring Rule or Index of Hydrogen Deficiency (IHD)

The molecular ion must be an odd-electron ion. So, if the elemental composition of the ion is known, the index of hydrogen deficiency may be used to recognize the molecular ion in question. There may be other odd-electron fragment ion besides the molecular ion in the spectrum which arise from rearrangement reactions. The index of hydrogen deficiency for a molecular ion (or any other odd electron fragment) must be a whole number (an integer).

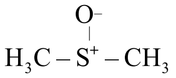
The index of hydrogen deficiency is the number of pairs of hydrogen atoms which must be removed from the saturated formula (e.g. C_nH_{2n+2} for alkanes) to give the molecular formula in question. Thus, the index of hydrogen deficiency is the sum of the number rings, the number of double bonds and twice the number of triple bonds. For a molecule $I_y\, II_n\, III_z\, IV_x$ (e.g., $C_xH_yN_zO_n$),

The index of hydrogen deficiency = $x - \frac{y}{2} + \frac{z}{2} + 1$ (5)

where I is any monovalent atom (e.g., H, F, Cl, Br, etc.), II is the O, S or any other divalent atom, III is the N, P or any other trivalent atom and IV is the C, Si or any other tetravalent atom.

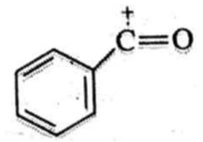
For example, acetone has an index of hydrogen deficiency of $\left(3 - \frac{6}{2} + 1\right) = 1$, because it has one C=O. Similarly, the index of hydrogen deficiency for pyrrole would be $\left(4 - \frac{5}{2} + \frac{1}{2} + 1\right) = 3.$

This is because it has two C=C and one ring. The calculated index of hydrogen deficiency for dimethyl sulphoxide (DMSO) is zero, which is in agreement with its following polar structure.



$$H_3C - \overset{\overset{\displaystyle O^-}{|}}{S^+} - CH_3$$

Eq. (8.5) can be applied to molecules, molecular ions and fragment ions. The index of hydrogen deficiency is always a whole number for odd-electron ions, whereas, it has a non-integral value (odd multiple of 0.5) for even-electron (all electrons paired) ions. Thus, the values of the index of hydrogen deficiency can be applied to molecular ions as well as fragment ions to get useful information. For example, $C_7H_5O^+$ has an index of 5.5 which suggests its following reasonable structure.



Metastable Peak: Metastable peaks have been observed from the unimolecular decomposition of an excited intermediate ion formed by ion-molecule reaction in a high-pressure chemical ionization source.

2.6.6 McLafferty Rearrangement and Nitrogen Rule

Many mass spectral fragmentations are associated with rearrangement process involving bond breaking and bond making. The most thoroughly studied example

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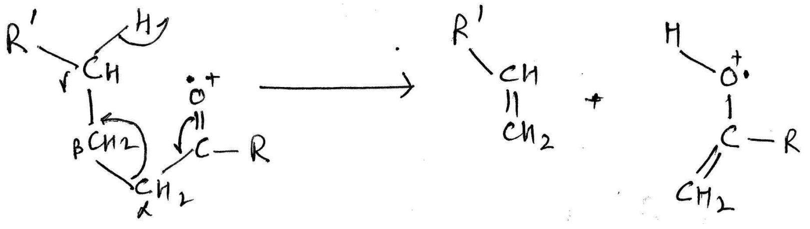
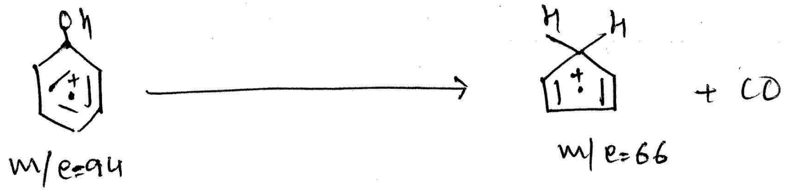
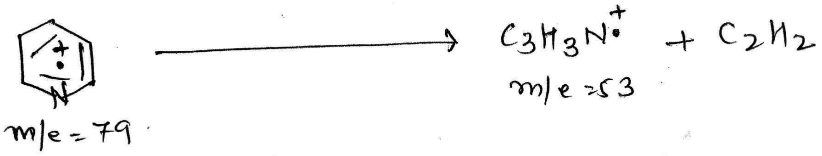
involves γ-hydrogen rearrangement commonly referred to as McLafferty rearrangement. This is of common occurrence in mass spectra of aldehydes (e.g., R=H), Ketones (e.g., R=alkyl), acids (R=OH) or esters (e.g., R= O–alkyl) containing a γ-hydrogen atom. The rearrangement process usually results in the formation of a changed 'enal' and a neutral 'olefin'. The rearrangement is easily recognized as the charged moiety having even *m/e* value.

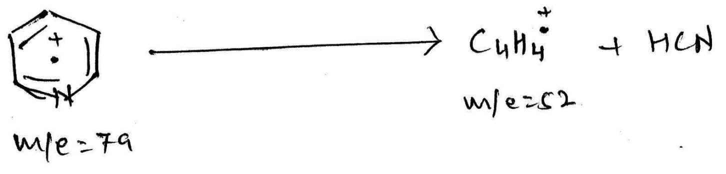


Nitrogen Rule

All stable organic molecules have an even integral molecular weight except for those which contain an odd nuclear of nitrogen atoms. The appearance of an odd number molecular ion, thus reveals the presence of a nitrogen atom in a molecule. On further extension we can say that an odd-electron ion, including a molecular ion, will have an even *m/e* value unless it contains an odd number of nitrogen atoms. For example,

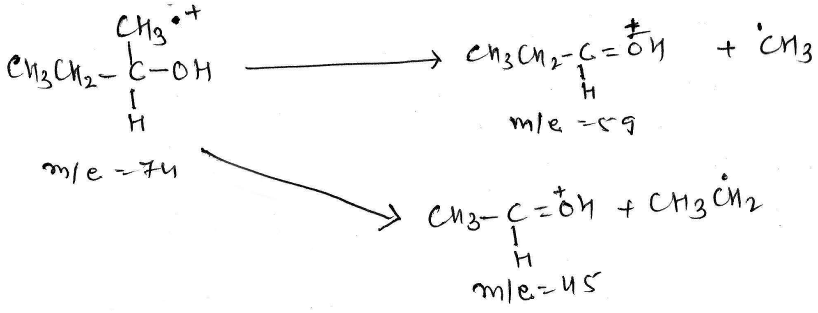




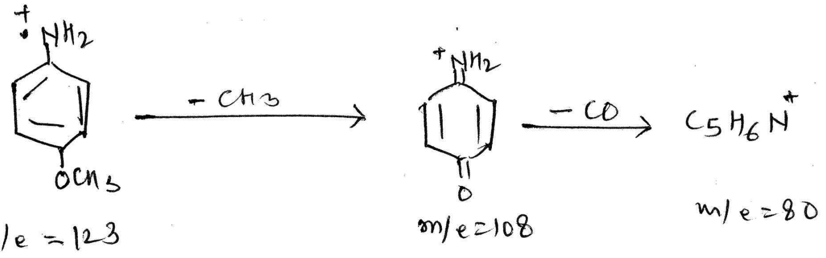


We can generalize that all even-electrons will have odd *m/e* values unless they contain an odd number of nitrogen atoms. For example,

(i)



(ii)



2.6.7 High Resolution Mass Spectrometry

The main compounds of a single focusing mass spectrometer are shown in fig ….. and discussed below.

(i) Inlet or Sample Handling System: This system allows the introduction of a small quantity (ranging from several milligrams to less than a microgram) of vapour of the sample under analysis into the ionization chamber. The pressure in the inlet system is greater than that in the ionization chamber.

(ii) Ionization Chamber: The vapour of the sample from the inlet system enters the ionization chamber (operated under high vacuum, at about 10^{-6} to 10^{-5} Torr) where it is bombarded by a beam of electrons of about 70 eV energy. The various positive ions thus produce are first accelerated by a repeller potential applied between A and B. Then they are accelerated to their final velocities by applying a large (-8 kV) accelerating potential V between B and C (figure 2.48)

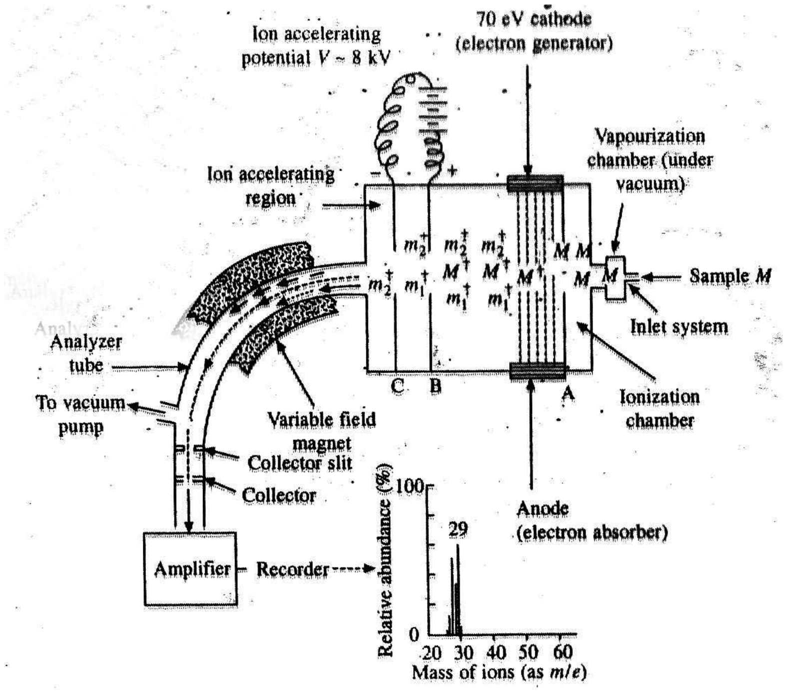


Fig. 2.48 Schematic Diagram of a Mass Spectrometer

(iii) Mass Analyzer: This part of the mass spectrometer separates ions according to their masses (strictly according to their *mle.* The accelerated positively charged ions from the ionization chamber enter the mass analyzer where they pass through a uniform perpendicular magnetic field H).

The kinetic energy of an ion of mass m and velocity v is $\frac{1}{2}mv^2$. Let the accelerating potential be V, then the energy given to each singly charged ion is eV. Hence, the kinetic energy possessed by the ion should be equal to this given energy, i.e.

$$\frac{1}{2}mv^2 = eV \tag{1}$$

The magnetic field H causes the ions to move in a circular path of radius r. The force of attraction (centripetal force) of the magnetic field is given by Hev which is balanced by the centrifugal force $\frac{mv^2}{r}$ at the equilibrium (Newton's second law of motion), i.e.

$$Hev = \frac{mv^2}{r} \tag{2}$$

Replace v with θ in the equations.

Squaring both sides, we get

$$H^2e^2v^2 = \frac{m^2v^4}{r^2}$$

$$H^2e^2 = \frac{m^2v^2}{r^2} \tag{3}$$

From Eq. (1) $\frac{1}{2}mv^2 = ev$

Therefore, $mv^2 = 2eV$

Putting the value of mv^2 in Eq. (3), we get

$$H^2e^2 = \frac{m.2eV}{r^2}$$

Or $$H^2e = \frac{2mV}{r^2}$$

Or $$m/e = \frac{H^2r^2}{2V} \tag{4}$$

It is clear from Eq. (4) that the radius r of the ion path can be changed by varying the magnetic field H at a constant accelerating voltage V or by varying V at a constant H which allows magnetic or voltage scanning of the mass spectrum respectively. The spectrum is generally obtained by magnetic scanning, i.e., H is increased keeping V constant. On increasing H, the ions of progressively higher m/e attain the necessary radius to pass through the collector slit sequentially.

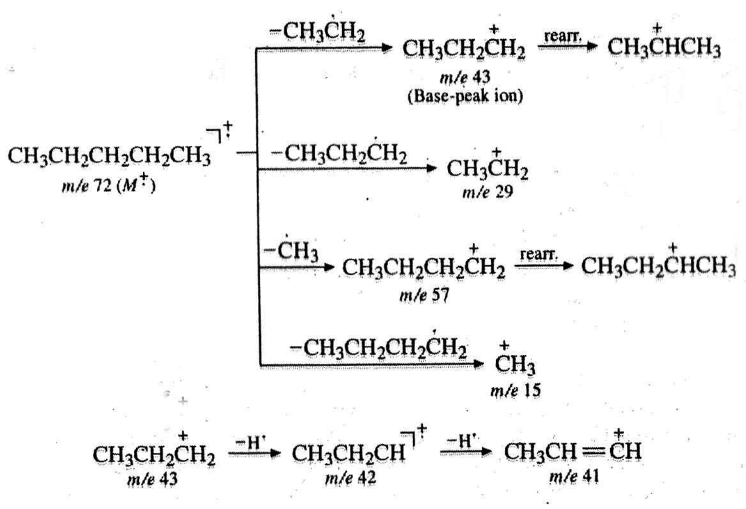
(iv) Ion Detector and Spectrum Recorder: The streams of ions of different m/e impinge into the ion collector and the amplified current from the ion collector is recorded as relative abundances of ions on y-axis of the recorder. The magnetic or voltage scanning is synchronized with the x-axis of the recorder and calibrated to appear as m/e.

2.6.8 Mass Spectral Fragmentation of Organic Compounds with Respect to Structure Determination

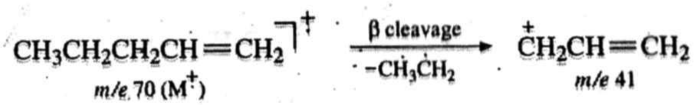
Various classes of organic compounds exhibit characteristic mass spectral features which are very useful in structure elucidation.

(A) Hydrocarbons

1. Alkanes (Straight Chains): Their mass spectra are characterized by groups of peaks separated by 14 (CH_2) mass units. The largest peak in each group corresponds to C_nH_{2+1} fragment, and it is accompanied by much smaller peaks due to C_nH_{2n} and C_nH_{2n-1} fragments formed by loss hydrogens. The most intense peaks are at m/e 43 and 57 due to and fragment ions, respectively. These ions are highly branched and arise via molecular rearrangements. Any molecular or fragment ion will give a peak at one mass unit higher due to the presence of ^{13}C. Abundance of this peak will be N × 1.1% of the abundance of the ^{12}C containing peak, where N is the number of carbon atoms in that ion and 1.1% is the natural abundance of ^{13}C. The molecular ion peak is always present in the mass spectra of straight-chain alkanes but its intensity decreases as the molecular mass increases. Mode of fragmentation of pentane show as:



2. Alkenes (Olefins): Similar to alkanes, acyclic olefins are also characterized by groups of peaks separated by 14 (CH_2) mass units. In these groups, the C_nH_{2n-1} and C_nH_{2n} peaks are more intense than the C_nH_{2n+1} peaks. Molecular ion peaks of unsaturated compounds are more intense than the corresponding saturated analogues. Because of facile migration of the double bond after electron impact ionization, its location is difficult in acyclic olefins. The most common fragmentation of alkenes is the allylic cleavage, i.e., cleavage of the bond β to the double bond resulting in the formation of a resonance stabilized allylic cation. Alkenes having a γ hydrogen with respect to the double bond also undergo the McLafferty rearrangement. For example, the prominent mode of fragmentation of 1-pentene is



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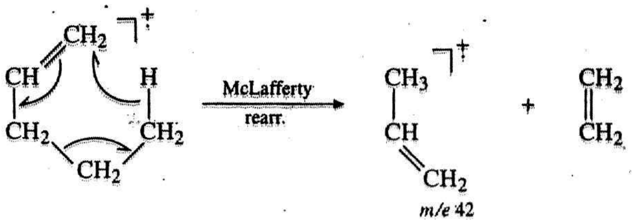
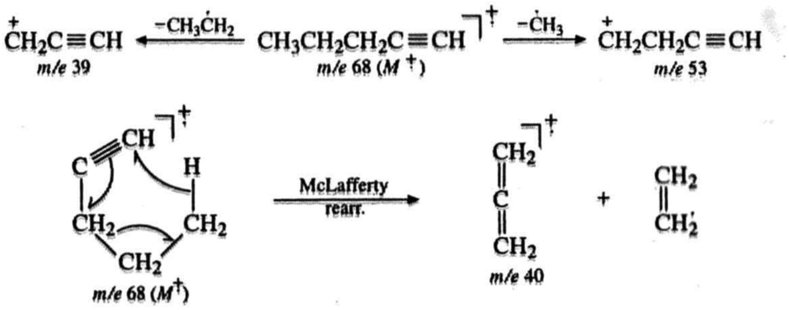
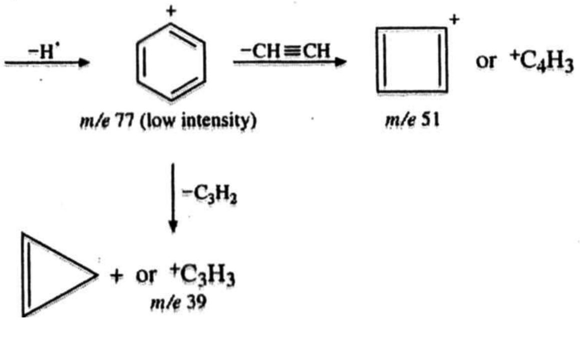


The formation of an even mass ion from an even mass molecular ion, and an odd mass ion from an odd mass molecular ion indicates that the fragmentation has occurred through a rearrangement involving the cleavage of two bonds. This is true only when the fragment ion contains all the nitrogen atoms (if any) of the molecular ion.

3. Alkynes: In alkynes, the fragment ions (with composition C_nH_{2n-3}) are generally formed by loss of alkyl radicals. Thus, M-15, M-29, M-43 etc. peaks are commonly present in the mass spectra of alkynes. Alkynes having a γ hydrogen with respect to the triple bond also undergo the McLafferty rearrangement. The molecular ion peaks in alkynes are usually distinct. In case of 1-butyne and 2-butyne, the molecular ion peak is the base peak. Taking the example of 1-pentyne, the fragmentation mode of alkynes is

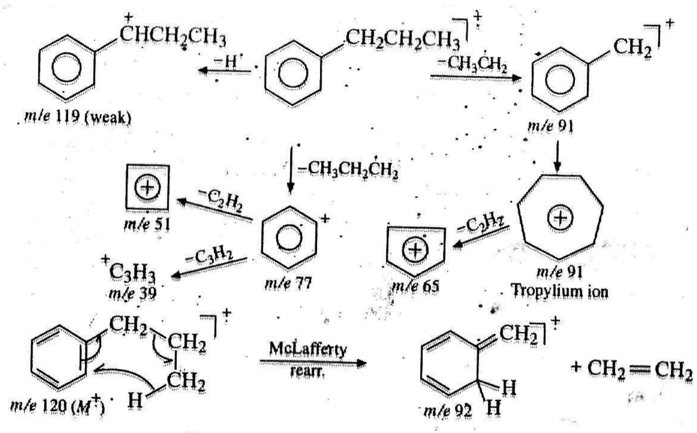


4. Aromatic Hydrocarbons: Molecular ion peaks in aromatic compounds are fairly large because an aromatic ring stabilizes the molecular ion. These are accompanied by M + 1 and M + 2 peaks due to ^{13}C and/or D. In alkyl-benzenes, the dominant fragmentation involves the cleavage of the bond β to the aromatic ring (benzylic cleavage) because it gives resonance stabilized carbocations.



The low intensity of the peak of phenyl cation is understandable because the positive charge of this cation is in empty sp^2 orbital and consequently cannot interact with π-electrons of the ring. Hence, the phenyl cation is not stabilized by resonance. Due to its less stability, intensity of its peak is low.

In alkyl-benzenes, β-cleavage is most favourable. It gives a benzyl cation which changes to the more stable troplium ion. When the side chain has at least three carbon atoms, McLafferty rearrangement also takes place. For example, the fragmentation of n-propyl-benzene is as follows:



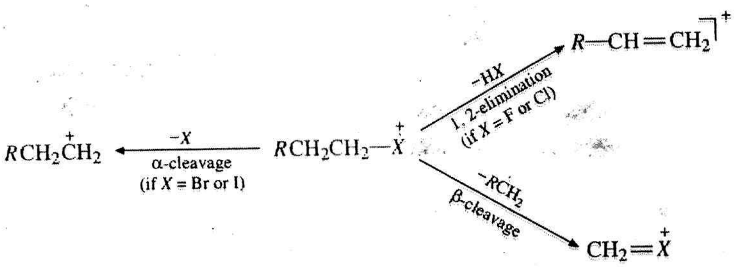
Fragmentation pattern of *n*-propylbenzene

5. Alkyl Halides: The intensities of molecular ion peaks of alkyl halides follow the order:

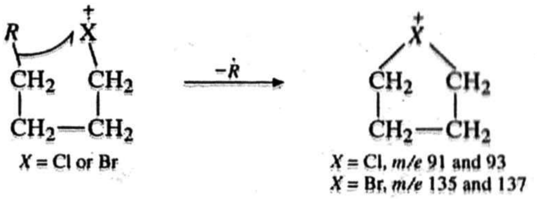
RI > RBr > RCl > RF

The intensity of the molecular ion decreases with increase in chain length and increases in branching.

Cleavage of a C–C bond β to the halogen atom is the favourable mode of fragmentation. Alkyl fluorides and chlorides also fragment by loss of HF and HCl to give peaks at M-20 in case of fluorides, and at M-36 and M-38 in case of chlorides. However, in alkyl bromides and iodides, loss of Br^+ and I^+ is preferred. For example,

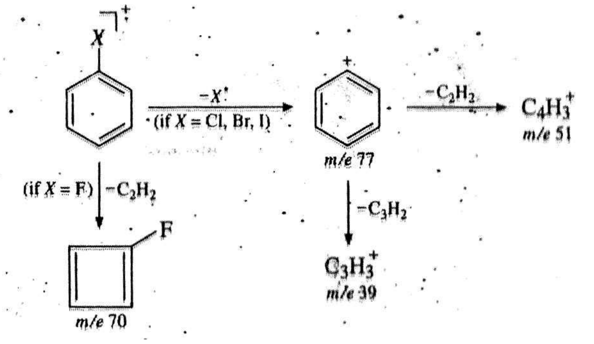


Straight-chain chlorides and bromides longer than C_6 give $C_3H_6X^+$, $C_4H_8X^+$ and $C_5H_{10}X^+$ ions. Of these, $C_4H_8X^+$ gives the most intense (sometimes the base) peak. (m/e 91 and 93 in chlorides, and m/e 135 and 137 in bromides). The intensity of these ions is attributed to the stability of the five-membered cyclic structure.

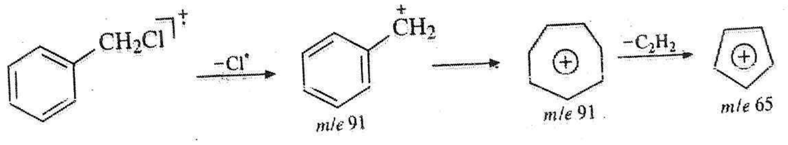


Small peaks due to HCl^+, HBr^+, Cl^+, Br^+ etc. may also be detected

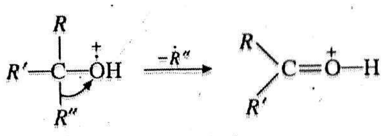
6. Aryl Halides: MX peak is intense for all compounds containing x- directly attached to the ring. For example, mode of fragmentation of a halobenzene is



Benzyl halides lose halogen to form benzyl cation which changes to the more stable tropylium ion. For example,



7. Aliphatic Alcohols: In all the three classes of alcohols, i.e., primary, secondary and tertiary alcohols, the α-cleavage of C–C bond is characteristic. The largest alkyl group is expelled most readily as a radical because a long-chain radical is stabilized by delocalization of the lone electron. When R and/or R' = H, a M-1 peak is often observed. In long-chain (long than C_6) alcohols, the fragmentation pattern is dominated by the hydrocarbon pattern.

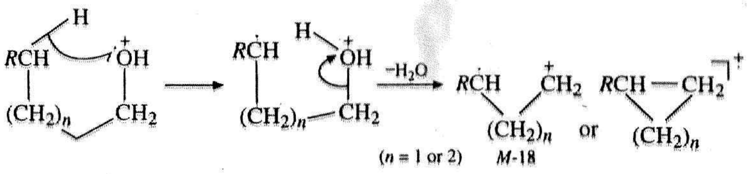


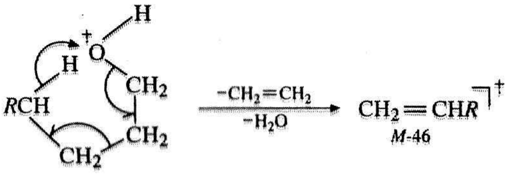
$R'' > R'$ or R = alkyl

The molecular ion peaks of primary or secondary alcohols are weak and that of tertiary alcohols are either very weak or undetectable. Long-chain primary alcohols show small M-2 and M-3 peaks.

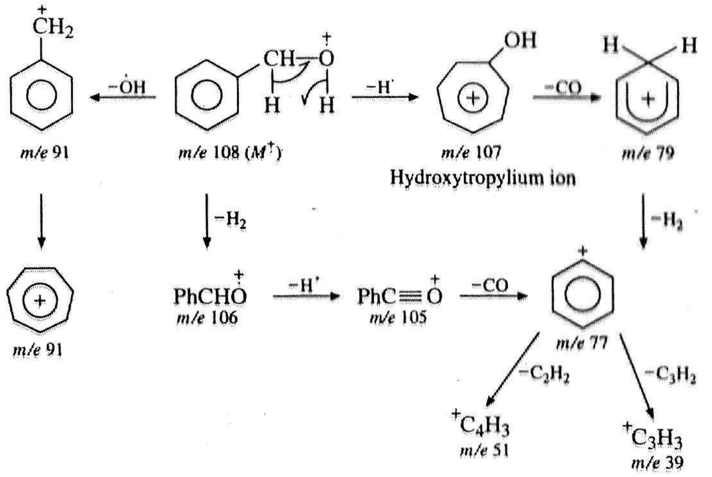
$$\underset{M\text{-}2}{R\text{—}\mathrm{CH}\overset{+}{\mathrm{O}}} \xleftarrow{-2\mathrm{H}} R\mathrm{CH_2}\overset{+}{\mathrm{O}}\mathrm{H} \xrightarrow{-3\mathrm{H}} \underset{M\text{-}3}{R\text{—}\mathrm{C}\equiv\overset{+}{\mathrm{O}}}$$

The most characteristic fragmentation of higher alcohols is associated with elimination of water to give a distinct peak at M-18. This peak is prominent in the mass spectra of primary alcohols

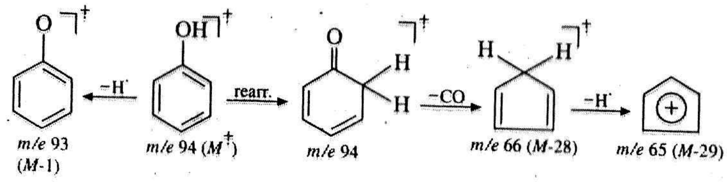




8. Aromatic Alcohols: Molecular ion peak is generally strong in benzyl alcohols. Benzylic cleavage occurs and the charge is retained by the aryl group. Prominent M-1, M-2 and M-3 peaks are noticed. As an example, the fragmentation mode of benzyl alcohol is given below:

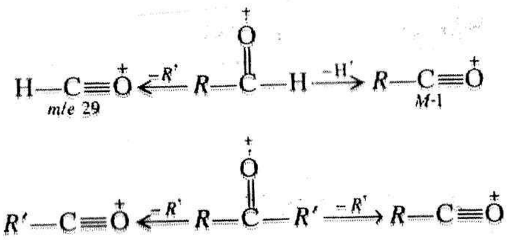


9. Phenols: Phenols exhibit prominent molecules ion peaks. In phenol itself, the molecular ion peak is the base peak. The most common fragmentations in phenols involve the loss of CO (M-28) and CHO (M-29). In addition, a small peak at M-1 is also observed due to loss of hydrogen radical.



10. Aldehydes and Ketones: Their molecular ion peaks are prominent and they undergo following two important types of cleavage:

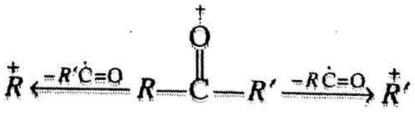
1. **α-Cleavage :** This involves the cleavage of the C – C bond next to the oxygen atom to give resonance-stabilized acylium ions as



$$\underset{m/e\ 29}{H{-}C{\equiv}\overset{+}{O}} \xleftarrow{-R'} R{-}\overset{\overset{+}{O}}{\overset{\|}{C}}{-}H \xrightarrow{-H'} \underset{M\text{-}1}{R{-}C{\equiv}\overset{+}{O}}$$

$$R'{-}C{\equiv}\overset{+}{O} \xleftarrow{-R'} R{-}\overset{\overset{+}{O}}{\overset{\|}{C}}{-}R' \xrightarrow{-R'} R{-}C{\equiv}\overset{+}{O}$$

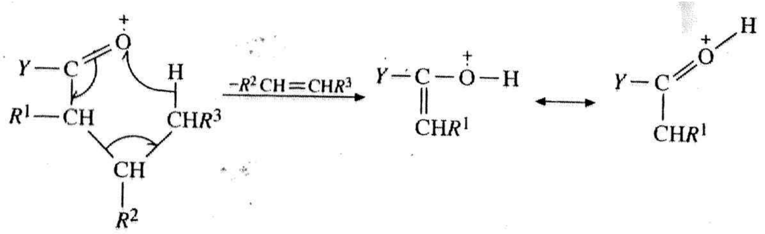
The M-1 peak is characteristic of aldehydes. In aliphatic aldehydes, (M–R ion) is more abundant than the M-1 (M – H) ion. In aliphatic ketones, the larger alkyl group is preferably lost as a radical. The α-cleavage in ketones may also occur with charge retention by the alkyl group.



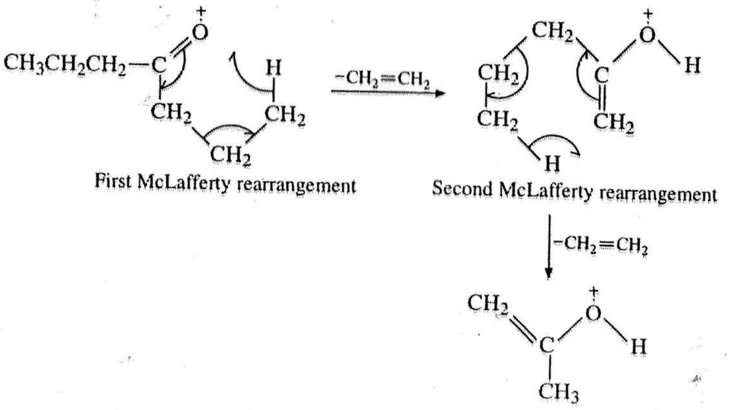
$$\overset{+}{R} \xleftarrow{-R'\dot{C}=O} R{-}\overset{\overset{+}{O}}{\overset{\|}{C}}{-}R' \xrightarrow{-R\dot{C}=O} \overset{+}{R'}$$

NOTES

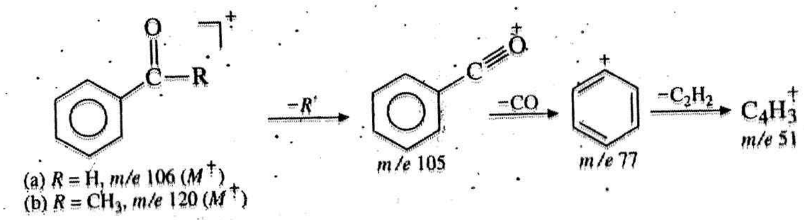
2. â-Cleavage (McLafferty rearrangement): Aldehydes and ketones containing a γ-hydrogen atom undergo β-cleavage via McLafferty rearrangement as:



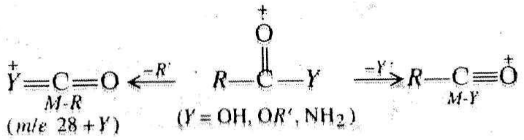
Aliphatic ketones undergo double McLafferty rearrangement if each of the alkyl groups attached to C=O group contains a three carbon or longer chain. For example, 4-heptanone:



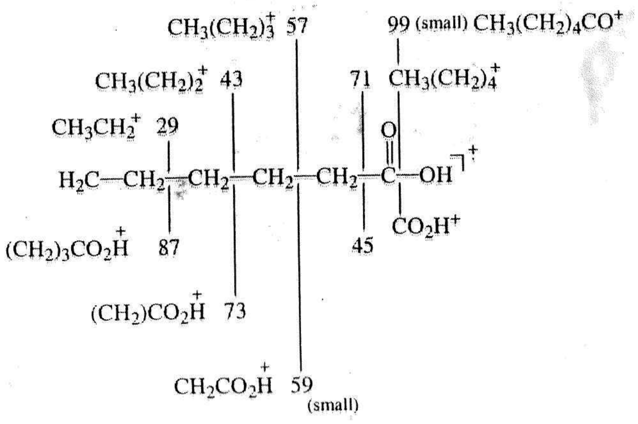
Aromatic aldehydes and ketones undergo α-cleavage to give characteristic ion which usually accounts for the base peak. Aromatic aldehydes show prominent M-1 peak, i.e. the loss of the aldehydic hydrogen from the molecular ion is favoured due to the stability of. Both benzaldehyde (a) and acetophenone (b) show strong peaks at m/e 105 due to and this further fragments as follows:



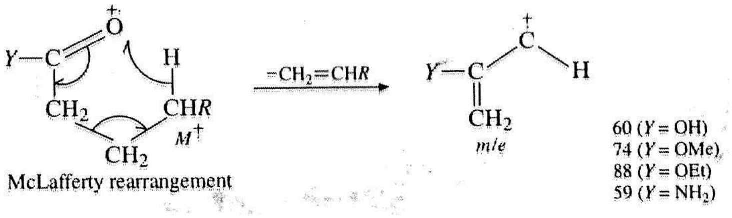
11. Carboxylic Acids, Esters and Amides: These organic compounds give detectable molecular ion peaks. Aliphatic acids, esters and amides undergo α-cleavage, i.e., cleavage of bonds next to C=O, and the positive change may remain with R or Y . R^+ and Y^+ may also appear.



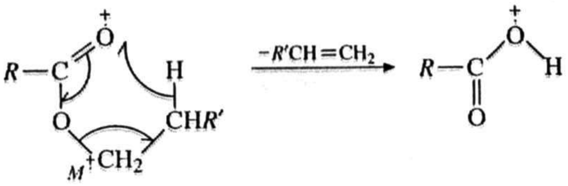
Long-chain acids exhibit two series of peaks resulting from cleavage at each C–C bond with retention of charge either on the oxygen-containing fragment (m/e 45, 59, 73, 87, …) or on the alkyl fragment (m/e 29, 43, 57, 71, 85 …). For example, this fragmentation pattern occurs in hexanoic acid (caproic acid) as:



Methyl esters of long-chain acids also follow the same fragmentation pattern. Carboxylic acids, esters and amides and amides undergo McLafferty rearrangement if they contain γ hydrogen.

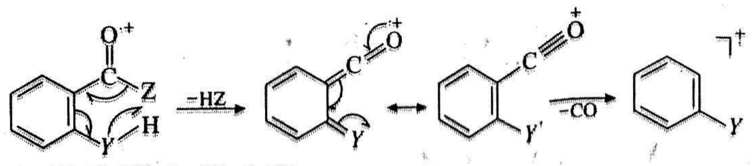


Esters containing ethoxy or longer alkoxy group also undergo another type of McLafferty rearrangement as:



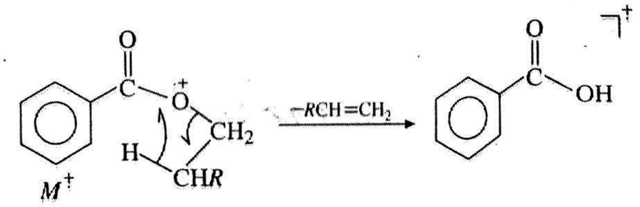
Aromatic acids, esters and amides show intense molecular ion peaks. These compounds undergo fragmentation mode similar to that of aromatic aldehydes and ketones. R=OH for acids, R=O Me for esters and R=NH_2 for amides.

Ortho Effect: When a substituent and a hydrogen are in close proximity to form a six-membered transition state, the loss of neutral molecules of H_2O, ROH or NH_3 occurs. This is called *ortho* effect. For example, the *ortho* effect is observed in aromatic carboxylic acids, esters and amides if an *ortho* substituent containing a hydrogen atom is present as shown below:

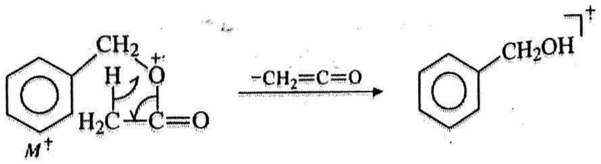


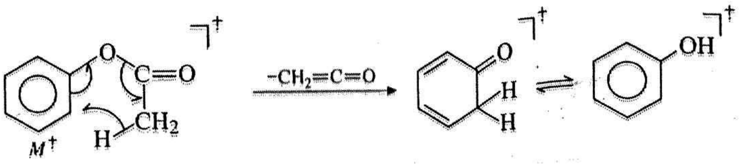
Z = OH, OR, NH_2; Y = CH_2, O, NH

Aromatic esters with ethyl or higher alkyl group eliminate alkene through hydrogen rearrangement similar to ethers.

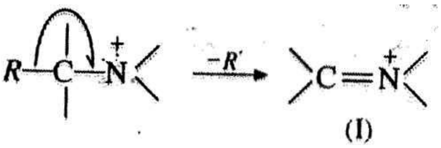


Benzyl and phenyl acetates eliminate ketenes to form the base peak. In case of benzyl acetate, peaks due to (m/e 43) and tropylium ion (m/e 91) are also prominent.

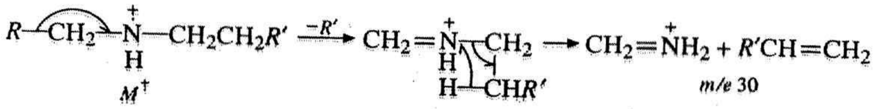




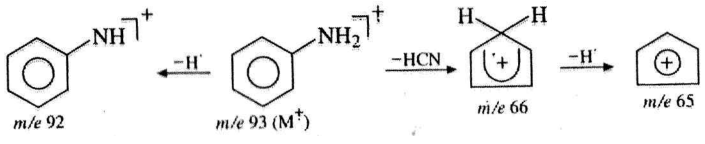
12. Amines: The cleavage of the C – C bond next to the nitrogen atom is most favourable fragmentation pattern in case of aliphatic amines. The cleavage is so favourable that the molecular ion peak is often not observed. This mode of fragmentation is similar to that of alcohols and ethers. In case of all primary, secondary and tertiary amines that are not branched at the α-carbon, the ion I accounts for the base peak. The largest alkyl group is lost as a radical in this cleavage. In amines containing an α hydrogen, usually M-1 peak is visible.



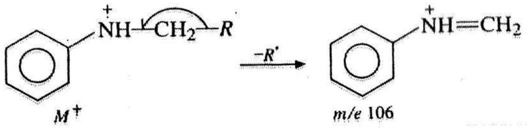
The primary fragment (I) from a secondary or tertiary amine undergoes fragmentation via hydrogen rearrangement similar to that described for aliphatic ethers to give a peak at m/e 30, 44, 58 or 72,…, e.g.



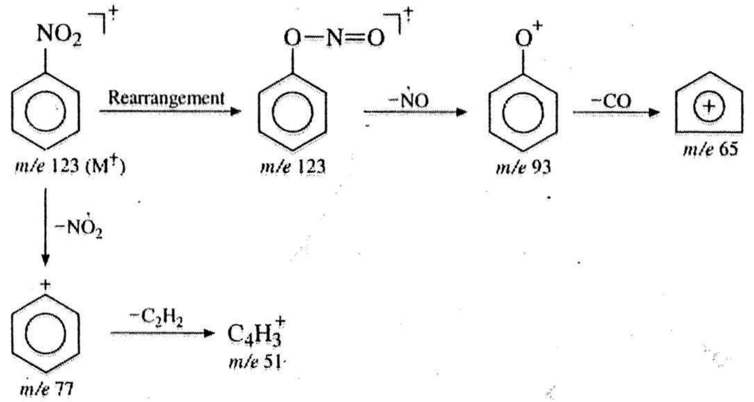
Aromatic amines show intense molecular in peak. Loss of one of the amines hydrogens of aniline gives an intense M-1 peak. Loss of HCN followed by loss of a H-atom also gives a prominent peak. Fragmentation pattern of aniline is given as:



The case of N-alkylanilines (alkyl aryl amines), cleavage of C–C bond next to the nitrogen atom is dominant, e.g.

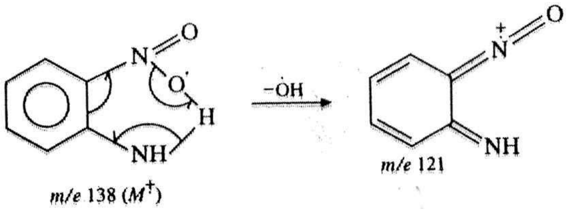


13. Aromatic Nitro Compounds: Their molecular ion peak are strong. Elimination of an NO_2 radical gives M-46 peak (the base peak in nitrobenzene) and neutral NO molecule is lost to give strong M-30 peak due to the phenoxy cation (m/e 93). For example, the fragmentation pattern of nitrobenzene is given as

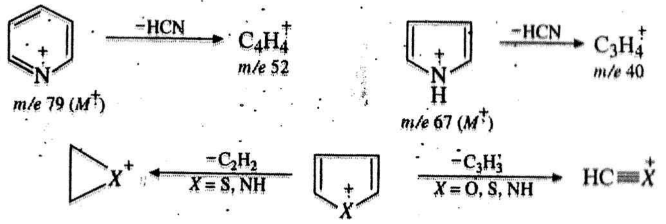


Peaks due to and are also observed at m/e 30 and 46, respectively, in the mass spectrum of nitrobenzene.

When a substituent is present in the m- or p- positions, e.g. in m- and p-nitroanilines, the fragmentation pattern similar to that of nitrobenzene is observed. However, when a hydrogen-containing substituent is present ortho to the nitro group, M-OH peak is also observed, e.g.



14. Heterocyclic Compounds: Aromatic heterocyclic compounds show intense molecular ion peak. They undergo fragmentation similar to benzene, e.g., benzene eliminates C_2H_2 from its molecular ion, whereas, pyrrole and pyridine loose ion. Pyrrole, thiophene and furan also eliminate C_3H_3 from their molecules ions to give and ions, respectively.



Check Your Progress

19. Who gave the Mass spectroscopy?
20. What is electron impact method of ion production?
21. Define the chemical ionization method of ion production.
22. State the nitrogen rule.

2.7 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Nuclear Magnetic Resonance Spectroscopy is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule.
2. The protons in molecules are surrounded by electrons which shield them from the applied magnetic field H to different extent. Hence the magnetic field experienced by different protons in different environments in a molecule is somewhat lower or

   $H_{\text{effective}} = (1-\sigma)H°$

   Where, σ is known as shielding constant.
3. The separation of resonance frequencies of protons in different structural environments from some arbitrary standard is termed as chemical shift.
4. The phenomenon of exchange of hydroxylic protons between different ethanol molecules is called chemical exchange.
5. Decoupling is the process of removing ^{13}C-^{1}H coupling interaction to simplify a spectrum and identify which pair of nuclei is involved in the J coupling.
6. Virtual coupling is a phenomenon in which the first-order multiplets contain the false coupling information.
7. Stereochemistry is a branch of chemistry that deals with the study of the relative spatial arrangement of atoms that form the structure of molecules and their manipulation.
8. Protons attached to the same carbon atoms and having different chemical environments are called geminal protons.
9. Protons attached to the adjacent atoms are called vicinal protons (I).
10. Karplus relationships are very useful for determining the stereochemistry of organic compounds.
11. NOESY spectroscopy has become especially useful in the study of large molecules, such as, proteins and poly nucleotides.
12. INEPT is a signal resolution enhancement method used in NMR spectroscopy.
13. The Attached Proton Test (APT) is a ^{13}C NMR experiment that is used as an aid to assignment by separating carbons unattached to protons and CH_2 signals from CH and CH_3 signals.

14. The INADEQUATE technique is used to measure ^{13}C-^{13}C coupling constants and for determining carbon-carbon connectivity by determining coupling magnitudes which are common to two carbon atoms.
15. Hyperfine coupling is a special feature of ESR caused by the interaction of electron spins with the magnetic nuclei in the sample.
16. Spin polarization is the degree to which the spin, i.e., the intrinsic angular momentum of elementary particles, is aligned with a given direction.
17. The spin-orbit coupling terms in the molecular electronic Hamiltonian have important, spectroscopically observable, effects. In states possessing an orbital degeneracy. They produce a first-order splitting of the various multiplet levels.
18. The g-tensor arises from the interaction of the electronic spin with external magnetic field.
19. Mass spectroscopy was first used by J.J. Thompson in 1912, F.W. Aston in 1919.
20. In electron impact method, the sample is bombarded in the vapour phase with a because of high energy electrons (70 eV).
21. In chemical ionization method, the sample is introduced into the ionization chamber near the atmospheric pressure with a large excess of an intermediate substance (methane, iso-butane or NH_3) also called the carrier gas.
22. Nitrogen rule states that; all stable organic molecules have an even integral molecular weight except for those which contain an odd nuclear of nitrogen atoms.

2.8 SUMMARY

- Nuclear Magnetic Resonance Spectroscopy is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule.
- The energy of radio frequency wave having frequency of 107 to 108 cycle per second is about 6.6 × 10– 20 to 6.6 × 10– 19 ergs.
- In NMR techniques, mainly organic compounds are exposed to a powerful magnetic field.
- The shielding effect is proportional to the magnitude of the applied magnetic strength and therefore the magnitude of chemical shifts is also dependent on the strength of applied magnetic field. Different kind of protons in organic compounds absorb at frequencies spread over 700 cycles per second at a magnetic field of 14,000 gauss.
- The chemical shift values of different nuclei in a molecule arise due to differences in the local magnetic field felt by nuclei in different parts of the molecule.

- The term chemical exchange is used to explain the fact that during a certain period of time, a single hydroxyl proton may be attached to a number of different ethanol molecules.
- Deuterium is easily introduced into a molecule and its presence in a molecule is not detected in the PMR spectrum because it absorbs at different field strengths.
- The vicinal coupling is the most useful information of dihedral angle, leading to stereochemistry and conformation of molecules.
- Virtual coupling is a phenomenon in which the first-order multiplets contain the false coupling information. In extreme cases, protons that are not actually coupled will show splitting.
- Stereochemistry is a branch of chemistry that deals with the study of the relative spatial arrangement of atoms that form the structure of molecules and their manipulation.
- The distance between the centers of two adjacent peaks in a multiplet is called coupling constant or spin-spin coupling constant, or spin-spin coupling constant, denoted by J.
- Protons attached to the adjacent atoms are called vicinal protons (I).
- Nuclear Overhauser Effect (NOE) is a change in the intensity of absorption of a nucleus on double irradiation of another nucleus. In this case, less intense radiation is used than that in spin tickling.
- Hyperfine shifts result from two mechanisms, contact shifts and pseudo-contact shifts.
- The effect of the contact shift arises from transfer of unpaired spin density to the observed nucleus.
- The effect of the pseudo-contact shift arises from magnetic anisotropy of the paramagnetic center (reflected in g-anisotropy in the EPR spectrum).
- Relaxation processes involve some non-radioactive transitions by which a nucleus in an upper transition state returns to the lower spin state.
- Spin polarization is the degree to which the spin, i.e., the intrinsic angular momentum of elementary particles, is aligned with a given direction.
- The g-tensor arises from the interaction of the electronic spin with external magnetic field.
- Transition metal complexes or coordination complexes are molecules that contain groups arranged around a central metal ion.
- The mass spectrum is a record of the relative numbers of different kinds of ions and is characteristics of energy compound, including isomers.
- Most of the fragmentation processes involve elimination of radicals from radical cations.
- The most thoroughly studied example involves γ-hydrogen rearrangement commonly referred to as McLafferty rearrangement.

2.9 KEY TERMS

- **NMR Spectroscopy:** Nuclear Magnetic Resonance Spectroscopy is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule.
- **Chemical Shift:** The separation of resonance frequencies of protons in different structural environments from some arbitrary standard is termed as chemical shift.
- **Chemical Exchange:** The phenomenon of exchange of hydroxylic protons between different ethanol molecules is called chemical exchange.
- **Vicinal Coupling:** The Vicinal coupling is the most useful information of dihedral angle, leading to stereochemistry and conformation of molecules.
- **Decoupling:** Decoupling is the process of removing ^{13}C-^{1}H coupling interaction to simplify a spectrum and identify which pair of nuclei is involved in the J coupling.
- **Virtual Coupling:** Virtual coupling is a phenomenon in which the first-order multiplets contain the false coupling information.
- **Stereochemistry:** Stereochemistry is a branch of chemistry that deals with the study of the relative spatial arrangement of atoms that form the structure of molecules and their manipulation.
- **Coupling Constant:** The distance between the centers of two adjacent peaks in a multiplet is called coupling constant.
- **Geminal Protons:** Protons attached to the same carbon atoms and having different chemical environments are called geminal protons.
- **Vicinal Protons:** Protons attached to the adjacent atoms are called vicinal protons (I).
- **Spin Polarization:** Spin polarization is the degree to which the spin, i.e., the intrinsic angular momentum of elementary particles, is aligned with a given direction.

2.10 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What do you mean by radio frequency absorption?
2. What do you understand by chemical shifts?
3. Define Shielding Effect.
4. Define spin-spin splitting
5. Define hindered rotation.
6. What do you understand by contact shift reagent?
7. Define resonance.

8. Define hyperfine coupling.
9. State the significance of g-tensor.
10. What do you understand by Ion analysis and ion abundance?

Long-Answer Questions

1. Explain the shielding mechanism.
2. Describe the effect of deuteration.
3. Explain in detail the two-dimensional NMR spectroscopy.
4. Describe the complex spin-spin interaction between various nuclei.
5. Explain in detail the Karplus Curve- Variation of Coupling Constant with Dihedral Angle.
6. Describe Nuclear Magnetic Double Resonance (Spin Decoupling) in detail.
7. Explain in detail the Nuclear Overhauser Effect (NOE).
8. Describe the factors affecting nuclear relaxation.
9. Explain in detail the 2D-NMR.

2.11 FURTHER READING

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NOTES

UNIT 3 APPLICATIONS OF SPECTROSCOPY: MOSSBAUER SPECTROSCOPY, OPTICAL ROTATORY DISPERSION, AND CIRCULAR DICHROISM

Structure

3.0 INTRODUCTION

Spectroscopy is the science concerned with the investigation and measurement of spectra produced when a material interacts with a source of light and emits electromagnetic radiation.

Mössbauer spectroscopy consists of the study of γ-ray absorption (or emission) spectra for transition between nuclear states. This technique has now become a very powerful tool for understanding problems in different branches of science.

Optical Rotatory Dispersion (ORD) is the change of specific rotation [α] or molar rotation [Õ] with the wavelength of light used. There is a difference in the absorbance of the left and right-handed components of circularly polarized light by a non-racemic sample. This differential absorption of left and right circularly polarized radiation in known as Circular Dichroism (CD).

Photochemistry is branch of chemistry which studies the chemical effects of light. Photochemistry is fundamentally referred as the principal mechanism for all of photobiology.

In this unit, you will study about the basic principles, usage, and applications of the Mössbauer spectroscopy, Optical Rotatory Dispersion (ORD), and Photochemistry.

3.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the concept of spectroscopy.
- Explain the principle and applications of Mössbauer spectroscopy.
- Discuss the applications of Optical Rotatory Dispersion (ORD).
- Define photochemistry and discuss its applications.

3.2 MÖSSBAUER SPECTROSCOPY

Mössbauer spectroscopy is named after Rudolf Mössbauer (1958), consists of the study of γ-ray absorption (or emission) spectra for transition between nuclear states. Though this type of resonant γ-ray absorption was first suggested by Kuhn in 1928. This technique has now become a very powerful tool for understanding problems in different branches of science.

3.2.1 Principles of Mössbauer Spectroscopy

Nuclear resonance absorption is expected to occur when γ –radiation emitted in a transition from E_i to E_f is reabsorbed by another nucleus of the same kind as shown in figure 3.1 However, this could not be achieved due to the high energy of the emitted photon.

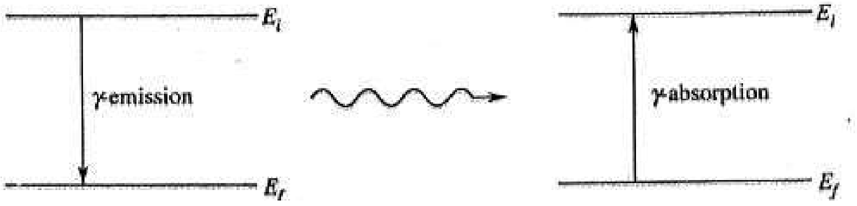


Fig. 3.1 Nuclear Resonance Absorption

Consider an isolated atom of mass M having a nuclear excited state E_i above the ground state E_f. Let E_0 be the energy difference $E_i - E_f$ and E_{re} be the kinetic energy of the recoil nucleus. If p is the recoil momentum, we have

$$E_{re} = \frac{P^2}{2M} \tag{3.1}$$

As this energy has to come from E_0, the emitted γ-ray will have an energy

$$E_\gamma = E_0 - E_{re} \tag{3.2}$$

Therefore, the centre of the emitted spectral line will be shifted from the expected position E_0 (figure 3.2).

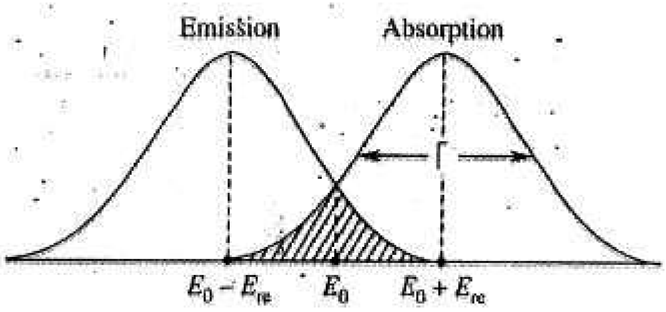


***Fig. 3.2** Overlap of Emission and Absorption Lines in a Nuclear Transition*

By the law of conservation of momentum,

Recoil momentum of the atom = Momentum of the emitted γ-ray

i.e., $$p = \frac{E_\gamma}{c} \tag{3.3}$$

where c is the velocity of light. Hence,

$$E_{re} = \frac{P^2}{2M} = \frac{E_\gamma^2}{2Mc^2} = \frac{\left(E_0 - E_{re}\right)^2}{2Mc^2} = \frac{E_0^2}{2Mc^2} \tag{3.4}$$

since E_{re} is small compared to E_0.

After absorption of the γ-ray by the same nucleus, the atom will have momentum and energy. This energy has to come from the radiation. Hence, in the absorption process, to excite the nucleus upon the same energy the γ-ray must have the energy E'_γ given by

$$E'_\gamma = E_0 + E_{re} \tag{3.5}$$

The effect of recoil is thus to introduce a difference of $\left(E'_\gamma - E_\gamma\right)$ between the energies of the emitted and absorbed γ-rays in a resonant process

$$E'_\gamma - E_\gamma = 2\ E_{re} = \frac{E_0^2}{Mc^2} \tag{3.6}$$

If $2E_{re} <<$ [, the FWHM of the line, the two curves would overlap and one would observe resonant absorption. Since E_{re} is proportional to E_0^2, it increases appreciably as we go from the optical region (~2 eV) to the gamma ray region

(~10 keV) of the electromagnetic spectrum. Figure 3.2 illustrates the overlapping of emission and absorption lines; greater the overlap greater is the absorption. Thus, maximum absorption will occur when the recoil energy is zero. This can be achieved when the emitting and absorbing nuclei are bound in crystal lattices. In such a case, the recoil energy is absorbed by the crystal lattice as a whole.

Mössbauer observed this resonance absorption. So, by placing a suitable unstable nucleus in a matrix which absorbs most of the recoil energy (Mössbauer source). When this γ-ray is passed through a material containing a similar nucleus, absorption will occur.

3.2.2 Spectral Parameter and Spectrum Display

In the experimental procedure, a solid matrix containing an excited nuclei of a given isotope called the source is placed next to a second matrix containing the same isotope in the ground state is called absorber. We have seen that the amount of overlap of the energy profiles for the source and absorber decides the strength of resonant absorption. A movement of the source and absorber relative each other with velocity 'V' produces a Doppler shift in frequency equal to (v/c) V, where C is the velocity of light and V is the frequency of γ-ray. If the effective resonance energies for the source and absorber exactly match at a particular velocity, V, the resonance absorption will be at a maximum. Thus, the principle of obtaining Mössbauer spectrum is to record the transmission of γ-rays from a source through are absorber as a function of Doppler velocity V between the source and absorber.

Mössbauer Spectrometer

Experimentally, two methods are possible for measuring the γ-ray transmission as a function of Doppler velocity. In one method, the source is mounted on a mechanical constant velocity device and the total number of counts is registered in a fixed true. The same is repeated at different velocities until the desired velocity is covered. A single channel analyser is used to limit the detection to only those pulses that have the required energy. In the second method, the source is mounted on an oscillating drive which gives it a varying velocity relative to the sample. The detector output is fed to a multichannel analyser which collects and sums the results. The general experimental arrangement of a Mössbauer spectrometer is given in Figure 3.3 and that of a detailed modern one, in Figure 3.4.

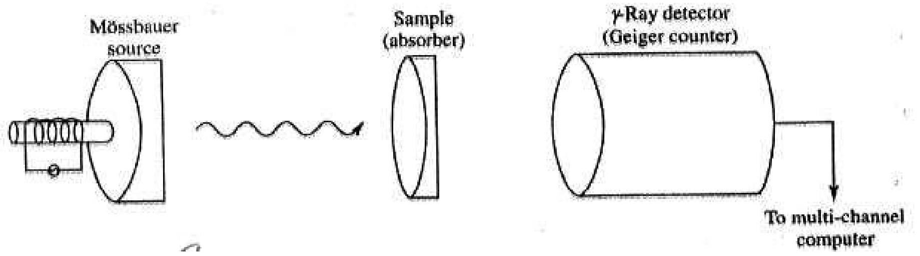


Fig. 3.3 Experimental Arrangement for Mössbauer Spectroscopy

The source ^{57}Co mounted on a loudspeaker coil whose motion is controlled by a waveform generator. A saw-tooth variation of velocity with time is generally used. This arrangement makes the sample to move back and forth at regular intervals. This oscillatory motion gives the source a varying velocity relative to the sample. The velocity will be zero at the turning points and maximum at the centre. The absorber which is also in the form of a foil covers the window of the detector. A scintillation counter or a gas filled proportional counter or a semiconductor detector is used according to the situation. The signal from the detector as a function of the loud speaker velocity is fed to a multichannel analyser which collects the results and sums it over each cycle. The discriminator rejects most of the non-resonant background radiation. The final Mössbauer spectrum is displayed as counts per second as a function of relative velocity between the source and absorber.

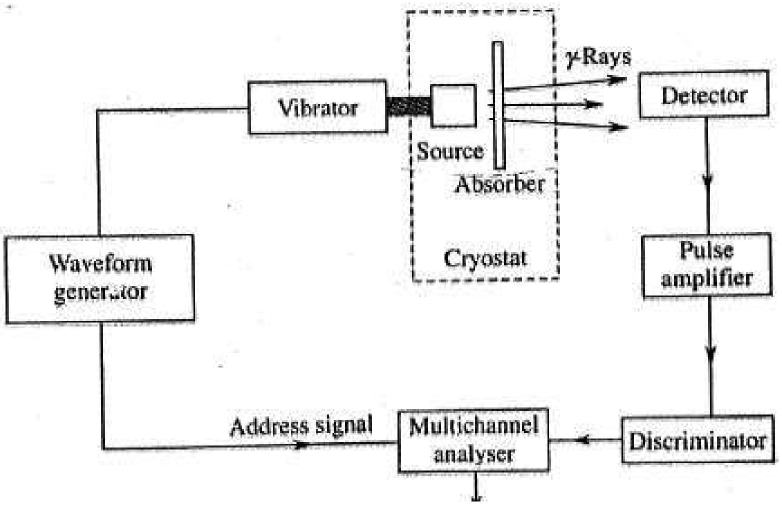


Fig. 3.4 *Schematic Arrangements of a Modern Mössbauer Spectrometer*

The absorption of the γ-ray by the sample is shown up by a fall in counts per second (Figure. 3.5). A relative velocity of 0.1 mm/s is sufficient to produce a market reduction in the absorption of the 14.4 keV ^{57}Fe transition. Though resonances are possible in certain cases at room temperature in many cases, one has to cool the absorber and the source to liquid helium temperatures. By cooling to low temperatures, the thermal motion of the lattice atoms and hence the resulting Doppler effect is reduced to a minimum. Then the Mössbauer effect shows up strongly.

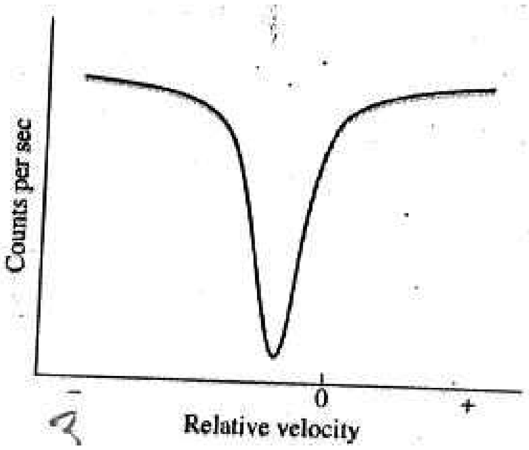


Fig. 3.5 *Typical Mössbauer Spectrum*

Mossbauer effect as such, would not have been of much use if the energy of the Mossbauer nucleus was not influenced by its chemical environment and other hyperfine interactions, the electric and magnetic hyperfine interactions.

Isomer Shift

In a Mössbauer experiment, if the environments of the emitting and absorbing nuclei are different, the energy of the nuclear transition E_0 may differ by a small amount. This energy difference is known as **isomer shift (δ) or chemical isomer shift.** The effect of isomer shift on the Mössbauer spectrum is to shift the resonance line from the zero position. The value of δ can be positive or negative depending on the sample (Figure 3.6). Isomer shift is the term more widely used since this effect depends on the energy difference in the ground and excited (isomeric) states.

Isomer shift arise because the nucleus of an atom is not a point charge as assumed, but has a finite charge distribution. The electrostatic interaction between the nuclear charge distribution and the electron charge distribution brings about a change in the energy levels of the nucleus. The shift in the energy levels of the nucleus is given by

$$\Delta E = \frac{2\pi}{5} Ze^2 R^2 \, |\psi(0)|^2 \tag{3.7}$$

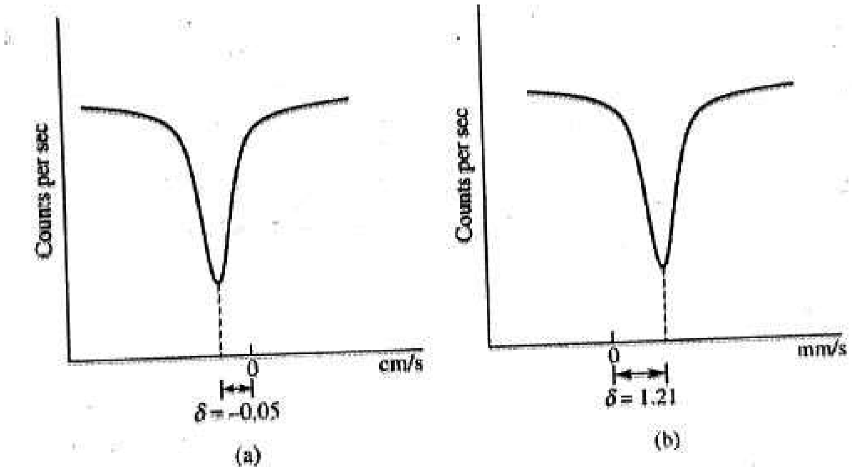


Fig. 3.6 *Isomer Shift in (a)* $[Fe(CN)_6]^{-4}$ *(b)* $(C_6H_5)_4 Sn$

where $|\psi(0)|^2$ represents the total electron density at the site of the nucleus. We are interested in the change in energy $\delta(\Delta E)$ between the nuclear ground and first excited state (Figure 3.7).

Hence,

$$\delta(\Delta E) = (\Delta E)_{ex} - (\Delta E)_{gr} = \frac{2\pi}{5} Ze^2 \, |\psi(0)|^2 \left(R_{ex}^2 - R_{gr}^2\right) \tag{3.8}$$

Writing R for radius of the equivalent sphere of uniform charge distribution and dR for $(R_{ex} - R_{gr})$, we get

$$\left(R_{ex}^2 - R_{gr}^2\right) = 2R \; dR = 2R^2 \frac{dR}{R}$$

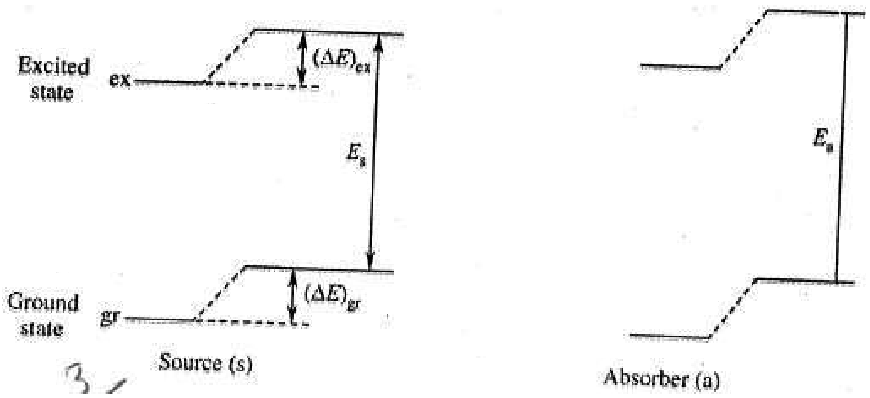


Fig. 3.7 Representation of Energy Shifts Responsible for Isomer Shift

In the experiment, a source-absorber pair is involved and one measures only a difference in the nuclear electrostatic energy changes of the source and the absorber. Hence, the isomer shift δ is given by

$$\delta = \delta\ (\Delta E)a - \delta\ (\Delta E)s$$

$$= \frac{4\pi}{5} ze^2DE\ \ R^2 \frac{dR}{R}\left[\left|\psi(0)\int_a^2 - |\ \psi(0)\int_s^2\ \right|\right] \qquad (3.9)$$

where subscripts a and s refer to absorber and source respectively.

Chemical isomer shift is the Mössbauer parameter that gives the maximum amount of chemical information.

Quadrupole Interaction

The spin of either or both of the Mössbauer nuclear levels may have a value greater than Y_2. In such a case, the interaction of the nuclear quadrupole moment eQ with the electric field gradient eq at the nucleus may lead to a splitting of the Mössbauer spectrum. The Hamiltonian representing the quadrupole interaction is given by

$$H = \frac{e^2qQ}{4I(2l-1)}\left[3I_z^2 - I(l+1) + \frac{n}{2}\left(l_+^2 + l_-^2\right)\right] \qquad (3.10)$$

where **Inserted word here Refer page number 6** is the asymmetry parameter of the field gradient tensor I_+ and I are the step up and step-down operators defined by

$$L_+ = L_x + i\,L_y \qquad \text{and} \qquad l = l_x - i\,l_y \qquad (3.11)$$

The energy eigenvalues E_{mi} of the Hamiltonian are doubly degenerate since plus and minus m_l values give the same energy.

$$E_{mi} = \frac{e^2qQ}{4I(2l-1)}\left[3m_I^2 - I(l+1)\right]\left(1 + \frac{n^2}{3}\right)^{1/2} \qquad (3.12)$$

As an example, consider the case for which the nuclear spin of the ground and first excited states are ½ and 3/2 respectively. Equation (3.12) leads to zero energy for the ground state which is understandable since it will not have nuclear quadrupole moment. For the excited state, from Equation (3.12)

$$E_{\pm 1/2} = \frac{3e^2qQ}{4I(2I-1)}\left(1+\frac{n^2}{3}\right)^{1/2} \quad (3.13)$$

$$E_{\pm 1/2} = \frac{3e^2qQ}{4I(2I-1)}\left(1+\frac{n^2}{3}\right)^{1/2} \quad (3.14)$$

Thus, the quadrupole interaction results in the splitting of the excited nuclear level into two levels. If the quadrupole moment is positive, the ±3/2 states will be above that of the ±1/2 states. A reverse situation exists when the quadrupole moment is negative. The selection rule for transition ml = 0, ±1 leads to two lines in place of one line. The energy level scheme of the system is illustrated in Figure 3.8. When quadrupole interaction alone is observed, a two line Mössbauer spectrum results with a separation Δ which is referred to as the quadrupole splitting, and is given by

$$\Delta = \frac{6e^2qQ}{4I(2I-1)}\left(1+\frac{n^2}{3}\right)^{1/2} \quad (3.15)$$

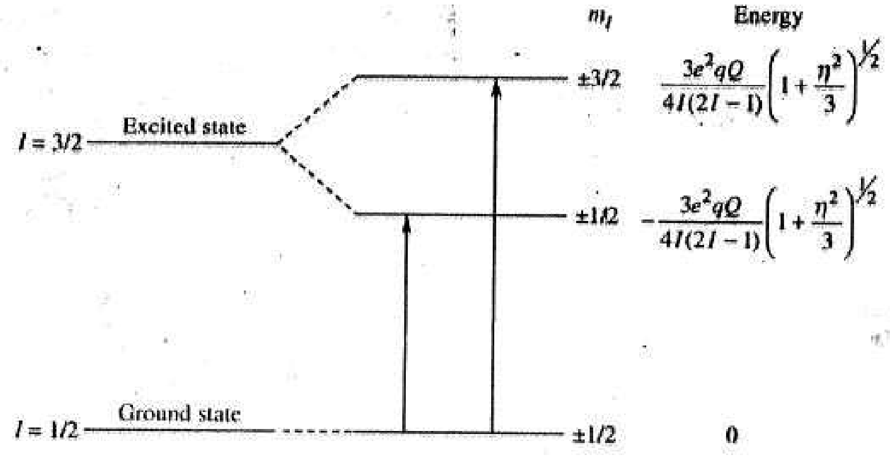


Fig. 3.8 *Quadrupole Interaction in a System having l = ½ in the Ground State and l = 3/2 in the Excited State*

Magnetic Hyperfine Interaction

Magnetic hyperfine splitting is a result of the interaction between the nucleus and any surrounding magnetic field, as described by the Zeeman Effect. Most of the Mössbauer nuclei have non zero spin in the ground and excited states and therefore both levels will directly interact with a magnetic field of flux density B giving rise to the interaction energy,

$E_{mI} = -g_N \mu_N B_{mI}$ (3.16)

where μ_N is the nuclear magneton, g_N the nuclear g factor and the magnetic quantum number m_I takes the values –l, –l + l, …+1. The magnetic field thus splits the grounds and excited Mössbauer levels into 2l + 1 nondegenerate equally spaced levels.

Again, we shall consider the case where the ground (double prime) and the first excited (single prime) nuclear states have spin $l_g'' = 1/2$ and $l_g' = 3/2$ respectively.

For the ground state,

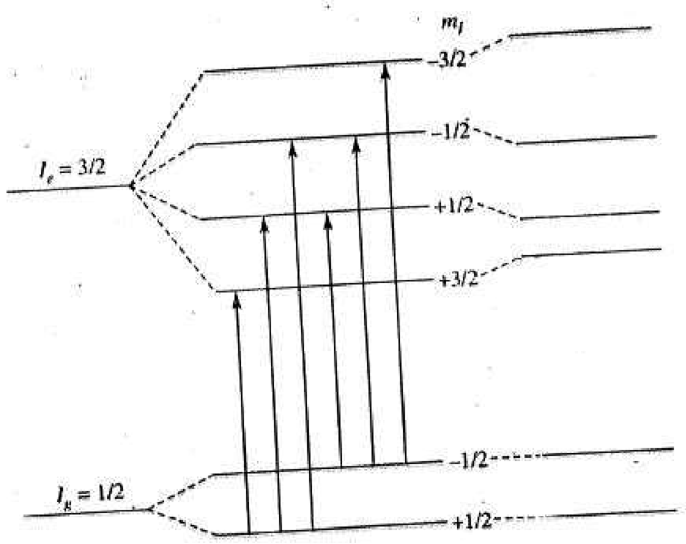
$$E_{1/2} = -\frac{1}{2} g'_N \ \mu_N B, \quad E_{-1/2} = \frac{1}{2} g''_N \ \mu_N B \tag{3.17}$$

For the excited state,

$$E_{1/2} = \frac{3}{2} g'_N \mu_N B, \qquad E_{-1/2} = \frac{3}{2} g''_N \ \mu_N B$$

$$E_{-1/2} = \frac{1}{2} g'_N \ \mu_N B, \quad E_{-1/2} = \frac{3}{2} g'_N \ \mu_N B \tag{3.18}$$

Six transitions are allowed between the $l''_g = 1/2$ and $l'_e = 3/2$ levels since the selection rule for dipole radiation is $\Delta m_l = 0, \pm 1$. Figure 3.9 illustrates the energy levels and transitions for such as system. In the figure g''_N and g'_N are taken as positive.



(a) *(b)* *(c)*

Fig. 3.9 ***(a)*** *The Ground and Excited Energy Levels of a* l_g *– 1/2* l_e *= 3/2 System*
(b) *The Energy Levels and Transitions Illustrating the Splitting Produced by Magnetic Field.*
(c) *The Energy Levels and Transitions Showing the Effect of a Simultaneous Magnetic and Electric Field.*

3.2.3 Applications of Mössbauer Spectroscopy

The observation of hyperfine structure in Mössbauer effect is an effective tool for the studies in solid state and chemistry. The narrow line width of nuclear transition involved made it possible to investigate small interactions between nucleus and orbital electrons which cannot be studied by other methods. Some of the applications of Mössbauer spectroscopy are discussed below.

1. **Electronic Structure of Fe^{2+}/Fe^{3+} Compounds.** The isomer shift is of greatest interest to chemists. It is a direct function of the s-electron density at the nucleus. Changes in shielding of s-electrons by p-d- and f-electrons

induces secondary effects. The removal or addition of a valence electron (a change in the oxidation state), may change the s-electron density at the nucleus and thereby the isomer shift. Hence from the knowledge of isomer shift, it is possible to get relative s-electron density and from it an estimate of bond character of atoms chemically bonded to the Mössbauer nucleus. Mössbauer experiments with spin free (high spin) compounds of iron in different valency states show a regular behaviour with respect to isomer shift. Characteristic values of the isomer shift obtained for different oxidation states is iron are shown in figure 3.10.

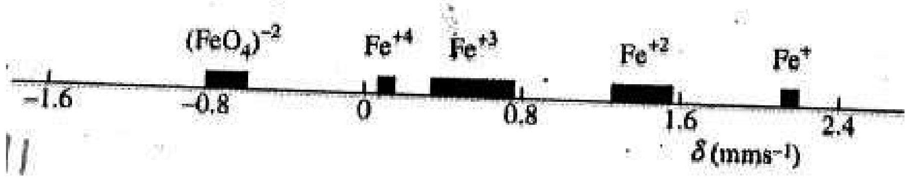


Fig. 3.10 *The Isomer Shifts Relative to 310 Stainless Steel for Spin Free (High Spin) Iron in Different Oxidation States*

This characteristic ^{57}Fe isomer shift was related to chemical bonding quantitatively. Plots of the total s-electron density versus 4s electron density for the various 3d^{n} configurations have also been constructed. It was thus possible to amount for the lower isomer shifts of weakly covalent spin free compounds of a fixed oxidation state. They also showed that the increase in the total s-electron density, hence a decrease in the isomer shift, in going from the higher oxidation state to the lower oxidation state due to a decrease in the shielding of the 3s electrons as a result of the removal of the d-electrons. Mössbauer spectra thus provide a method of estimating s-electron covalency in transition metal complexes.

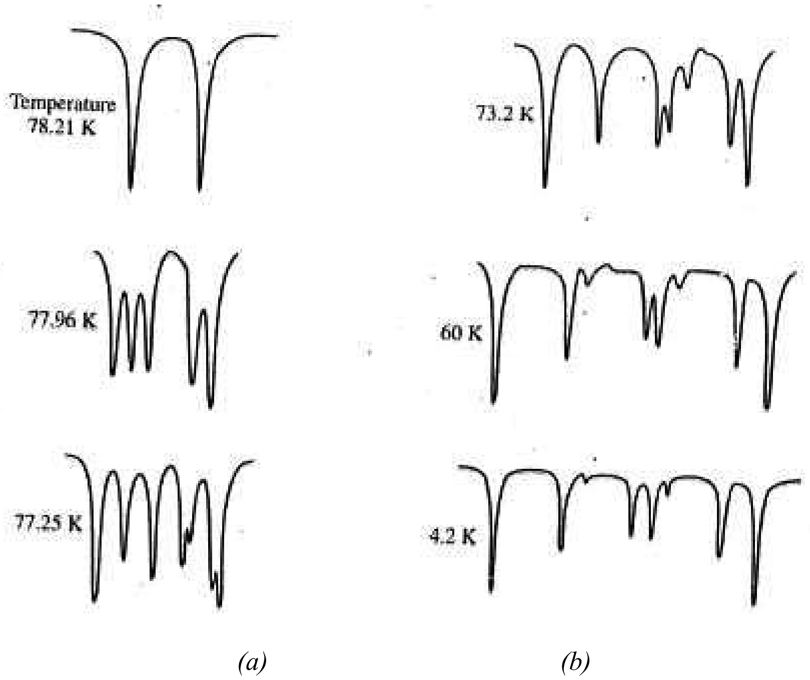
For spin paired (low spin) compounds of iron, the isomer are independent of the oxidation state and lie in the region of zero velocity relative to stainless steel. From isomer shifts, it is also possible to get information on the extent of the back donation of the electrons from the metal to the ligand in low spin complexes such as $K_3Fe(CN)_6$, $K_4[Fe(CN)_6].3H_2O$, … From Mössbauer studies on a series of hexacyanoferrate derivatives $Fe(CN)_5L^{-n}$ in which a cyano group is replaced by some other ligand L, it is established that the increasing values of the observed isomer shift correspond to the decreasing π bond strength of the ligands:

$$\delta \xleftarrow[\text{Increasing } \pi\text{-bond strength}]{NO^{+}\quad CO\quad CN^{-}\quad SO_3^{-2}\quad Ph_3P\quad NO_2^{-}\quad NH_3}$$

2. **Sn^{2+} and Sn^{4+} Oxidation States.** As discussed, the magnitude of the isomer shifts is influenced by the electron density at the concerned nucleus. We know that p, d etc., orbitals have zero electron density at their nuclei; consequently, it is the s-electron density which is important. From measurement of chemical shifts, one may this obtain relative s-electron density and from it an estimate of the bond character of atoms chemically attached to the Mössbauer

nucleus. For example, the Mössbauer nucleus ^{119}Sn exhibits chemical shifts of 0,0.21 and 0.37 cm/s, respectively, in compounds containing tin in Sn^{4+}, 4-covalent (tetrahedral) and Sn^{2+} valence states; the values are seen to match almost linearly with the number of s electrons in the respective electron configurations (for outer shell): s^0p^0, sp^3 and s^2p^0. Mössbauer spectroscopy thus affords a relatively simple means of ascertaining the valence state of an unknown tin compound.

3. **Crystal Symmetry and Magnetic Structure.** We have discussed that the presence of magnetic hyperfine interaction causes line splitting and this magnetic field could be intrinsic as well. In certain cases, an analysis of the spectra would be able to provide information about crystal symmetry and intrinsic magnetic field. An interesting example for illustrating the combined use of magnetic hyperfine splitting and quadrupole interaction studies is provided by the temperature dependent spectra of ^{57}Fe in FeF_2 given in figure 3.12.



(a) (b)

Fig. 3.11 The Hyperfine Structure of ^{57}Fe In Fef_2: (A) The Quadrupole Interaction is Stronger than the Magnetic Interaction, (B) The Magnetic Interaction is Stronger than the Quadrupole Interaction. At 78.21 K The Spectrum Shows a Sharp Doublet Typical of a Case where Quadrupole Coupling is much Stronger than the Magnetic Coupling. At Temperatures 77.96K, 77.25K, 73.2 K And 60 K, The Effect of both Magnetic and Quadrupole Interactions are Present, Giving Rise to a more Complicated Spectrum.

The line positions and relative intensities contain more information than is available from the quadrupole spectrum alone. However, at 4.2 K, the six-line spectrum is typical of a situation wherein magnetic coupling is much stronger than the quadrupole coupling. The data at 4.2 K lead to B = 32.9 T, $\Delta = \frac{1}{2} e^2 qQ = 2.85$ ms^{-1} and an asymmetry parameter **10** = 0.40. The line positions and intensities suggest that the principal axis of the electric field gradient tensor is perpendicular to the spin axis. Thus, analysis of a combined magnetic and quadrupole interactions gives detailed information about the crystal symmetry and the magnetic structure.

4. **Biological Applications.** Many of the large protein molecules control biological functions through the oxidation and reduction properties of a transition metal atom. For example, the hemoglobin proteins which acts as an oxygen carrier, function by a direct bonding of oxygen molecules to an iron atom. The Mössbauer spectrum of the iron site reflects the ligand field of the surrounding organic groups and therefore usual procedures for understanding of electronic structures can be applied. However, there is a difference as the individual iron atoms are separated by distances of the order of 25 Å which changes the relaxation properties considerably. In such cases, the Mössbauer spectrum of low temperatures usually show a paramagnetic hyperfine splitting which slowly collapse with rising temperatures. Hence, application of an external magnetic field is often necessary.

   Consider the case of haemo-proteins, the carriers of oxygen in blood. The oxygen is transported by chemically binding it to an iron atom which is in the centre of a planar porphyrin structure known as protoporphyrin IX. Four co-ordinations of the iron are to the four nitrogens of the planar porphyrin unit and the fifth one is to the protein through the nitrogen of the histidine unit below the plane. The sixth coordination position of the iron on the other side of the porphyrin is vacant and provides a suitable site for labeling of small molecules such as oxygen.

   The iron III chloride derivative of protoporphyrin (haemin) gives the spectrum of a high spin $S = 5/2$ configuration while the reduced iron II derivative (haeme) has a low spin $S = 0$. The reduced form of hemoglobin gives the spectrum of a high spin $S = 2$ iron II compound whereas the carbon monoxide and oxygen derivatives of hemoglobin (HbCO and HbO_2) show the spectrum for a low spin $S = 0$ iron II configuration. The resultant spectra are characteristic of each compound and are as sensitive probe of the environment of the iron. The large quantity of data provided by experimental observations coupled with the results of theoretical investigations provide highly detailed informations which are not obtainable by other methods.

Nature of M-L Bond: Coordination Number and Structure

A metal–ligand multiple bond describes the interaction of certain ligands with a metal with a bond order greater than one. Coordination complexes featuring multiply bonded ligands are of both scholarly and practical interest. Transition metal carbene complexes catalyze the olefin metathesis reaction. Metal oxo-intermediates are pervasive in oxidation catalysis. Oxygen evolving complex.

The classification of a metal ligand bond as being "multiple" bond order is ambiguous and even arbitrary because bond order is a formalism. Furthermore, the usage of multiple bonding is not uniform. Symmetry arguments suggest that most ligands engage metals via multiple bonds. The term 'metal ligand multiple bond" is often reserved for ligands of the type CRn and NRn (n = 0, 1, 2) and ORn (n = 0, 1) where R is H or an organic substituent, or pseudohalide. Historically, CO and NO+ are not included in this classification, nor are halides.

The number and strength of metal-ligand bonds: The greater the number of ligands, and the stronger the bonds, the greater the thermodynamic stability of the resulting complex, i.e., in general the more ligands the better. Larger metals can accommodate more ligands. In general coordination numbers are greater for the earlier transition metals (groups 4 – 7) compared to the later ones. Coordination numbers for lanthanide complexes are generally higher than for transition metals. d^8 square planar complexes are stable because 4 strong bonds are collectively stronger than 6 bonds that would be collectively weaker for this electron configuration.

Coordination Number and Structure

The coordination number, also called ligancy, of a central atom in a molecule or crystal is the number of atoms, molecules or ions bonded to it. The ion/molecule/atom surrounding the central ion/molecule/atom is called a ligand. This number is determined somewhat differently for molecules than for crystals.

For molecules and polyatomic ions the coordination number of an atom is determined by simply counting the other atoms to which it is bonded (by either single or multiple bonds). For example, $[Cr(NH_3)_2Cl_2Br_2]^{-}$ has Cr^{3+} as its central cation, which has a coordination number of 6 and is described as *hexa-coordinate*. The common coordination numbers are 4, 6 and 8.

The coordination numbers are well defined for atoms in the interior of a crystal lattice: one counts the nearest neighbors in all directions. The number of neighbors of an interior atom is termed the bulk coordination number. For surfaces, the number of neighbors is more limited, so the surface coordination number is smaller than the bulk coordination number.

Coordination Number of a Central Atom

In the case of polyatomic ions and molecules, the coordination number corresponding to a given atom can be calculated by counting the total number of atoms it is bonded to, be it a single bond or a double/triple bond.

Considering the example of the polyatomic ion given by the formula [Cr(NH3)2Cl2Br2]–, the coordination number of the central cation (Cr3+) can be counted by the total number of atoms bonded to the chromium atom, which is found to be 6.

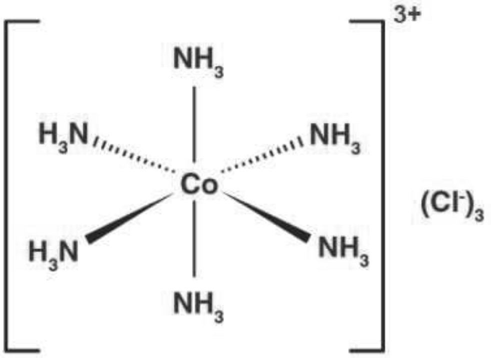


Fig. 3.12 Coordination Number and Structure of a Polyatomic Ion

There exist multiple possible geometric combinations for each value of the coordination number for the central atom. These possible geometric shapes are mentioned in the table 3.1 below:

Table 3.1 *Various Coordination Number and Structures*

Coordination Number	**Geometric Structure**
2	Linear
3	Trigonal planar, T-shaped, or trigonal pyramidal
4	Square planar or tetrahedral
5	Trigonal bipyramidal or square pyramid structures
6	Trigonal prism structure, hexagonal planar, or octahedral
7	Pentagonal bipyramidal, capped octahedron, or a capped trigonal prism structure.
8	Cubic, hexagonal bipyramidal, square antiprism, or dodecahedron
9	Three-face centered trigonal prism
10	A bicapped square antiprism structure
11	All faced capped trigonal prism structure
12	Cuboctahedron structure

Detection of Oxidation State and Inequivalent MB Atoms

The oxidation state, or oxidation number, is the hypothetical charge of an atom if all of its bonds to different atoms were fully ionic. It describes the degree of oxidation (loss of electrons) of an atom in a chemical compound. Conceptually, the oxidation state may be positive, negative or zero. While fully ionic bonds are not found in nature, many bonds exhibit strong ionicity, making oxidation state a useful predictor of charge.

The oxidation state of an atom does not represent the "real" formal charge on that atom, or any other actual atomic property. This is particularly true of high oxidation states, where the ionization energy required to produce a multiply positive ion is far greater than the energies available in chemical reactions. Additionally, the oxidation states of atoms in a given compound may vary depending on the choice of electronegativity scale used in their calculation. Thus, the oxidation state of an atom in a compound is purely a formalism. It is nevertheless important in understanding the nomenclature conventions of inorganic compounds. Also, several observations regarding chemical reactions may be explained at a basic level in terms of oxidation states.

Oxidation states are typically represented by integers which may be positive, zero, or negative. In some cases, the average oxidation state of an element is a fraction, such as 8/3 for iron in magnetite Fe_3O_4. The highest known oxidation state is reported to be +9 in the tetroxoiridium (IX) cation (IrO^+_4). It is predicted that even a +12 oxidation state may be achievable by uranium in the unusual hexoxide UO_6. The lowest oxidation state is "5, as for boron in Al_3BC.

Check Your Progress

1. Define spectroscopy.
2. What do you understand by Mössbauer Spectroscopy?
3. Who gave the concept of Mössbauer Spectroscopy?
4. Define isomer shift.
5. What do you understand by magnetic hyperfine interaction?
6. Define coordination number.

3.3 OPTICAL ROTATORY DISPERSION (ORD) AND CIRCULAR DICHROISM

Optical Rotatory Dispersion (ORD) is the change of specific rotation [α] or molar rotation [Õ] with the wavelength of light used. There are differences in the absorbance of the left and right-handed components of circularly polarized light by a non-racemic sample. This differential absorption of left and right circularly polarized radiation in known as Circular Dichroism (CD).

The optical techniques like polarimetry, ORD and CD which can differentiate between the two enantiomers of a chiral compound are called ***chiroptical techniques***.

When a linearly polarized light beam passes through an optically active medium, its two circularly polarized components show different refractive indices (i.e., interaction is diastereomeric). The medium is said to circularly birefringent. The differences in refractive indices correspond to differences in light velocities. Both the circularly polarized components are slowed down relative to their equal velocities prior to entrance into the optically active medium but to a different extent. As the two circularly polarized components travelled with unequal velocities the optically active medium, the two components now are not in phase and the resultant i.e., linear polarization vectors get rotated by an angle (α) to the original plane of polarization. Optical rotation at sodium D-line is used to detect and quantitate optical activity. On the other hand, optical rotations determined over a range of wave lengths as in ORD has been used to establish absolute configurations. [The refractive index n for any medium equals Co/C where C is the velocity of light in that medium and Co is the velocity of light in a vacuum (It may be noted that when left and right circularly polarized beams pass through an achiral sample or a racemic mixture, they travel with the same velocity and therefore, enter and exit, the medium in phase. Consequently, there is no rotation of the plane of linearly polarized light as it passes through and exit the medium)]

In summary, if one of the circularly polarized components passes through an optically active medium more slowly compared to the other, the plane of polarization will be rotated (for this to happen the refractive index of the medium for one circularly polarized component must be different than the other and the phenomenon is called circular birefringence.

Due to the circular birefringence of the optically active medium, the two circularly polarized components of light not only sustain a differential retardation but are also absorbed to different extents in the region of absorption and thus the optically active medium has an unequal molar absorptivity coefficient (ε) for the right and left circularly polarized light. This difference in molar absorptivity is called circular dichroism (CD). Moreover, due to unequal absorption of left and right circularly polarized light by an optically active medium, the emergent beam has an imbalance between the strengths of two circularly polarized beams, as a result, the emergent beam is not truly linearly polarized but has been converted to elliptically polarized light (Figure 3.13)

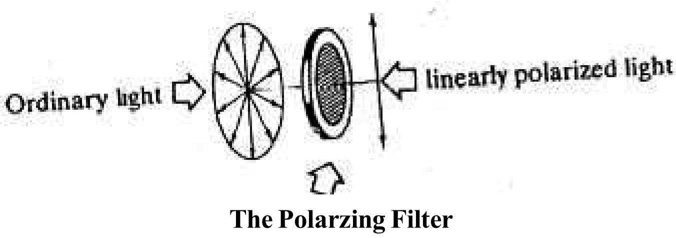


Fig. 3.13 *Elliptically Polarized*

3.3.1 Deduction of Absolute Configuration

The combined phenomenon of circular birefringence and circular dichroism are called Cotton Effect. Important features of ORD, CD, and cotton effect are summarized below:

1. Both CD and ORD are displayed clinal compounds and not observed for aclinal compounds or racemic mixtures.
2. ORD involves measurement of rotation and therefore can be detected over all wave lengths. CD on the other hand involves the measurement of an absorption i.e., the differential absorption of left and right-handed circularly polarized radiation. Thus, CD occurs only in the vicinity of an absorption bond.
3. A CD curve can be positive or negative (Figure 3.14) and is displayed as Δε (difference in molar absorptivity) or molar ellipticity [θ] versus π, these being difference spectra displaying the difference in absorption of left and right circularly polarized light. Each CD curve for each electronic absorption also represents a positive or negative cotton effect.

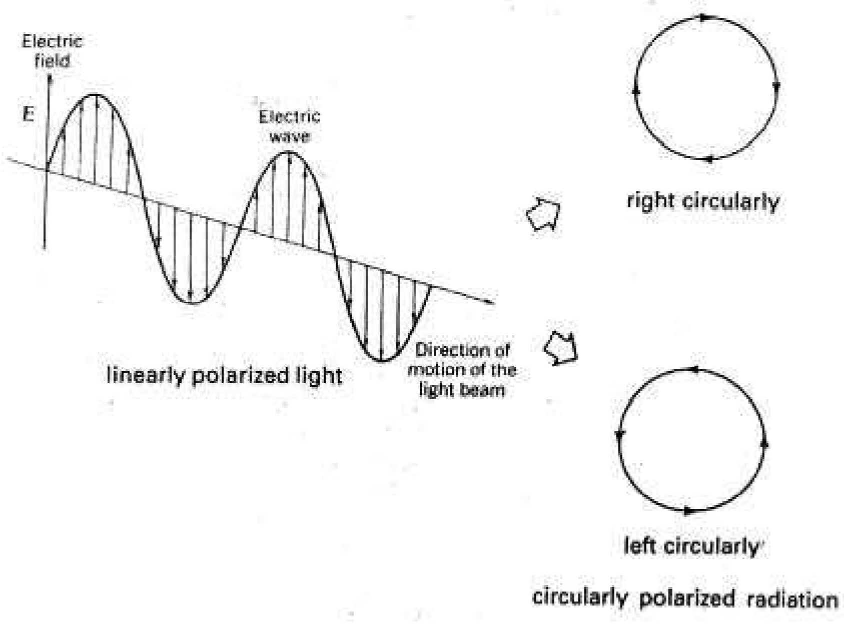


Fig. 3.14 A CD Curve

4. The ORD curves for many compounds only show typically the plain curve (+ or –) variance (Figure 3.15). However, if the compound with a symmetric chromophore e.g., C = O group has also an adjacent asymmetric unit e.g., a stereocenter, an anomalous ORD curve called a Cotton effect curve is obtained. The sign of the Cotton Effect of such a chromophore is determined by a chirality of the adjacent perturbing environment of the chromophore. The carbonyl group acts as a chromophore due to excitation of an electron in non-bonding orbital n (oxygen lone pair) into low-lying anti bonding orbital (π bond). Thus, the ORD curve of an optically active ketone in the region of $n \rightarrow \pi^*$ transition band (~290 mm) one will observe the Cotton Effect.
5. The Cotton effect (CE) could be either positive or negative (Figure 3.15). The curve is called positive when the rotation first increases as the wave length decrease on the other hand it is termed negative when the rotation magnitude first decreases when going towards shorter wave lengths.
6. For a CD Cotton effect (at a given wavelength) for a compound there also exists a corresponding ORD Cotton effect (Fig 3.14) for the transition, i.e., at a given wave length, both phenomena ORD and CD reflect the interaction of polarized light with the same chirotopic chromophore (a chromophore present in chiral environment). The wavelength (λ_0) at the sign change cross-over point of the ORD curve corresponding to λ_{max} of the CD curve.

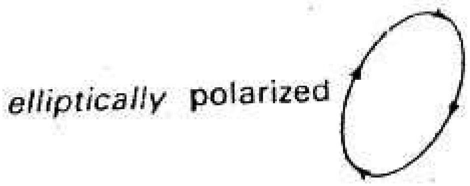


Fig. 3.15 Positive Cotton Effects

3.3.2 The Octant Rule

As discussed, the sign of the Cotton Effect reflects the stereochemistry of the environment of the chromophore, e.g., of a chiral ketone. A rule referred as Octant rule is used to predict the sign of the cotton effect in ORD and CD curves from a knowledge of the spatial arrangement (axial or equatorial) of the substituents around the carbonyl group. This rule is used to predict the absolute configuration or stereo structure of the compounds.

The application of the octant rule with a cyclohexanone ring in the chair conformation having an equatorial methyl group is as under:

1. The ring containing the carbonyl group is shown in figure 3.16 i.e., the carbonyl group is seen so oriented that it occupies the head of the chair closest to the observer.
2. Three planes at right angles are drawn through the carbonyl group to produce eight octants (figure 3.16)

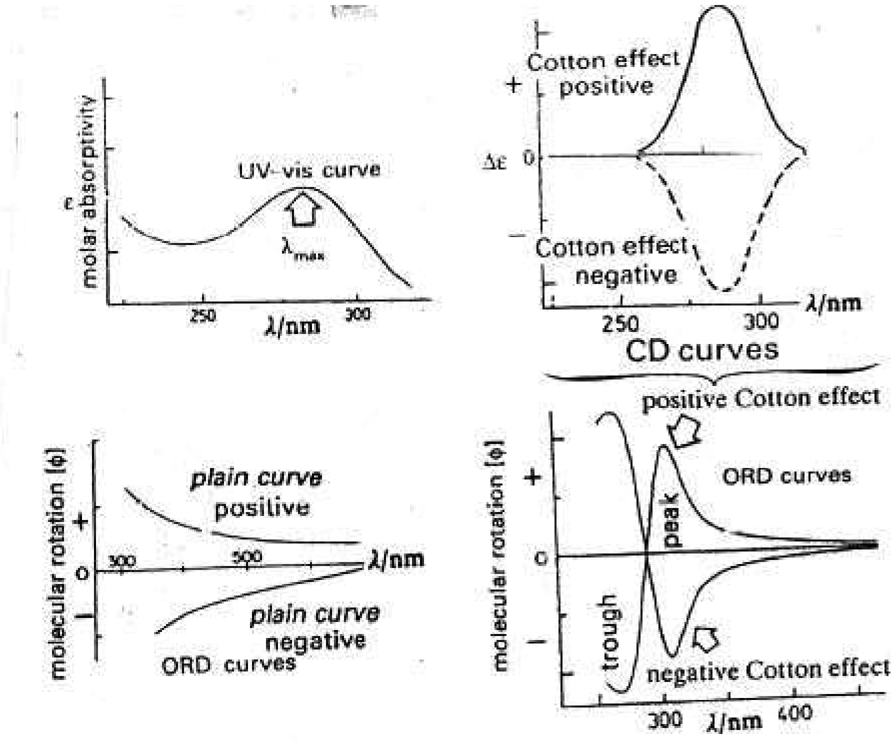


Fig. 3.16 The Ring Containing the Carbonyl Group

3. Since only rarely substituents bend over the carbonyl group toward the oxygen and beyond, the four octants which are nearest to the observer, i.e., the front octants are usually vacant. Thus, one may study the octant rule with the simplified depiction considering only the rear octants (Fig. 3.18) and the following points may be considered. The method of application of octant rule with a cyclohexanone ring in the chair conformation with an equatorial methyl group at C-3 is an under:

(a) First plane (A) (vertical in diagram) passes through the carbonyl group C-I and C-4.

(b) Second horizontal plane (B) is put through C-I and the cyclohexanone is so tilted that it also passes through C-2 and C-6.

(c) Third plane (C) passes about midway through the C = O bond at right angles (its consideration would be useful only for front octants.)

4. The overall sign of the n → π^* Cotton effect is then determined by the contribution of the groups in these octants.
5. According to octant rule:

   The substituents lying on the coordinate planes make negligible (and therefore ignorable) contribution to the n → π^* Cotton effect. Thus, as seen (Figure. 3.17) equatorial substituents at C-2 and C-6

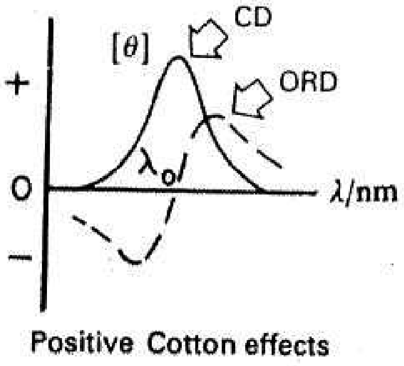


Fig. 3.17 Effects on Cotton Effects

Application of ORD, CD and Octant Rule for Ketones

The techniques ORD and CD provides complementary information, CD has now replaced ORD as the main chiroptical techniques to study chiral compounds. The applications of these techniques are discussed below:

1. Study of Absolute Configuration and Stereochemistry

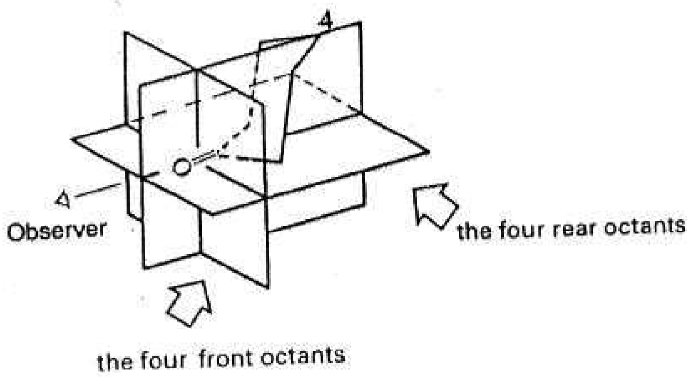


Fig. 3.18 The Sign of Cotton Effect

The sign of Cotton Effect gives information about the stereochemistry in the nearly environment of the chromophore, i.e., the carbonyl group (n $\rightarrow \pi^*$ absorption of the carbonyl group around 280 nm) acts as a probe of the chirality of its environment. Consider the following points:

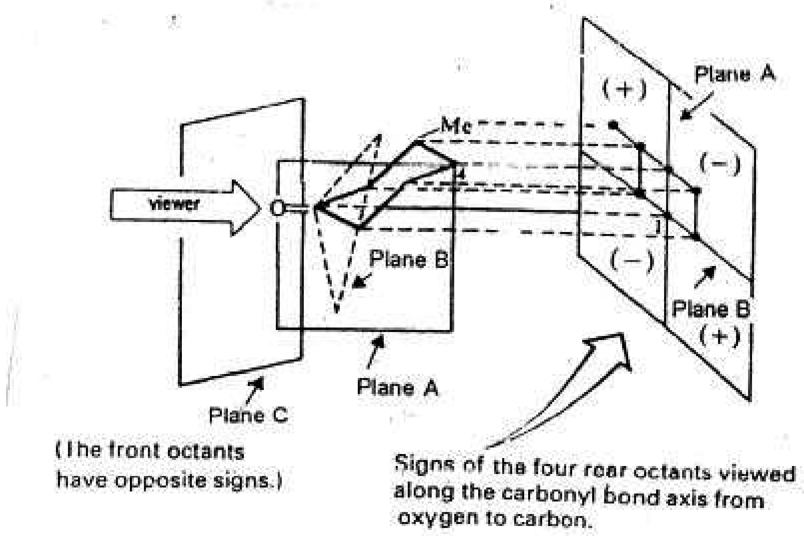
(i) When two compounds display curves of the same sign and shape, the stereochemical features near the chromophore are same.

(ii) When two compounds show Cotton effects of opposite sign then the stereochemical features near the chromophore are mirror image type.

(iii) The compounds are not enantiomers (these are different compounds), however, their ORD curves have an almost mirror image relationship. Thus, the compounds have an object: mirror image i.e., enantiomeric stereochemistry of the groups in the immediate vicinity of the carbonyl group and this is A/B ring junction.

2. Position of Functional Group

CD curves allows a clear distinction between a given pair from among, e.g., the isomeric 1-, 2- and 3- oxo – 5 α- steroids (which is impossible from UV or IR spectra). The *3-oxo-derivative* displays a positive cotton effect while the *l-oxo* derivative shows a negative cotton effect. A steroidal alkaloid rubigervine a preferential oxidation gives 12-keto derivative whose ORD resembled that of 12-oxo keto derivative whose ORD curve resembled that of a 12-oxo steroid to show the position of keto group (II) at C-12.



(The front octants have opposite signs.)

Signs of the four rear octants viewed along the carbonyl bond axis from oxygen to carbon.

Fig. 3.19 *ORD Curves of Ketones*

So, the position of a functional group (which is a chromophore) can be determined in an unknown compound.

3. Study of Conformation

When the absolute configuration of a conformationally mobile system is known, the preferred conformation can be determined by the application of octant rule. Consider (+) -3- methylcyclohexanone which is known to have the *R-configuration.*

(i) One would predict that the chair form with equatorial methyl group would be energetically favoured over the conformer with the axial methyl group (III, scheme 3.2, the stereocenter in III, maintains the R configuration although the equatorial methyl has become axial. Recall that a compound can have infinite number of conformations but only one configuration).

Check Your Progress

7. What do you mean by Optical Rotatory Dispersion?
8. Define chiroptical techniques.
9. State the octant rule.

3.4 PHOTOCHEMISTRY (PHOTOCHEMICAL REACTIONS)

Photochemistry is the branch of chemistry which studies the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm). In nature, photochemistry is of immense importance as it is the basis of photosynthesis, vision, and the formation of vitamin D with sunlight. Photochemical reactions proceed differently than temperature-driven reactions. Photochemical paths access high energy intermediates that cannot be generated thermally, thereby overcoming large activation barriers in a short period of time, and allowing reactions otherwise inaccessible by thermal processes. Photochemistry is also destructive, as illustrated by the photodegradation of plastics.

Photochemistry is fundamentally referred as the principal mechanism for all of photobiology. The moment a molecule absorbs a photon of light, its electronic structure changes or alters, and hence it reacts differently with the other molecules. The absorbed energy from the light results in photochemical changes that will occur in the absorbing molecule, or in an adjacent molecule, for example photosensitization. The energy can also be evolved in the form of heat, or in the form of light as lower energy light, for example fluorescence or phosphorescence, so that the molecule can return to its ground state. Different molecules have different preference for these mechanisms in order to get rid of absorbed photon energy, for example photosensitization, fluorescence or phosphorescence.

Continuous flow photochemistry has multiple advantages over batch photochemistry. Photochemical reactions are driven by the number of photons that are able to activate molecules causing the desired reaction. The large surface area to volume ratio of a microreactor maximizes the illumination, and at the same time it also permits for efficient cooling, which decreases the thermal side products.

Principles of Photochemistry

In the case of photochemical reactions, light provides the activation energy. Principally, the light is referred as mechanism for providing the activation energy required for many different reactions. If laser light is used, then it is possible to select a molecule and stimulate or excite it for producing a desired electronic and vibrational state. Similarly, the emission from a particular state may be individually or selectively monitored, providing a measure of the population of that state. If the chemical system is at low pressure, then it is possible to observe the energy distribution of the products of a chemical reaction before the differences in energy have been smeared out and averaged by means of repeated collisions.

The absorption of a photon of light through a reactant molecule may also permit a reaction to occur not just by bringing the molecule to the necessary activation energy, but also by changing the symmetry of the molecule's electronic configuration, enabling an otherwise inaccessible reaction path, as stated by the Woodward–Hoffmann selection rules. A 2+2 cycloaddition reaction is an example of a pericyclic reaction that can be analysed using these rules or by the related frontier molecular orbital theory.

Some photochemical reactions having numerous orders of magnitude are referred as faster than thermal reactions, i.e., reactions as fast as 10^{-9} seconds and associated processes as fast as 10^{-15} seconds are frequently observed.

The photon can be absorbed directly through the reactant or by means of a photosensitizer, which absorbs the photon and transfers the energy to the reactant. The opposite process is called quenching when a photo excited state is deactivated by a chemical reagent.

Most photochemical transformations occur through a series of simple steps known as primary photochemical processes. One common example of these processes is the excited state proton transfer.

Following are common examples of photochemical reactions:

1. **Photosynthesis in Plants.** Plants use solar energy to convert carbon dioxide and water into glucose and oxygen.
2. Human formation of vitamin D through exposure to sunlight.
3. **Bioluminescence in Insects.** In fireflies, an enzyme in the abdomen catalyses a reaction to produce light.
4. Polymerizations happening due to photoinitiators, which decompose upon absorbing light to produce the free radicals for radical polymerization.
5. **Photodegradation of Many Substances,** for example polyvinyl chloride and Fp_2. Medicine bottles are often made with darkened glass to prevent the drugs from photodegradation. Cyclopentadienyliron dicarbonyl dimer is an organometallic compound with the formula $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, often abbreviated as $Cp_2Fe_2(CO)_4$, $[CpFe(CO)_2]_2$ or even Fp_2, with the colloquial name 'Fip Dimer'. It is a dark reddish-purple crystalline solid, which is readily soluble in moderately polar organic solvents, such as chloroform and pyridine, but less soluble in carbon tetrachloride and carbon disulfide.
6. **Photodynamic Therapy.** Light is used to destroy tumours by the action of singlet oxygen generated by photosensitized reactions of triplet oxygen. Typical photosensitizers include tetraphenylporphyrin and

methylene blue. The resulting singlet oxygen is an aggressive oxidant, capable of converting C–H bonds into C–OH groups.

7. Diazo printing process is based on photochemical reactions.
8. Photoresist technology, used in the production of microelectronic components.
9. Vision is initiated by a photochemical reaction of rhodopsin.
10. Toray photochemical production of ε-caprolactame.
11. Photochemical production of artemisinin, an anti-malaria drug.
12. Photoalkylation, used for the light-induced addition of alkyl groups to molecules.

3.4.1 Interaction of Electromagnetic Radiation with Matter

The 'Electro-Magnetic Radiation, also termed as EM radiation or EMR, refers to the waves or their quanta, photons of the electromagnetic field, propagating (radiating) through space, carrying electromagnetic radiant energy. It includes radio waves, microwaves, infrared, (visible) light, ultraviolet, X-rays, and gamma rays.

Classically, electromagnetic radiation consists of electromagnetic waves, which are synchronized oscillations of electric and magnetic fields. In a vacuum, electromagnetic waves travel at the speed of light. In homogeneous, isotropic media, the oscillations of the two fields are perpendicular to each other and perpendicular to the direction of energy and wave propagation, forming a transverse wave. The wavefront of electromagnetic waves emitted from a point source, such as a light bulb, is a sphere. The position of an electromagnetic wave within the electromagnetic spectrum can be characterized by either its frequency of oscillation or its wavelength. Electromagnetic waves of different frequency are termed or named by different names since they have different sources and effects on matter. In order of increasing frequency and decreasing wavelength these are named as radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays.

Electro Magnetic waves or EM waves are waves that are created as a result of vibrations between an electric field and a magnetic field. In other words, EM waves are composed of oscillating magnetic and electric fields. Principally, the electromagnetic waves are formed when an electric field comes in contact with a magnetic field, hence termed as 'Electromagnetic' waves. The electric field and magnetic field of an electromagnetic wave are perpendicular (at right angles) to each other. They are also perpendicular to the direction of the EM wave.

Electromagnetic waves are generally emitted by electrically charged particles undergoing acceleration, and these waves can subsequently interact with other charged particles, exerting force on them. EM waves carry energy, momentum and angular momentum away from their source particle and can impart those quantities to matter with which they interact. Electromagnetic radiation is associated with those EM waves that are free to propagate themselves, i.e., 'Radiate' without the continuing influence of the moving charges that produced them, because they have achieved sufficient distance from those charges. Thus, EMR is also sometimes referred to as the far field; the near field refers to EM fields near the charges and current that directly produced them, specifically electromagnetic induction and electrostatic induction phenomena.

The effects of EMR upon chemical compounds and biological organisms depend both upon the radiation's power and its frequency. EMR of visible or lower frequencies, i.e., visible light, infrared, microwaves, and radio waves, is called non-ionizing radiation, because its photons do not individually have enough energy to ionize atoms or molecules or break chemical bonds. The effects of these radiations on chemical systems and living tissue are caused primarily through heating effects from the combined energy transfer of many photons. On the contrary, the high frequency ultraviolet, X-rays and gamma rays are called ionizing radiation, since individual photons of such high frequency have enough energy to ionize molecules or break chemical bonds. These radiations have the ability to cause chemical reactions and can damage living cells.

Electromagnetic radiation consists of waves of electric and magnetic fields traveling in space at right angles to one another (Refer Figure 3.20).

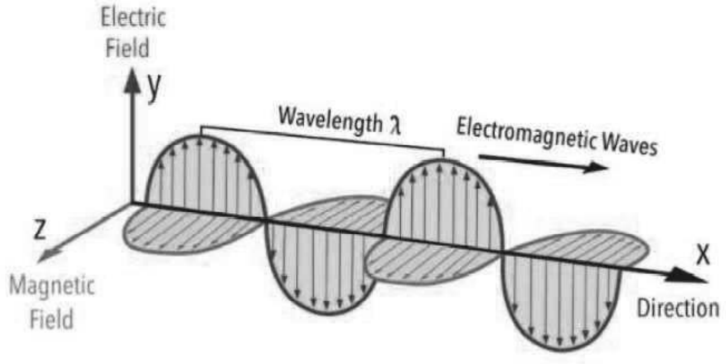


Fig. 3.20 *Electromagnetic Wave*

Figure 3.20 illustrates an electromagnetic wave displaying the perpendicularly oriented waves of electric field, magnetic field, and the characteristic wavelength (λ) of the radiation.

Natural sources produce EM radiation across the spectrum. EM radiation with a wavelength between approximately 400 nm and 700 nm is directly detected by the human eye and perceived as visible light. Other wavelengths, especially nearby infrared (longer than 700 nm) and ultraviolet (shorter than 400 nm) are also sometimes referred to as light. As frequency increases into the visible range, photons have adequate energy to change/modify the bond structure of some individual molecules.

The electromagnetic spectrum is composed of different wavelengths of light having different photon energies, and is classified into the regions shown in Figure 3.21. Note that the regions of interest for photochemistry, i.e., visible and UltraViolet (UV), are only a small part of the full electromagnetic spectrum. Longer wavelengths, such as far infrared, tend to cause the vibrational excitation of molecules, which results in heating. Shorter wavelength X-rays cause ionization.

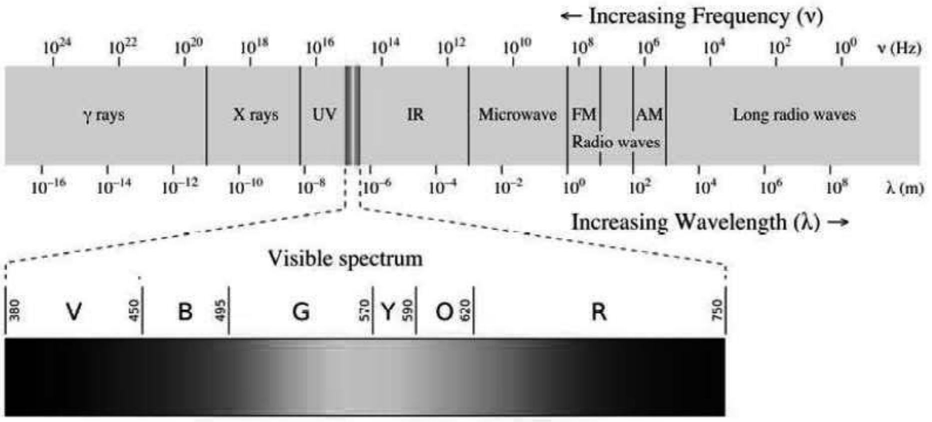


Fig. 3.21 *Electromagnetic Spectrum*

Figure 3.21 illustrates the electromagnetic spectrum highlighting the visible region, which along with the ultraviolet region can produce the photochemical changes in molecules.

Interaction of Radiation with Matter

In the photoelectric (photon-electron) interaction, a photon transfers all its energy to an electron located in one of the atomic shells. Basically, the electron is emitted or ejected from the atom by means of this energy and initiates to pass through the surrounding or adjoining matter. The electron quickly loses its energy and moves/travels only a comparatively short distance from its original location. The photon's energy is, therefore, deposited in the matter close to the site of the photoelectric interaction. The transfer process of energy includes two steps, the photoelectric interaction in which the photon transfers its energy to the electron and the depositing of the energy in the surrounding or adjoining matter through the electron.

Photoelectric interactions are most probable when the electron binding energy is only slightly less than the energy of the photon. If the binding energy is more than the energy of the photon, a photoelectric interaction cannot occur. This interaction is possible only when the photon has sufficient energy to overcome the binding energy and remove the electron from the atom.

When a beam of monochromatic radiation falls upon a system, it can be transmitted, refracted, scattered or absorbed. Grothuss and Draper in 1818 established a relationship between the light absorbed and the chemical change occurring in a photochemical reaction. According to this law, 'Only the light that is absorbed by a substance is effective in producing a photochemical change.' This is also sometimes referred to as the principle of photochemical activation. The converse of the law is not true. All absorbed light does not bring about chemical action. For example light is strongly absorbed by solutions of potassium permanganate, but no chemical effect is produced. The fraction of the incident light absorbed by a homogeneous medium depends on the depth or the thickness of the medium. This is known as Lambert's law which states that when a beam of monochromatic radiation passes through a homogeneous absorbing medium, equal fractions of the incident radiation are absorbed by successive layers of equal thickness of the light absorbing substance. It can be expressed as,

$$-\frac{dl}{I} = a.\,dx \qquad ...(1)$$

Where l is the intensity of light and x is the thickness of the medium, a is called the absorption coefficient. On integration, Equation (1) gives,

$$I = I_0 e^{-ax} \qquad ...(2)$$

With the boundary condition $I = I_0$ at $x = 0$. The intensity I_a, of the light absorbed is given by,

$$I_a = I_0 - I$$

$$I_a = I_0 - I_0 e^{-ax}$$

Or $$I_a = I_0\,(1 - e^{-ax}) \qquad ...(3)$$

When the absorbing medium is solution or gas, the relationship between the intensities of the incident and transmitted radiations is given by Beer's law, which states that equal fractions of the incident radiation are absorbed by equal changes in concentration of the absorbing substance in a path of constant length; that is,

$$I_a = I_0 e^{-\varepsilon Cx} \qquad ...(4)$$

where c is the molar concentration and $\in$ is the molar extinction coefficient. The amount of light absorbed is,

$$I_a = I_0 - I_0 e^{-\varepsilon Cx}$$

$$= I_0(1 - e^{-\varepsilon Cx}) \qquad ...(5)$$

The Beer's law is valid only in dilute solution and when monochromatic light is used. The extinction coefficient ε varies a great deal from substance to substance and also with the wavelength of the light used. The nature and position of the absorption band determines the colour of the substance.

3.4.2 Types of Excitations

The Jablonski diagram is widely used in fluorescence spectroscopy to illustrate the excited states of a molecule and the radiative and nonradiative transitions that can occur between them. The Jablonski Diagram is named after Polish physicist Aleksander Jabłoński who, due to his many pioneering contributions, is regarded as the father of fluorescence spectroscopy.

In molecular spectroscopy, a Jablonski diagram is a diagram that illustrates the electronic states of a molecule and the transitions between them. The states are arranged vertically by energy and grouped horizontally by spin multiplicity. Nonradiative transitions are indicated by squiggly arrows and radiative transitions by straight arrows. The vibrational ground states of each electronic state are indicated with thick lines, the higher vibrational states with thinner lines. The diagram is named after the Polish physicist Aleksander Jabłoński.

Figure 3.22 illustrates the Jablonski diagram showing the excitation of molecule A to its singlet excited state (^{1}A*) followed by intersystem crossing to the triplet state (^{3}A) that relaxes to the ground state by phosphorescence.

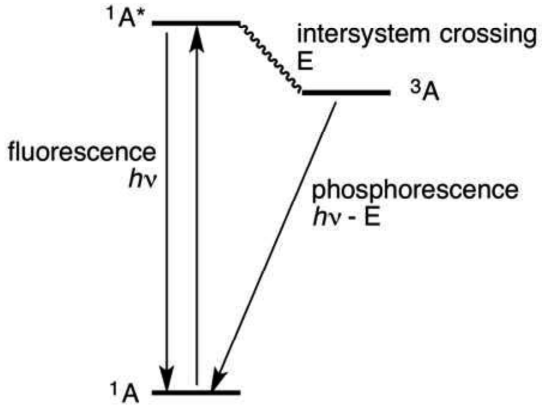


Fig. 3.22 Jablonski Diagram Showing the Excitation of Molecule

(***Source:*** Wikipedia)

Radiative transitions involve the absorption of a photon, if the transition occurs to a higher energy level, or the emission of a photon, for a transition to a lower level. Nonradiative transitions arise through several different mechanisms, all differently labelled in the diagram (Refer Figure 3.22). Relaxation of the excited state to its lowest vibrational level is called vibrational relaxation. This process involves the dissipation of energy from the molecule to its surroundings, and thus it cannot occur for isolated molecules. A second type of nonradiative transition is Internal Conversion (IC), which occurs when a vibrational state of an electronically excited state can couple to a vibrational state of a lower electronic state. A third type is InterSystem Crossing (ISC); this is a transition to a state with a different spin multiplicity. In molecules with large spin-orbit coupling, intersystem crossing is much more important than in molecules that exhibit only small spin-orbit coupling. ISC can be followed by phosphorescence. Figure 2.23 illustrates the Jablonski diagram including vibrational levels for absorbance, non-radiative decay, and fluorescence.

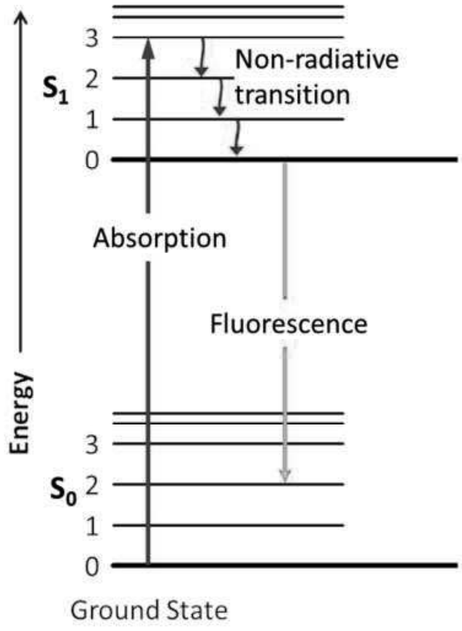


Fig. 3.23 Jablonski Diagram Showing Different Vibrational Levels

(***Source:*** Wikipedia)

Principally, the Jablonski diagram is a principal tool for visualising the possible transitions that can occur after a molecule has been photoexcited. Figure 3.24 illustrates the typical Jablonski diagram.

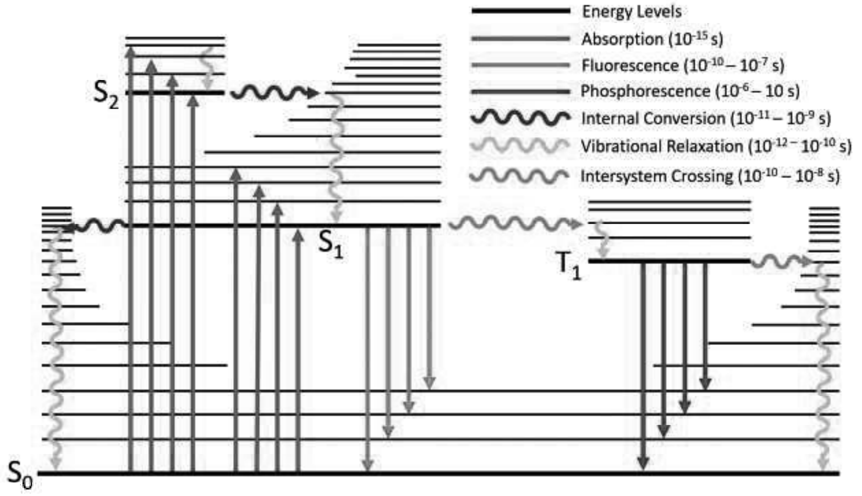


Fig. 3.24 *Typical Jablonski Diagram Showing the Possible Radiative And Non-Radiative Transitions*

Following are the key components and transitions that constitute the diagram.

Energy Levels: The energy levels of a molecule are represented by the horizontal black lines; with energy increasing along the vertical axis of the diagram. The bold lines represent the lowest vibrational level of each electronic state, with the higher vibrational levels represented by thinner lines. The vibrational levels become more closely spaced as energy increases and eventually form a continuum; for clarity, only a subset of these vibrational levels are represented on the diagram.

The naming of the electronic states is based on the spin angular momentum configuration of each state. Singlet states (a total spin angular momentum of zero) are denoted by an **S** and triplet states (a total spin angular momentum of one) by **T**:

$\mathbf{S_0}$ is the singlet ground state of the molecule.

$\mathbf{S_1}$ is the first excited singlet state and $\mathbf{S_n}$ is the nth excited singlet state.

$\mathbf{T_1}$ is the first excited triplet state and $\mathbf{T_n}$ is the nth excited triplet state.

Radiative and Non-Radiative Transitions

The arrows symbolise the various transitions that can transfer energy between the molecular states and are typically divided into radiative and non-radiative transitions.

Radiative transitions are transitions between two molecular states where the energy difference is emitted or absorbed by photons and are represented in a Jablonski diagram by straight arrows.

Non-radiative transitions are transitions between two molecular states without the absorption or emission of photons and are represented in a Jablonski diagram by undulating arrows.

Absorption: A radiative transition from a lower to a higher electronic state of a molecule. The energy of the photon is converted to the internal energy of the molecule.

Vibrational Relaxation: A non-radiative transition to a lower vibrational level within the same electronic state. After a molecule has been stimulated to an excited state by absorption, it is in a non equilibrium state and will eventually dissipate the energy that it has gained and return to the ground state.

Internal Conversion: A non-radiative transition between two electronic states of the same spin multiplicity. A molecule in a higher lying singlet electronic state may also undergo internal conversion to a lower lying singlet electronic state.

Fluorescence: A radiative transition between two electronic states of the same spin multiplicity.

Intersystem Crossing: A non-radiative transition between two isoenergetic vibrational levels belonging to electronic states of different spin multiplicity.

Phosphorescence: A radiative transition between two electronic states of different spin multiplicity.

3.4.3 Fate of Excited Molecule

Luminescence the emission of radiation from excited species is one of the several paths by which the excess energy may be lost as shown in Figure. 3.25. The general phenomenon of light emission from electronically excited species is known as luminescence. Luminescent emission provides some of the most reliable information about the nature of primary photochemical processes. Competition exists between emission and other factors of excited species (quenching, reaction, decomposition, etc.) and the dependence of emission intensity on temperature, reactant concentrations, and so on, may yield valuable information about nature and efficiencies of various processes.

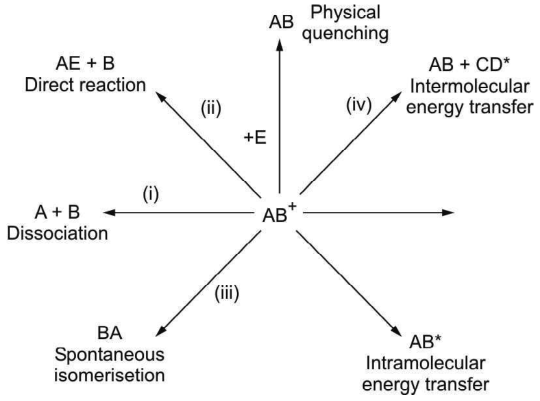


Fig. 3.25 Several Routes to Loss of Electronic Excitation

The various individual luminescent phenomena are named according to the mode of excitation of the energy rich species. We are concerned primarily with excitation by absorption of radiation and emission from species excited in this way is referred to as fluorescence or phosphorescence.

Fluorescence

An electronically excited atom must lose its energy by emission of radiation or by collisional deactivation chemical decomposition is not possible, and radiationless degradation is extremely improbable. At low enough pressures, therefore, fluorescent emission is expected from all atoms. Many molecular species who either, do not exhibit fluorescence or fluoresce weakly even when bimolecular reaction or physical deactivation does not occur. Some general principles can suggest whether a polyatomic organic molecule is likely to be strongly fluorescent. First absorption must occur at a wavelength long enough to ensure that chemical dissociation does not take place. Absorption to an unstable state is clearly very unlikely to result in fluorescence. Secondly, intramolecular energy transfer must be relatively slow compared to the rate of radiation.

In the excited state the molecule is subjected to collision with the environment, i.e., solvent molecules. Its thermal energy is discarded as thermal motion of the surroundings. The collisions succeed on lowering the molecule down the ladder of vibrational energy levels, but they may be made to withdraw the larger electronic energy difference and quench the electronic excitation energy. The molecules might therefore live long enough to undergo a spontaneous emission and to emit the excess energy as radiation as it drops to the lower electronic state. The downward step occurs vertically in accord with the Franck Condone δ principle and a series of lines appear as the fluorescence spectra Figure. 3.26. The vibrational structure of the spectrum is characteristic of the lower electronic state of the system and the fluorescence spectra provides a valuable method of studying the vibrational characteristic of the ground state. This mechanism accounts for the observations that fluorescence radiation has a lower frequency than the incident radiation, the fluorescence occurs after some energy has been absorbed into the solvent. This mechanism suggests that the intensity of fluorescence should depend on the ability of the solvent to withdraw the larger quantum of energy required to lower the molecule from one electronic state to the other. It has been observed that fluorescence can be eliminated by selecting a different solvent. For example a solvent with widely spaced vibrational energy levels (such as water) may be able to accept the large quantum of electronic energy but one with more closely spaced levels (such as heavy flabby $SeOCl_2$) night not.

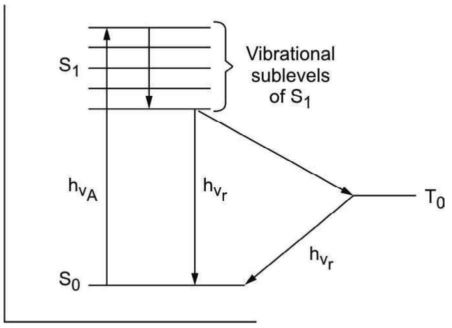


__Fig. 3.26__ The Sequence of Steps Leading to Fluorescence

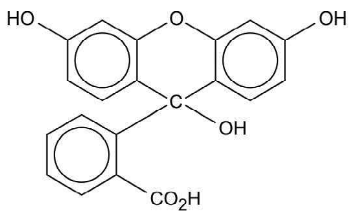
The absorption of light hv_A by the groundstate molecule leads to promotion of one electron from a ground state MO. to one of the vibrational sublevels of the excited state MO.,S_1 (or to some higher electronic excited, state S_2, S_3, etc.) This rapidly deactivates in solution, by a radiationless process to the lowest vibrational sublevel of S_1.

For the electron to return from S_1 to the ground state, it must emit radiation (hv_{A}) which is clearly of lower energy and thus of longer wavelength than hv_A the fluorescent radiation corresponds to hv_F.

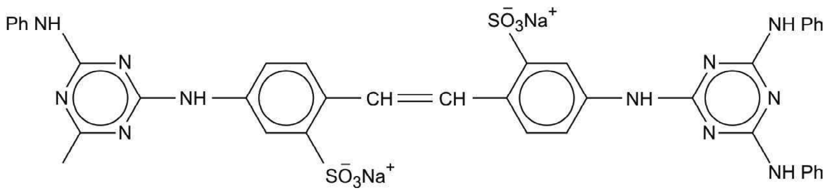
An alternative path involves loss of energy from S_1 to T_1, the principle difference between S_1 and T_1 is electron spin orientation.

The two electrons originally occupying the ground state MO under consideration, their must be antiparallel from the Pauli's exclusion principle. The excitation followed spins by the decay to the lowest vibrational level of S_1 does not alter the spin of the promoted electron, but the transition S_1 to T_1 does. Energy states containing only spin paired electrons are called singlet states (S_0,S_1,S_2) and those energy states containing parallel spin electrons are called trip lot states (T_1...), etc. Triplet states are more stable than singlet states and are longer lived, as they survive after the exciting radiation has been removed. These then decay to S_0 and in doing so emit radiation hv_{P}, called phosphorescent radiation. This has been explained in Figure. 3.23.

Important uses of fluorescence phenomenon are represented by the molecules of fluorescein and the optical 'brightener' derivative of 4,4′-diaminostilbene.



Florescein (acid iorm)



The intense green fluorescence of aqueous fluorescein in solutions makes it an excellent material to add to water systems for leak detection, an excellent 'Maker' for sea rescue operations, etc. Minute quantities of optical brighteners are added to detergents and are retained on the fabrics after washing in sunlight they fluoresce blue and add brightness to the fabrics after washing. Other applications of fluorescence depend on its extremely low detection limit, it is used in polymer chemistry to detect and identify plasticisers, and in the study of impurities. Fluorescent material dissolved in solution or in solid plastic bases can also detect radioactive decay, this forms the basis of scintillation counting of β-emitters, etc. The three dimensional structure of proteins can be studied by measuring the proximity of known fluorescent group within the protein, these fluorescent groups can be aromatic amino acids.

In addition to this fluorescence finds wider applications in testing the conditions of food stuffs, for detecting ring worm. Fluorescent tubes are used for lighting purposes. The great importance of photochemistry as a branch of science lies principally in the fact that it provides the chemical potential which is necessary for biological chemistry to operate. From its earliest abiological stages, the chemical origin of life were almost certainly photochemical reactions and the food and fuel of life today is provided by photosynthesis. The discovery of laser has further helped in the growth of photochemistry.

Phosphorescence

The phenomenon of phosphorescence is similar to fluorescenie with some difference. Figure 3.27 depicts the phenomenon of phosphorescence. The first steps are the same as in fluorescence but the presence of a second excited state of the molecule play a decisive role and is present only in phosphorecence. The second excited state is called the tripled state. It differs from the first state (single state) in that in a tripled state spins of two of its electrons are paralled where as in the singlet state the spins are opposed.

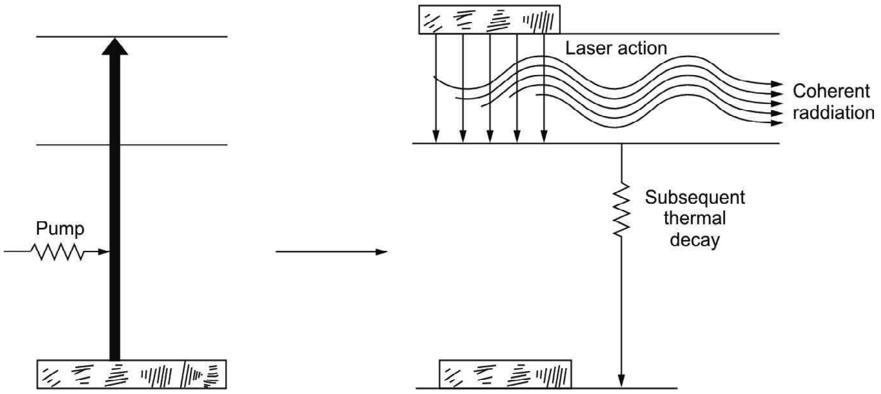


Fig. 3.27 *Phosphoresence*

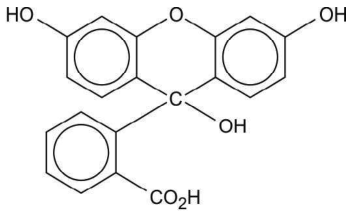
At a point indicated in the Figure. 3.27 the excited state curves cross the two states have the same geometry. This singlet or triplet switching is known as inter system crossing. In most systems this singlet to triplet state crossing is forbidden while in some other systems it is weakly allowed. This happens in case of the molecules which contain a heavy atom because its strong spin-orbit interaction

molecules which contain a heavy atom because its strong spin-orbit interaction

can reverse the relative orientations of pairs of electrons.

When a molecule crosses over into the triplet it continues to deposit the energy into the environment and as it drops down the triplet ladder of vibrational energies. The ladder terminates at the ground vibrational state of the excited triplet. The energy of the molecule thus gets trapped. The solvent can not extract the final large quantum of electronic excitation energy and the molecule can not radiate the energy because a return to the ground state involves a forbidden singlet triplet transition. The radiative transition is not completely forbidden, because the spin-orbit coupling is present and breaks the selection-rule. The molecules are therefore able to emit slowly and the emission may last long after the original excited state is formed.

The mechanism explains experimental observation that the energy seems to be trapped in a slowly leaking reservoir. It also suggests that phosphorescence should be most intense in solid sample. This is due to the fact that the environment then colloides less effectively with the molecule and intersystem crossing step has time to occur as the singlet excited state slowly loss vibrational energy and falls past the intersection point. The above mechanism also suggests that the amount of phosphorescence depends on the presence of a heavy atom and due to the presence of unpaired electrons the excited reservoir state should be magnetic. This has been experimentally confirmed by observance of magnetism in phosphorescent excited molecules. The common examples of phosphorescent substances are fluorescein (I), 1-hydroxy-2 naphthoic acid (I) and triphenylene (III) in boric acid.



Florescein (acid Form)

Lasers

Both fluorescence and phosphorescence are modes of return to the ground state by spontaneous emission. Laser action, as the aronym laser (light amplification by stimulated emission of radiation) suggests, depends on emission by stimulated processes.

A typical laser arrangement is shown in Figure. 3.28. By some means a majority of molecules in the ample are excited into the upper state. For example, a chemical reaction be used to prepare the species in that state. The sample is contained in a cavity between two mirrors, and when a molecule emits spontancously the photon, it generates ricochets backwards and forwards. Its pressure stimulates other molecules to emit. They add more photons of the same frequency to the cavity, and these photons stimulate more molecules to emit. The cascade of energy builds up very rapidly and if one of the mirrors is half-silvered the radiation may be tapped.

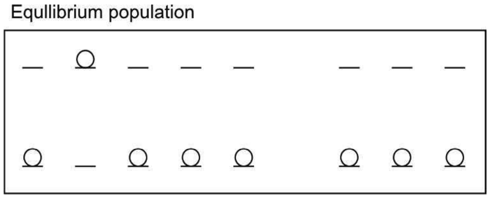


Fig. 3.28 *Laser Action by Emission Radiation*

The characteristics of laser radiation follow from its manner of generation. It is monochromatic (because photons travelling at angles to the cavity axis are not tapped and do not stimulate others).

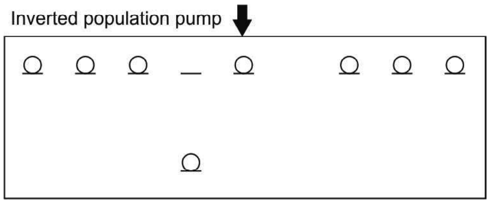


Fig. 3.29 Laser Action by Inverting a Ground State Population

In practice it is often more convenient to use the three-level system shown in Figure. 3.29. This is because inverting a ground state population (getting majority molecules into excited states) is often impossible, but it is often easier to obtain a relative excess in the upper of two excited states. A typical arrangement would be to use a powerful source to stimulate the transitions between the first and third level (e.g., a Xenon lamp, or another laser), this is called pumping and then to observe laser action to the middle, unpopulated level. The pumping can be done either with a powerful optical flash as in the ruby laser, or chemically, as in the chemical laser.

$$H_2 + F_2 \rightarrow 2HF^*$$
$$HF^* \rightarrow HF + \text{photon}$$

Another method depends on a collision of the laser molecule with a species excited by a radio frequency discharge. This is used in the He–Ne laser, where some of the neon excited energies just match those in the helium atom; excitation of neon, followed by collisions with helium atoms, can therefore lead to excited states when the energy is transferred.

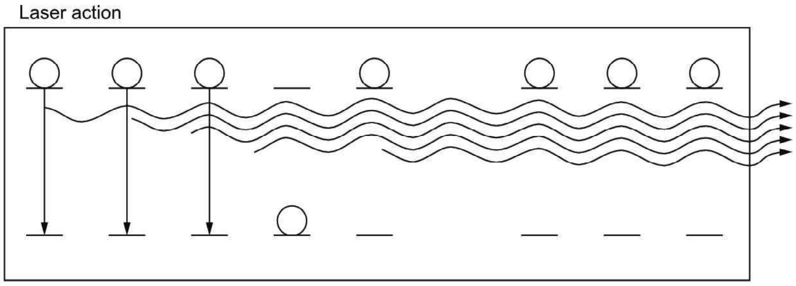


Fig. 3.30 Laser Action by Collision

***Solar Energy Conversion*:** The need to find a substitute for dwindling reserves of fossil fuels is becoming increasingly apparent. The power from nuclear emission is becoming unpopular because of the anxieties about the control of reactors and protection of their waste products. Nuclear power offers the prospects of almost unlimited energy supply if the formidable technical difficulties can be overcome. Although tidal and geothermal energy could become locally important they cannot make a major contribution to global demands. By contrast solar energy is available everywhere and the total supply for outstrips human's requirements as the radiant energy reaching the earth's surface in one hour approximates to the global requirements for one year. At noon 1 m^2 of the Sahara Desert receives about 1kW of solar power. The efficiency with which the incident radiation can be converted into usable power will be one of the man factors determining the exploitation of solar energy where $C_6H_{12}O_6$ stands for the basic synthesis product of the reaction which has glucose structure. The combustion reaction, complementary to the above process, can be written:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$\Delta S = 43.6 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta G^{o} = -686 \text{ kcal. mole}^{-1}$$

$$\Delta H^{o} = -673 \text{ kcal. mole}^{-1}$$

3.4.4 Quantum Yield

The law of photochemical equivalence is applicable only to primary photochemical process, i.e., when as a result of absorption of light, only one molecule decomposes and the products enter no further reaction. The Einstein law is usually marked by secondary reactions and radiative and non-radiative transitions which present a simple 1 : 1 relationship between the number of photon absorbed and the number of molecules of final products in the reaction. The results of photochemical process are frequently expressed in terms of the *quantum yield or quantum efficiency* of the reaction. It is the number of moles of reactant consumed or product formed for each einstein of light absorbed. This quantity is defined as

$$\text{Quantum Yield, } \Phi = \frac{\text{Number of Moles Reacting}}{\text{Number of Einstiens Absorbed}}$$

An experimental arrangement for a photochemical study is shown in Figure. 3.31. The light from the source passes through a monochromotor which yields light of definite wavelength (λ). The light from a monochromotor enters a reaction cell filled with the reaction mixture. The part of light which is not absorbed strikes the detector, mostly a thermopile. The intensity of light is measured with the empty cell and with a reaction mixture.

Photoelectric cell can also be used as detectors, but they must be calibrated for each frequency. Chemical actinometers are often used to measure the intensity of light radiation. It utilises a chemical reaction which has been accurately investigated in its photochemical behaviour. One of the most reproducible reactions is the decomposition of oxalic acid in presence of uranyl sulphate. The reaction can be written as,

$$UO_2 + hv \rightarrow (UO_2^{++})^*$$

$$(UO_2^{++})^* + (COOH)_2 \rightarrow UO_2^{++} + CO_2 + CO + H_2O$$

The oxalic acid concentration can be determined by titration with permanganate. This reaction has a quantum yield of 0.50.

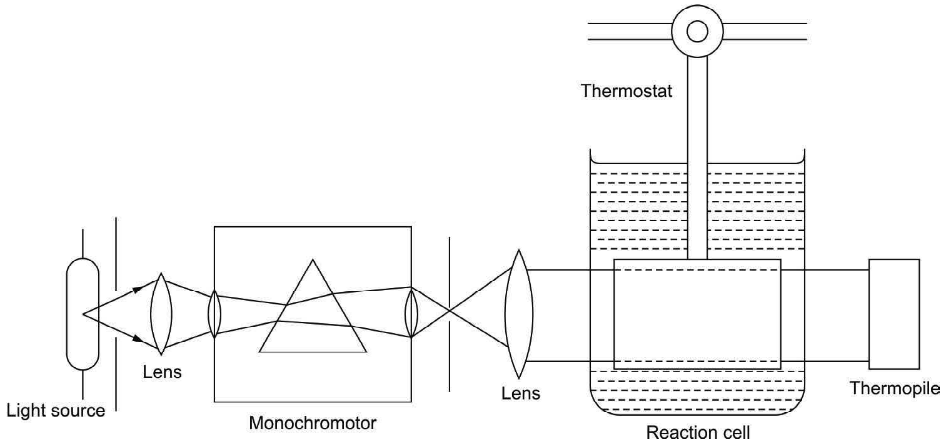


Fig. 3.31 *Arrangement for Photochemical Studies*

It has been found that the law of photochemical equivalence applies only to the primary process of the reaction since only in a few cases the quantum yield is unity as required by the law of the photo-chemical equivalence. The values of quantum yields range from almost zero to very large values, e.g., 10^5.

Example 1: In the photobromination of cinnamic acid to dibromocinnamic acid, using light of wavelength 4358 at 30.6° a light intensity of 14,000 ergs sec^{-1} produced a decrease of 0.075 millimole of bromine during an exposure of 1105 sec. The solution absorbed 80.1 per cent of the light passing through it. Calculate the quantum yield.

Solution. $E = h\nu = \frac{hc}{\lambda}$

$$E = (6.62 \times 10^{-27})\,(3 \times 10^{10})\,(4.358 \times 10^{-5})$$

$$E = 4.54 \times 10^{-12} \text{ erg per quantum}$$

$$\text{Number of quanta absorbed} = \frac{(14.000)\,(0.801)\,(1105)}{4.54 \times 10^{-12}}$$

$$= 2.74 \times 10^{16}$$

Number of molecules of Br_2 reacting

$$= (7.5 \times 10^{-5})\,(6.02 \times 10^{23})$$

$$= 45.2 \times 10^{18}$$

$$\text{Quantum Efficiency } (\Phi) = \frac{45.2 \times 10^{8}}{2.74 \times 10^{18}} = 16.5$$

Example 2: From the following data for the uranyl uxalate system, evaluate the quantum efficiency at each wave length.

Wave length $m\mu$	*Fraction of oxalate decomposed*	*Molecules decomposed* $\times 10^{18}$	*Photons absorbed* $\times 10^{-18}$
365.5	0.0592	5.18	10.58
435.8	0.0242	2.10	3.64
435.8	0.0208	1.79	3.10

Solution. At 365.5 mμ

$$\phi = \frac{\text{number of molecules decomposed}}{\text{number of photons absorbed}}$$

$$= \frac{5.18 \times 10^{18}}{10.58 \times 10^{18}} = 0.490$$

At 435.8 mμ

$$\phi = \frac{2.10 \times 10^{18}}{3.64 \times 10^{18}} = 0.576$$

At 435.8 mμ

$$\phi = \frac{1.79 \times 10^{18}}{3.10 \times 10^{18}} = 0.577$$

3.4.5 Transfer of Excitation Energy

When a molecule is electronically excited the total energy of the molecule may be written as

$$E_{\text{total}} = E_{\text{ electronic}} + E_{\text{ vibrational}} + E_{\text{ rotational}}$$

A change in the total energy of the molecule may be written as,

$$\Delta E_{\text{total}} = \Delta E_{\text{ele}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}}.$$

Or $$\Delta\varepsilon_{\text{total}} = \Delta\varepsilon_{\text{ele}} + \Delta\varepsilon_{\text{vib}} + \Delta\varepsilon_{\text{rot}}.$$

The approximate orders of magnitudes of these changes are,

$$\Delta\varepsilon_{\text{ele}} \approx \Delta\varepsilon_{\text{vib}} \times 10^3 \approx \Delta\varepsilon_{\text{rot}}. \times 10^6$$

Franck-Condon principle states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance during the transition.

If a diatomic molecule undergoes a transition into an upper electronic state in which excited molecule is stable with respect to dissociation into its atoms. There are three possibilities in such a case as shown in Figure. 3.32.

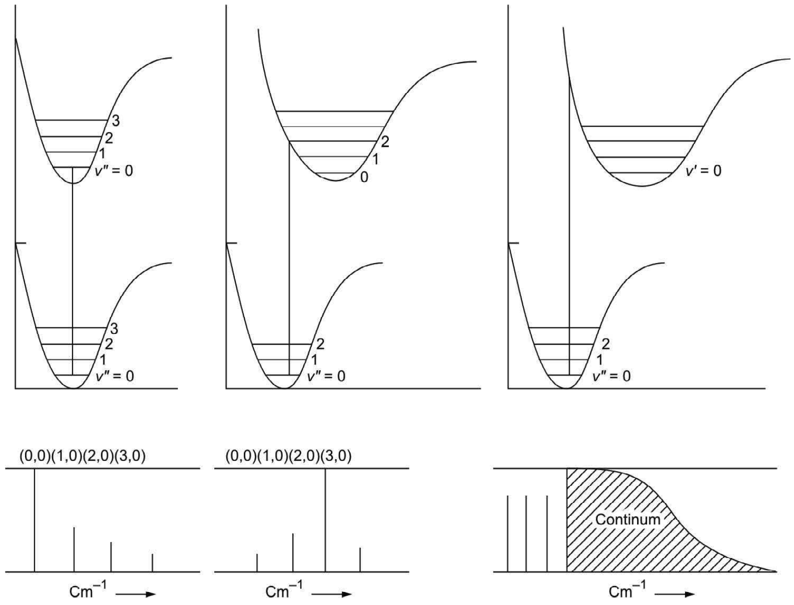


Fig. 3.32 Illustrates of Franck Condon Principles

Figure 3.32 illustrates the three possibilities, namely (*i*) Internuclear distances equal in upper and lower states (*ii*) Upper state inter nuclear distance is little greater than that in the lower state and (*iii*) Upper state distance is considerably greater.

In possibility (*i*) we show the upper electronic state having the same equilibrium inter nuclear distance as the lower. The transition occurs vertically since the inter nuclear distance does not change. Thus, the strongest line will be (0, 0).

In possibility (*ii*) a case is shown where the excited electronic state has a slightly higher inter nuclear separation than the ground state. A vertical transition from $v'' = 0$ to $v' = 2$ will most likely occur. (Z,0) transition will thus most intense. Possibility (*iii*) the upper state separation is drawn as considerably greater than that in the lower state. The electronically excited molecule is fragmented into two or more components. The onset of dissociation can be detected by observing where the vibrational structure of the molecule ends this is the dissociation limit of the spectrum. This helps us in determining the dissociation energy of the molecule. In some cases however the vibrational structure disappear as but the molecule returns to higher energies. This behaviour is called predissociation and can be interpreted in terms of the molecular energy curves shown in Figure. 3.32. When the molecule makes a transition in the vibrational energy levels in the region when one molecular potential energy curve crosses the other, there may be reorganisation of its electrons switching from one state to another. The nuclear geomet158ry at the crossing point of the two states is the same. This process is called internal conversion. When a molecule changes to another state in may have enough to dissociate. Hence the energy levels in the vicinity of the intersection of the curves may have a unbound character and the vibrational structure of the spectrum blurs into a continunum. The moment the excitation source supplies energy sufficient enough to raise the molecule into the dissociative state. The vibrational structure becomes well defined and the spectrum acquires a fine structure.

3.4.6 Actinometry

Actinometers are the devices specifically used for measuring the heating power of radiation and also used in meteorology for measuring the solar radiation as pyranometers, pyrheliometers and net radiometers.

Principally, ***an actinometer is a chemical system or physical device which determines the number of photons in a beam integrally or per unit time***.

The name actinometer is commonly given to devices that are used in the ultraviolet and visible wavelength ranges. For example, solutions of iron or Fe (III) oxalate can be used as a chemical actinometer, while bolometers, thermopiles, and photodiodes are physical devices which provide a reading that can be correlated to the number of photons detected.

In chemistry, an actinometer is defined as a device that is used to measure the intensity of solar radiation. It is a chemical system that determines the number of photons by measuring the rate of change of photoinduced responses in a chemical system.

Figure 3.33 illustrates the actinometer device that is designed by Jules Violle and is specifically used for estimating the temperature of the surface of the Sun.

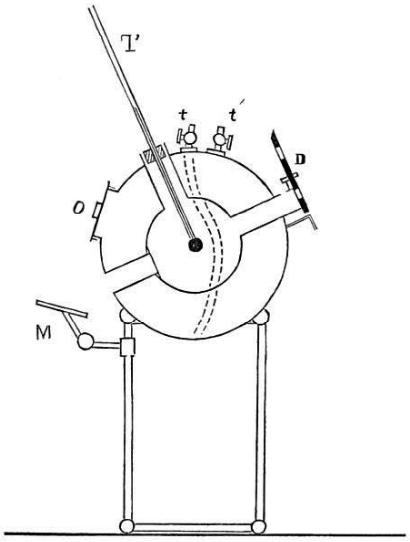


Fig. 3.33 *Actinometer Designed by Jules Violle*

The actinometer was first invented by John Herschel (1825) who introduced the term actinometer. The prefix '***actin***' in the term 'actinometer' means scientific instruments, effects and processes. The actinograph is other related device that is used to estimate the actinic power of lighting for photography.

Chemical Actinometry

Chemical actinometry includes measuring radiant flux via the yield from a chemical reaction. It essentially requires a chemical with a known quantum yield and easily analyzed reaction products.

Selecting an Actinometer

For analysing the reaction products, we need a proper actinometer. Potassium ferrioxalate is commonly used, because it is simple to use and sensitive over a wide range of relevant wavelengths, basically 254 nm to 500 nm. Other actinometers include malachite green leucocyanides, vanadium (V) – iron (III) oxalate and monochloroacetic acid, however all of these undergo dark reactions, i.e., they react in the absence of light. Organic actinometers, such as the butyrophenone or piperylene are analysed by gas chromatography. Some other actinometers are more specific in terms of the range of wavelengths at which quantum yields have been determined. Reinecke's salt with chemical formula $K[Cr(NH_3)_2(NCS)_4]$ reacts in the near-UV region although it is thermally unstable. Uranyl oxalate has been used historically but it is very toxic and cumbersome to analyze.

Recent studies on nitrate photolysis have defined the use of 2-nitrobenzaldehyde and benzoic acid as a radical scavenger for hydroxyl radicals that is produced in the photolysis of hydrogen peroxide and sodium nitrate. Though, they originally used ferrioxalate actinometry to calibrate or regulate the quantum yields for the hydrogen peroxide photolysis. Radicals evidenced a feasible method of measuring production of hydroxyl radical.

Chemical Actinometry in the Visible Range

Meso-diphenylhelianthrene can be used for chemical actinometry in the visible range, i.e., from 400–700 nm. Though this chemical measures in the 475–610 nm range, but it can also measure the wider spectral ranges with this chemical if the emission spectrum of the light source is known.

Working Principle of Chemical Actinometer

In chemistry, the actinometer is considered as a substance or a mixture of substances that reacts through the action of light. Because the quantitative relationship between the extent of the reaction and the energy of the absorbed light can be easily determined, hence it is frequently used as a standard for measurement of light energies involved in photochemical work.

A typical actinometer is a liquid solution of oxalic acid containing uranyl sulfate. Light in the wavelength range of about 2,080 to 4,350 angstroms, i.e., ultraviolet to violet light decomposes the oxalic acid into a mixture of carbon dioxide, carbon monoxide and water through a complex process involving initial absorption of the light energy by the uranyl ion. Generally, a standard solution is irradiated with light of the proper wavelength and of known intensity, and then the quantity of oxalic acid decomposed is accurately measured by titration with potassium permanganate.

In the experiment, the relationship between the quantity of oxalic acid transformed and the quantity of light energy absorbed is determined using a scale to predict either quantity when the other is known or measured. In addition to the oxalic acid–uranyl sulfate solution, other substances that are normally used as chemical actinometers include acetone, hydrogen bromide, carbon dioxide and a solution of ferrioxalate in sulfuric acid.

For an efficient actinometer, this quantum yield has to be independent of oxygen, trace impurities, temperature and excitation wavelength. The following are the basic steps employed in the working principle of chemical actinometers:

- The specified gas is filled into a photolysis reactor.
- The actinometer is exposed to heat radiation.
- The photochemical rate is measured.

Basically, the actinometer gas is considerably exposed to actinic flux without altering the radiation intensity and spectral composition and from the measurement or reading obtained the photolysis frequency can be easily evaluated.

During the measurement, the actinometer is uncovered and exposed to heat radiation for a fixed interval of time, then the actinometer is closed again and analyzed for change in the gas composition. When the gas passes through the reactor, its composition is analyzed using an online gas detector. Photolysis frequencies can be continuously monitored in this mode.

The actinometers are mostly used in meteorology for measuring solar radiation that is transmitted by the sun, reflected by the earth or scattered by the atmosphere, in photochemical experiments that involve complex irradiation geometry, and for calibrating photochemical detectors used for radiation measurements.

Check Your Progress

10. Define photochemistry.
11. What do you understand by electro-magnetic radiations?
12. Define quantum yield.
13. What do you understand by actinometer?
14. Define chemical actinometry.

3.5 DETERMINATION OF REACTION MECHANISM

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

3.5.1 Classification

All photochemical processes can broadly be classified into two types: (1) The Primary Process and (2) The Secondary Process.

1. **The Primary Process:** As a first step, a photochemical reaction requires absorption of energy. The molecule is thus raised to a higher energy level.

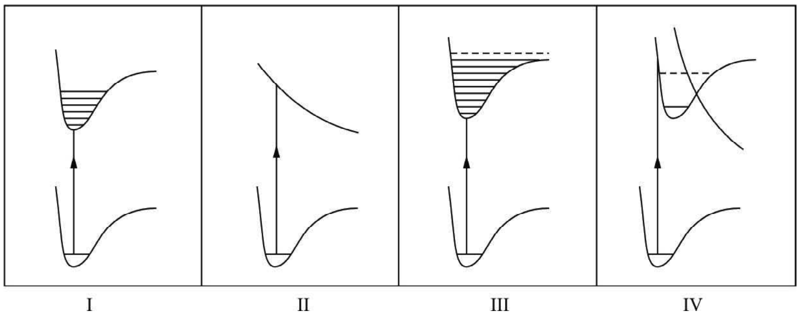


Fig. 3.34 *Primary Photochemical Process*

This can lead to four different types of behaviour as shown in Figure. 3.34. In type I, transition is from a stable-ground state to a stable excited state. The corresponding spectrum consists of discontinuous bands with a fine structure of closely packed lines as shown. Type II represents a transition to an unstable state which immediately undergoes dissociation. Type III also leads to dissociation because the energy level reached lies above the binding energy of the molecule. Type IV is a combination of Type II and Type III. The initial transition is from one stable state to another but, the upper state is intersected by the potential energy surface of an unstable state. When the molecule is vibrating in the excited state, as soon as it reaches a point where the two curves cross, it undergoes dissociation. This type of behaviour is referred to as predissociation.

2. **The Secondary Process:** This process involves the excited atoms, molecules or free radicals. A large number of paths are available to a molecule, some of them may lead to the return of the molecule to the ground state by emission of excess energy while the others produce chemical decomposition.

3.5.2 Rate Constants and Life Time of Reactive Energy States Determination of Rate Constants of Reactions

In chemical kinetics a **reaction rate constant** or **reaction rate coefficient**, *k*, quantifies the rate and direction of a chemical reaction.

For a reaction between reactants A and B to form product C

$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow c\,\mathrm{C}$

the reaction rate is often found to have the form:

$$r = k(T)[\mathrm{A}]^m[\mathrm{B}]^n$$

Here $k(T)$ is the reaction rate constant that depends on temperature, and [A] and [B] are the molar concentrations of substances A and B in moles per unit volume of solution, assuming the reaction is taking place throughout the volume of the solution. (For a reaction taking place at a boundary one would use instead moles of A or B per unit area.)

The exponents *m* and *n* are called partial orders of reaction and are *not* generally equal to the stoichiometric coefficients *a* and *b*. Instead, they depend on the reaction mechanism and can be determined experimentally.

Rate constant can be calculated for elementary reactions by molecular dynamics simulations. One possible approach is to calculate the mean residence time of the molecule in the reactant state. Although this is feasible for small systems with short residence times, this approach is not widely applicable as reactions are often rare events on molecular scale. One simple approach to overcome this problem is Divided Saddle Theory. Such other methods as the Bennett Chandler procedure, and Milestoning are also developed for rate constant calculations.

Divided Saddle Theory

The theory is based on the assumption that the reaction can be described by a reaction coordinate, and that we can apply Boltzmann distribution at least in the reactant state. A new, especially reactive segment of the reactant, called the *saddle domain*, is introduced, and the rate constant is factored:

$$k = k_{\mathrm{SD}} \cdot \alpha_{\mathrm{RS}}^{\mathrm{SD}}$$

Where $\alpha_{\mathrm{RS}}^{\mathrm{SD}}$ is the conversion factor between the reactant state and saddle domain, while k_{SD} is the rate constant from the saddle domain. The first can be simply calculated from the free energy surface, the latter is easily accessible from short molecular dynamics simulations.

3.5.3 Effect of Light Intensity on the Rate of Photochemical Reactions

Light energy (uv or visible radiation) can initiate or catalyse particular chemical reactions. As well as acting as an electromagnetic wave, light can be considered as an energy 'bullets' called photons and they have sufficient 'impact energy' to break chemical bonds, that is, enough energy to overcome the activation energy. The greater the intensity of light (visible or ultra-violet) the more reactant molecules are likely to gain the required energy (activation energy) and react, so the reaction speed increases.

3.5.4 Types of Photochemical Reactions: Photodissociation

Photodissociation, photolysis, or photodecomposition is a chemical reaction in which a chemical compound is broken down by photons. It is defined as the interaction of one or more photons with one target molecule. Photodissociation is not limited to visible light. Any photon with sufficient energy can affect the chemical bonds of a chemical compound. Since a photon's energy is inversely proportional to its wavelength, electromagnetic waves with the energy of visible light or higher, such as ultraviolet light, x-rays and gamma rays are usually involved in such reactions.

3.5.5 Gas-Phase Photolysis

Photolysis occurs in the atmosphere as part of a series of reactions by which primary pollutants such as hydrocarbons and nitrogen oxides react to form secondary pollutants such as peroxyacyl nitrates.

The two most important photodissociation reactions in the troposphere are firstly:

$$O_3 + h\nu \rightarrow O_2 + O\ (^1D) \quad \lambda < 320\ \text{nm}$$

Which generates an excited oxygen atom which can react with water to give the hydroxyl radical:

$$O\ (^1D) + H_2O \rightarrow 2\ {}^{\bullet}OH$$

The hydroxyl radical is central to atmospheric chemistry as it initiates the oxidation of hydrocarbons in the atmosphere and so acts as a detergent.

Secondly the reaction:

$$NO_2 + h\nu \rightarrow NO + O$$

is a key reaction in the formation of tropospheric ozone.

The formation of the ozone layer is also caused by photodissociation. Ozone in the Earth's stratosphere is created by ultraviolet light striking oxygen molecules containing two oxygen atoms (O_2), splitting them into individual oxygen atoms (atomic oxygen). The atomic oxygen then combines with unbroken O_2 to create ozone, O_3. In addition, photolysis is the process by which CFCs are broken down in the upper atmosphere to form ozone-destroying chlorine free radicals.

Check Your Progress

15. Define the reaction rate constant.
16. State the divided saddle theory.
17. What do you understand by photo-dissociation?

3.6 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Spectroscopy is the science concerned with the investigation and measurement of spectra produced when a material interacts with a source of light and emits electromagnetic radiation.
2. Mössbauer spectroscopy consists of the study of γ-ray absorption (or emission) spectra for transition between nuclear states.
3. Mössbauer spectroscopy is named after Rudolf Mössbauer (1958).
4. In a Mössbauer experiment, if the environments of the emitting and absorbing nuclei are different, the energy of the nuclear transition E_0 may differ by a small amount. This energy difference is known as isomer shift (δ).
5. Magnetic hyperfine splitting is a result of the interaction between the nucleus and any surrounding magnetic field, as described by the Zeeman Effect.
6. The coordination number, also called ligancy, of a central atom in a molecule or crystal is the number of atoms, molecules or ions bonded to it.
7. Optical Rotatory Dispersion (ORD) is the change of specific rotation [α] or molar rotation [Õ] with the wavelength of light used.
8. The optical techniques like polarimetry, ORD and CD which can differentiate between the two enantiomers of a chiral compound are called *chiroptical techniques*.
9. A rule referred as Octant rule is used to predict the sign of the cotton effect in ORD and CD curves from a knowledge of the spatial arrangement (axial or equatorial) of the substituents around the carbonyl group.
10. Photochemistry is that branch of chemistry which studies the chemical effects of light.
11. The 'Electro-Magnetic Radiation, also termed as EM radiation or EMR, refers to the waves or their quanta, photons of the electromagnetic field, propagating (radiating) through space, carrying electromagnetic radiant energy.

12. The quantum yield or quantum efficiency of the reaction. It is the number of moles of reactant consumed or product formed for each Einstein of light absorbed.
13. An actinometer is a chemical system or physical device which determines the number of photons in a beam integrally or per unit time.
14. Chemical actinometry includes measuring radiant flux via the yield from a chemical reaction.
15. A reaction rate constant or reaction rate coefficient, *k*, quantifies the rate and direction of a chemical reaction.
16. The theory is based on the assumption that the reaction can be described by a reaction coordinate, and that we can apply Boltzmann distribution at least in the reactant state.
17. Photo-dissociation is a chemical reaction in which a chemical compound is broken down by photons.

3.7 SUMMARY

- Mössbauer spectroscopy is named after Rudolf Mössbauer (1958).
- Mössbauer spectroscopy consists of the study of γ-ray absorption (or emission) spectra for transition between nuclear states.
- Nuclear resonance absorption is expected to occur when γ –radiation emitted in a transition from E_i to Ef is reabsorbed by another nucleus of the same kind.
- After absorption of the γ-ray by the same nucleus, the atom will have momentum and energy.
- In a Mössbauer experiment, if the environments of the emitting and absorbing nuclei are different, the energy of the nuclear transition E_0 may differ by a small amount.
- The effect of isomer shift on the Mössbauer spectrum is to shift the resonance line from the zero position.
- Isomer shift arise because the nucleus of an atom is not a point charge as assumed, but has a finite charge distribution.
- The spin of either or both of the Mössbauer nuclear levels may have a value greater than Y_2. In such a case, the interaction of the nuclear quadrupole moment eQ with the electric field gradient eq at the nucleus may lead to a splitting of the Mössbauer spectrum.
- Magnetic hyperfine splitting is a result of the interaction between the nucleus and any surrounding magnetic field, as described by the Zeeman Effect.
- The isomer shift is of greatest interest to chemists. It is a direct function of the s-electron density at the nucleus.

- For spin paired (low spin) compounds of iron, the isomer are independent of the oxidation state and lie in the region of zero velocity relative to stainless steel.
- The Mössbauer spectrum of the iron site reflects the ligand field of the surrounding organic groups and therefore usual procedures for understanding of electronic structures can be applied.
- Light is an electromagnetic radiation and associated with time-dependent electric and magnetic fields. In ordinary light radiation the electric field associated with the light waves oscillates in all directions perpendicular to the direction of propagation.
- Linearly polarized light can be regarded as the resultant of two equal and opposite beams of circularly polarized light, i.e., as a contribution of left and right circularly polarized light.
- ORD (Optical Rotatory Dispersion) is the change of specific rotation [α] or molar rotation [$\tilde{O}$] with the wavelength of light used.
- The optical techniques like polarimetry, ORD and CD which can differentiate between the two enantiomers of a chiral compound are called chiroptical techniques.
- The sign of the Cotton Effect reflects the stereochemistry of the environment of the chromophore e.g., of a chiral ketone.
- The techniques ORD and CD provides complementary information, CD has now replaced ORD as the main chiroptical techniques to study chiral compounds.
- When the absolute configuration of a conformational mobile system is known, the preferred conformation can be determined by the application of octant rule.
- Photochemistry is that branch of chemistry which studies the chemical effects of light.
- Photochemistry is fundamentally referred as the principal mechanism for all of photobiology.
- The ‘Electro Magnetic Radiation, also termed as EM radiation or EMR, refers to the waves or their quanta, photons of the electromagnetic field, propagating (radiating) through space, carrying electromagnetic radiant energy.
- In the photoelectric (photon-electron) interaction, a photon transfers all its energy to an electron located in one of the atomic shells.
- Luminescence the emission of radiation from excited species is one of the several paths by which the excess energy may be lost.
- An electronically excited atom must lose its energy by emission of radiation or by collisional deactivation chemical decomposition is not possible, and radiationless degradation is extremely improbable.

- The law of photochemical equivalence is applicable only to primary photochemical process, i.e., when as a result of absorption of light, only one molecule decomposes and the products enter no further reaction.
- Actinometers are the devices specifically used for measuring the heating power of radiation and also used in meteorology for measuring the solar radiation as pyranometers, pyrheliometers and net radiometers.
- Chemical actinometry includes measuring radiant flux via the yield from a chemical reaction. It essentially requires a chemical with a known quantum yield and easily analyzed reaction products.
- All photochemical processes can broadly be classified into two types: (1) The Primary Process and (2) The Secondary Process.
- A metal–ligand multiple bond describes the interaction of certain ligands with a metal with a bond order greater than one.
- The classification of a metal ligand bond as being "multiple" bond order is ambiguous and even arbitrary because bond order is a formalism.
- The coordination number, also called ligancy, of a central atom in a molecule or crystal is the number of atoms, molecules or ions bonded to it.
- In the case of polyatomic ions and molecules, the coordination number corresponding to a given atom can be calculated by counting the total number of atoms it is bonded to, be it a single bond or a double/triple bond.

3.8 KEY TERMS

- **Mössbauer Spectroscopy:** It consists of the study of γ-ray absorption (or emission) spectra for transition between nuclear states.
- **Isomer Shift:** In a Mössbauer experiment, if the environments of the emitting and absorbing nuclei are different, the energy of the nuclear transition E_0 may differ by a small amount. This energy difference is known as isomer shift (δ).
- **Magnetic Hyperfine Interaction:** Magnetic hyperfine splitting is a result of the interaction between the nucleus and any surrounding magnetic field, as described by the Zeeman Effect.
- **Optical Activity:** The optical activity of the compound is its ability to rotate the plane of polarized light.
- **Optical Rotatory Dispersion (ORD):** It is the change of specific rotation $[\alpha]$ or molar rotation $[\tilde{O}]$ with the wavelength of light used.
- **Photochemistry:** Photochemistry is that branch of chemistry which studies the chemical effects of light.
- **Electromagnetic Radiation:** The 'Electro Magnetic Radiation, also termed as EM radiation or EMR, refers to the waves or their quanta, photons of the electromagnetic field, propagating (radiating) through space, carrying electromagnetic radiant energy.

- **Actinometer:** An actinometer is a chemical system or physical device which determines the number of photons in a beam integrally or per unit time.
- **Chemical Actinometry:** Chemical actinometry includes measuring radiant flux via the yield from a chemical reaction.
- **Photodissociation:** Photodissociation is a chemical reaction in which a chemical compound is broken down by photons.

3.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short-Answers Questions

1. State the principle of Mössbauer spectroscopy.
2. Define spectral parameter and spectrum display.
3. What do you understand by Mössbauer spectroscope?
4. What are the biological applications of Mössbauer spectroscopy?
5. Define circular dicroism.
6. State the octant rule.
7. State the Divided Saddle Theory.
8. What do you understand by gas-phase photolysis?

Long-Answers Questions

1. Explain the working of the Mössbauer spectroscope.
2. Explain quadrupole interactions.
3. Describe the applications of Mössbauer spectroscopy.
4. Describe the crystal symmetry and magnetic structure.
5. Explain in detail the applications of ORD, CD, and Octant Rule.
6. Explain the process of determination of reaction mechanism

3.10 FURTHER READING

Greenwood N.N., T.C. Gibb, 2012, *Mössbauer Spectroscopy,* Springer Netherlands: Netherlands.

Langouche Guido, Yutaka Yoshida, 2012, *Mössbauer Spectroscopy- Tutorial Book,* Springer Berlin Heidelberg: Berlin.

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UNIT 4 PHOTOCHEMISTRY

NOTES

Structure

4.0 INTRODUCTION

Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm).

Photochemical reactions proceed differently than temperature-driven reactions. Photochemical paths access high energy intermediates that cannot be generated thermally, thereby overcoming large activation barriers in a short period of time, and allowing reactions otherwise inaccessible by thermal processes.

Some photochemical reactions are several orders of magnitude faster than thermal reactions; reactions as fast as 10^{-9} seconds and associated processes as fast as 10^{-15} seconds are often observed.

In this unit, you will study about the various aspects of photochemistry in aliphatic and aromatic compounds.

4.1 OBJECTIVES

NOTES

After going through this unit, you will be able to:

- Understand the concept of photochemistry.
- Explain the various photochemical reactions.
- Describe the photochemical reactions of aliphatic compounds.
- Describe the photochemical reactions of aromatic compounds.
- Conceptualize various miscellaneous photochemical reactions.

4.2 PHOTOCHEMISTRY OF ALKENES

The members of this class of compounds have two hydrogen atoms less than the corresponding alkenes (saturated hydrocarbons). The members of this homologous series are represented by the general formula C_nH_{2n} and are also known as **Olefins** (*Olefiant* = oil forming) because lower gaseous members of the series react with chlorine to form oily products. The simplest olefin has the formula C_2H_4 and is commonly known as **ethylene**. Study of the structure of an olefin reveals that the two hydrogen atoms are lacking at adjacent carbon atoms as compared to saturated hydrocarbons. When two atoms form two covalent bonds with each other, implying the sharing of two pairs of electrons, they are considered to be joined by a **double bond**. The carbon-carbon double bond is known as **olefinic linkage** or ethylenic linkage after the name of the first member. In IUPAC system, olefins are termed as **Alkenes**.

The nature of carbon-carbon double bond is best explained terms of molecular orbitals. The hybridization state of carbon atoms united to only three other atoms is sp^2. The three sp^2 hybrid orbitals are planar and are at an angle of 120° to one another. In case of ethylene each carbon atom, forms two C—H bonds by overlap of sp^2 orbital of carbon with 1 *s* orbital of hydrogen and the two carbon atoms are joined by the overlap of sp^2 orbitals of each one of them. All of these bonds are σ-bonds and all bond angles are 120° as shown in Fig. 9.1. The remaining unpaired electron at each carbon atom is in the *p*-orbital which is perpendicular to the plane of the three σ-bonds of the carbon. These two *p*-orbitals can form another bond between two carbon atoms by a parallel or sideways overlap. Such a bond is known as π-bond to distinguish it from σ-bond.

The overlapping of two *p*-orbitals is relatively poor and therefore, a π-bond is less stable than a π-bond. The energy associated with a carbon-carbon π-bond is only 58 kcal whereas for carbon-carbon σ-bond it is 85 kcal. Thus the total bond strength of the carbon-carbon double bond is 143 kcal. It is, therefore, stronger than a carbon-carbon single bond and the greater reactivity of the π-bond is because of the tendency to form more stable σ-bonds. Again because of a stronger double bond, the distance between carbon atoms decreases, as compared to singly bonded carbon atoms, so as to allow maximum overlap of *p*-orbitals to form a π-bond. The bond distance of a carbon-carbon single bond is 1.53 Å whereas that of a carbon-carbon double bond is 1.33 Å.

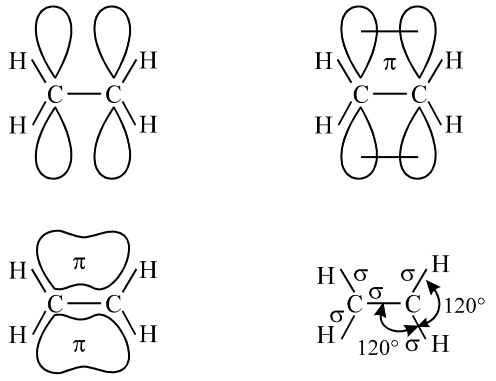


Fig. 4.1. *Formation of a double bond in ethylene molecule.*

4.2.1 Intramolecular Reactions of the Olefinic Bond-Geometrical Isomerism

The alkenes are in general very reactive in contrast to the inert behaviour of alkanes. This high reactivity of alkenes is due to the presence of double bond in the molecule. According to Baeyer's strain theory any deviation from the normal valency angle (109.5°) of the carbon atom results in a strain on the molecule. The greater is the deviation the greater will be the consequent strain. In a molecule having a double bond there is considerable (in fact the bond angle is theoretically reduced to zero) distortion of valency angle which causes a severe strain and therefore such a molecule has a tendency to release the strain by breaking the double bond yielding saturated compound.

The nature and structure of the double bond in terms of molecular orbital concept has already been explained earlier and it can be recalled that formation of a π bond results in the enveloping of the carbon atoms by π electron clouds on either side. Thus a molecule having a carbon-carbon double bond may be considered as a substrate rich in electrons and thus reagents seeking electrons, *i.e.* electrophilic reagents are most likely to react with alkenes. The most important reaction of alkenes will, therefore, be **electrophilic reaction**.

The π electrons of a double bond are quite mobile and highly reactive because of polarizability brought about by the attacking reagent (**electromeric shifts**).

The molecule of an alkene may be considered to be made up of two units—(*i*) **A double bond** and (*ii*) **Alkyl group(s)**. They will thus show the reactions of both.

Addition Reactions

Alkenes undergo addition at double bond with a large number of reagents to form saturated compounds. These addition reactions are electrophilic addition reactions.

1. **Addition of Hydrogen or Hydrogenation**. The alkenes when heated with hydrogen gas in presence of catalysts like Ni (*Sabatier-Senderens reduction*), Pt, Pd etc., give alkanes.

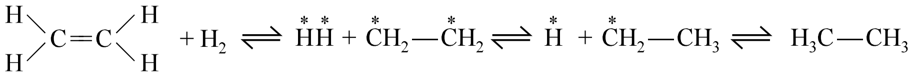
$$\underset{\text{Alkene}}{R.CH{=}CH_2} + H_2 \xrightarrow[200\text{–}300°C]{Ni} \underset{\text{Alkane}}{R.CH_2.CH_3}$$

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + H_2 \xrightarrow[200°C]{Ni} \underset{\text{Propane}}{CH_3.CH_2.CH_3}$$

In presence of finely powdered Pt, Pd and Raney nickel[1] the hydrogenation can be affected at room temperature and atmospheric pressure.

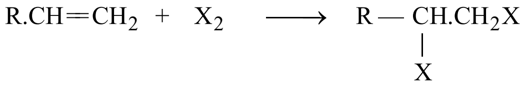
The addition of hydrogen to a double or triple bond is known as hydrogenation.

The mechanism of catalytic hydrogenation is uncertain. It is widely accepted that alkene and hydrogen get adsorbed at the surface of the catalyst where hydrogen is present as atoms. Smith and coworkers (1942) suggested that addition of the adsorbed hydrogen atoms occurs one at a time and the reaction is reversible.



(Asterisks indicate the adsorbed state at metallic sites)

2. **Addition of Halogens.** Alkenes react with halogens to form dihalogen derivatives by an addition reaction. The order of reactivity of halogens for a given alkene is Chlorine > Bromine > Iodine.



$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Halogen}}{X_2} \longrightarrow \underset{\substack{\textit{vic}\text{-Dihalide or}\\ \text{1,2-Dihaloalkane}}}{R-\underset{X}{\underset{|}{CH}}.CH_2X}$$

$$\underset{\text{Ethene}}{CH_2{=}CH_2} + Cl_2 \longrightarrow \underset{\substack{\text{Ethylene chloride or}\\ \text{1,2-Dichloroethane}}}{CH_3CI.CH_2CI}$$

$$\underset{\text{Porpene}}{CH_3.CH{=}CH_2} + Br_2 \longrightarrow \underset{\text{1,2-Dibromopropane}}{CH_2.CHBr.CH_2Br}$$

The mechanism of the reactions has already been discussed (Sec. 5.22).

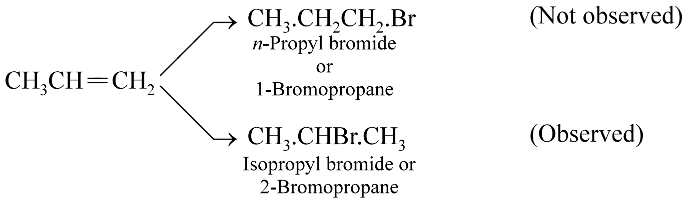
3. **Addition of Halogen Acids.** Alkenes react with aqueous solution of halogen acids to form alkyl halides. The order of reactivity of the halogen acids is HI > HBr > HCI.

$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\substack{\text{Halogen}\\ \text{acid}}}{HX} \longrightarrow \underset{\substack{\text{Alkyl halide or}\\ \text{Haloalkane}}}{R.CHX.CH_3}$$

$$\underset{\text{Ethene}}{CH_2{=}CH_2} + HCI \longrightarrow \underset{\text{Ethyl chloride}}{CH_3.CH_2.Cl}$$

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + HBr \longrightarrow \underset{\substack{\text{Isopropyl bromide or}\\ \text{2-Bromopropane}}}{CH_3.CHBr.CH_3}$$

In the addition reaction of propene it may be noted that because of unsymmetrical nature of alkene two products are theoretically possible. Thus:



Out of these only one is obtained predominantly, *i.e.*, 2-bromopropane. Markovnikov studied a large number of addition reactions of unsymmetrical olefins and gave **Markovnikov's rule**. This rule states that: *In the addition to an unsymmetrical olefin the negative part of the reagent or addendum goes to that carbon constituting the double bond which is poorer in hydrogen.* However in the presence of peroxides the addition occurs anti to Markovnikov's rule and in the above example: 1-bromopropane will then be obtained predominantly. This is known as **Kharasch peroxide effect**.

Regiochemistry. When the alkene is unsymmetric and the adding reagent is also unsymmetric then the regiochemistry (which group adds to which carbon) becomes important. Thus addition of HBr to propene under acidic conditions can give rise to two regio isomeric products of which 2-bromopropane is the main product implying that the reaction is *regiospecific*.

The additions of HF, HCl and HI are not affected by the presence of peroxides. As the peroxide effect comes from the free radical nature of the reactions, the unusual behaviour of HF and HCl is understandable because the high bond energy prevents the formation of free radicals. On the other hand HI readily dissociates to give iodine free radical but firstly these combine to form iodine molecule and secondly these are insufficiently reactive due to their bigger size.

4. **Addition of Hypohalous Acids.** Hypohalous acids, *viz.*, hypochlorous and hypobromous acids readily add to the double bond of alkenes to give halohydrins.

$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Hypohalous acid}}{HOX} \longrightarrow \underset{\text{Halohydrin}}{R.CHOH.CH_2X}$$

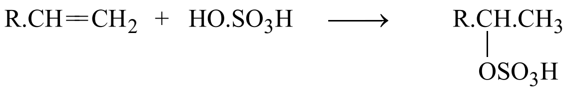
$$\underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Hypochlorous acid}}{HOCI} \longrightarrow \underset{\substack{\text{Ethylene chlorohydrin}\\ \text{or 2-Choloroethanol}}}{CH_2OH.CH_2CI}$$

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + \underset{\text{Hypobromous acid}}{HOBr} \longrightarrow \underset{\text{Propylene bromohydrin}}{CH_3CHOH.CH_2Br}$$

The halogens of the hypohalous acids constitute the positive part with respect to the hydroxyl (—OH) groups and therefore, in the addition of hypohalous acid to unsymmetrical olefins, —OH group goes to carbon poorer in hydrogen. Addition of hypobromous acid to propene, therefore gives 1-bromo-2-propanol and not 2-bromo-1-propanol.

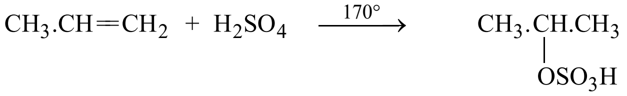
The hypoiodous acid is practically non-reactive in this reaction.

5. **Addition of Sulphuric Acid.** Alkenes add sulphuric acid at double bond to form alkyl hydrogen sulphates.



$$\underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Sulphuric acid}}{HO.SO_3H} \longrightarrow \underset{\text{Alkyl hydrogen sulphate}}{R.\underset{\substack{|\\OSO_3H}}{C}H.CH_3}$$

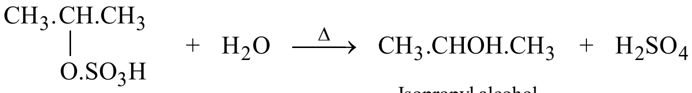
$$\underset{\text{Ethene}}{CH_2{=}CH_2} + H_2SO_4 \xrightarrow{170°} \underset{\text{Ethyl hydrogen sulphate}}{CH_3.CH_2.O.SO_3H}$$



$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + H_2SO_4 \xrightarrow{170°} \underset{\text{Isopropyl hydrogen sulphate}}{CH_3.\underset{\substack{|\\OSO_3H}}{C}H.CH_3}$$

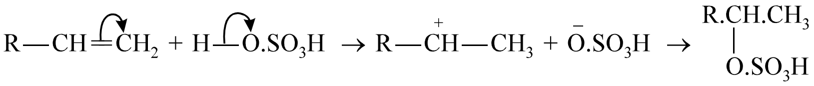
Addition of sulphuric acid to unsymmetrical alkenes, like propene, takes place in accordance with Markovnikov's rule and —SO_3H group adds to the carbon linked to lesser number of hydrogens. These alkyl hydrogen sulphates on boiling with water decompose to give corresponding alcohols.

$$\underset{\text{Ethyl hydrogen sulphate}}{CH_3.CH_2.O.SO_3H} + H_2O \xrightarrow{\Delta} \underset{\text{Ethyl alcohol}}{CH_3.CH_2.OH} + H_2SO_4$$



$$\underset{\text{Isopropyl hydrogen sulphate}}{CH_3.\underset{\substack{|\\O.SO_3H}}{C}H.CH_3} + H_2O \xrightarrow{\Delta} \underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3} + H_2SO_4$$

The mechanism of the reaction may be written as:



$$R{-}CH{=}CH_2 + H{-}O.SO_3H \rightarrow R{-}\overset{+}{C}H{-}CH_3 + \overset{-}{O}.SO_3H \rightarrow R.\underset{\substack{|\\O.SO_3H}}{C}H.CH_3$$

Alkenes, thus, can be converted to corresponding alcohols on treatment with sulphuric acid and subsequent hydrolysis. Large amounts of ethyl alcohol and isopropyl alcohol are industrially obtained from ethene and propene produced by cracking of petroleum fractions.

6. **Addition of Water or Hydration.** Alkenes may be hydrated to alcohols by the application of above reaction. However, alkenes having a secondary or tertiary carbon atom may be hydrated directly by boiling with dilute acids or acid acting as catalyst. Isobutylene gives tertiary butyl alcohol under these conditions.

$$\underset{\text{Isobutylene}}{(CH_3)_2.C{=}CH_2} + H_2O \xrightarrow{H^+} \underset{\textit{ter}\text{-Butyl alcohol}}{(CH_3)_3C.OH}$$

The following mechanism has been proposed for hydration

$$H_2O + H^+ \longrightarrow H_3\overset{+}{O}$$

$$(CH_3)_2C{=}CH_2 + H{-}\underset{+}{O}H_2 \xrightarrow[-H_2O]{\text{Slow}} \underset{t\text{-Butyl carbocation}}{(CH_3)_2\overset{+}{C}.CH_3} \text{ or } (CH_3)_3\overset{+}{C}$$

$$(CH_3)_3\overset{+}{C} + H_2O \xrightarrow{\text{Fast}} (CH_3)_3C{-}\overset{+}{O}H_2 \xrightarrow[\text{Fast}]{-H^+} \underset{t\text{-Butyl alcohol}}{(CH_3)_3C.OH}$$

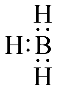
The slow step addition of a proton to alkene gives a carbocation. This carbocation in the fast step adds a molecule of water followed by the elimination of a proton to give addition product, alcohol.

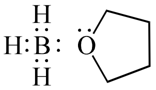
7. **Hydroboration-Oxidation.** This is another method of hydration of alkenes where hydration takes place anti to Markovnikov's rule. Diborane $(BH_3)_2$ adds to alkene and the trialkyl borane obtained gives alcohol when reacted with alkaline hydrogen peroxide.

$$3\,R-CH{=}CH_2 \xrightarrow{(BH_3)_2} (R.CH_2CH_2)_3B \xrightarrow[OH^-]{H_2O_2} 3\,R.CH_2CH_2OH + H_3BO_3$$

The reaction details are given below.

Alkenes react with diborane in ether to undergo hydroboration to yield alkylboranes. It is a case of simple addition of BH_3 to double bond. Diborane is the dimer of the hypothetical BH_3 and in the reaction given below it acts as if it were BH_3. In fact it exists as BH_3 (monomer) in solvents like tetrahydrofuran in the form of acid base complex.

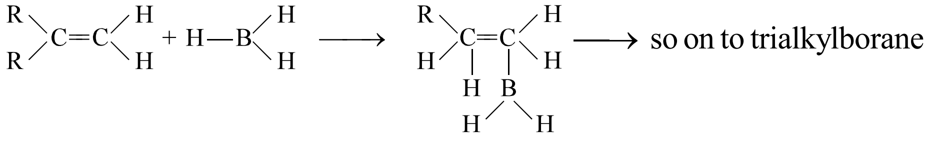




Boron THF complex

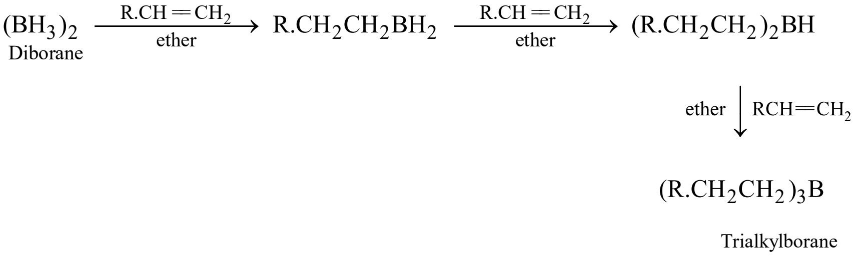
Formation of alkylboranes

(*i*)



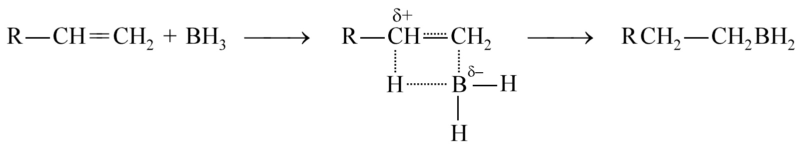
Alkylborane

(*ii*)



$$\underset{\text{Diborane}}{(BH_3)_2} \xrightarrow[\text{ether}]{R.CH=CH_2} R.CH_2CH_2BH_2 \xrightarrow[\text{ether}]{R.CH=CH_2} (R.CH_2CH_2)_2BH \xrightarrow[\text{RCH=CH}_2]{\text{ether}} \underset{\text{Trialkylborane}}{(R.CH_2CH_2)_3B}$$

Mechanism: Boron has only six electrons in BH_3 hence it acts as an electrophile. It seeks π electrons of the double bond between two carbon atoms of alkenes. When it approaches alkene it starts attaching itself to carbon with a negative charge but in the meantime the other carbon atom constituting the double bond starts getting a positive charge on losing π electrons. With positive charge developing this carbon begins to take charge of the hydrogen of BH_3 which is near it. Boron which has gained π electrons is willing to part with this hydrogen to acidic carbon atom. Thus a transition state develops which then results in the addition of BH_3 to alkene.

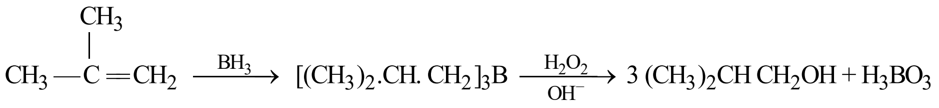


$$R-CH=CH_2 + BH_3 \longrightarrow \text{Transition state} \longrightarrow RCH_2-CH_2BH_2$$

Transition state

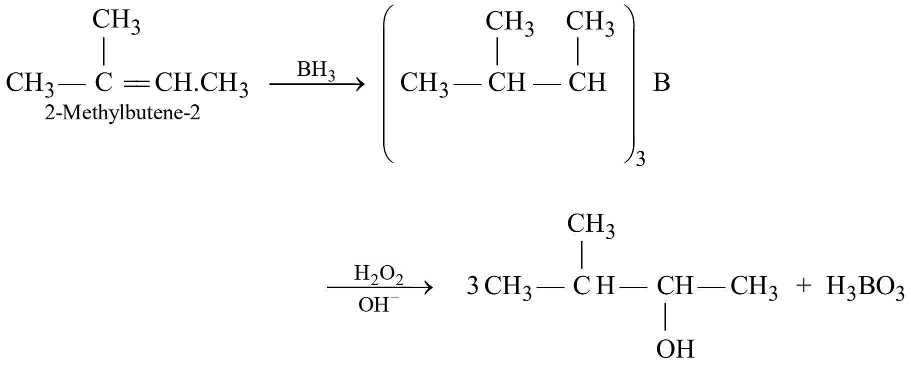
The process goes on till trialkyl borane is formed.

Trialkyl boranes are useful because they can be oxidised to alcohol by using alkaline H_2O_2.



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{BH_3} [(CH_3)_2.CH.\ CH_2]_3B \xrightarrow[OH^-]{H_2O_2} 3\ (CH_3)_2CH\ CH_2OH + H_3BO_3$$

Isobutylene Isobutyl alcohol (1°)



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH.CH_3 \xrightarrow{BH_3} \left(CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}\right)_3 B$$

2-Methylbutene-2

$$\xrightarrow[OH^-]{H_2O_2} 3\,CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{OH}{|}}{CH}-CH_3 + H_3BO_3$$

3-Methylbutanol-2 (2°)

Thus hydroboration-oxidation process gives alochol in which water adds in anti-Markovnikov's manner to alkene.

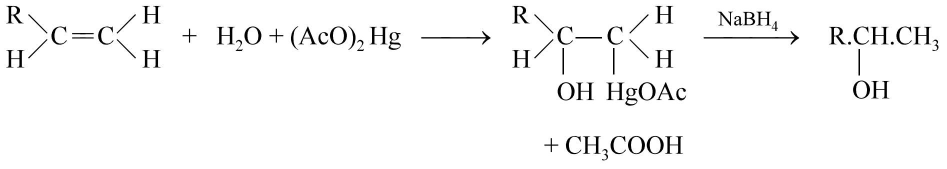
Trialkyl boranes can also be used to get alkanes or aldehydes.

$$(R.CH_2CH_2)_3B \xrightarrow[\Delta]{CH_3COOH} R.CH_2.CH_3$$

$$(R.CH_2CH_2)_3B \xrightarrow[\Delta]{H_2Cr_2O_7} R.\ CH_2.CH=O$$

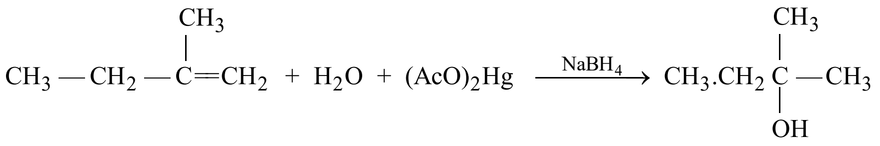
8. **Oxymercuration.** This is another method of hydration of alkenes where hydration takes place according to Markovnikov's rule.

Alkene is added to an aqueous solution of mercuric acetate diluted with tetrahydrofuran at room temperature. The reaction is complete in a very short time. Hydroxy-mercurial compound is first formed which is reduced by sodium borohydride *in situ*.



$$RHC=CH_2 + H_2O + (AcO)_2Hg \longrightarrow RH\underset{\underset{OH}{|}}{C}-\underset{\underset{HgOAc}{|}}{C}H_2 + CH_3COOH \xrightarrow{NaBH_4} R.\underset{\underset{OH}{|}}{CH}.CH_3$$

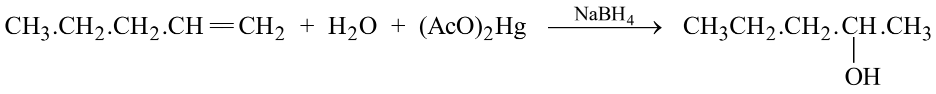
The yields are very good; often over 90%. Oxymercuration is highly regioselective and gives alcohols in accordance with Markovnikov's rule.



$$CH_3-CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}}}=CH_2 + H_2O + (AcO)_2Hg \xrightarrow{NaBH_4} CH_3.CH_2\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2-Methylbutene-1 2-Methylbutanol-2

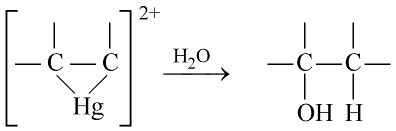
(*tert*-Pentyl alcohol)



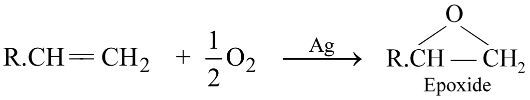
$$CH_3.CH_2.CH_2.CH=CH_2 + H_2O + (AcO)_2Hg \xrightarrow{NaBH_4} CH_3CH_2.CH_2.\underset{\underset{OH}{|}}{CH}.CH_3$$

Pentanol-2

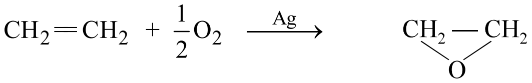
Oxymercuration involves the electrophilic addition to carbon-carbon double bond, mercuric ion acting as an electrophile. Cyclic mercurinium ion formed is attacked by nucleophilic solvent water to yield the addition product. Mercury is recovered in elemental state.



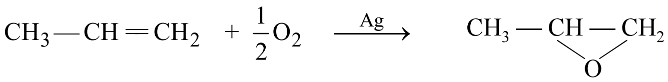
9. **Epoxidation (Addition of oxygen)**. When mixed with oxygen or air and passed over a silver catalyst at high temperature and pressure, lower alkenes add an atom to oxygen to form epoxides (alkene-oxides)



Epoxide

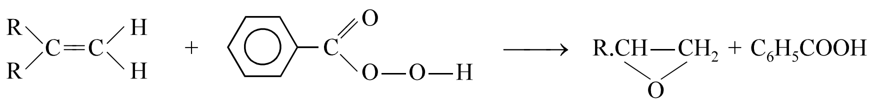


Ethylene oxide or Oxirane



Propylene oxide or Methyl oxirane

Epoxides are also obtained when alkenes are reacted with peracids like perbenzoic acid.



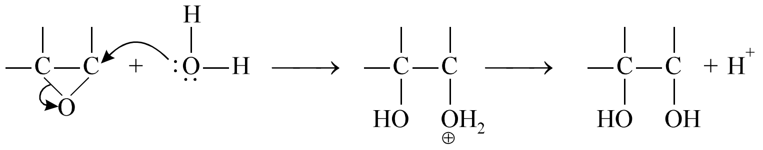
Perbenzoic acid

Epoxide or Oxirane

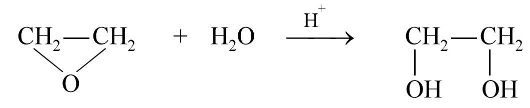
Peroxybenzoic acid and alkene are allowed to stand in chloroform or ether solution. Reaction takes place resulting in epoxide formation along with benzoic acid.

Epoxides are very useful and give glycols and other alcohols under varying conditions.

(*a*) In acid catalysed cleavage protonation of epoxide takes place which can then be attacked by nucleophilic agent like water or ethyl alcohol.

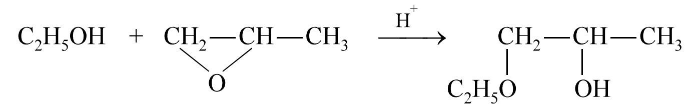


(*i*)



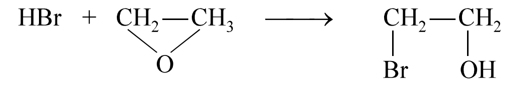
Ethylene glycol

(*ii*)



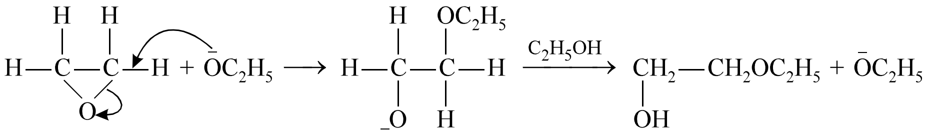
3-Ethoxy propanol-2

(*iii*)

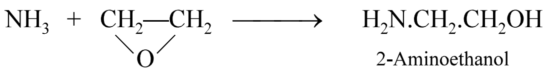


Ethylene bromohydrin

(*b*) In base catalysed cleavage the epoxide itself undergoes nucleophilic attack. The non-protonated epoxide has lower reactivity hence only strong nucleophilic reagents like alkoxides and ammonia can straight away attack non-protonated epoxide.

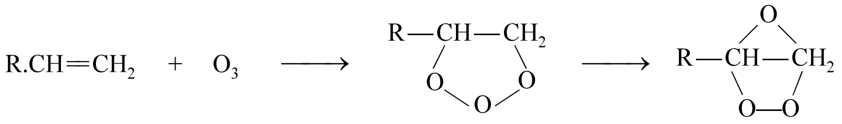


2-Ethoxyethanol

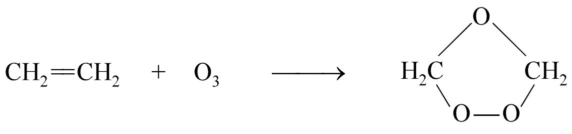


2-Aminoethanol

10. **Addition of ozone and ozonolysis.** When a stream of ozone or ozonised oxygen is passed through a solution of alkene in an inert solvent like ether or carbon tetrachloride it adds a molecule of ozone at the double bond to give an ozonide.

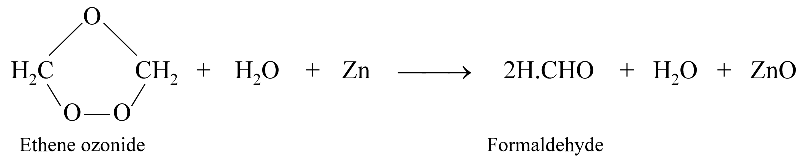


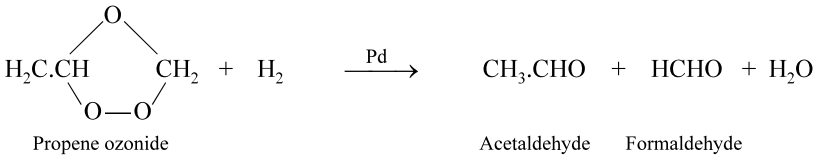
Alkene Ozone Iso-ozonide Ozonide



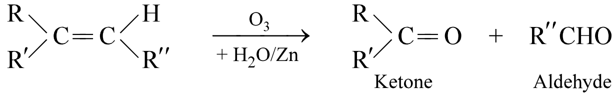
Ethene Ethene ozonide

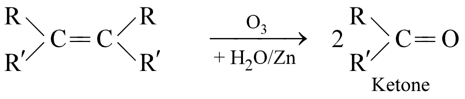
The ozonides are explosive and on reduction with hydrogen in presence of a catalyst (Pt or Pd) or on boiling with water containing traces of zinc dust, split to give aldehydes and/or ketones. The fission of the molecules takes place at the position occupied by the double bond.





An alkene of the type R.R′.C═CHR″ gives a mixture of aldehyde and ketones whereas R.R′.C ═ C.R.R′ type alkene gtives ketones only.





The process of the formation of ozonide and its decomposition to give carbonyl compounds is known as **Ozonolysis**. The mechanism of ozonolysis has been discussed in Sec. 6.24.

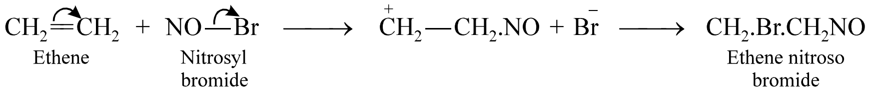
11. **Addition of hydrogen peroxide.** The addition of H_2O_2 to alkenes is catalyzed by acids and gives a mixture of hydroperoxides and peroxides, for example:

$$\underset{\text{Isobutylene}}{(CH_3)_2C{=}CH_2} + H_2O_2 \xrightarrow{H^+} \underset{\textit{ter}\text{-Butyl-hydroperoxide}}{(CH_3)_3C—O—O—H}$$

$$(CH_3)_2C—O—O—H + CH_2{=}C.(CH_3)_2 \xrightarrow{H^+} \underset{\textit{ter}\text{-Butyl-peroxide}}{(CH_3)_2C—O—O—C(CH_3)_3}$$

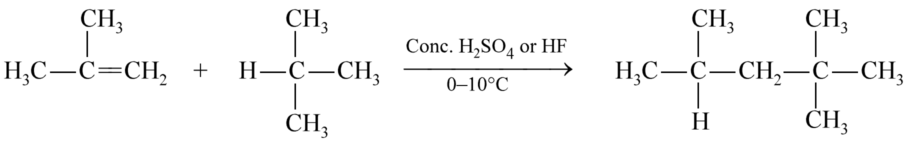
12. **Addition of nitrosyl halide.** Alkenes add nitrosyl chloride or bromide at the double bond to give crystalline nitrosohalides.

$$\underset{\text{Alkene}}{R.CH = CH_2} + \underset{\text{Nitrosyl halide}}{NO — X} \longrightarrow \underset{\text{Nitroso halide}}{R.CHX.CH_2NO}$$



$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + \underset{\text{Nitrosyl chloride}}{NO—Cl} \longrightarrow \underset{\text{Intermediate carbocation}}{CH_3.\overset{+}{C}HCH_2NO} + Cl^- \longrightarrow \underset{\text{Propene nitroso chloride}}{CH_3CHClCH_2NO}$$

13. **Addition of alkanes to alkenes (Alkylation).** When 1 part of isobutane and 1 part of isobutene are allowed to react in presence of acid catalyst like HF, H_2SO_4, $AlCI_3$ etc. then alkylation of isobutene takes place to form 2,2,4-trimethylpentane. Alkane used for alkylation should have a tertiary hydrogen.

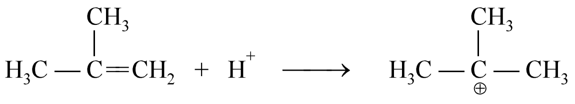


$$H_3C-\overset{\overset{CH_3}{|}}{C}=CH_2 + H-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[\text{0–10°C}]{\text{Conc. } H_2SO_4 \text{ or HF}} H_3C-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Isobutene Isobutane 2,2,4-Trimethyl pentane (Iso-octane)

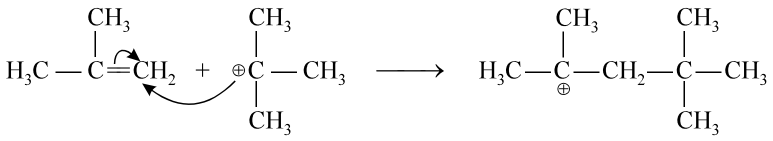
The alkylation is supposed to take place in 3 steps:

(*i*) Isobutene accepts a proton to provide *tert*-butyl carbocation:



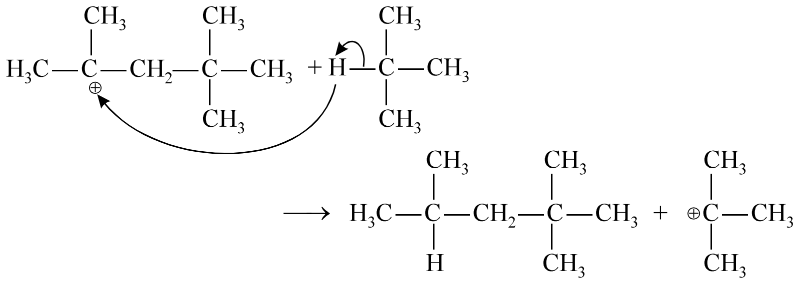
$$H_3C-\overset{\overset{CH_3}{|}}{C}=CH_2 + H^+ \longrightarrow H_3C-\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

(*ii*) The carbocation goes to site of π electrons to add up to isobutene.



$$H_3C-\overset{\overset{CH_3}{|}}{C}=CH_2 + \oplus\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow H_3C-\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

(*iii*) The carbocation formed in step (*ii*) abstracts a hydride ion from isobutane.



$$H_3C-\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + H-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

$$\longrightarrow H_3C-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + \oplus\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Iso-octane

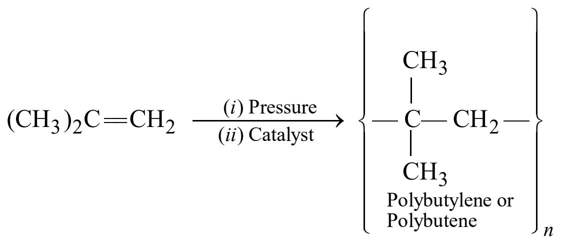
The conditions of the reactions have to be controlled to avoid other reactions.

Iso-octane is formed yielding *tert*-butyl carbocation to continue the chain reaction. 2,2,4-Trimethylpentane is a high grade gasoline and its efficiency as a fuel is used for rating other gasolines.

14. **Self-addition or Polymerization.** Alkenes in the presence of acid catalysts and high temperature and pressure undergo self-addition (addition of one molecule to another alkene molecule) to give a new alkene. The product alkene has twice the molecular weight of initial alkene and is called a **dimer**. Addition of another alkene to this dimeric alkene can give a new trimeric alkene. The process can repeat itself to give a polymeric product (polymer) of high molecular weight. The process by which polymer is formed is known as polymerization. The mechanism and details of polymerization have been explained in Sec. 5.28.

$$\underset{\text{Ethene}}{CH_2=CH-H} + CH_2=CH_2 \xrightarrow[\substack{(ii)\text{ Pressure,}\\(iii)\text{ Catalyst}}]{(i)\text{ High temp.}} \underset{\text{Butene}}{CH_2=CH-CH_2-CH_3}$$

$$\xrightarrow{CH_2=CH_2} \underset{\text{Polyethylene or Polythene}}{(-CH_2-CH_2)_n}$$



$$(CH_3)_2C{=}CH_2 \xrightarrow[(ii)\ \text{Catalyst}]{(i)\ \text{Pressure}} \left\{ -\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2- \right\}_n$$

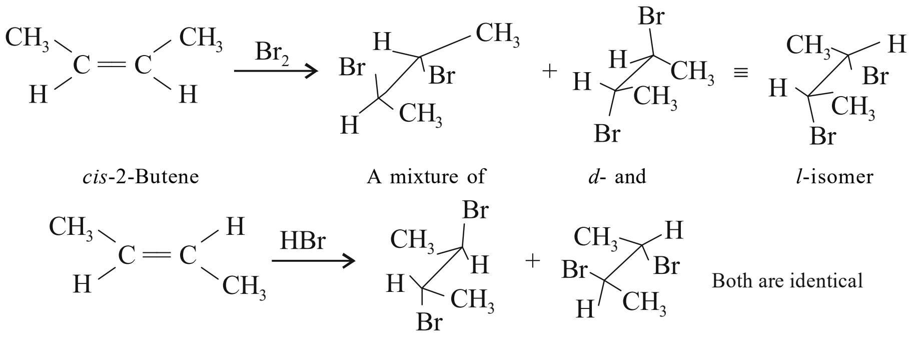
Polybutylene or Polybutene

Polythene and polybutene are plastics of industrial importance.

Stereochemistry of Addition Reactions. In a carbon-carbon double bond, since the carbon atoms are sp^2 hybridized, all the six atomes (two carbon and four atoms attached to them) lie in one plane. During addition reactions, both the adding groups may come from the same side leading to *syn*- addition or from opposite side leading to *anti*- addition.

Let us take the case of 2-butene which exists as *cis*- and *trans*- isomers. Addition of bromine results in the formation of two asymmetric centres in the molecules. If *syn*- and *anti- additions both take place randomly then the reaction is non-stereospecific. If the additions are only syn*- or only *anti*- then we get one set of stereisomers from *cis*-2-butene and a different set of stereoisomers from *trans*-2-butene. Such reactions are called stereospecific.

In actual practice, addition of bromine to *cis*-2-butene gives a *dl*-mixture while addition of bromine to *trans*- 2-butene gives a meso compound suggesting that it is a stereospecific *anti*-addition



cis-2-Butene A mixture of *d*- and *l*-isomer

trans-2-Butene *meso*- isomer

Oxidation Reactions

Alkenes undergo oxidation reactions readily with a wide variety of reagents to give different products depending upon the nature of oxidizing agent and the conditons of the reactions.

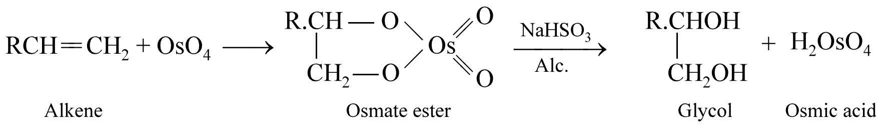
(*i*) **Oxidation with mild oxidizing agents**. *When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline potassium permanganate solution (**Baeyer's reagent**) at low temperatures, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols*. The pink colour of potassium permanganate solution is discharged during the reaction and so this reaction is used as a test for the unsaturation in molecules.

$$\underset{\text{Alkene}}{R.CH{=}CH_2} + H_2O + O \xrightarrow{\text{Alk. }KMnO_4} \underset{\text{Glycol}}{R.CHOH.CH_2OH}$$

$$CH_3.CH{=}CH_2 + H_2O + O \xrightarrow{\text{Alk. KMnO}_4} \underset{\text{Propylene glycol or Propene-1,2-diol}}{CH_3.CHOH.CH_2OH}$$

NOTES

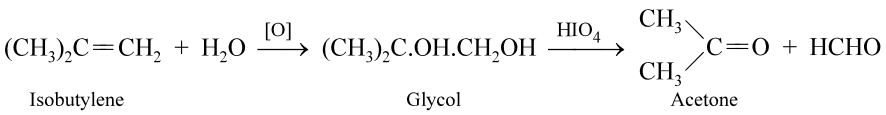
Glycols are also formed when osmium tetraoxide is added to the olefin and then refluxed with alcoholic $NaHSO_3$ solution.



In these addition reactions both the —OH groups are added to the same side of the double bond resulting in a *syn*- addition.

(*ii*) **Oxidation with periodic acid or lead tetra acetate**. These are moderately strong oxidizing agents and the oxidation of alkene first results in the formation of glycol which is subsequently oxidized to aldehydes or ketones.

$$\underset{\text{Alkene}}{R.CH{=}CH_2} + H_2O \xrightarrow[(CH_3COO)_4Pb]{HIO_4\text{ or}} RCHOH.CH_2OH \xrightarrow{HIO_4} \underset{\text{Aldehyde}}{R.CHO} + \underset{\text{Formaldehyde}}{HCHO}$$



The overall addition of two –OH groups occurs on opposite sides of the double bond leading to overall *anti*-addition.

(*iii*) **Oxidation with acidic potassium permanganate or potassium dichromate.** Alkenes when oxidized with acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ first give glycols which are further oxidized to aldehydes, ketones and acids.

$$\underset{\text{Alkene}}{R.CH{=}CH_2} + H_2O \xrightarrow{O} \underset{\text{Glycol}}{R.CHOH.CH_2OH} \xrightarrow[KMnO_4]{\text{Acid}} \underset{\text{Aldehydes}}{R.CHO + HCHO}$$

$$\xrightarrow{KMnO_4} \underset{\text{Acids}}{HCOOH + RCOOH}$$

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} + H_2O + O \xrightarrow[\text{Acid}]{KMnO_4} \underset{\text{Glycol}}{CH_3.CHOH.CH_2OH}$$

$$\xrightarrow{KMnO_4} \underset{\text{Acetaldehyde}}{CH_3.CHO} \quad + \quad \underset{\text{Formaldehyde}}{HCHO}$$

$$\downarrow KMnO_4\text{ (acid)} \qquad \downarrow$$

$$CH_3COOH$$

HCOOH

$$\underset{\text{Butene}}{(CH_3)_2C{=}CH_2} + H_2O + O \xrightarrow[K_2Cr_2O_7]{\text{Acid}} \underset{\text{Glycol}}{(CH_3)_2COH.CH_2OH}$$

$$\downarrow \text{Acid } K_2Cr_2O_7$$

$$CH_3CO.CH_3 + HCHO \xrightarrow{\text{Acid } K_2Cr_2O_7}$$

HCOOH

These oxidation reactions are used for locating the presence of the double bond by identifying the reaction products.

(*iv*) **Combustion.** Alkenes when burnt in air, are completely oxidised resulting in the formation of carbon dioxide and water.

$$C_nH_{2n} + \frac{3}{2}nO_2 \longrightarrow nCO_2 + nH_2O$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

They form an explosive mixture with air or oxygen and burn with luminous flame.

Isomerisation Reactions

When alkenes are heated in the presence of a catalyst or alone, they undergo isomerisation to form isomeric alkenes. The double bond generally shifts towards centrally located carbon atoms. In some cases hydrogen or alkyl groups migrate to form a branched chain alkene.

$$\underset{\text{1-Pentene}}{CH_3.CH_2.CH_2CH{=}CH_2} \xrightarrow[200\text{–}300°C]{Al_2(SO_4)_3} \underset{\text{2-Pentene}}{CH_3CH_2.CH{=}CH.CH_3}$$

$$\underset{\text{3-Methyl-1-butene}}{(CH_3)_2CH.CH{=}CH_2} \xrightarrow[200\text{–}300°C]{Al_2(SO_4)_3} \underset{\text{2-Methyl-2-butene}}{(CH_3)_2C{=}CH.CH_3}$$

$$\underset{\text{2-Butene}}{CH_3.CH{=}CHCH_3} \xrightarrow{Al_2(SO_4)_3} \underset{\text{2-Methyl-1-propene}}{(CH_3)_2C{=}CH_2}$$

Substitution Reactions

The alkyl group of alkenes undergo substitution reactions at higher temperatures. Thus when alkenes like ethene and propene are chlorinated at 500°C the double bond does not break up but hydrogen of alkyl group is substituted by chlorine, for example:

$$CH_2{=}CH_2 + Cl_2 \xrightarrow{500°C} CH_2{=}CHCl$$

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + Cl_2 \xrightarrow{500°C} \underset{\text{Allyl chloride}}{CH_2{=}CH{—}CH_2Cl} + HCl$$

The substitution reactions proceed by a free radical mechanism and is similar to substitution of alkanes. If the alkyl group contains more than one carbon atom, even then the substitution occurs at the carbon α- to the double bond or at allylic carbon atom.

$$\underset{\text{1-Butene}}{CH_3.CH_2.CH{=}CH_2} + Cl_2 \xrightarrow{500°C} \underset{\text{3-Chloro-1-butene}}{CH_3.CHCl.CH{=}CH_2}$$

Geometrical isomerism. Alkenes except ethene and propene also exhibit geometrical isomerism. Because of restricted rotation about the double bond two isomers are generally possible; one where the two hydrogens occupy same side of the double bond and the other where these are placed on opposite side of the double bond.

4.2.2 Cyclisation Reactions

Cyclisation reactions of carbocations are powerful methods for the synthesis of fused polycyclic organic molecules. The process involves an initiating electrophile that produces a cationic center and terminating nucleophile, usually an alkene, alkyne or an electron-rich aromatic ring.

When a radical center and a double bond are situated so that formation of either a five- or a six-membered ring is possible, the smaller ring generally is produced. The reason for forming the smaller ring is that the strain engendered in reaching the transition state for a six-membered ring is greater than that required for reaching a five-membered one.

For formation of a five-membered ring the calculated angle of approach of the atom bearing the radical center to the multiple bond is 106o, an angle similar to the 104° calculated for the trans-ition state in the strain-free addition of the methyl radical to propene. For six-mem-bered ring formation the trans-ition state has a calcu-lated angle of approach of 94°. This consider-able angle deformation away from a strain-free situation is a major factor in raising the energy of the transition state leading to a six-membered ring.

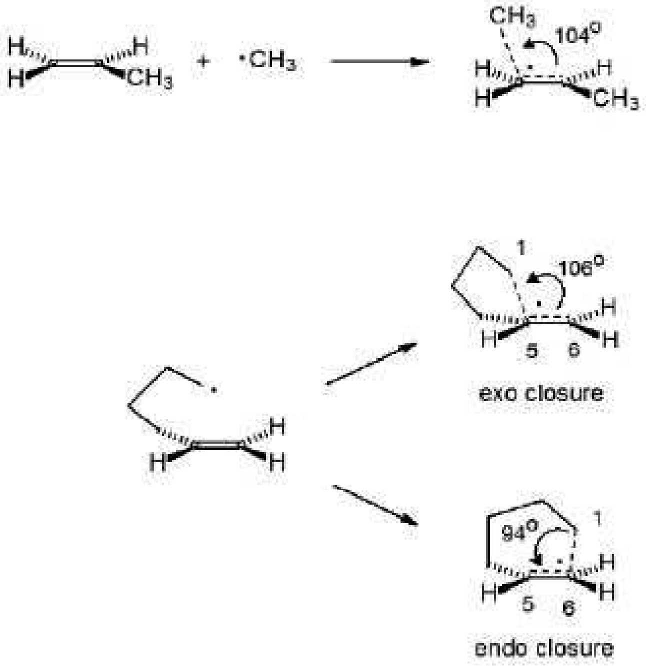


Fig. 4.2: *Transition State Structure for Addition of Methyl Radical to Propene and Cyclisation of 5-hexenyl Radical.*

In addition to describing cyclization reactions by the size of the ring produced, the terms exo and endo indicate the way in which the ring is formed. When the exo/endo terminology is used to describe ring for-ma-tion from reaction of the 5-hexenyl radical, the five-membered ring is seen as arising from exo closure and the six-membered one from endo closure.

4.2.3 Rearrangements of 1,4 and 1,5 Dienes

Physical Rearrangement. Butadiene is a gas at room temperature (b.p. –2.6°C) whereas isoprene is a liquid (b.p. 30°C). The heats of combustion and hydrogenation of butadiene and isoprene are lower than the expected value.

The bond distances of carbon atoms in butadiene are neither those of pure single nor of pure double bond and they have intermediate value. Thus C_1 to C_2 or C_3 to C_4 bond length is 1.35 Å and C_2 and C_3 bond length is 1.47 Å.

Butadiene absorbs at 217 mμ and isoprene at 222 mμ in UV spectrum; while in IR region they absorb at 1650 and 1600 cm^{-1} due to the presence of conjugated double bonds.

Chemical Rearrangement. Butadiene, isoprene and other conjugated dienes show the usual reactions of alkenes such as hydrogenation, ionic and free radical additions but they do so more readily. However they also undergo abnormal additions and polymerize readily.

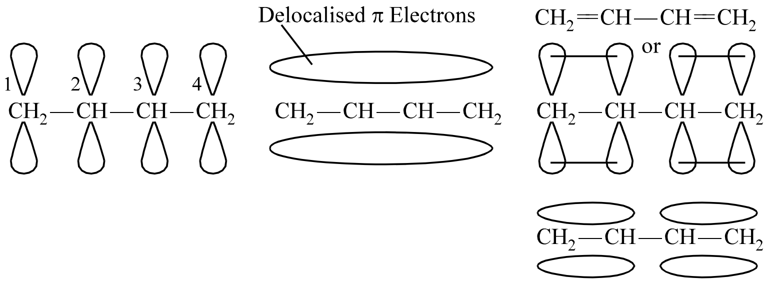
In 1899 Thiele observed that when butadiene and other conjugated dienes are reacted with one molecule of addendum usually a mixture of 1,4- and 1,2-addition products result; 1,4-addition product predominating. To account for such anomalous behaviour he gave **Theory of Partial Valency** which assumes that valencies of carbon atoms involved in double bonds are not fully satisfied and each carbon is left with some *residual* or *partial valency* and the addition to double bond occurs through these residual valencies. He also pointed that in case of conjugated dienes the partial valencies of carbon atoms 1 and 4 are free, while those of carbon 2 and 3 get mutually satisfied and hence the addition to 1,3-butadiene is preferentially 1,4-addition.

$$\underset{\substack{\text{3,4-Dichlorobutene-1}\\\text{(1,2-addition product)}}}{CH_2Cl.CHCl.CH{=}CH_2} \xleftarrow{Cl_2} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow{Cl_2} \underset{\substack{\text{1,4-Dichloro-2-butene}\\\text{(1,4-addition product)}}}{Cl.CH_2.CH{=}CH.CH_2Cl}$$

However, the theory is of only historical interest now. These reactions, greater reactivity and greater stability of butadiene and other conjugated dienes are now better explained in terms of resonance or molecular orbital concept.

It is believed that butadiene and other conjugated dienes are resonance hybrids of many structures. The dipolar structures account for 1,4 additions in butadiene.

$$CH_2{=}CH{-}CH{=}CH_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{C}H_2 \longleftrightarrow \overset{-}{C}H_2{-}CH{=}CH{-}\overset{+}{C}H_2$$



p-Orbitals before delocalisation

Delocalised p-orbitals

Localised p-orbitals

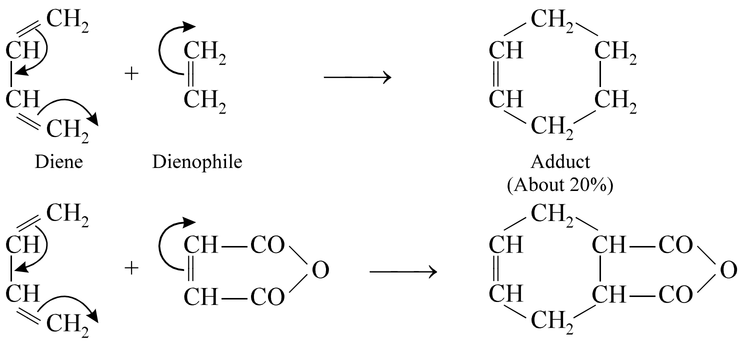
Fig. 4.3. Butadiene M.O. representation.

NOTES

In the MO concept each carbon atom of butadiene is considered to be in sp^2 hybridized state so that each carbon has an unhybridized *p*-orbital. The localized bonds are formed by sidewise overlap of these *p*-orbitals. Thus the *p*-orbital at carbon-2, can overlap with either *p*-orbital of carbon-1 or that of carbon-3. Similarly the orbital at carbon-3 can overlap with that of carbon-2 or carbon-4 to form π bonds. The net effect is the formation of polycentric uniform orbital overlap giving delocalized bond orbitals over all the four carbon atoms. The delocalization of electrons imparts greater stability. It is supported by bond length measurements, and study of heat of combustion and hydrogenation:

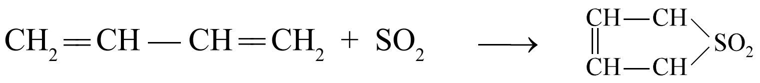
Some of the reactions of conjugated dienes different from isolated dienes are given below:

(1) **Diels-Alder reaction**. Conjugated dienes add to alkenes by 1,4-addition to form cyclic compounds. The reaction is known as Diels-Alder reaction after the names of its discoverers. The alkene is usually referred to as dienophile and is generally having electron attracting group like —COOH; —CN; —COR etc.



The mechanism of this reaction has been explained in Sec. 5.30.

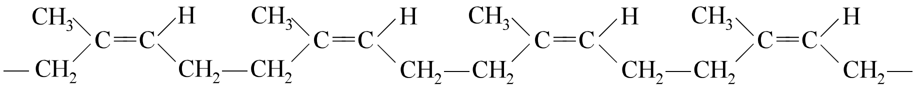
(2) **Combination with sulphur dioxide.** Butadiene and isoprene react with SO_2 to give cyclic sulphones. Thus:



$$CH_2{=}CH-CH{=}CH_2 + SO_2 \longrightarrow \begin{matrix}CH-CH\\ \| \\ CH-CH\end{matrix}\!>SO_2$$

(3) **Polymerization.** Polymerization is a common feature of all alkenes. However, in case of conjugated dienes the polymer chain may grow either by 1,4- or 1,2-addition depending upon whether it is acid or peroxide catalyzed.

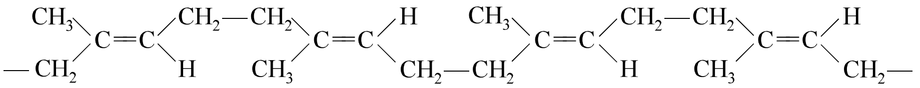
When 1,4-addition occurs to give polymers in acidic conditions it may be either *cis* or *trans*. The two types have widely differing properties. Thus natural rubber[1] is *cis*-1,4-polyisoprene and **gutta percha** is *trans*-1,4-polyisoprene and the two compounds have different properties.



cis-1,4-Polyisoprene (Natural rubber)

Uses. Butadiene and isoprene readily polymerise in presence of sodium and give products resembling natural rubber and leather substitutes.

These are used in Diels-Alder reaction for the synthesis of cyclic compounds. These are also used to prepare emulsion paints.



trans-1,4-Polyisoprene (Gutta-percha)

Check Your Progress

1. Define olefins.
2. What do you understand by ethylene?
3. What are the components of an alkene molecule?
4. State the Markovnikov's rule.
5. How alkenes can be converted to alcohols?
6. What is a dimer?
7. State the theory of partial valency.

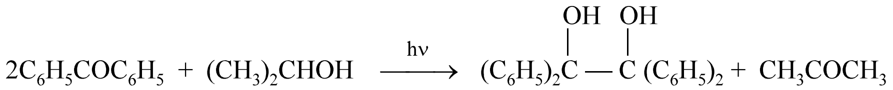
4.3 PHOTOCHEMISTRY OF CARBONYL COMPOUNDS

Carbonyl compounds undergo various photochemical reactions in both gas and liquid phases. The electronic excited states of saturated ketones are n $\rightarrow \pi$ states, whereas of conjugated ketones are $\pi \rightarrow \pi^*$ states. Both these excited states in singlet or triplet states take part in chemical reactions. The activation energies for singlet and triplet states of saturated ketones are about 80–85 and 75–80 kcal/mol, respectively, whereas of unsaturated ketones, these are in the range of 45–75 kcal/mol. For this reason, the photoreactions of saturated ketones occur in the UV region, 270–290 nm, and of unsaturated ketones in the UV region, 310–330 nm. The excited carbonyl compounds have radical characters at both carbon and oxygen atoms of the carbonyl group, and hence most of their photoreactions proceed through radical intermediates. The important photoreactions of carbonyl compounds are the reduction of carbonyl compounds by hydrogen abstraction, fragmentation reactions, cycloaddition to alkenes, and rearrangement reactions.

4.3.1 Intramolecular Reactions of Carbonyl Compounds (Saturated, Cyclic and Acyclic Unsaturated Compounds)

Amongst a wide variety of organic compounds by far the most studied and understood are the photochemical reactions of carbonyl compounds.

Photoreduction of benzophenone to benzopinacol occurs when a solution of benzophenone and isopropyl alcohol is irradiated with radiation of 345 nm. Isopropyl alcohol does not absorb at this wavelength and absorption of radiation by benzophenone causes $n \rightarrow \pi^*$ transition



$$2C_6H_5COC_6H_5 + (CH_3)_2CHOH \xrightarrow{h\nu} (C_6H_5)_2\overset{\overset{\Large OH}{|}}{C}-\overset{\overset{\Large OH}{|}}{C}(C_6H_5)_2 + CH_3COCH_3$$

Benzophenone Isopropyl alcohol Benzopinacol Acetone

NOTES

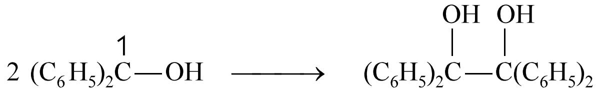
Initial light absorption produces S_1 state which then undergoes rapid *intersystem crossing* to give T_1 states.

$$(C_6H_5)_2CO \xrightarrow{h\nu} [(C_6H_5)_2\overset{1}{C}-O\downarrow]^{S_1} \xrightarrow[\text{crossing}]{\text{Intersystem}} [(C_6H_5)_2-\overset{1}{C}-O1]^{T_1}$$

The T_1 triplet state has a structure resembling alkoxy radical and abstracts α-hydrogen of isopropyl alcohol forming two radicals I and II.

$$[(C_6H_5)_2\!\sim\!\overset{1}{C}-O1]^{T_1} + CH_3CHOHCH_3 \longrightarrow \underset{\text{I}}{(C_6H_5)_2\!\sim\!\overset{1}{C}-OH} + \underset{\text{II}}{(CH_3)_2\overset{1}{C}-OH}$$

Combination of two units of I gives benzopinacol



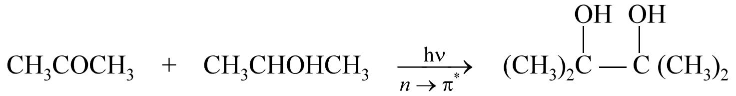
$$2\,(C_6H_5)_2\overset{1}{C}-OH \longrightarrow (C_6H_5)_2\overset{\overset{\Large OH}{|}}{C}-\overset{\overset{\Large OH}{|}}{C}(C_6H_5)_2$$

Benzopinacol

The quantum yield for the formation of benzopinacol is approximately 1, hence the second molecule of I is not formed by absorption of another quantum of light but is formed by reaction between benzophenone and radical obtained from isopropyl alcohol after hydrogen abstraction (II).

$$(CH_3)_2\overset{1}{C}-OH + (C_6H_5)_2CO \longrightarrow (C_6H_5)_2\overset{1}{C}-OH + (CH_3)_2CO$$

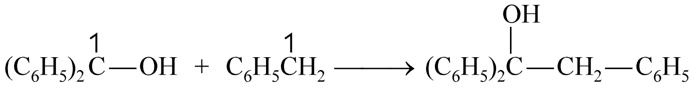
The reaction is a general one and can be observed in case of large number of aliphatic as well as aromatic ketones and α-ketoesters in presence of wide varieties of solvents such as toluene, cyclohexane, methanol etc.



$$CH_3COCH_3 + CH_3CHOHCH_3 \xrightarrow[n \to \pi^*]{h\nu} (CH_3)_2\overset{\overset{\Large OH}{|}}{C}-\overset{\overset{\Large OH}{|}}{C}(CH_3)_2$$

$$\underset{\text{Benzophenone}}{(C_6H_5)_2CO} + \underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[n \to \pi^*]{h\nu} \underset{\text{(I)}}{(C_6H_5)_2\overset{1}{C}-OH} + \underset{\text{Benzyl radical}}{C_6H_5\overset{1}{C}H_2}$$

In the above reaction dibenzyl and benzyl diphenyl carbinol are also formed probably due to following side reactions:



$$\underset{\text{(I)}}{(C_6H_5)_2\overset{1}{C}-OH} + \underset{\text{Benzyl radical}}{C_6H_5\overset{1}{C}H_2} \longrightarrow \underset{\text{Benzyl diphenyl carbinol}}{(C_6H_5)_2\overset{\overset{\Large OH}{|}}{C}-CH_2-C_6H_5}$$

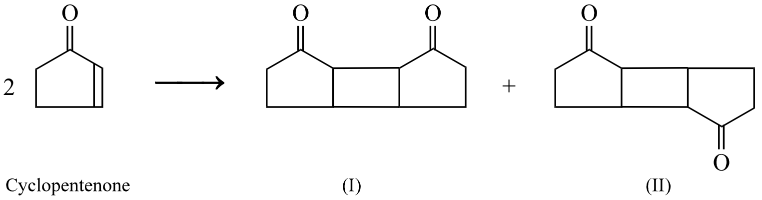
$$\underset{\text{Benzyl radical}}{2\;C_6H_5\overset{1}{C}H_2} \longrightarrow \underset{\text{Dibenzyl}}{C_6H_5-CH_2-CH_2-C_6H_5}$$

Evidence for the participation of T_1 state rather than S_1 state in benzopinacol formation comes from the quenching studies. Naphthalene is a known **quencher** which deactivates the excited states. Irradiation of benzoquinone and isopropyl alcohol mixture mixed with small amounts of naphthalene appreciably reduces the quantum yield. This can only happen if excited benzophenone molecule transfers its energy to naphthalene and returns to the ground state. Obviously such an energy transfer is not possible with short lived S_1 state but only in T_1 states which has sufficient long life to collide with naphthalene (which is in low concentration) resulting in energy transfer.

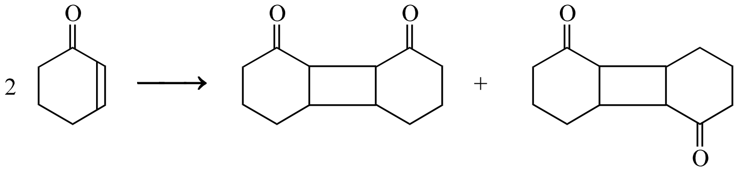
Photochemistry of α,β-Unsaturated Ketones

In α,β-unsaturated ketones due to conjugation the energy gap between π and π* is much less as compared to a saturated ketone. Consequently $\pi \rightarrow \pi^*$ transition occur at much longer wavelength. Ultraviolet absorption spectra of a common α,β-unsaturated ketone show two absorption maxima — one around 220 nm (for $\pi \rightarrow \pi^*$) and other around 310 nm (for $n \rightarrow \pi^*$). Irradiation of such a ketone may result in any of these transitions but excited state has more of $\pi \rightarrow \pi^*$ character than $n \rightarrow \pi^*$ triplet character which undergoes either *photocyclodimerization* or olefin addition at the double bond of α,β-unsaturated ketone.

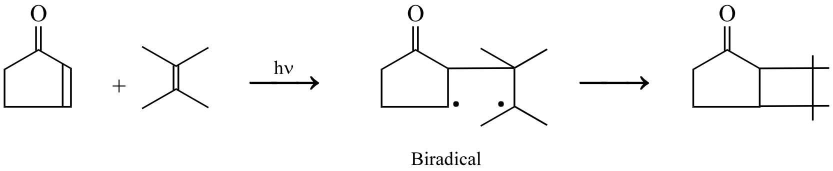
Photodimerization of cyclic α,β-unsaturated ketone like cyclopentenone yields two different dimers in almost equal amounts — one in which two units are joined head to head (I) and the other in which two units are joined head to tail (II).



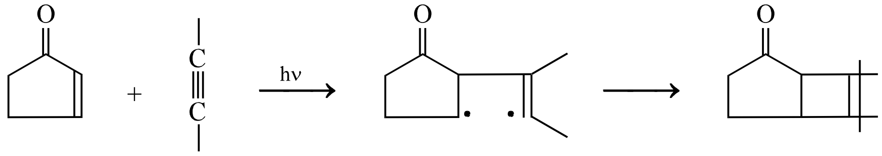
Similarly cyclohexenone also gives two major products



Photocycloaddition of alkenes to cyclic α,β-unsaturated ketones generally involves the initial formation of a carbon-carbon bond between the α-carbon of α,β-unsaturated ketone and the olefin giving a biradical which then cyclizes.



Reaction of α,β-unsaturated ketones into acetylenes results in formation of cyclobutene derivatives



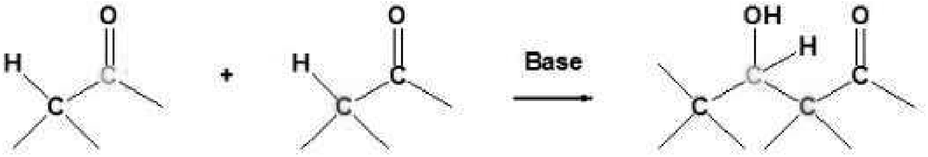
4.3.2 Cyclohexadienones

Cyclohexadienones are produced from the reactions of unsaturated carbene complexes and alkynes when the beta-carbon of the carbene complex is disubstituted. This is presumed to be the result of the fact that if substituents R1 and R2 in intermediate are both non-hydrogen, then tautomerization to the aromatized phenol is not possible and as a result the cyclohexadienone is isolated after the metal is lost. This reaction is quite general for a variety of alkenyl complexes as is illustrated by the reaction of complex with alkyne. This process can also be extended to indole carbene complexes. The reaction complex with 3-hexyne gives the cyclohexadienone annulated product in 95 % yield. In this reaction, part of the aromaticity of the indole ring is lost. The aromaticity can be restored by a 1,5-sigmatropic shift in the cyclohexadienone. This compound can be isolated, or if heated to 140°C, it will undergo a rearrangement to the isomeric cyclohexadienone.

Asymmetric induction in the cyclohexadienone annulation can occur in several different modes. The cyclohexadienone annulation produces a new chiral center at carbon 6 in the cyclohexadienone. Therefore, there can be a central-to-central chirality transfer from a center of chirality that is present in either the alkyne, the carbene carbon substituent or in the heteroatom stabilizing substituent on the carbene complex.

4.3.3 Intermolecular Cycloaddition Reactions-Dimerisation and Oxetane Formation

A useful carbon-carbon bond-forming reaction known as the Aldol Reaction is yet another example of electrophilic substitution at the alpha carbon in enolate anions. The fundamental transformation in this reaction is a dimerization of an aldehyde (or ketone) to a beta-hydroxy aldehyde (or ketone) by alpha C–H addition of one reactant molecule to the carbonyl group of a second reactant molecule. Due to the carbanion like nature of enolates they can add to carbonyls in a similar manner as Grignard reagents. For this reaction to occur at least one of the reactants must have alpha hydrogens.

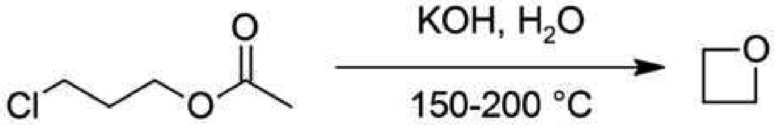


Oxetane Formation

Oxetane, or 1,3-propylene oxide, is a heterocyclic organic compound with the molecular formula C_3H_6O, having a four-membered ring with three carbon atoms and one oxygen atom. The term “an oxetane” or “oxetanes” refer to any organic compound containing the oxetane ring.

Production of Oxetane

A typical well-known method of preparation is the reaction of potassium hydroxide with 3-chloropropyl acetate at 150 °C



Yield of oxetane made this way is c. 40%, as the synthesis can lead to a variety of by-products.

Another possible reaction to form an oxetane ring is the Paternò–Büchi reaction. The oxetane ring can also be formed through diol cyclization as well as through decarboxylation of a six-membered cyclic carbonate.

4.4 PHOTOCHEMISTRY OF AROMATIC COMPOUNDS

Photo-induced aromatic compounds in their excited singlet and triplet states undergo various chemical reactions. The triplet states of relatively long-life times are involved in photochemical reactions in most cases. Photochemical reactions of aromatic compounds are mainly of eight types, isomerization, [2+2]- and [4+2]-cycloadditions, hydrogen abstraction and addition, electrocyclization, dimerization, oxidation, substitution and rearrangement reactions.

4.4.1 Isomerization

Isomerization is the process in which a molecule, ion or molecular fragment is transformed into an isomer with a different chemical structure. The isomerization of unsubstituted azulene to naphthalene was the first reported thermal transformation of an aromatic hydrocarbon, and has consequently been the most widely studied rearrangement.

Many mechanisms have been suggested for this isomerization, yet none have been unequivocally determined as the only correct mechanism. Five mechanisms were originally considered: a reversible ring-closure mechanism, a norcaradiene-vinylidene mechanism, a diradical mechanism, a methylene walk mechanism, and a spiran mechanism. It was quickly determined that the reversible ring-closure mechanism was inaccurate, and it was later decided that there must be multiple reaction pathways occurring simultaneously. This was widely accepted, as at such high temperatures, one mechanism would have to be substantially energetically favored over the others to be occurring alone. Energetic studies displayed similar activation energies for all possible mechanisms.

NOTES

The photoisomerization of liquid benzene at 55° to fulvene via the first optical transition was originally reported in 1957. Recently, benzvalene has been shown to be also formed under similar conditions, especially when the benzene is diluted by a paraffinic solvent. Benzvalene slowly reverts solely to benzene at room temperature, and there is as yet no definite evidence whether fulvene is wholly or only partly formed from it under photochemical conditions. The formation of both these isomers of benzene is promoted by increasing temperatures.

4.4.2 Addition and Substitution Reactions

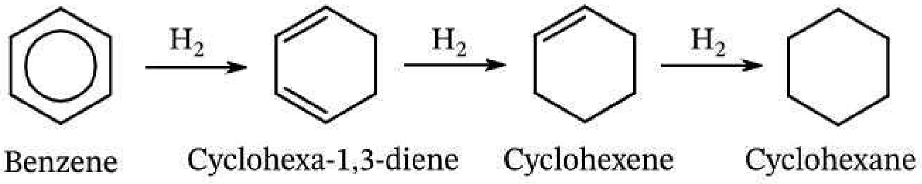
Benzene (C_6H_6) is the most common example of an aromatic system. Benzene is substantially more resistant to hydrogenation than a simple alkene like cyclohexene as the delocalization of electrons in the ring confers extra stability.

Addition Reactions

An addition reaction is a type of reaction where 2 or more molecules combine to form a larger molecule, without any by-products forming. The hydrogenation of benzene, or the hydrogen addition reaction of benzene, involves the addition of 2, 4, or 6 hydrogens to the carbons of benzene. Cyclohexane is produced when benzene is completely hydrogenated. Cyclohexane is a useful solvent and a precursor in the production of other chemicals.

Hydrogen Addition Reaction: A hydrogen addition reaction is a type of reaction where a molecule combines with 1 or more molecules of hydrogen to form a larger molecule, without any by-products forming. The hydrogenation of benzene involves the addition of 1 or more hydrogen molecules to each molecule of benzene in the reaction.

In excess hydrogen, we can expect that benzene will be completely hydrogenated.

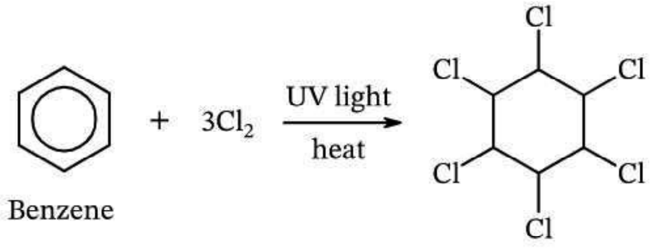


These reactions are performed using a nickel, palladium, or platinum catalyst, and moderate temperatures and pressures. A minimum of <“70‴C is necessary, but reactions are usually performed at 150‴C–190‴C.

Halogen Addition Reaction: A halogen addition reaction is a type of reaction where a molecule combines with 1 or more halogen molecules to form a larger molecule, without any by-products forming. The halogenation of benzene, or halogen addition reaction of benzene, involves the addition of 2, 4, or 6 halogens to the carbons of benzene. Various hexachloroethane have been used to make pesticides that have since been banned.

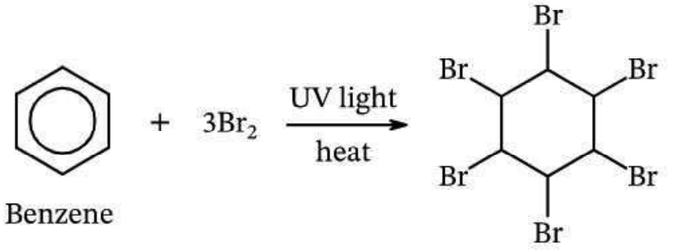
NOTES

Addition of chlorine to benzene can be as follows:



1,2,3,4,5,6-Hexachlorocyclohexane

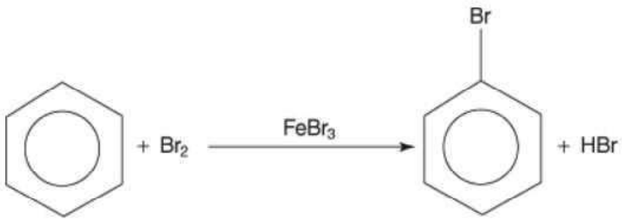
Addition of bromine to benzene can be represented as:



1,2,3,4,5,6-Hexabromocyclohexane

Substitution Reactions

Although aromatic compounds have multiple double bonds, these compounds do not undergo addition reactions. Their lack of reactivity toward addition reactions is due to the great stability of the ring systems that result from complete À electron delocalization (resonance). Aromatic compounds react by electrophilic aromatic substitution reactions, in which the aromaticity of the ring system is preserved. For example, benzene reacts with bromine to form bromobenzene.



Many functional groups can be added to aromatic compounds via electrophilic aromatic substitution reactions. A functional group is a substituent that brings with it certain chemical reactions that the aromatic compound itself doesn't display.

Substitution reactions in aromatic compounds are of two types:

Nucleophilic Aromatic Substitutions: In a nucleophilic aromatic substitution reaction, a nucleophile displaces a substituent on an aromatic ring. The replaced species is typically a good leaving group, like nitrogen gas or a halide ion. The presence of an electron-withdrawing group on the ring can speed up the progress of this class of reactions. Chemically, this is similar to an addition reaction to a Michael acceptor or other electron-deficient, unsaturated system, followed by an elimination reaction.

Electrophilic Aromatic Substitutions: In an electrophilic aromatic substitution reaction, a substituent on an aromatic ring is displaced by an electrophile. These reactions include aromatic nitration, aromatic halogenation, aromatic sulfonation, and Friedel-Crafts acylations and alkylations. These reactions can involve a resonance-stabilized carbocation intermediate known as a sigma complex. The reactivity can be thought of in terms of an alkene attacking a cationic species, such as in the first step of an acid-catalyzed hydration of an alkene.

Check Your Progress

8. What are Cyclohexadienones?
9. Define isomerization.
10. What do you understand by a halogen addition reaction?
11. What do you understand by a hydrogen addition reaction?
12. Define a nucleophilic substitution reaction.
13. Define an electrophilic substitution reaction.

4.5 MISCELLANEOUS PHOTOCHEMICAL REACTIONS

Photochemical reactions are the chemical reactions initiated by the absorption of energy in the form of light. The consequence of molecules' absorbing light is the creation of transient excited states whose chemical and physical properties differ greatly from the original molecules.

The photochemical reaction is, in fact, the thermal reaction of the electronically excited state of the molecule while the dark reaction of the molecule is the thermal reaction of the ground state.

The mechanism of a photo reaction should ideally include a detailed characterization of the primary events as outlined by the classification of photochemical reaction pathways. The quantum yields and hence the rate constants of all relevant photophysical and photochemical processes, in addition to the information about the structure and fate of any reactive intermediates, their lifetimes and reactivities.

4.5.1 Photo-Fries Rearrangements and Photo-Fries reactions of Anilides

This reaction in values migration of a group across a double bond (1,3 migration on 1,5 migration). It is an intermolecular rearrangement, where acyl and alkyl groups migrate to *ortho*- and *para*-position on irradiation. In this rearrangement, the substrate dissociates into phenoxy and acyl radicals which recombine within the solvent cage to give intermediates on aromatization to the product.

For example, phenol esters in solution on photolysis given a mixture of O- and p- acylphenols. In the gas phase, where solvent cage effects are not operative many other products arc formed. In Fries rearrangement, however, a catalyst is required. Photo Fries reaction doesn't need a catalyst and is a predominantly an intermolecular free radical process. The mechanism can be illustrated as:

When Photo-Fries rearrangement is carried out in gaseous phase, only phenol is obtained, which confirms the formation of solvent cage.

Photo-Fries Reactions of Anilides

These rearrangements occur through intermediate formation of free radicals.

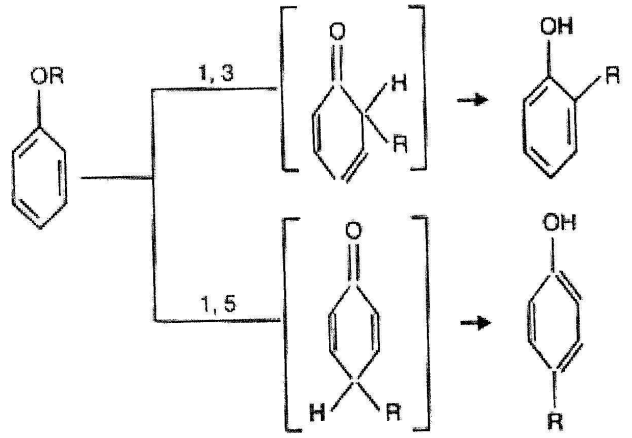


Fig. 4.4 *Photo fries rearrangement reaction.*

4.5.2 Barton Reaction

Photolytic conversion of organic nitrites into nitroso alcohols is known as Barton reaction. When a compound consists of C-O-NO group and a C-H bond is brought into close proximity (generally 1,5 position), the alkoxyl radicals are formed by photolysis of nitrites, in the solution phase, which have sufficient energy to bring about selective intermolecular abstraction of hydrogen atom and produce a carbon radical.

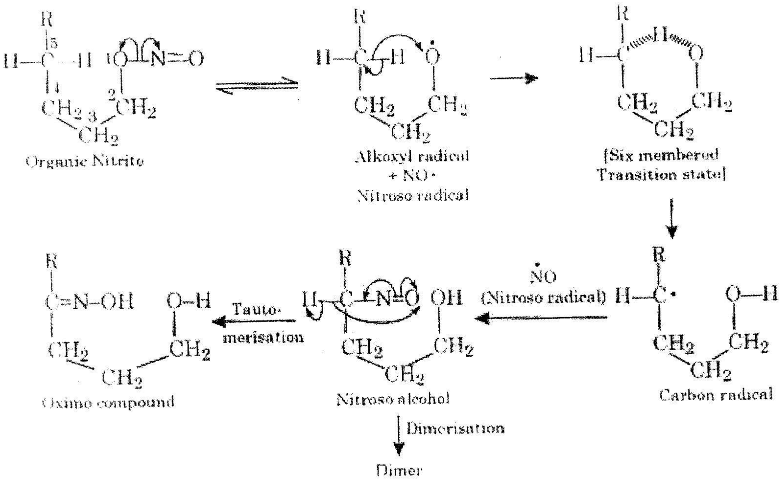
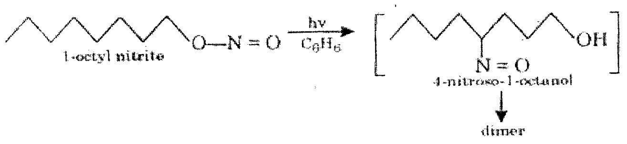


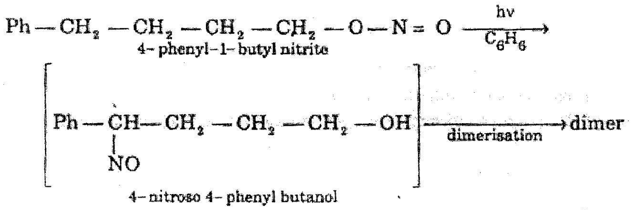
Fig. 4.5 *Mechanism of Barton reaction.*

Some examples of Barton reaction are given below:

(i)



(ii)



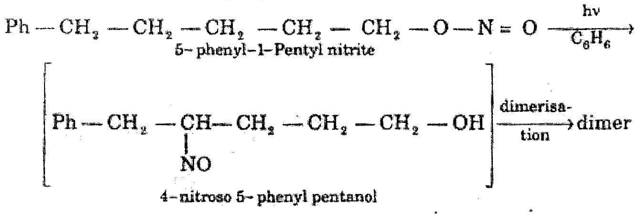
$$Ph-CH_2-CH_2-CH_2-CH_2-O-N=O \xrightarrow[C_6H_6]{h\nu}$$

4- phenyl-1- butyl nitrite

$$\left[Ph-\underset{\displaystyle NO}{\underset{|}{CH}}-CH_2-CH_2-CH_2-OH\right] \xrightarrow[\text{dimerisation}]{} \text{dimer}$$

4- nitroso 4- phenyl butanol

(iii)



$$Ph-CH_2-CH_2-CH_2-CH_2-CH_2-O-N=O \xrightarrow[C_6H_6]{h\nu}$$

5- phenyl-1-Pentyl nitrite

$$\left[Ph-CH_2-\underset{\displaystyle NO}{\underset{|}{CH}}-CH_2-CH_2-CH_2-OH\right] \xrightarrow[\text{tion}]{\text{dimerisa-}} \text{dimer}$$

4-nitroso 5- phenyl pentanol

The produced carbon radical reacts with nitrogen monoxide (NO) and gives nitroso alcohol. The nitroso alcohol can be isolated from the solution by the process of dimerisation.

As the Barton reaction consist of great selectively in the hydrogen abstraction step, it has found application mainly in the field of steroids.

4.5.3 Singlet Molecular Oxygen Reaction

Singlet oxygen is gaseous inorganic chemical with the formula Q = O also written as O_2, which is a state in which all electros are paired. In terms of reactivity, singlet oxygen in for more reactive forwards organic compounds. It is responsible for the photo degradation of many materials and have been used in preparative methods in organic chemistry.

Singlet oxygen refers to one of the two singlet electronic excited states. The two singlet excited states of oxygen one denoted by Δ_g and $'\Sigma_g^+$. The ground and first two singlet excited states of oxygen and triplet oxygen can be showed in following Figure.

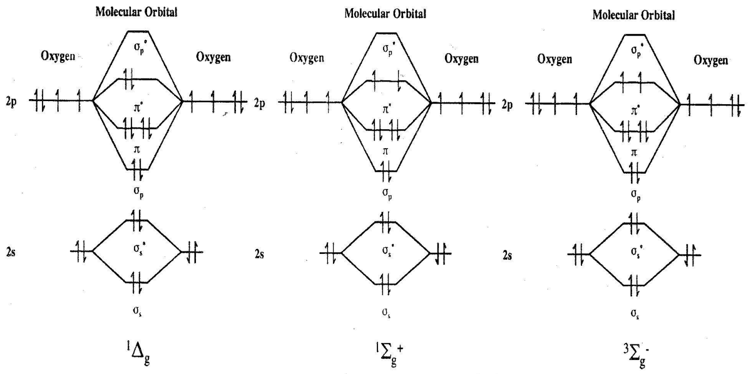
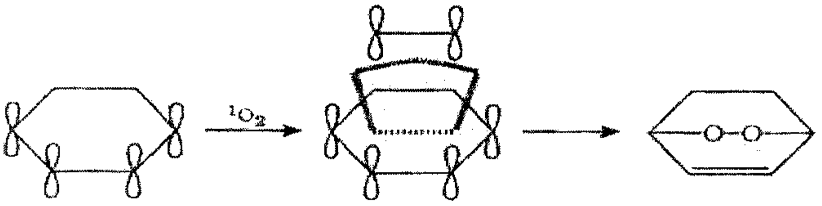


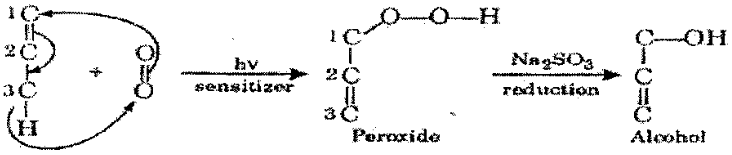
Fig. 4.6 The Ground and Excited states of Oxygen and Triplet Oxygen

The Loner, O_2 (Δ_g or O_2) state in commonly referred to as singlet oxygen.

Photo-Oxygenation Reaction

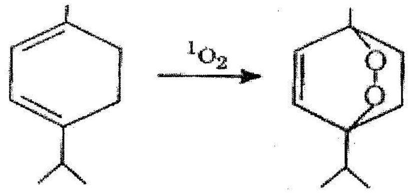
1. Singlet oxygen given additions reactions with cisoid dienes. This reaction proceeds in concerted manner by formation of fix membered transitions state. Mono-alkenes give 1, 4-cycloadditon reaction with singlet oxygen.



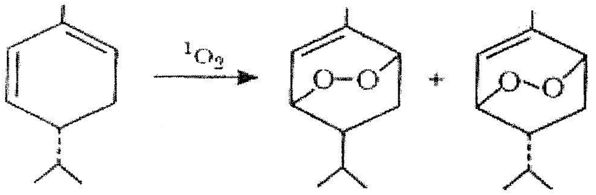


Some more examples of photo-oxygenation relations are:

(i)



(ii)



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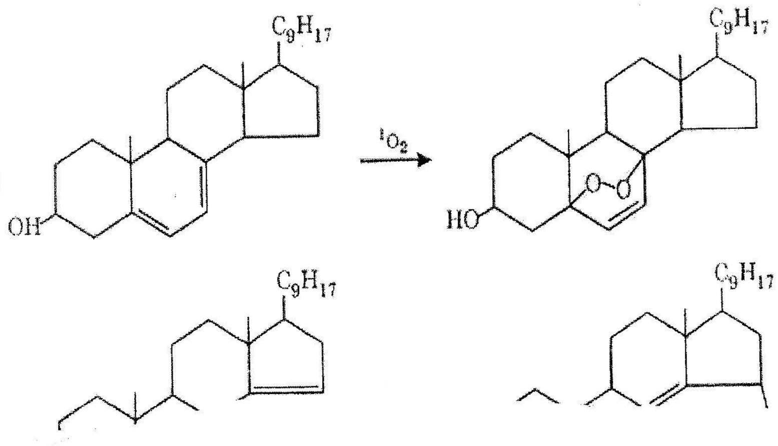
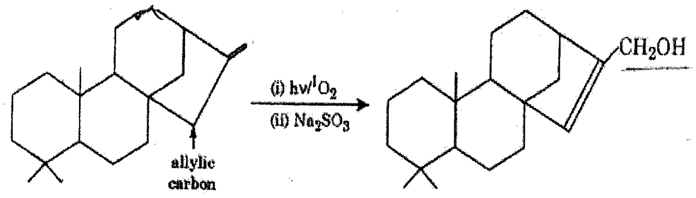
(ii)

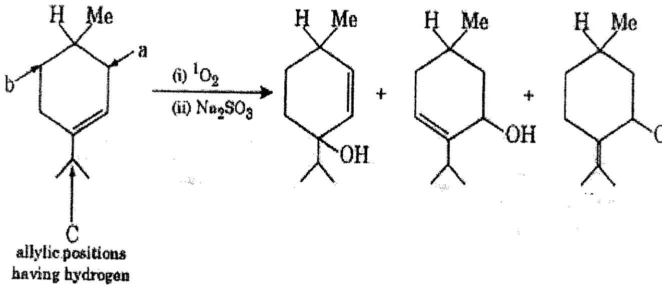


2. Ene Reaction: olefines give hydroperoxy compounds on reacting with singlet oxygen, the reaction is called Ene Reaction.

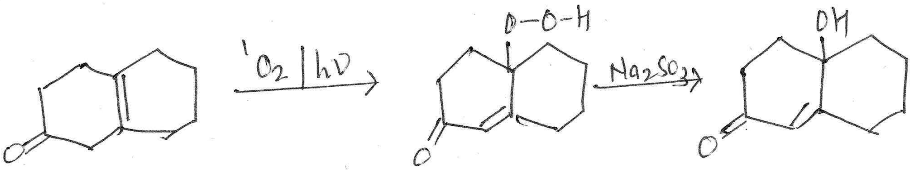
(i)



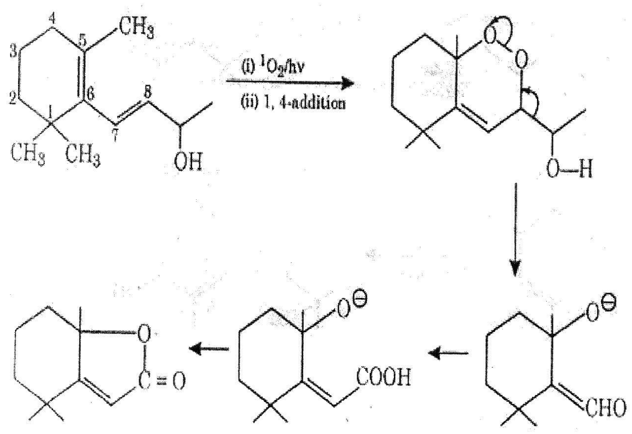
(ii)



3. α–β unsaturated ketones also undergo photo oxygenation reaction.



4. Photo Oxygenation of carotenoid and terpenoids give ketene derivatives in addition to normal products.



Importance of Singlet Molecular Oxygen

1. Singlet molecular oxygen participates in various dye sensitized photo oxygenation reactions of olefins, denies and aromatic hydrocarbons.
2. It is used in the quenching of the excited singlet and triplet states of molecules.
3. It is involved in the chemiluminescent phenomena, Photo dynamic reactions, photo carcinogenicity and in metal catalysed oxygenation reactions.

4.5.4 Photochemical Smog

Hydrocarbons in the atmosphere by the natural resources, particularly trees; by the anaerobic decomposition of organic matter in water, sediments and soils: domesticated and human activities contributing about 15% of the hydrocarbons to the atmosphere each year. Hydrocarbons are removed from the atmosphere by several chemical and photo chemical reactions. They are thermodynamically unstable towards oxidation and tend to be oxidized through a series of steps. The end products are CO_2 and solid cyanic particulate matter which finally famous acids and aldehydes in the atmosphere, which are washed by rain.

Harmful effects of hydrocarbon pollution are not due to the hydrocarbons themselves but the products of photochemical reactions in which they are involved. Hydrocarbons do not react readily with sunlight, but they are reactive towards other substances produced photochemical. An important characteristic of atmospheres which is loaded with large quantities of automobile exhausts, trapped by an inversion layer (stagnant air masses) and at the same time exposed to intense sunlight, is the formation of photochemical oxidants in the atmosphere. This gives rise to the phenomenon of photochemical smog which is observed in localities like Los Angeles and Denver, USA. It may be mentioned that 'smog' originally means and odd combination of smoke and fog prevalent in London. This is, however, chemically reducing with high levels of SO2 and is called reducing smog, whereas, photochemical smog is an oxidising smog having a high concentration of oxidants. Photochemical smog is characterised by brown, hazy fumes which irritates the eyes and lungs, and also leads to the cracking of rubber and extensive damage of plant life.

The probable mechanism of smog forming reaction is shown in the following flowchart.

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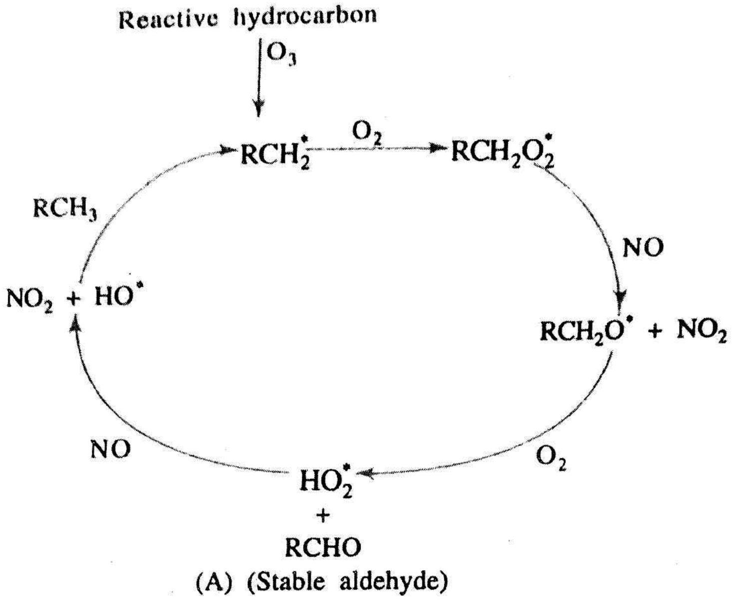


(B) Route to PAN formation

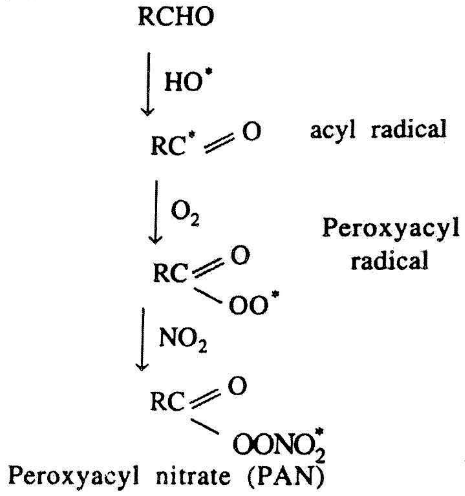


Fig. 4.7 *Smog-formation reactions (B) PAN formation reactions.*

(i) Reactive hydrocarbons (those with C = C groups) from auto-exhaust interact with O_3 to form a hydrocarbon-free radical RCH_2.

(ii) RCH_2 rapidly reacts with O_2 to form another free radical RCH_2O_2. (Check symbols on compounds. Refer page 9 of hard copy attached).

(iii) RCH_2O_2 reacts with NO to produce No_2 and the free radical RCH_2O_2.

(iv) This new free radical next interacts with O_2 to yield a stable aldehyde, RCHO, and hydroperoxyl radical HO_2.

(v) HO_2 then reacts with another molecule of NO to give NO_2 and HO.

(vi) HO is extremely reactive and rapidly reacts with a stable hydrocarbon RCH_3 to yield H_2O and regenerate the hydrocarbon-free radical RCH_2, thereby completing cycle. This goes on and on as a chain reaction. One complete cycle yields two molecules of NO_2. One molecule of aldehyde RCHO, and regenerates the free radical RCH_2 to start all over again. Very soon there is a rapid build-up of smog products.

(vii) The aldehyde RCHO may initiate another revote by interaction with the HO^- radical, leading to the function of an acyl (R C = O), peroxyalyl ($RCCO_2$) and finally peroxyacyl nitrate (PAN). PAN is one of the most potent eye irritants found in smog.

Photochemical smog shows characteristic variation of the parameters (smog ingredients) with the time of day. The hydrocarbon level is maximum during early morning traffic rush hours, then decreases during the remaining daylight hours as it is consumed in the smog-formation reactions described above. Nitric oxide concentration has a peak value at the same time and then falls as NO_2 concentration increases. Subsequently, there is a rise in the concentration of oxidants (aldehyde, PAN), which are active oxidising agents and contain the irritating ingredients of smog. A typical concentration profile of smog-forming chemicals in Los Angeles air in USA in shown in figure4.8.

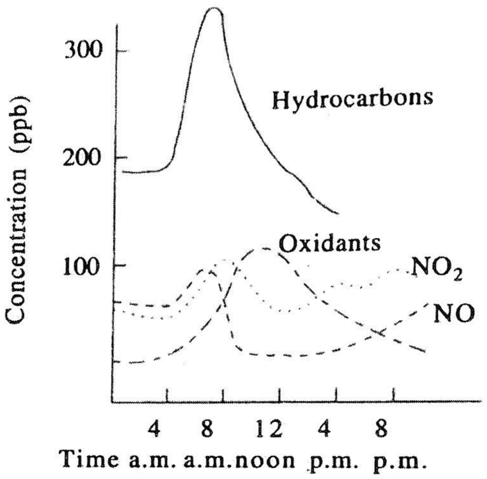


Fig. 4.8 *Concentration profiles of smog-forming chemical in Los Angeles air (Source: J.A. Kerr, J.G. Calvert and K.L. Demerjian, Chem. B. 8(1971): p. 253.)*

Reducing the Occurrence of Photochemical Smog

Major sources for the occurrence of Photochemical smog are the oxides of nitrogen and volatile agamic compounds (VOCs) produced biogenically in nature and the anthropogenic emission.

1. Reduction of Nitrogen Oxides: The levels of nitrogen can be lowered by a process called catalytic reduction used in industries and motor vehicles. For example, a catalytic connecter fitted to a car's exhaust system connects much of the nitric oxide from the engine exhaust gases to nitrogen and oxygen.

Nitrogen is not in the actual fuels used in motor vehicles or power stations; it is introduced from the air when combustion occurs. Using less air in combustion can reduce emissions of nitrogen oxides.

Temperature also has an effect on emission – the lower the temperature of combustion, the lower the production of nitrogen oxides. Temperatures can be lowered by using processes such as two-stage combustion and flue gas recirculation, water injection, or by modifying the design of the burner.

2. Reduction of VOCs

There are various ways to reduce VOC emissions from motor vehicles. These include the use of liquefied petroleum gas (LPG) or compressed natural gas (CNG) rather than petrol, decreasing distances vehicles travel by using other modes of transport, such as buses and bikes, and implementing various engine and emission controls now being developed by manufactures.

The other major contributors to VOCs emission, however, are not simple to control as solvent evaporation occurs in many different places, from longed factories to backyard sheds.

4.5.5 Photo-Degradation of Polymers

Most of the polymers are affected by exposure to sunlight in conjunction with other natural weathering forces such as oxygen, water, and heat. The consequences of photo-degradation depend on the nature of the polymer and can cause polymer chain scission and cross-linking leading to changes at the molecular level. These irreversible processes eventually change the physical and visible properties of polymers to such extent that it cannot serve its purpose. A variety of synthetic and natural polymers absorb solar ultraviolet radiation and undergo photolytic, photo oxidation, and thermo oxidative degradation which results in breaking of the polymers chain, produce radicals, and reduces the molecular height, causing deterioration of mechanical properties and leading to useless materials.

Damage by UV radiation is commonly the main reason for the decolouration of dyes and pigments, weathering and yellowing of plastics, loss of gloss and mechanical properties, sunburnt skin, skin cancer, and other problems associated with UV height.

Factors Causing the Photo-Degradation

Factors leading to photo degradation of polymers can be broadly divided into two groups.

1. **Internal Impurities:** These include chromophores that are introduced in macromolecules during polymerization processing and storage, these include:
    - (i) Hydroperoxide
    - (ii) Carbonyl
    - (iii) Unsaturated bonds (C=C)
    - (iv) Catalyst Residue (CT)
    - (v) Charge transfer/complex with oxygen

2. **External Impurities:** These include chromophores groups like;
   - (i) Traces of solvents, catalyst, etc.
   - (ii) Compounds from a polluted atmosphere and smog, e.g., poly-nuclear hydrocarbons such as naphthalene and anthraces in propylene and polybntadiene.
   - (iii) Additive (pigments, dyes, thermal stabilizers, photo-stabilizers, etc.)
   - (iv) Traces of metal and metal oxides from processing equipment's and containers such as, Fe, Ni or Cr.

Mechanism of Photoxidative Degradation of Polymers

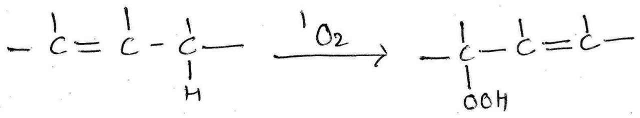
Photo oxidative degradation of polymers take place via radical processes similar to thermal oxidation reaction. Two mechanisms have been proposed to explain the photo oxidation of polymers in conformity with similar observations made on low molecular weight compounds this mechanism are discussed below.

1. The Singlet Oxygen Mechanism of Oxidation.

Many photosensitized oxidation reactions proceed with participation of oxygen in an electronically excited singlet state. The photochemical production of singlet oxygen is mainly due to quenching of the excited triplet state of suitable sensitizers:

$$3S + 3O_2 \rightarrow {}^1SO + {}^1O_2$$

Singlet oxygen exhibits several specific reactions and the one that has been most often invoked in the photooxidation of polymers is the formation of a hydro peroxide by oxidation of an olefin containing and allylic hydrogen, and which could further decompose and lead to chain scission and formation of a terminal of carbonyl group.



2. The Free Radical Mechanism of Oxidation

The radical mechanism of photo oxidation of polymers proceeds through a chain reaction similar to that for homogeneous liquid phase oxidations:

Initiation: Polymers → Radicals

Propagation: Radical $+O_2 \rightarrow RO_2$

$RO_2 + RH \rightarrow ROOH + R$

$ROOH \rightarrow RO + OH$

Termination: $2RO \rightarrow$ non-radical product

Photo Oxidation Cycle for Polymers

The Photo oxidation cycle for polymers can be shown as (figure 4.9).

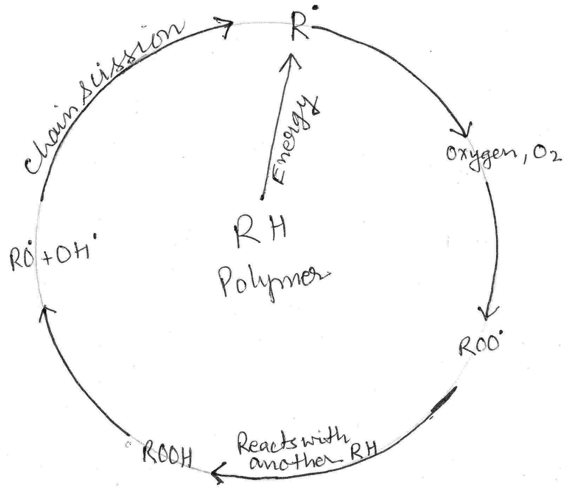


Fig. 4.9 *Photooxidation cycle for polymers*

Examples of Photo Degradation

1. Photo Degradation of Polymethyl Methacrylate (PMMA) by UV Radiations: PMMA in a molten state on irradiation with UV rays gives an almost quantitative yield of the monomer. It is generally believed that free radicals are initially formed during photo degradation, and in many cases, the subsequent cause of the reaction of the free radicals depends on the physical state of the polymer. Thus, while matter polymer gives a quantitative yield of the monomer, the solid polymer doesn't give any significant quantity of the monomer. Small quantities of methyl formate are, however, formed during the photo degradation of the solid PMMA, as shown below:

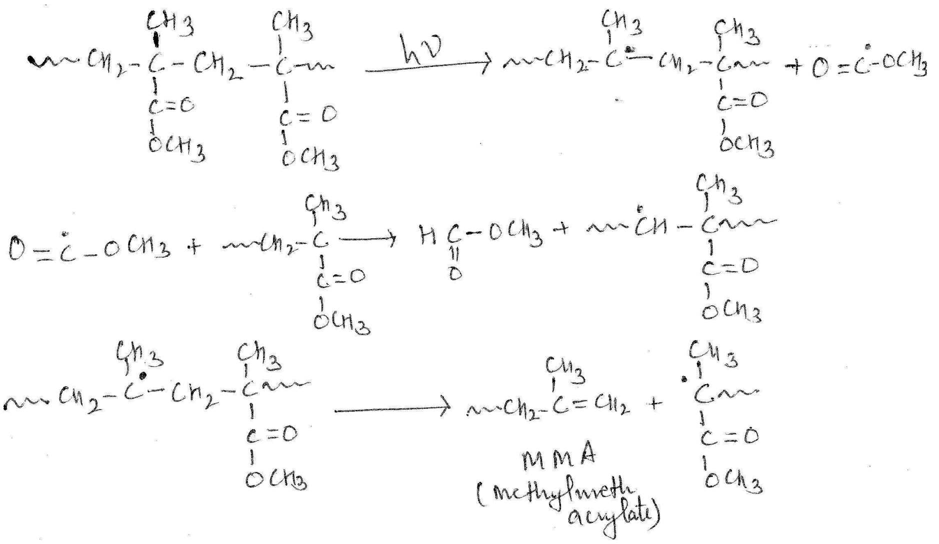
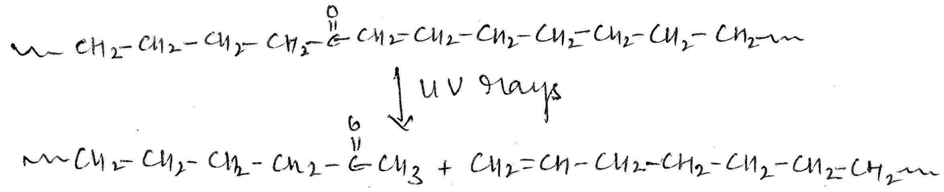


Photo degradation of poly α-methyl styrene, shows similar type of photo degradation.

2. Photo Degradation of Polyethene (PE) : It has been shown that polyethylene molecules, due to structural defects as impurities, due to structural defects as impurities, quite often contain a C = C as C = O linkage which makes the nearby bonds susceptible to photo degradation in following manner:



$$\sim CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2\sim \xrightarrow{\text{UV rays}} \sim CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_3 + CH_2=CH-CH_2-CH_2-CH_2-CH_2-CH_2\sim$$

4.5.6 Photo Chemistry of Vision

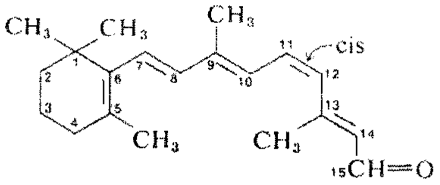
The process of vision involves absorption of light by a pigment in a photo receptor cell and the photo chemistry that ensures the process ultimately produces a transient electrical signal that is transmitted to the brain and interpreted as visual image. The photo chemistry of vision is not fully understood but we will discuss chemistry involved in brief.

Chemistry of vision

Eye is an extra ordinarily sensitive instrument, its wavelengths restricted to 400-800 nm. But its degree of sensitivity in such that a fully dank adapted eye can clearly detect objects in height so dim as to correspond to a height input over the restive of only about 10000 quanta per second

The retina is made up of two kinds of light-sensitive (photoreceptor) cells, known as rods and cones. The rods are the more sensitive and are responsible for vision in dim light. The cones are much fewer in number than the rods and provide detail and colour vision in good light. The part of the retina that corresponds to the centre of the visual field contains only cones. A red pigment called rhodopsin is the photosensitive substance in the rod cells of the retina. It absorbs most strongly in the cone vision appears of the visible spectrum (λ_{max} 500 nm) and is essentially unaffected by the far-red end of the spectrum. Cone vision appears to involve a different pigment called iodeosin, which absorbs farther toward the red than does rhodopsin.

Rhodopsin is a combination of a protein called scotopsin, and the highly conjugated aldehyde, 11-cis-retinal.



11-*cis*-retinal (λ_{max} 370 nm)

The structure of scotopsin is unknown, but its prosthetic group (11-cis-retinal) is bonded to it through an imine (Schiff base) function formed between the aldehyde group of the retinal and the side-chain amino function of a lysine unit of opsin.

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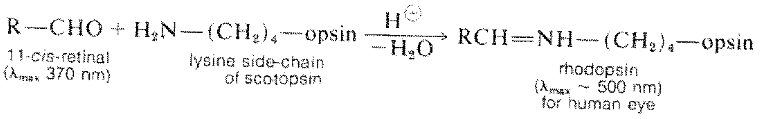

$$\underset{\substack{11\text{-}cis\text{-retinal}\\(\lambda_{max}\ 370\ \text{nm})}}{R{-}CHO} + \underset{\substack{\text{lysine side-chain}\\\text{of scotopsin}}}{H_2N{-}(CH_2)_4{-}\text{opsin}} \xrightarrow[-H_2O]{H^{\oplus}} \underset{\substack{\text{rhodopsin}\\(\lambda_{max} \sim 500\ \text{nm})\\\text{for human eye}}}{RCH{=}NH{-}(CH_2)_4{-}\text{opsin}}$$

Scotopsin itself is colourless, whereas 11-cis-retinal absorbs strongly at 370nm. The combination of scotopsin with 11-cis-retinal produces a remarkable shift of λ_{max} to longer wavelength (430 nm to 620 nm, depending on the species). Similar shifts in wavelength for 11-cis-retinal in combination with simple amines are observed only up to λ_{max} of 440 nm, add only then for the protonated Schiff base. From this evidence, the chromphore in rhodopsin is believed to be protonated add to be profoundly modified by the structure of the scotopsin.

Rhodospin – Retinal Visual cycle

When light energy is absorbed by rhodopsin, the rhodopsin begins to decompose within a very small fraction of a second, as shown at the top of figure 4.5 The cause if this is photo activation of electrons in the retinal portion of the rhodopsin, which leads to instantaneous change of the cis form of retinal into an all-trans form that still has the same chemical structure as the cis form but has a different physical structure- a straight molecule rather than an angulated molecule. Because the three-dimensional orientation of the reactive sites of the all-trans retinal no longer fits with the orientation of the reactive sites on the protein scotopsin, the all-trans retinal begins to pull-away from the scotospin.

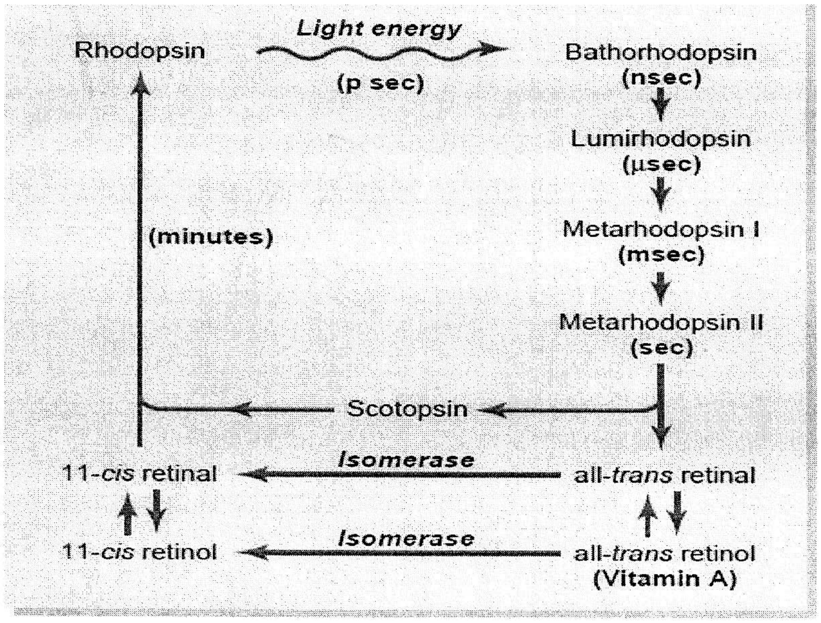

Fig. 4.10 *Effect of Light Energy on Rhodospin*

The immediate product is **patharhodospin,** which is extremely unstable and decays in nanoseconds to **lumirhodospin**. This then decays to **metarhadospin I**, then in about a millisecond to **metarhadospin II** and finally much more slowly (in second) into **scotospin** and all **trans-retinal**.

Refoundation of Rhodopsin: As shown in fig. the all *trans*-retinal reconnects 11 –*cis* retinal. This process requires metabolic energy and is catalysed by the enzyme retinal isomerase. 11-cis retinal formed combines with scotopsin to reform rhodopsin, which remains stable until its decomposition is again triggered by the absorption of light energy.

Role of Vitamin A in the formation of Rhodospin: As seen in fig, there is a second route by which all *trans*-retinal is connected into 11-*cis* retinal. This is by conversion of all *trans* retinal first into all *trans* retinol, which is one form of vitamin A. Then the all-trans retinal is converted into 11-*cis* retinol under the influence of enzyme isomerase. Finally, 11-cis retinal is connected into 11-*cis* retinol, which combines with scotopsin to form new rhodopsin.

Vitamin A is present both in the cytoplasm of the rods and in the pigment layer of the retina. Therefore, vitamin A is normally always available to form new retinal when needed. Conversely, when there is excess retinal in the retina, it is converted back into vitamin A, thus reducing the amount of light-sensitive pigment in the retina. We shall see later that this interconversion between retinal and vitamin A is especially important in long-term adaptation of the retina to different light intensities.

Night Blindness: Night blindness occurs in persons with severe vitamin-A deficiency. This is because without vitamin A, the amounts of retinol and rhodopsin that can be formed are severely depressed. This condition occurs when a person remains vitamin A deficient diet for months, because large quantities of Vitamin A are normally stored in the liver and can be made available to the eyes.

Photochemistry of Colour Vision by the Cones

Photo chemical in the cones have almost exactly the same chemical composition as that of the rhodopsin in the rods. The only difference is that the protein (*photopsin*) in the cones is slightly different from the *scotopsin* of the rods. The retinal proteins of all usual pigments are exactly the same in the cones as in the rods. The colour sensible pigments of the cones, therefore, are combination of retinal proteins and photopsins. Only one of the three types of colour pigments is present in each of the different cones, thus making the cones selectively sensitive to different colour like blue, green or red. These colour pigments are called, blue-sensitive pigment, green-sensitive pigment, and red-sensitive pigment. The absorption characteristics of the pigments in the three types of cones show peak absorbance's at light wavelength of 445, 535, and 570nm respectively.

These are also the wavelengths for peak light sensitivity for each type of cone, which begins to explain how the retina differentiates the colours. The approximate absorption curves for these three pigments are shown in figure 50-7. Also is the absorption rhodopsin of the rods, with a peak at 505 nanometres.

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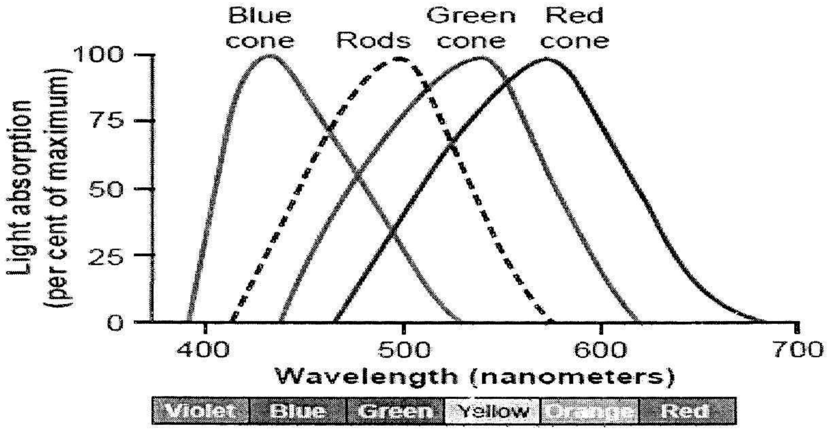

Fig. 4.11 *Light absorption by the pigment of the rods and by the pigments of the three color-receptive cones of the human retina.*

Light and D208ark Adaptations

If a person has been in bright light for hours, large portions of the photo chemicals in both the rods and the cones will have been reduced to retinal and opsins. Furthermore, much of the retinal of both the rods and the cones will have been converted into vitamin A. Because of these two effects, the concentration of the photosensitive chemicals remaining in the rods and cones are considerably reduced, and the sensitivity of the eye to light is correspondingly reduced. This is called light adaptation.

Conversely, if a person remains in darkness for a long time. The retinal and opsins in the rods and cones are converted, back into the light-sensitive pigments. Furthermore, vitamin A is converted back into retinal to give still more light-sensitive pigments. The final limit being determined by the amount of opsins in the rods and cones to combine with the retinal, this is called dark adaptation.

Check Your Progress

14. What do you understand by Barton's reaction?
15. What is a singlet oxygen?
16. What do you understand by photochemical smog?
17. State the components of retina.
18. Give the components of rhodopsin.

4.6 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The members of alkene series are represented by the general formula CnH_2n and are also known as Olefins.
2. The simplest olefin has the formula C2H4 and is commonly known as ethylene.

3. The molecule of an alkene may be considered to be made up of two units; a double bond and an alkyl group.
4. This rule states that: In the addition to an unsymmetrical olefin the negative part of the reagent or addendum goes to that carbon constituting the double bond which is poorer in hydrogen.
5. Alkenes can be converted to corresponding alcohols on treatment with sulphuric acid and subsequent hydrolysis.
6. Alkenes in the presence of acid catalysts and high temperature and pressure undergo self-addition to give a new alkene. The product alkene has twice the molecular weight of initial alkene and is called a dimer.
7. This theory assumes that valencies of carbon atoms involved in double bonds are not fully satisfied and each carbon is left with some residual or partial valency and the addition to double bond occurs through these residual valencies.
8. Cyclohexadienones are produced from the reactions of unsaturated carbene complexes and alkynes when the beta-carbon of the carbene complex is disubstituted.
9. Isomerization is the process in which a molecule, ion or molecular fragment is transformed into an isomer with a different chemical structure.
10. A halogen addition reaction is a type of reaction where a molecule combines with 1 or more halogen molecules to form a larger molecule, without any by-products forming.
11. A hydrogen addition reaction is a type of reaction where a molecule combines with 1 or more molecules of hydrogen to form a larger molecule, without any by-products forming.
12. In a nucleophilic aromatic substitution reaction, a nucleophile displaces a substituent on an aromatic ring.
13. In an electrophilic aromatic substitution reaction, a substituent on an aromatic ring is displaced by an electrophile.
14. Photolytic conversion of organic nitrites into nitroso alcohols is known as Barton reaction.
15. Singlet oxygen is gaseous inorganic chemical with the formula Q = O also written as O_2, which is a state in which all electros are paired.
16. Photochemical smog is an oxidising smog having a high concentration of oxidants.
17. The retina is made up of two kinds of light-sensitive (photoreceptor) cells, known as rods and cones. The rods are the more sensitive and are responsible for vision in dim light. The cones are much fewer in number than the rods and provide detail and colour vision in good light.

18. Rhodopsin is a combination of a protein called scotopsin, and the highly conjugated aldehyde, 11-cis-retinal.

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4.7 SUMMARY

- Alkenes are represented by the general formula CnH2n and are also known as Olefins.
- The simplest olefin has the formula C2H4 and is commonly known as ethylene.
- The carbon-carbon double bond is known as olefinic linkage or ethylenic linkage after the name of the first member. In IUPAC system, olefins are termed as Alkenes.
- Alkenes undergo addition at double bond with a large number of reagents to form saturated compounds.
- Alkenes in the presence of acid catalysts and high temperature and pressure undergo self-addition (addition of one molecule to another alkene molecule) to give a new alkene.
- Alkenes in the presence of acid catalysts and high temperature and pressure undergo self-addition (addition of one molecule to another alkene molecule) to give a new alkene.
- When alkenes are heated in the presence of a catalyst or alone, they undergo isomerisation to form isomeric alkenes
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- When alkenes are heated in the presence of a catalyst or alone, they undergo isomerisation to form isomeric alkenes.
- Isomerization is the process in which a molecule, ion or molecular fragment is transformed into an isomer with a different chemical structure.
- Isomerization is the process in which a molecule, ion or molecular fragment is transformed into an isomer with a different chemical structure.
- Photochemical reactions are the chemical reactions initiated by the absorption of energy in the form of light.
- Photolytic conversion of organic nitrites into nitroso alcohols is known as Barton reaction.
- Harmful effects of hydrocarbon pollution are not due to the hydrocarbons themselves but the products of photochemical reactions in which they are involved.

- Photo oxidative degradation of polymers take place via radical processes similar to thermal oxidation reaction.
- The process of vision involves absorption of light by a pigment in a photo receptor cell and the photo chemistry that ensures the process ultimately produces a transient electrical signal that is transmitted to the brain and interpreted as visual image.
- Eye is an extra ordinarily sensitive instrument, its wavelengths restricted to 400-800 nm.
- Rhodopsin is a combination of a protein called scotopsin, and the highly conjugated aldehyde, 11-cis-retinal.
- The structure of scotopsin is unknown, but its prosthetic group (11-cis-retinal) is bonded to it through an imine (Schiff base) function formed between the aldehyde group of the retinal and the side-chain amino function of a lysine unit of opsin.

4.8 KEY TERMS

- **Olefins:** The members of alkene series are represented by the general formula CnH_2n and are also known as Olefins.
- **Ethylene:** The simplest olefin has the formula C2H4 and is commonly known as ethylene.
- **Ozonolysis:** The process of the formation of ozonide and its decomposition to give carbonyl compounds is known as Ozonolysis.
- **Photochemistry:** Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm).
- **Cyclohexadienones:** Cyclohexadienones are produced from the reactions of unsaturated carbene complexes and alkynes when the beta-carbon of the carbene complex is disubstituted.
- **Isomerization:** Isomerization is the process in which a molecule, ion or molecular fragment is transformed into an isomer with a different chemical structure.
- **Barton Reaction:** Photolytic conversion of organic nitrites into nitroso alcohols is known as Barton reaction.
- **Photochemical Smog:** The photochemical smog is an oxidising smog having a high concentration of oxidants.

4.9 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answers Questions

1. Define the geometrical isomerism in alkenes.
2. State the hydrogenation reaction of alkenes.
3. Define Kharasch peroxide effect.
4. State the hydroboration-oxidation reaction of alkenes.
5. State the hydrogen addition reaction of benzene.
6. State the halogen addition reactions of benzene.
7. What are the harmful effects of the photochemical smog?
8. What do you understand by photo degradation of polymers?
9. What do you understand by the singlet oxygen mechanism of oxidation?

Long-Answers Questions

1. Explain in detail the various reactions of alkenes.
2. Describe the rearrangement of 1,4 dienes.
3. Describe the photochemistry of a,b-unsaturated ketones.
4. Describe the cyclisation reaction of carbonyl compounds.
5. What do you understand by Photo-Fries Rearrangements and Photo-Fries reactions of Anilides?

6 Describe in detail the photochemistry of vision.

4.10 FURTHER READING

Wardle Brian, 2009, *Principles and Applications of Photochemistry,* Wiley: New Jersey.

Olivucci Massimo, 2005, *Computational Photochemistry*, Elsevier Science: USA.Arnold D. R., N. C.

Baird, J. R. Bolton, 2014, *Photochemistry An Introduction,* Elsevier Science: USA.

Mukherjee K. K. Rohatgi, 1978, *Fundamentals of Photochemistry,* Wiley: New Delhi.

UNIT 5 SOLID-STATE CHEMISTRY

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Structure

5.0 INTRODUCTION

Solid-state chemistry is the study of the synthesis, structure, and properties of solid phase materials, particularly, but not necessarily exclusively of, non-molecular solids. Solids can be classified as crystalline or amorphous on basis of the nature of order present in the arrangement of their constituent particles.

Crystal defect, imperfection in the regular geometrical arrangement of the atoms in a crystalline solid. Crystallographic defects are interruptions of regular patterns in crystalline solids. They are common because positions of atoms or molecules at repeating fixed distances determined by the unit cell parameters in crystals, which exhibit a periodic crystal structure, are usually imperfect.

Organic solids are the materials containing carbon as one of many compounds. Carbon is a general compound. Organic solids are generally soft with low melting points and poor electrical conductivity.

In this unit, you will study about the various solid state reactions, crystal defects, band theory, and organic solids etc.

5.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the solid state reactions.
- Explain the crystal defects and non-stoichiometric processes.
- Conceptualize the band theory and electronic properties.
- Describe the organic solids.
- Discuss the various types of semi-conductors.

5.2 SOLID STATE REACTIONS

Solid state reactions are the reactions which occurs among solids. The reactions where the product is solid and the two reactants must be solid are included in this type, but practically many reactions are categorized as solid state reactions even though both the reactants are not solid. For example in rusting of iron, of the reactant is solid while the other is gaseous. Reactions among solids is not very common, but certain reactions have been found to occur among solids. The study of solid-state reaction has gained importance because this is one of the most important procedures for the synthesis of polycrystalline solids, which have great significance in material science.

Solid state reactions are usually difficult to occur. The reason is that it has a well-defined geometrical spinel structure. So usually these reactions can occur only at high temperature normally above 1000°C. In some cases the reaction can occur also at room temperature but progress of reaction in such cases cannot be monitored unless the temperature is raised to certain optimum value.

Types of Reactions

In the preparation of a homogeneous solid, it is not possible to restrict the reactions to solid- solid reactions only. Many useful solids are founded formed by reactions between solid-liquid or solid and a gas. Preparation of a solid depending upon the physical state of the reactants and products involved in the reaction can be classified into following shown below.

Type I $A\ (s) \rightarrow B(s) + C(g);$

Type II $A\ (s) + B\ (s) \rightarrow C(s);$

Type III $A(s) + B(s) \rightarrow C(s)$ and $D\ (g);$

Type IV $A(s) + B(g) \rightarrow C\ (s);$

Type V $A(s) + B(g) \rightarrow C(s) + D(g);$

Type VI $A(s) \rightarrow B\ (g) + C(g)$

Most of these reactions take place where the reactants are subjected to heating.

5.2.1 Classification of Solid-State Reactions

Solid state reactions are diffusion controlled process (migration of ion). In solid state reaction mixing doesn't occur at the molecular level and at least one of the reactant must diffuse towards the other reactant.

Decomposition Reactions (Occurrence and Kinetics)

Thermal decomposition of a solid may give one or more solid or gaseous products. Reaction types I and VI belong to thermal decomposition. Let us consider Type I reactions, where in a solid on heating gives another solid and a gaseous product. Decomposition of a solid *A* to give a new solid *B* on heating may or may not have an induction period. Typical plots of the fraction (α) of *A* decomposed versus time *(t)* may be represented by any of the curves shown in Figure 5.1. At some stage of heating, nuclei of *B* will be formed that will be embedded in *A*. Since the structure of *B* is generally different from that of *A*, at some stage of growth of *B* sufficient local deformation will be present giving rise to strain energy. There exists a critical size of *B* at which the thermodynamic stability of *B* will overcome the strain energy created by its formation. Below this size, nuclei of *B* will revert back to *A*. If the nuclei of *B* are bigger than the critical size, transformation of *A* to *B* will continue.

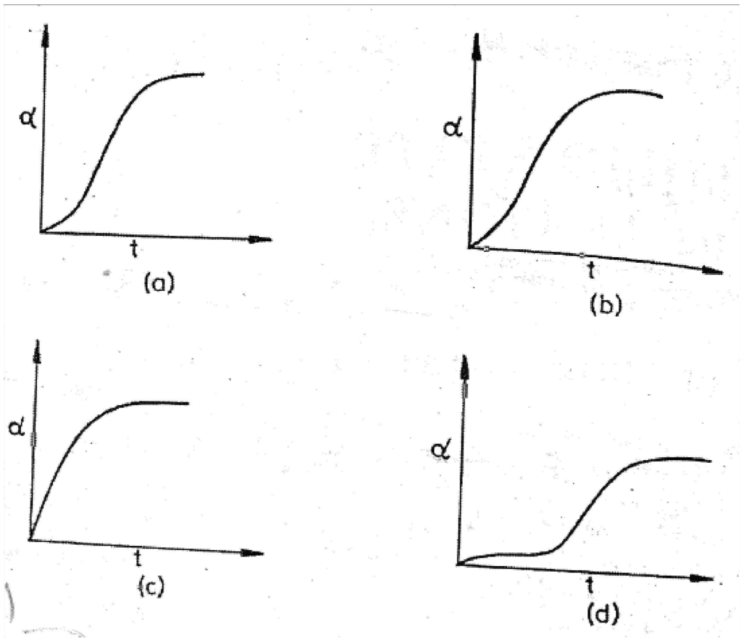

***Fig. 5.1** Fraction of the solid decomposed versus time: (a) self-catalysed, (b) short induction followed by rapid decomposition, (c) no induction period, (d) initial slow gas evolution.*

Free energy of the reaction

$$\Delta G = m\Delta G_b + a\gamma \tag{5.1}$$

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Where m is the number of molecules in the nucleus of B, ΔG_b is the bulk free energy of the reaction, a is a shape factor and γ is the strain energy per unit area of the interface between A and B. If the particles are spherical, $a = 4\pi r^2$ and $m = m = \frac{4}{3}\frac{\pi r^3}{v_m}$ where r is the radius of the nucleus of B and v_m is the volume per molecule of the phase B. In equation (8.1), ΔG_b is a negative quantity and γ is positive. So the growth of B makes opposite contribution to the free energy ΔG of the reaction. There is a critical value of m, i.e. m" at which $\Delta G = 0$.

Jacobs and Tomkins has shown that

$$\text{m}^* = m = \left(\frac{2\gamma}{3\Delta\, Gb} \right) 336\pi v 2m \tag{5.2}$$

When $m > m$", $(\frac{\partial \Delta G}{\partial m})$ is negative and the reaction will proceed, the nucleus of B will grow. When $m < m^*$, the change of ΔG with m becomes positive and B will revert back to A. This is shown in Figure 5.2.

If the formation of the nuclei is followed by rapid growth, it will be autocatalytic in nature. If the activation energy of the reaction is less than that of the formation of the nuclei, the reaction will proceed only nuclei as is the case for many dehydration reactions. When the activation energy of nucleation and growth are comparable, there will be - practically no induction period. These cases are shown in Figure.5.1 (a-c).

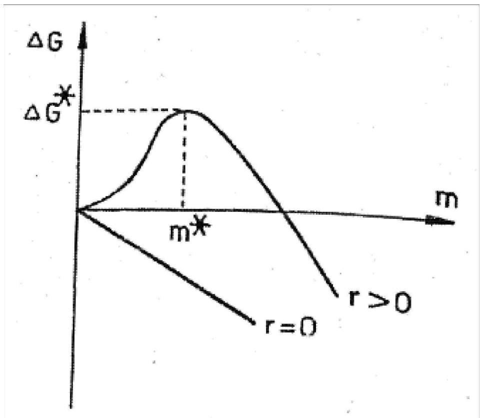

Fig. 5.2 *AG of the reaction* A(s) + B(s) + C(g) *as a function of number of molecules per nuclei of* B. *m* is the critical number.*

Initially, a number of nuclei are formed after which growth proceeds rapidly all over. We see that the a versus t plots can be explained in terms of the nucleation and growth of the newly formed solid phase. It should be realised that for reactions of Type I, nucleation can occur only at the surface so that the gaseous product can escape.

Laws Governing Nucleation

Nuclei of the product solid will be formed in the reactant solid matrix at different points if the local fluctuations of the atoms are sufficient to overcome the energy of activation of nucleation Nucleation generally occurs at some lattice defects.

If nucleation requires decomposition of a single molecule, it can be shown that

$$\frac{dn}{dt} = K_1 N_{0\exp} (k1t) \quad (5.3)$$

Where N is the number of nuclei present at time t, N_0 is the number of potential nucleation sites and K_1 is a rate constant. If the energy as activation of nucleation is large, K_1 is small ant it becomes

$$\frac{dn}{dt} = k_1 N_0 \quad (5.4)$$

Under these conditions, the number of nuclei increases linearly with time. If K_1 is very large,

$$N = N_o \quad (5.5)$$

This is the situation when the nucleation is instantaneous. If nucleation in values stepwise decomposition of two or three molecules, the rate follows a power law such as

$$\frac{dn}{dt} = At^{\beta-1} \quad (5.6)$$

where A is a constant and ß is equal to two or three.

Growth of Nuclei

If nucleation follows power law and growth is linear, it can be shown that

$$\alpha = Ct^n \quad (5.7)$$

Where, C and n are constants. For the reactions of Type I, the pressure (p) developed in a closed system is proportional to α. Hence

$$p = Dt^n \quad (5.8)$$

Where D is a new constant.

The power law equation holds good for many reactions of Type I such as decomposition of barium and calcium azides, aged mercury fulminate and aged silver oxalate. It has been found at times that n changes if the temperature of decomposition is varied. Discrepancy was also noticed using finely powdered crystals. This could be explained by assuming that the growth is much slower if the crystals are small. In order to explain the observed high values of n (between 11.2 and 22.8) in the case of the decomposition of mercury fulminate, Garner and Hailes assumed that the nuclei are linear branching chains. This assumption led to the expression

$$\alpha = Ce^{kt} \quad (5.9)$$

Where k is a branching coefficient.

The pressure developed during decomposition inside a closed system is

$$p = de^{kt} \quad (5.10)$$

Type I Reactions

These may be endothermic or exothermic. The most commonly studied to endothermic reactions is the dehydration of a metal salt hydrate and the decomposition of the metal carbonates.

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The decomposition product of some metal hydrates has a crystal lattice identical with that of the parent solid. In some cases, the product is devoid of any well defined crystal structure. In the third case the product shows a distinctly different phase. The dehydration of the crystalline hydrate forms a highly disordered product. Rearrangement of this may give a new crystalline phase. During the reaction, they are present as shown in Fig 5.3. There is a shrinkage in the volume due to the new phase giving rise to cracks of molecular dimensions through which the water, molecules will have to escape. Slow diffusion through the cracks slow down the rate of dehydration. This possibly is the reason why there is a, initial fall in the rate of dehydration of $CuSO_4.5H_2O$.

The rate of dehydration depends not only on the rate at which water is lost at the interface between the reactant and the product solids, but also on the rate of diffusion of the water vapour. If the product is amorphous, it hardly can develop any crack to give a diffusion path. This will make diffusion difficult as found in the case of the dehydration of copper sulphate hydrate. If the product is highly crystalline as found in the case of the dehydration of chrome alum, large radial cracks develop in the new phase facilitating diffusion and thereby dehydration.

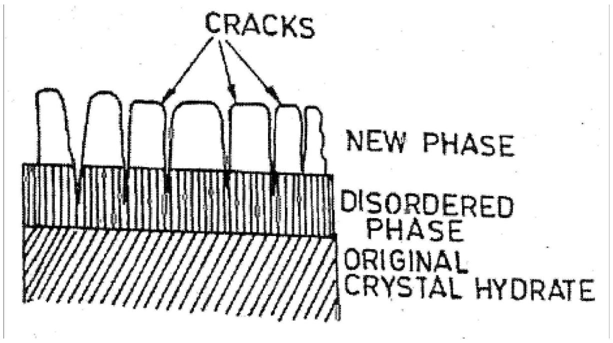

Fig. 5.3 *A model for the thermal decomposition of the hydrate of a metal salt.*

Decomposition of the metal carbonates is another widely studied solid state reaction. Many carbonates decompose to the corresponding oxides with the formation of a basic carbonate as an intermediate. In many cases, the rate follows a first order law and the energy of active is nearly equal to the heat of the reaction. A typical example is he decomposition of calcium carbonate

$CaCO_3(s)$ ——— $CaO(s) + CO_2(g)$

In such cases the reverse reaction does not need any activation energy.

5.2.2 Reactions between Two solids (Addition Reaction) or The Type II reaction

$A(s) + B(s) \rightarrow C(s)$

It is considerably different from the reactions taking place in the gas phase or in a solution. Whereas the reaction in the gas phase or in solution depends on the chance of the reactant molecules meeting each other, the solid state reactions of Type II take place between two solid phases in which the atoms have very restricted movement. The reaction can take place only at the points of contact of the two phases and a product layer builds up. Further reaction depends on the

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diffusion of the reactants through this product layer. Rate of a solid-solid reaction depends on the rate of transfer of atoms or ions through this layer. For a reaction to take place, the free energy ΔF should be negative. Since the entropy change in such a process is small, the change in enthalpy determines whether the reaction is possible. This means that the enthalpy change of the process should be negative making reaction Type Il exothermic in nature. If the solids A and B do not solid solution to any appreciable extent. ΔF will remain unchanged during the reaction and equilibrium will not be reached. The reaction will go to completion.

Studying the kinetics of such reactions is often difficult as there is no mass loss or gas evolution. The reaction is generally followed by observing the X-ray Diffraction (XRD). This is difficult if the product crystallinity. Kinetic study becomes more difficult if the product is formed through some intermediate.

Often, there is mention of a reaction temperature. Since these reactions are exothermic, temperature of the simple rises during the reaction due inefficient heat transfer from the simple to the surroundings resulting in an increase in the rate of the reaction. The temperature at which the reaction rate is maximum is generally taken as the **reaction temperature**. It is convenient to follow such reactions by Differential Thermal Analysis (DTA) where the temperature of the DTA peak is taken as the reaction temperature.

Because the reaction proceeds by diffusion of the reactants through the initially formed product layer, the reaction depends on the structure of the product phase B. The diffusion path can be effectively shortened by using finely divided particles of the reactants. The newly formed phase is often poorly crystalline and contains a large concentration of defects that makes diffusion easy.

The growth of the product *C(s)* depends on the rate of diffusion of A and B through C. Three cases may be distinguished depending on the ability of A and B to diffuse through the bulk of C. These are (i) A diffuses through the bulk of the product to react with B. (i) B diffuses and reacts and (iii) both A and B diffuse through the product to react.

Representative of Type Il reaction is the addition reaction such as

$$ZnO + Al_2O_3 \rightarrow ZnAl_2O_4$$

$$2AgI + HgI_2 \rightarrow Ag_2HgI_4$$

Zinc aluminium has the spine structure in which only a fraction of the available tetrahedral and octahedral sites are occupied. Diffusion of zinc and aluminium ions are facilitated through the vacant sites. In the second reaction, both Ag^+ and Hg^{2+} diffuse at high rates. There are three cations for every four cationic sites in the product Ag_2HgI_4 and diffusion takes place through these cationic vacancies.

Exchange Reactions

The exchange reactions are possible in following ways:

(1) $A + BC \rightarrow AC + B$

For example,

$Mg + ZnS \rightarrow MgS + Zn$

(2) $AB + CD \rightarrow AD + CB$

For example,

$$HgCl_2 + Na_2CO_3 \rightarrow HgCO_3 + 2NaCl$$

Gas Solid Reaction

Tarnishing reactions are very common examples of this types. Tarnishing is a process to which involves a solid reaction with the gas and forms a solid compound which builds a thick layer of the product between the two reactants. Oxidation of metals are very common examples of this type. This reaction generally depends upon on the compactness of the product layer which is formed between the reactants.

Solid Liquid Reaction.

The corrosion of anodic dissociation and electrode decomposition of metals are very common examples of this type of reaction. The hydration of cement is also an example of this type.

$$\text{cement} + \text{moisture} \rightarrow \text{solid}$$

5.2.3 Preparative Methods for Solids (Experimental Procedure)

A diverse array of methods are available to synthesize solid compounds and materials. In the preparation of solid care must be taken for stoichiometric quantities, pure starting materials and ensure that reaction has gone to completion:

1. Solid State Ceramic Method

This method consists of treating two non-volatile solids which react to form the required product. The solid-state method can be used to prepare a whole range of materials including mixed metal oxides, sulphides, nitrides, aluminosilicates etc.

$$ZrO_2(s) + SiO_2(s) \xrightarrow{1300^\circ C} ZrSiO_4(s)$$

This method can be used to prepare an extremely large number of compounds. Important features to be taken into consideration in the method include:

(1) Thorough grinding is necessary to achieve a homogenous mixture of reactants.

(2) The number of crystallites in contact may be increased by pelletizing the powders using a hydraulic press.

(3) The reaction mixture is typically removed and reground to bring fresh surfaces in contact, which speeds up the reaction.

(4) Reaction times are sometimes hours, but may range into several days or weeks for a complete reaction, with intermediate grinding.

(5) Sample purity is typically examined using powder X-ray diffraction.

(6) Furnaces use resistance heating with metal, SiC, or $MoSi_2$, heating elements.

(7) Conversion of electrical energy into heat (to 2300 K). An electrical arc directed at the sample may achieve 3300 K. A CO_2 laser can give temperatures up to 4300 K.

(8) Containers for the reaction (crucibles) must be able to withstand high temperatures and be sufficiently inert to the reactants. Common crucibles are silica (to 1430 K), alumina (to 2200 K), zirconia (to 2300 K), or magnesia (2700 K). Platinum (m.p. 2045 K) and silver (m.p. 1235 K) are also used for some reactions.

The Disadvantages of the Process Include

(1) High temperatures are generally required (500-2000°C), because it takes a significant amount of energy to overcome the lattice energy so a cation or anion can diffuse into a different site.

(2) The desired compound may decompose at high temperatures.

(3) The reaction may proceed very slowly, but increasing the temperature speeds up the reaction since it increases the diffusion rate.

(4) Generally, solids are not raised to their melting point, so reactions take place in the solid state (subsolids).

2. Sealed Tube Methods

If reactants are volatile or air sensitive, then heating in an open atmosphere is inappropriate. In such cases evacuated tubes are used, e.g.

$\mathrm{Sm(s)} \rightarrow \mathrm{SmS}$

Sulphur has a low boiling point 717k, so the reaction mixture is placed in an evacuated tube to prevent it from boiling off and being lost.

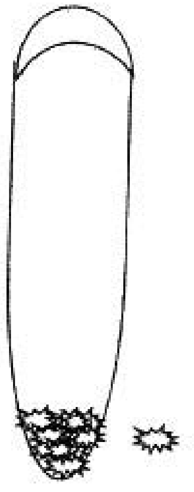

Fig. 5.4 Sealed Tube Method

The tube is often made of Pyrex or silica, since these are fairly inert and can be flame sealed with a Pyrex vacuum system. Usable to about 1000-1100 K. The sample is grounded, then heated in a tantalum tube for high temperature reactions (to 2300 K). The Ta tube must be sealed by welding the tube. An electric current is passed through the tube, generating high pressures and temperatures. Safety precautions must be taken in case of tube rupture.

3. Special Atmosphere

Synthesis of some compounds require a special atmosphere, for example,

(1) A noble gas, argon, may be used to prevent oxidation to higher oxidation state.

(2) An oxidizing gas, oxygen, might be used to form a high oxidation state.

(3) A reducing gas, hydrogen, might be used to form a low oxidation state. Reactions usually take place in a small boat crucible placed in a tube in a horizontal tube furnace.

(4) Gas is passed of a period of time to expel all air from the apparatus, then continues to flow during the heating and cooling cycle. A bubbler is used to ensure positive pressure is maintained.

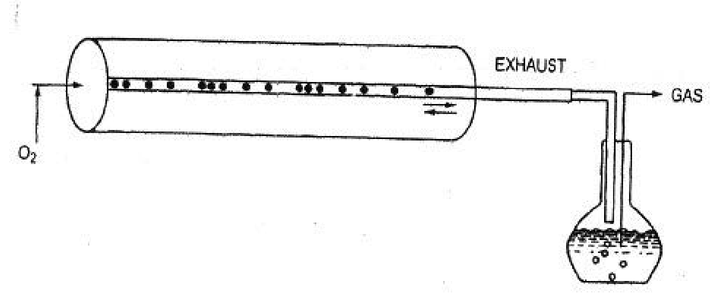

Fig. 5.5 Experimental Setup Showing the Process of Solid Preparation

5.2.4 Co-precipitation and Precursor Methods

Co-precipitations is a process in which normally soluble compounds are carried out of solution and precipitating them as hydroxides, citrates, oxalates, or formates. The mixture is filtered, dried, and then heated to give the final product. This method may result in impurities within the desired precipitates. These impurities may cause either negative or positive errors. There are four types of co-precipitation methods.

1. Surface Adsorption

It is a common source of co-precipitation that causes significant contamination of precipitates with large specific surface areas. It has no significance in crystalline precipitates for example, coagulated silver chloride is contaminated with primarily adsorbed Ag^+ along with nitrate or other amines.

Adsorbed impurities can be minimized by following methods.

1. **Washing:** A coagulated colloid with a solution containing a volatile electrolyte.-
2. **Digestion**: It involves expulsion of water from the solid to give a denser mans that has a smaller specific surface area for adsorption.
3. **Re-precipitation:** In this process, the filtered solid is redissolved and re-precipitated.

2. Mixed Crystal Formation

In this type of co-precipitation a contaminant on replaces an ion in the lattice of a crystal. Mixed crystal formation may occur in both colloidal and crystalline precipitates for example, SrO_4 in $BaSO_4$, $MgKPO_4$ in Mg (NH_4) (PO_4), MnS in CdS. This can be minimized by using another more selective precipitative reagent.

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3. Occlusion

In this type a compound and reprecipitation: (foreign ions in counter ion layer) is physically trapped within a precipitate during rapid precipitatate formation. This can be minimized by digestion which ensures that occluded material is exposed to the supernatant solution.

4. Mechanical Entrapment

It is a type of co-precipitation in which co-precipitated physically trap a pocket of solution within a precipitate during rapid precipitate formation. It can be reduced by digestion

5. Precursor Method

It involves atomic level mixing by forming a solid compound (precursor) in which the metals of the desired compound are present in the proper stoichiometry. For example, a mixed salt of an oxyacid (e.g. acetate) containing M and M' in the ratio of 1:2 is formed in the case of formation of MM'_2O_4.

(1) The precursor is heated to decompose it to the desired product.

(2) Homogeneous products are formed at relatively low temperatures.

(3) It is not always possible to find a suitable precursor

For example, formation of oxides ($BaTiO_3$) by precursor method.

$$Ti(OBu)_4\ aq + 4H_20 \rightarrow Ti\ (OH)_4\ (6) + 4B_4OH\ (aq)$$

Excess oxalic acid re-dissolves the precipitate

$$Ti\ (OH)_4\ (s) + (COO)_2^{2-}\ (aq) \rightarrow TiO\ (COO)_2\ (aq) + 2\ OH\ (aq)\ H_2O\ (l)$$

$$Ba^{2+}(aq) + (OO)_2^{2-}(aq) + TiO\ (COO)_2\ (aq) \rightarrow Ba\ [TiO(COO)_2)_2](s)$$

Decomposition by heating (920K) gives the desired oxide phase

$$Ba\ (TiO((COO)_2)_2\ \ BaTiO_3\ (s) + 2CO_2(s) + 2CO_2(g) + 2CO(g)$$

Decomposition of oxalates is also used to form ferrites (MFe_2O_4). Products from precursor methods often contain small particles with large surface area, which is desired for certain applications.

Improving the Reactivity of Solid-State Reactions

The reactivity of solids so that the product can be obtained in a shorter time and under milder conditions needs to be explored. Several ways of improving the sold-state reactions are discussed below.

Increasing the surface area.

Since solid state reactions begin at the surface of the reactant, inreasing its surface area is always helpful. This gives a larger area of contact between them where the reaction begins, small particle size of the high surface area material also reduces the diffusion path. Thus, it is advantageous to use solid reactants with high surface area.

High surface area oxides can be prepared in a number of ways. Since oxides are generally prepared by thermal decomposition of a precursor solid, it is easy to prepare an oxide with high surface area by the decomposition of a precursor also with high surface area. The precursor with high surface area can be prepared in a number of ways. It can be achieved by precipitation of a precursor that has low solubility in the medium used. It can also be done by spray drying or freeze drying. The precursor may be a metal hydroxide or a carboxylate or some other compound that decomposes at a relatively low temperature to give the oxide.

Addition of impurities

Impurities may be introduced in a solid during crystallization deliberately or otherwise these impurities play an important role in determining the reactivity of solids. They may introduce a distortion in the crystal structure thereby weakening the chemical bonds. The impurity cation may be present as an interstitial defect. If it is present at a substitutional position but has a higher cationic change than that of the host lattice cation, it will produce cation vacancies. The diffusion of the ions may then be enhanced due to the presence of the defects by any of the diffusion mechanisms. Thus, it has been found that when silver oxalate is doped with divalent copper, there is decrease in the decomposition rate constant with the concentration of the copper ion. Doping with Cu^{2+} ions increase cation concentration which in turn decreases the interstitial cation concentration This brings down the decomposition rate.

Doping affects the rate of reduction of nickel oxide. Generally, doping with cations with higher than +2 charge enhances reduction. Doping with a monovalent cation, on the other hand, decreases the rate of reduction.

Structural defect

The reactivity of a solid is related to its structure. This has led to the investigation of solid state reactions just below and above the temperature of its polymorphic transformation. Such changes in reactivity have been observed even in the cases of second order phase transformation, for example, in the antiferromagnetic to paramagnetic transition of NiO.

Coupling Effect

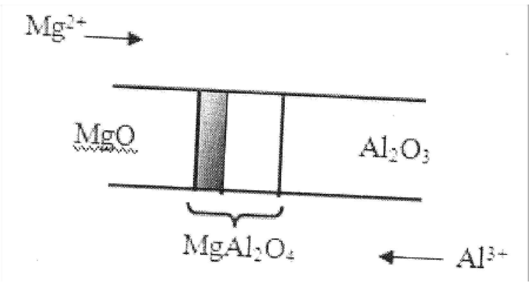
This general term stands for combining the effect of one transformation in the solid with another reaction. In this general sense, the higher reactivity of a solid at the temperature of its phase transition is also a coupling effect. The coupling effect, however, relates to the higher reactivity of a newly formed solid. Suppose instead of mixing two metal oxides and heating them to obtain a new single phase mixed oxide we heat their carbonates or the oxalates. The carbonates or oxalates with initially decompose to the respective oxides. These instantaneously formed oxides will react much more rapidly giving the product.

Mechanism of Solid-State Reaction (Wagner Reaction- (Wegner Reaction Mechanism)

Counter diffusion of cations in solid state reactions and the formation of product at the interface as a result of migration of the magnesium ions and aluminium ions is popularly known as Wegner reaction mechanism. This is the most common mechanism among solid state reactions. For example, in the reaction between MgO and Al_2O_3 in solid state, the magnesium ions move to right side and aluminium ions move to left side as a result of this migration of counter ions, product is formed at the interface between these two reactants.

With the progress of the reaction more and more product is formed at the interface between the two and also two interfaces developed at the right side.

1. Interface between MgO/ $MgA1_20_4$



$$2A1^{3+} - 3Mg^{2+} + 4MgO \rightarrow MgAl_2O_4$$

2. At interface of $MgAl_2O_4$/ Al_2O_3

$$3Mg^{2+} - 2A1^{3+} + 4A1_20_3 \rightarrow 3MgA1_20_4$$

Overall Reaction

$$4MgO + 4A120_3 \rightarrow 4MgA1_2O_4$$

By this reaction mechanism the electrochemistry or the electro valency during the course of the reaction is maintained as for every 3 magnesium ions which are moving to right side, 2 aluminium ions are moving to left hand side. So the charges and mass during the course of reaction is being maintained. This mechanism also explain the observance of product at the interface between the two reactants in the ratio of 1:3 as 1/3 product is formed on one side whereas the 3 proportions is formed on the other side because of the migration of relative amount of magnesium and aluminium to the reaction side

5.2.5 Kinetics of Solid State Reactions

The study of solid-state reaction can be done in terms of thermodynamics and kinetics. In thermodynamics, the spontaneity of solid-state reactions is studied in terms of energy changes, whereas in kinetics, the growth of the product is studied with time.

In doing kinetics, the formation and the growth of the product is monitored with the help of microscope and the growth is plotted against time at different constant temperature. In most of the cases the rate equation is found to follow parabolic rate law and applying this rate equation one can determine the rate constant for the reaction and from rate constant, by plotting against inverse temperature using Arrhenius expression, one can determine the activation energy of the reaction. With the value of activation energy one can understand the rate of reaction as well as the medium of the reaction, can be understood.

NOTES

Check Your Progress

1. What do you understand by solid state chemistry?
2. Define the solid state reactions.
3. What do you understand by reaction temperature?
4. What do you understand by co-precipitation?
5. Define coupling effect.

5.3 CRYSTAL DEFECT AND NON-STOICHIOMETRY

According to the definition of crystalline solids, an ideal crystal is one which has a regular repeating arrangement of unit cell throughout the crystal. This type of perfectly ordered arrangement is observed in the crystals formed at absolute zero. However, in practice, almost all the crystals suffer from defects of one kind or the other. The defect increases with the rise in temperature. The defects or imperfections in crystals may arise due to any one of the following reasons:

- One of the constituent particle is missing from the crystal lattice. It creates a vacancy or hole in the crystal.
- Displacement of atom or ion from its lattice site to the interstitial position.
- Presence of impurity at the lattice site.
- Presence of an impurity in the void or the interstitial site.

Such defects when developed in the crystal lattice, alter the properties of the solids, for example, change in density, conduction of current, coloration and shining (metallic lusture) in the crystals, etc.

Stoichiometric and Non-Stoichiometric Crystals

Stoichiometric ionic crystals are those in which the ratio of positive and negative ions present in the compound are the same as required by the ideal formula of the compound. On the other hand, non-stoichiometric compounds are those in which the ratio of positive and negative ions present in the compound differ from that which is required by ideal chemical formula of the compound. For example, vanadium (II) oxide is non-stoichiometric oxide, since it has the formula VO_x where $x = 0.6 – 1.3$. Similarly iron (II) oxide samples contain more oxygen atoms than iron atoms, while samples of zinc (II) oxide usually has excess of zinc atoms than oxygen atoms. In each case electrical neutrality is maintained.

Defects in Crystals

In an ideal crystal the arrangement of constituent ions is perfect. The defect in crystals means that the perfect arrangement of the constituent ions is destroyed due to the presence of cationic and anionic vacancies in the lattice points, dislocations of ions in the lattice, the presence of the same type of ions in the different oxidation states and the presence of impurities in the lattice points. Such defects when developed in crystal lattice, alter the properties of the crystals, such as change in density, conduction of current, colorations, mechanical strength and shining in crystals, etc. A brief classification of these defects is shown in Figure 5.6.

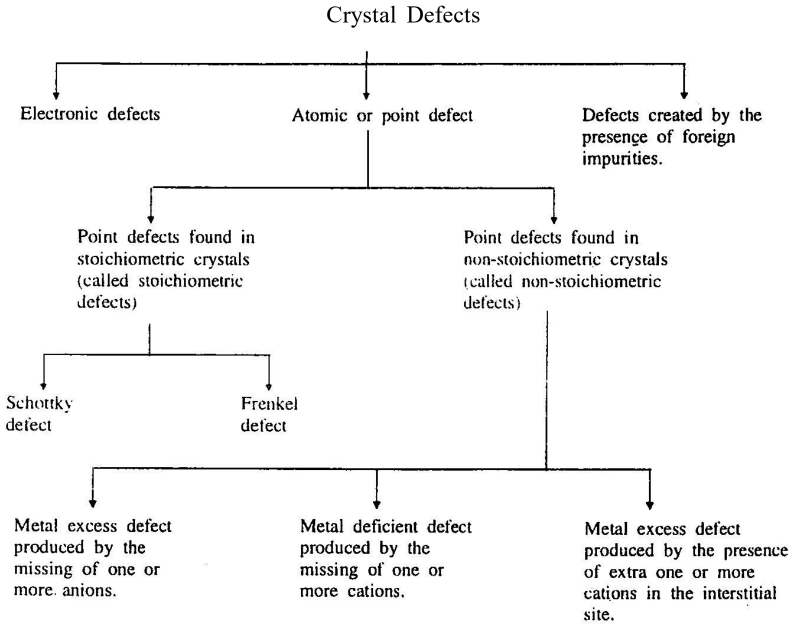


Fig. 5.6 *Classification of Crystal Defects found in Ionic Crystals*

5.3.1 Perfect and Imperfect Crystals

Crystalline materials (mainly metals and alloys, but also stoichiometric salts and other materials) are made up of solid regions of ordered matter. These regions are known as crystals.

A perfect crystal is a crystal that contains no point, line, or planar defects. There are a wide variety of crystallographic defects.

A crystal in which the regular, periodic structure is interrupted by various defects is imperfect crystal.

5.3.2 Intrinsic and Extrinsic Defects

A point defect is an isolated distortion of the crystal lattice with intrinsic or extrinsic origin.

The intrinsic defect is related to the presence of vacancies (missing atoms), interstitial atoms (added atoms), or anti-sites (exchanged atoms for polar material).

Extrinsic defects are caused by the presence of foreign atoms in the crystal structure. These foreign atoms can be either substitutional (replacing original lattice atoms) or interstitial.

5.3.3 Point Defects

Point defects are produced in an ionic crystal when equal number of cations and anions are missing from their regular lattice positions and thus an equal number of cation and anion vacancies are produced in the structure of the crystal or when an ion (cation or anion) of an ionic crystal is missing and is shifted to a vacant interstitial site existing in the structure of the crystal. Point defects may occur in stoichiometric as well as non-stoichiometric crystals. The point defects found in stoichiometric crystals are called **stoichiometric defects** while the point defects in non-stoichiometric crystals are known as **non-stoichiometric defects**.

5.3.4 Line and Plane Defect

Line defects are the lines along which whole rows of atoms in a solid are arranged anomalously. The resulting irregularity in spacing is most severe along a line called the line of dislocation. Line defects can weaken or strengthen solids.

On planes of single crystals, steps between atomically flat terraces can also be regarded as planar defects. It has been shown that such defects and their geometry have significant influence on the adsorption of organic molecules.

5.3.5 Vacancies: Schottky an Frenkel Defect

The compounds in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called stoichiometric defects.

Schottky Defect: This defect was discovered by the German scientist, Schottky in 1930. When one positive ion and one negative ion, from any site in the crystal lattice, are missing from their respective sites then it creates a pair of holes or vacancies. Such paired cation-anion vacancies in ionic crystals is termed as Schottky defect as shown in Figure 5.7.

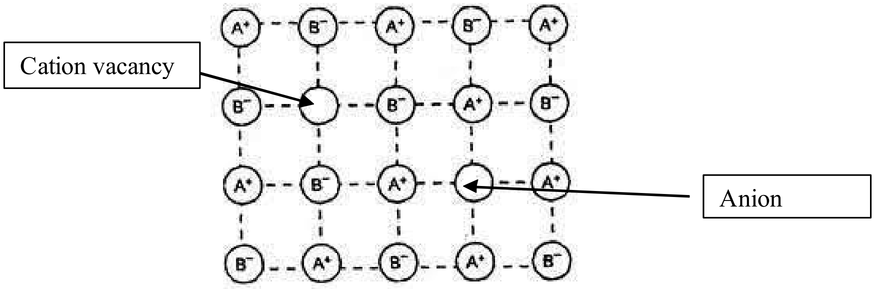


Fig 5.7 *Schottky Defect*

Schottky defect is generally developed in highly ionic compounds with either one or both of the following characteristics:

(i) With high co-ordination number in crystal structure.

(ii) Where sizes of cation and anion are almost equal.

Crystal structure of NaCl, KCI, KBr and CsCI usually exhibit this type of defect. Crystallographic studies have shown that in NaCl crystal one paired vacancy is observed in 10^{16} lattice sites at room temperature. The increase of temperature increases the vacancies, i.e., defect becomes more prominent at high temperature.

Frenkel Defect: This defect occurs when some of the ions (usually cations) shift from their normal lattice sites to the interstitial positions in the crystal lattice, then the vacancies are developed at the original sites. Since cations are generally smaller in size than anions, cations can easily be displaced to the voids as depicted in Figure 5.8.

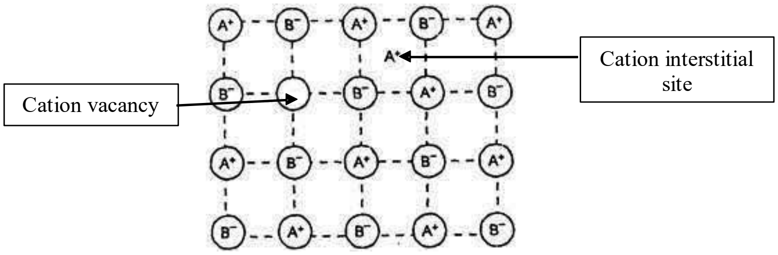


Fig 5.8 *Frenkel Defect*

This type of defect is generally found in crystals in which

(i) Anion is much larger in size than the cation.

(ii) Low co-ordination number is shown between anions and cations.

Therefore, during shifting of cation to interstitial site, lesser amount of energy is required to overcome the forces of attraction. Crystal structure of ZnS, AgBr and AgCl are good examples for illustrating Frenkel defect. The Table 5.1 differentiates between Schottky and Frenkel defects.

Table 5.1 *Differences between Schottky and Frenkel Defects*

S. No.	Schottky Defect	Frenkel Defect
1.	In this defect, the ion pair (cation as well as the anion) are missing from their respective lattice sites in the crystal.	In Frenkel defect, the ion takes the interstitial position rather than its original lattice site.
2.	In occurs in highly ionic compounds with high coordination number	It occurs in compounds showing less coordination number amongst ions.
3.	This defect is observed in compounds in which cations and anions are of almost same size.	Frenkel defect is shown by compounds having large difference between the size of cation and anion.
4.	In Schottky defect, the density of the crystal decreases.	No change in density is observed due to Frenkel defect in the crystal
5.	The stability of crystal decreases and the electrical conductivity increases due to the formation of voids.	Decrease in stability and increase in electrical conductivity is observed. Due to the presence of ions in interstitial position (void), this defect increases the dielectric constant of the crystals.

Consequences of Schottky and Frenkel Defects:

- It is due to the presence of these defects that the crystal is able to conduct electricity through it when an electric field is applied on it. This tendency of the crystal can be explained as follows. When an electric field is applied on a crystal, having both types of defects, a nearby ion moves from its position to occupy a hole. This results in creating a new hole and another nearby ion moves into it and so on. This process continues and a hole, thereby, moves from one end to the other end. Thus it conducts electricity across the whole crystal.

- Density of the crystals, having Schottky defects, decrease, as expected.
- The presence of holes also decreases the lattice energy or the stability of the crystal. The presence of too many holes decreases the stability of the crystal to such an extent that a partial collapse of the lattice energy may take place.
- We have seen that in a crystal having Schottky defect, the similar ions (charges) come closer to each other and hence the dielectric constant of the crystal increases.

5.3.6 Thermodynamics of Schottky and Frenkel Defect Formation

The Schottky defect and Frankel defect are called thermodynamic defects because the number of these defects depends on the temperature. Solids have perfect crystal at 0 K. But as the temperature increases (T>0), the crystal starts deviating from the perfectly ordered arrangement. This leads to increase in the entropy and enthalpy leading to spontaneous defect formation.

5.3.7 Colour Centers

Colour centre is the defect in the regular spacing of atoms within a solid that absorbs the visible light of a particular colour or infrared or ultraviolet radiation, thus it lends a characteristic colour to the specific solid. Each colour centre involves the absence of an atom from the place it would normally occupy in the solid and the relation of an electron with a vacancy.

There are many types of colour centres. The best understood one, called an F-centre that results from the absence of a negatively charged ion from a particular point in an ionic solid. This vacancy, which acts like a positively charged particle, attracts and traps an electron, and their combination constitutes an F-centre.

F-centres in sodium chloride absorb only blue light, giving the solid a yellow-orange tinge. Sodium chloride is usually colourless, however, because its electrons are not free to move to vacancies formed by removal of negative chloride ions from the solid.

5.3.8 Non-Stoichiometric Defects

When the ratio of the cations and anions present in the imperfect ionic solid differs from that required by the ideal or perfect chemical formula of the compound, the defect is known as non-stoichiometric defect. This defect is caused either by excess cation (anion vacancies) or by excess anion (cation vacancies) in the crystal. The crystal becomes electrically neutral by acquiring either extra electrons or extra positive charge on the cation. The ionic compounds having such defects are called as non-stoichiometric or Berthollide compounds. The chemical composition of such compounds varies from the ideal chemical formula and the variation depends upon the amount of impurities present in the crystal.

The non-stoichiometric defects are classified into the following types:

- Metal excess defect due to anion vacancies
- Metal excess defect due to interstitial cation
- Metal deficiency defect due to cation vacancies
- Cation deficiency defect due to impurities

Metal Excess Defect due to Anion Vacancies: This type of defect is developed when some of the anions are missing from their respective lattice sites creating holes. These vacant anion positions (holes) are occupied by the electrons in order to maintain the electrical neutrality of the crystal as shown in the Figure 5.9.

The vacant sites occupied by electrons are termed as F-centres (F stands for Farbe, meaning colour). The presence of F-centres impart colour to the otherwise colourless ionic crystal. Greater the number of such F centres greater will be the intensity of coloration.

Electron at the anion site

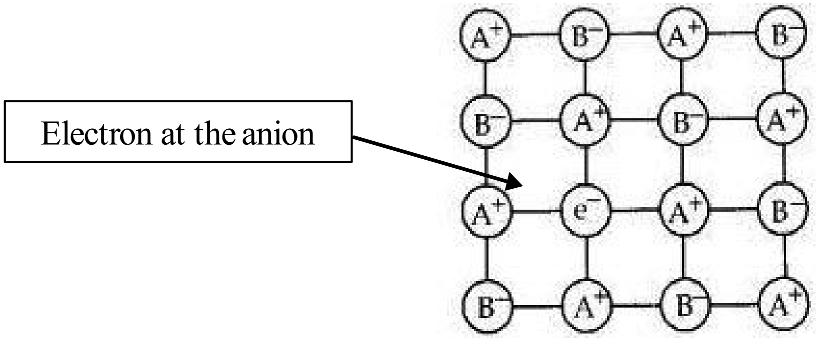


Fig. 5.9 *Metal Excess Defect due to Anion Vacancies*

This type of defect of anionic vacancies is usually found in crystals likely to possess Schottky defect. In alkali halides this defect is developed when alkali halide crystal is heated in an atmosphere of alkali metal vapours. The alkali metal atoms condense on the surface of the crystal where these combine with halide ion of the lattice by diffusion. The electrons released during oxidation of metal atoms to ions diffuse into crystal lattice and occupy the sites vacated by anions.

$$M + X^- \rightarrow M^+ X^- + e^-$$

The consequences of anion vacancies or F-centre defect are as follows:

- Crystals with F-centres are paramagnetic because the trapped electrons in the anionic vacancies are unpaired.
- Excess of metal ions impart colour to the crystal, for example, excess of Li in LiCl gives pink colour to crystal and the excess of K in KCI crystal turns it to violet.
- The crystals with F-centres on irradiation with light becomes photoconductors.

Metal Excess Defect due to Interstitial Cation: This type of defect is observed in crystals containing extra positive ion in the interstitial position. The electrical neutrality is maintained by the electrons also occupying the interstitial sites as illustrated in the Figure 5.10.

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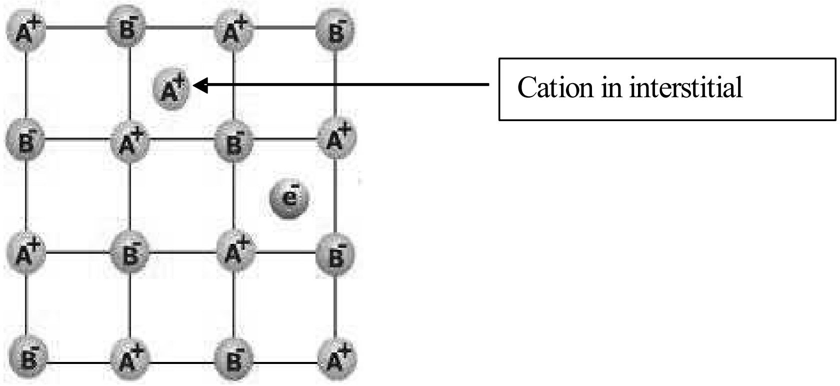

Fig. 5.10 *Metal Excess Defect due to Interstitial Cation Vacancy*

This type of defect is usually observed in crystals which are likely to develop 'Frenkel defect'. The example illustrating this kind of defect is the crystal of ZnO. When ZnO is heated, it loses oxygen reversibly and turns yellow. The excess of the Zn^{2+} ions formed on heating ZnO is accommodated in the interstitial site and the electrons in the neighbouring interstitial position.

$$2\,ZnO \xrightarrow{\text{Heating}} 2\,Zn\,2^{+} + O_2 + 4\,e^{-}$$

Crystals having this type of defect show increased electrical conductivity due to the presence of free electrons in the interstitial position.

Metal Deficiency Defect due to Cation Vacancies: This type of defect is generally found in ionic solids in which metal ions have variable valency. This defect is developed in the crystal when a positive ion is missing from its lattice site and the charge is balanced (i.e., electrical neutrality is maintained) by oxidation of some of the cations to higher oxidation states as shown in the Figure 5.11. The crystal lattice shows the deficiency of metal ion.

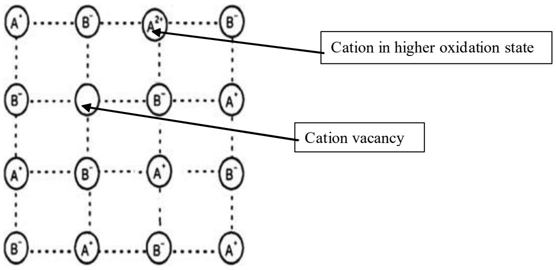

Fig. 5.11 *Metal Deficiency Defect due to Cation Deficiency*

The metal deficient ionic compounds, as shown in the above figure, are classified as p-type semiconductors. These conduct electricity through positive hole conduction mechanism.

Illustrative examples of this type are FeO, FeS, NiO and TiO. In FeS crystal, one Fe^{2+} lattice site is vacant and the other two cation sites are occupied by Fe^{3+}

ions (produced by oxidation of Fe^{2+} ions.), in order to maintain the electrical neutrality. The existence of Fe^{2+} and Fe^{3+} ions side by side results in free exchange of electrons between two such sites. So it gives metallic lustre to the crystal.

Cation Deficiency Defect due to Impurity: This type of defect arises due to the presence of impurity cation (foreign atom), of almost same size but of higher oxidation state, at the lattice site instead of host cation. It results in the formation of vacant site, for example, the presence of Cd^{2+} ion impurity in the crystal lattice of AgCl as shown in Figure 5.12.

Cation vacancy

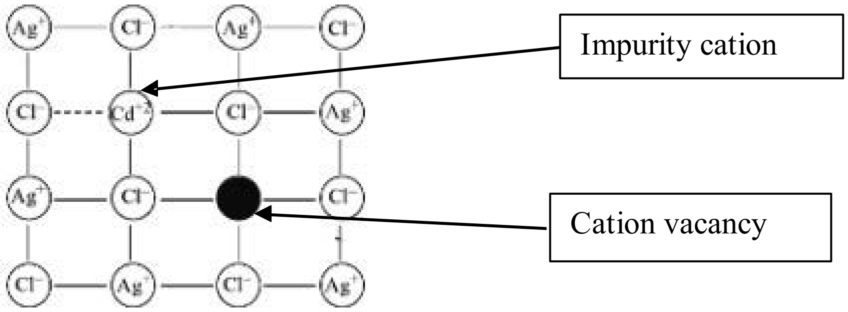

Fig. 5.12 Silver Chloride Crystal having Cd^{2+} Ion as Impurity

In the crystal lattice of AgCl, two Ag^+ ions are missing from their lattice sites; one of the vacant site is occupied by Cd^{2+} ion (impurity cation) and the other remains vacant. The vacant site helps in conduction of electricity through AgCl. The mechanism of conduction of electricity involves the migration of Ag^+ ion from lattice point into the vacant site creating a new vacancy. This kind of movement of vacancy in the opposite direction to the movement of Ag^+ makes the crystal p-type of semiconductor.

Consequences of Metal Deficient Defects: Crystals having metal deficient defects are semiconductors. The conductivity is due to the movement of an electron from one cation to the other cation. When an electron moves from one cation, it is changed into a cation with higher positive oxidation state. The movement of a cation is also called the movement of a positive hole and the substances are called p-semiconductors.

Check Your Progress

6. Define perfect crystals.
7. What do you understand by imperfect crystals?
8. Define intrinsic defects.
9. Define extrinsic defects.
10. What do you understand by line defect?
11. What do you understand by plane defect?
12. Define colour centre.

5.4 ELECTRONIC PROPERTIES OF SOLIDS AND BAND THEORY

NOTES

Electrical properties of solids are measured in terms of conductivity. Conductivity may be defined as the ease with which electric current can pass through a given substance. All solids do not conduct electricity in equal amounts. Some of them have high conductivity, whereas some of them do not conduct electricity at all. On the basis of conduction of electricity, solids can be broadly divided into three categories:

Conductors or Metals: Conductors are the solids that allow easy passage of electric current through them. Metals are generally good conductors of electricity. Electrical conductivity in metals is due to the presence of mobile electrons. The conductivity of metals is of the order of $107(\Omega m)^{-1}$. There is no gap between the conduction band and the valence band. Thus, electrons can easily flow from the valence band to the conduction band under the influence of electric field, making them good conductors of electricity.

Semiconductors: The gap between the conduction band and the valence band is very less; therefore whenever sufficient energy is provided to the electrons in a semiconductor, electrons jump from the valence band to the conduction band. The conductivity of the semiconductors increases with an increase in temperature, for semiconductors, it lies in between 10-6 to 10-4 (Ωm)-1.

Insulators: These materials do not conduct electricity. The band gap between the valence band and conduction band is very large. Even if a large amount of energy is provided to these solids, they do not conduct electricity. Example: Wood, plastics etc.

Band Theory

Band theory is based on the principle of molecular orbital theory of covalent bonds. According to the molecular orbital theory, when two equivalent atomic orbitals (AO) combine, two Molecular Orbitals (MO) are formed, one is bonding MO (BMO) and other is anti-bonding MO (ABMO), each with its own discrete energy. Three equivalent AOs on combination yields three ABMOs, one BMO, one ABMO and one non-bonding MO (NBMO) each with its own discrete energy. In general, AOs on combination will yield n MOs. In metals where large number of atoms exist together very closely electron delocalisation (conduction) occurs.

This can be understood with the example of construction of a crystal of lithium metal by adding Li-atoms one at a time, forming first Li_2 then Li_3, Li_4, Li_5 Li_6 and so an until finally we have L_N where N is very large number of order 10^{20}. Now in Li_2 molecule, each Li-atom has electronic configuration $1s^2$, $2s^1$, with a single 2s valence electron.

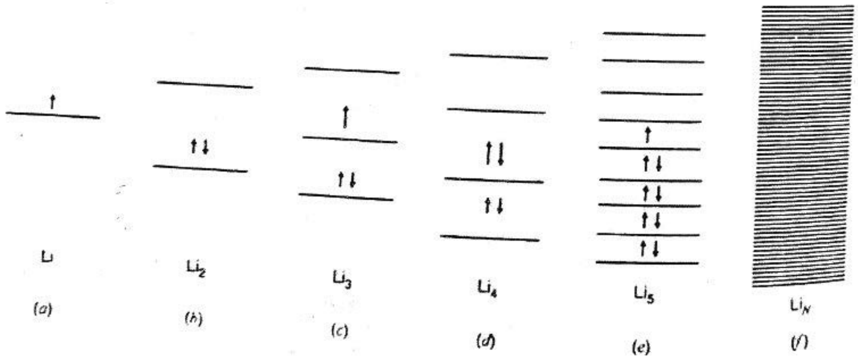

Fig. 5.13 *Illustration of band theory of solids: (a) single Li-atom with one 2s-valence electron, (b) Li $_2$ with two MO one filled and one vacant. (c) Li$_3$ with three M.O. (d) Li$_4$ with four M.O. (e) Li$_9$ with nine MO half filled (f) Li$_N$ with a band of NMO. Note that as the number of Li-atoms increases, the spacing between the MO decreases.*

Two 2s atomic orbitals, one from each Li atom, overlap to form two molecular orbitals σ (2s) and σ* (2s). The σ* (2s) orbital is vacant (See figure 2 b). In general, n atomic orbitals combine to form n molecular orbitals. Now in Li$_{3,}$ the three 2s-orbitals overlap to form three MO (see figure 2 c). Electrons in the MO are spread over the three Li nuclei and are the property of the entire Li$_3$ molecules, and not of any one Li atom.

For N Li -atoms, there are NMO that arise from the overlap of the 2s-valence atomic orbitals of all the N Li-atoms. The separation between the M.O. decreases as the number of atoms (N) increases, so that there is a band of N closely spaced M.O. (see Fig. 2f) The band is half-full, since each MO can hold 2 electrons, and there are only N valence electrons. The band containing the outer or valence electrons, is called the **valence bond.**

It may be pointed here that the empty 2p atomic orbitals of the Li atoms also overlap to form a wide band of M.O. Since the 2s and 2p orbitals do not differ much in energy, the band of MO. formed from the 2p orbital, joint continuously, and are called a **conduction band**. A band that is either partly or completely vacant, is called **conduction band**. Electrons in the lower filled levels of the conduction band can easily be unpaired and excited to vacant levels of the band. In these delocalized orbitals, they can circulate throughout the crystal. When an electric field is applied across a lithium crystal, the electrons start moving in direction and consequently, lithium is a good conductor of electricity. The bands in the next alkali metal, sodium, is shown in Figure 5.14.

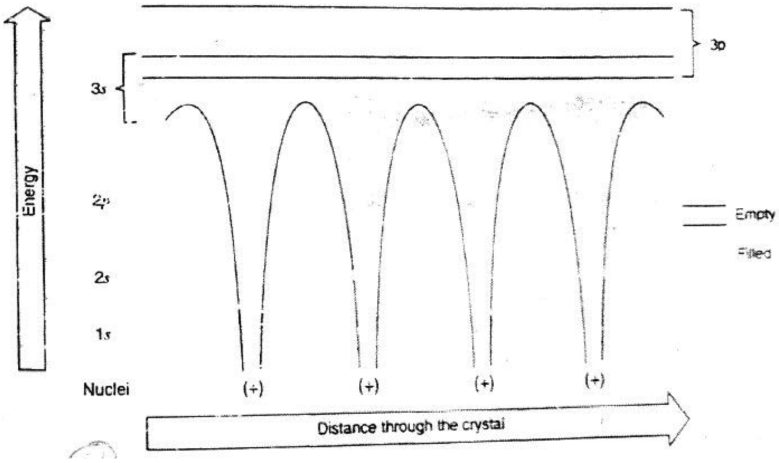

Fig. 5.14 *Band in metallic sodium. The 3s-band is half-filled, it is the valence band. The 3p-band is empty. The 3s and 3p bands overlap to form conduction band.*

For the alkaline-earth metals, the valence band is filled by two valence electron per atom. For example, Mg has completely filled 3s-band. However, the overlap of the 3s and 3p-bands creates action band that is only partially-filled. Hence, solid Mg can conduct electricity.

Important Features of Band Theory

1. Solids are giant molecules in which large number of spherical atoms are arranged in a regular close backed pattern in the formed crystals.
2. When the atoms are brought together in solids, the atomic orbital of the valence shells interact forming molecular orbitals.
3. In a solid there are approximately 10^{23} atoms in 1 cm^3. During interaction between different atoms, they influence each other to such an extent that their outer shells (empty as well as partially filled) constitute one simple system of electrons, common to entire array of atoms in crystal, while inner shells remain intact and are not affected.
4. When n energy levels of identical atoms interact, each energy level number of infinitesimal energy levels. As a result of this, each original energy level becomes a band of very closely-spaced levels of extremely small energy differences. The individual energy band are so close together that for all purposes, the energy band may be continuous. Consequently, an electron in a solid crystal can thus occupy any of the energy level, within the band. Thus, a band is a group of infinitesimal energy levels in a solid/crystal.
5. Depending upon the composition of a solid/crystal, the bands are of two types:
   (a) **Overlapping Band** (see Figure 5.15 (a),i.e., higher band overlapping lower band to some extent. For example, the valence 2s-band overlaps with the empty 2p-band in beryllium ($1s^2$, $2s^2$, $2p^6$) and the valence 3s-band overlaps with empty 3p-band in magnesium ($1s^2$, $2s^2$, $2p^6$, $3s^2$,$3p^0$)

(b) **Non-overlapping or Separate Bands** (see Figure 5.15 (b)]. For example, lithium ($1s^2$, $2s^1$), and copper ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^1$).

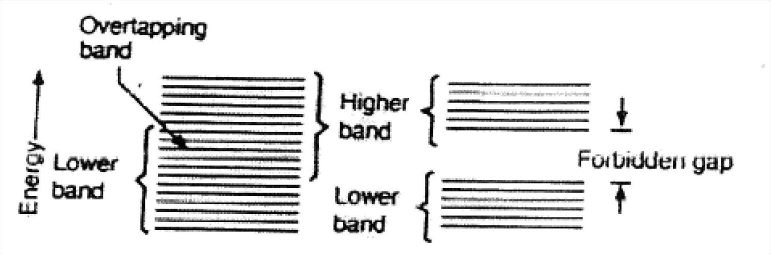

Fig. 5.15 (a) Overlapping of bands. and (b) forbidden gap

6. The band of energy levels occupied by the valence electrons (or highest occupied energy band), is called valence band. It may be occupied by: (a) partially, or-filled with electrons, e.g., in Na($3s^1$), Al ($3s^2$.$3p^1$), and Cu ($3d^{10}$, $4s^1$). (b) Completely filled with electrons, e.g., Be ($1s^2$, $2s^2$), and Mg ($1s^2$, $2s^2$, $2p^6$, $3s^2$),

7. The next higher permitted band, above the valence band, is called the conduction band, and the electrons occupying this band are called **conduction electrons**. The electrons present in the conduction and are "*free electrons*" and once an electron enters the conduction band, it moves freely. The conduction band may be empty or partially-filled with the electrons.

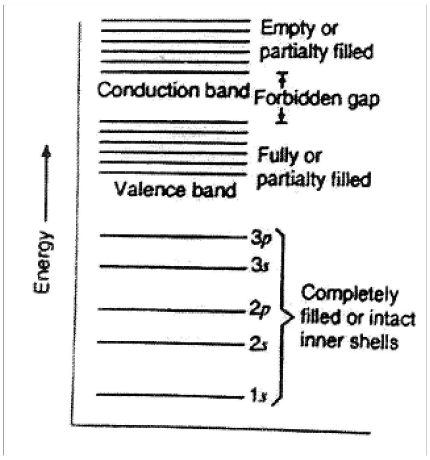

Fig. 5.16 Valence and Conduction Bands Solids

The gap between the valence bend and the conduction band is called forbidden gap. No electron can exist in forbidden gap. The width of the forbidden gap is called energy gap (Eg).

9. **Conductors:** A solid is a conductor, if it has either a partially filled valence band (e.g., Li, Na, Al) or a filled valence band overlapping with the next higher empty band e.g., Be, or Mg), conduction in conductors occurs in fallowing two way:

Conduction with Partially-Filled Valence Band:

Electrons in half-filled bands and can move throughout the solid like "free electrons" When a potential is some of these free electrons are raised to the conduction band. Here these electrons begin to conduct. For example, in metals Li, Na, Al, Cu, etc., there exists half-filled conduction bands. The transfer of electrons to the conduction band can also be accompanied by light photo old photo-conduction) is observed in metals like selenium.

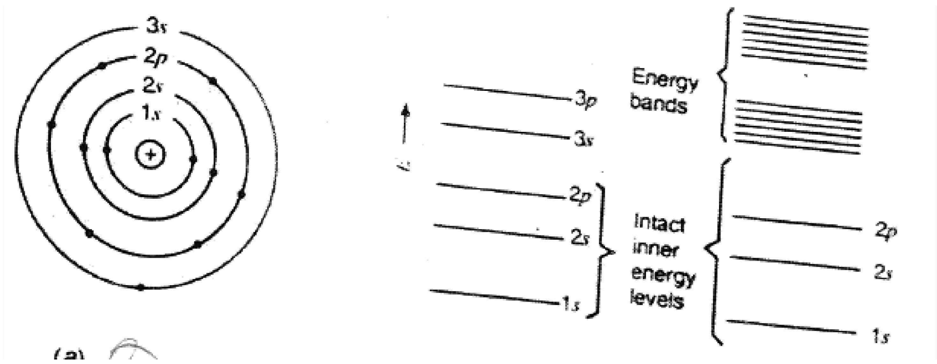

Fig. 5.17 Energy levels in: (a) an isolated sodium atom, (b) sodium crystal.

Conduction in conductors with filled-valence band overlapping with the next higher empty band: Consider metal magnesium ($1s^2$; $2s^2$, $2p^6$, $3s^2$) with all the available bands completely-filled with electron

In this element, the 3s-valence band overlaps with the empty 3p-band, thereby resulting in a partially filled band. Hence, Mg is a conductor like Na, Al, Cu, etc.

The electrical conductivity of a metal decreases with the rise in temperature, because increased thermal vibrations of the metal atoms causes scattering of electrons, thereby obstructing their free flows.

5.4.1 Insulators

In solids where the valence bands are tightly bound to their parent nuclei and require very large electric fields to remove electrons to conduction band are known as insulators. These solid materials possess a full valence band, completely empty conduction band, and large energy gap (Eg). These include materials like diamond, glass, solid NaCl, plastics, porcelain and ceramics.

Conduction in Insulations a CUliga0.025 ev, and this is far less th electrons in valence ban at room temperatur energy to overcome the are now free to move temperature of an insulat rise in temperature.

Conduction in Insulators: Thermal energy of an insulating material at room temperature is 0.025 eV and this is far less than energy gap (E.). Consequently, at room temperature, there is no electrons in valence band to jump to conduction band. Hence, these substances show best insulating temperature. However, at high temperatures, some of the valence band electrons acquire energy to overcome the forbidden gap and enter the conduction band. These electrons in the conduction band are now free to move and hence, the insulators exhibit conductivity with increased temperature.

5.4.2 Semiconductors

NOTES

A solid is a semi-conductor, i.e., a material having electrical conductivity in between those of insulators and conductors. These solids have an almost filled valence band, an almost empty conduction band and a very narrow energy gap. (1 ev or less). Energy gap of Si and Ge are 1.0 and 0.7 eV respectively.

Effect of Temperature on Conductivity of Semiconductors: At 0 K, all semiconductors are insulators. At finite temperature, conduction in semiconductors starts, due to thermal energy. Some valence electrons gain enough thermal energy to jump over the energy gap (E.) into the conduction band. The probability of the promotion of electrons from valence band to conduction band: (a) decreases exponentially with the energy gap (EQ), and (b) increases exponentially with Kelvin temperature. Consequently, the conductivity of a semiconductor increases with a rise in temperature. At 0K, all semiconductors are insulators.

Figure 5.18 demonstrates the energy bands of an insulator, a conductor and a semiconductor.

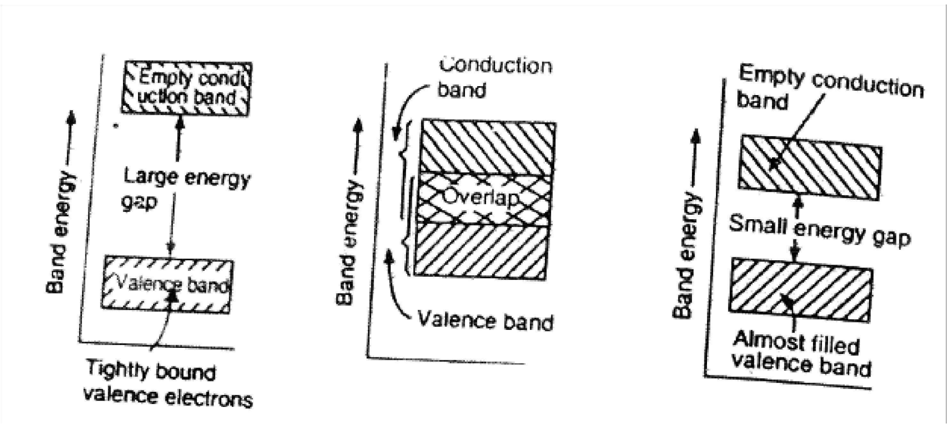

Fig. 5.18 Energy band in: (a) insulators, (b) conductors, and (c) semiconductors.

Types of Semiconductors

Broadly semiconductors are classified as:

1. Intrinsic Semiconductors: These are extremely pure (above 99.9999% pure) elements like silicon, germanium, and selenium, having four valence electrons in their atoms and their forbidden energy gap is about 1 eV. These metals have crystalline structures in which each atom forms four covalent bonds by sharing with four neighbouring atoms.

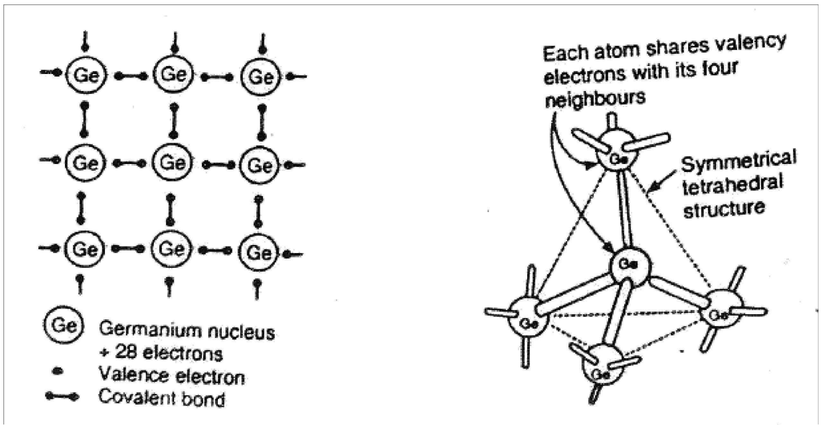

Fig. 5.19 (a) Two-dimensional, and (b) three-dimensional view of germanium crystal.

In such semiconductors, the energy gap is so small (about leV) that even at ordinary temperature, there are many valence electrons, which possess sufficient energy to jump across the forbidden gap to conduction band.

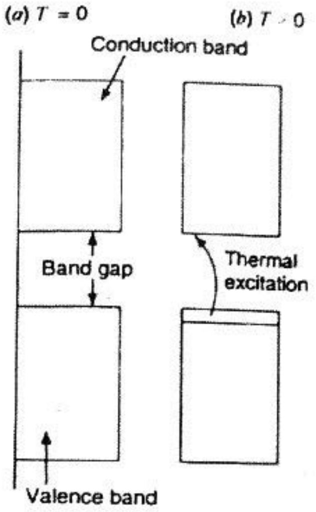

Fig. 5.20 (a) When the valence band is full, the material Si or Ge is an insulator at T=0 K (b) At temperature T > 0K, electrons populate the levels of the upper conduction band at expense the filled valence band and the solid is a semiconductor.

Conduction Process In an intrinsic semiconductors, the energy gap (Eg) is very small, even at room temperature. So, there are a few valence electrons, which possess sufficient thermal energy to jump across the forbidden gap to conduction band, when an electron from the valence band is ejected, a covalent bond is broken and a positively charged hole is left in the valence band. This hole can travel to an adjacent atom by accepting an election from the latter one. This process involves in re-establishing a new covalent bond breaking an existing covalent bond by filling up the previous hole and creating a new hole. In this way, the hole from one atom to the adjacent atoms in the crystal lattice. Consequently, when an electric field is applied across an intrinsic semiconductor at room temperature, electrons in the conduction band more to the anode while the positively charged holes in the valence band move to the cathode. Hence, current in an intrinsic semiconductor consists of simultaneous movement of conduction band electrons and valence band holes in the opposite directions (see Figure 5.21). In other words, electrons and holes in equal numbers are the charge-carriers in an intrinsic semiconductor.

NOTES

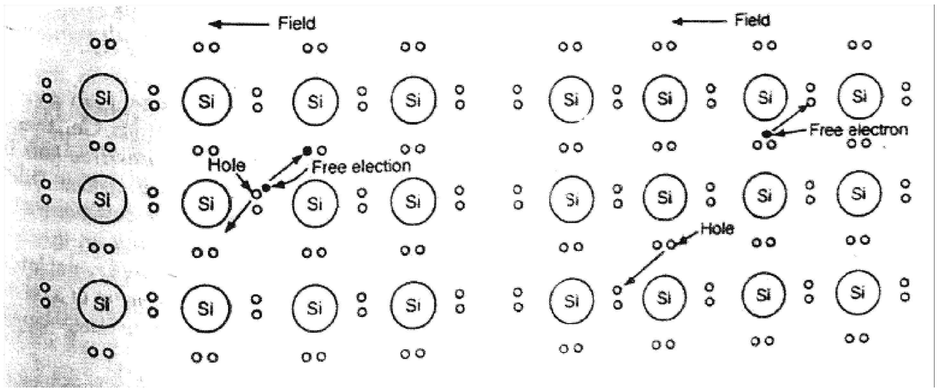

Fig .5.21 Current in an Intrinsic Semiconductor is Out to Simultaneous Movement of Electrons and Holes in the Opposite Directions

2. Extrinsic semiconductors.

There are produced by doping or addition of impurity elements in extremely small amounts to the intrinsic semiconductors.

The addition of doping agent reduces the energy gap (E.), Thereby allowing more electrons to flow from valence band to the empty conduction band. Usually, 1 part of the doping agent is added to 10^6 parts of parent element (Si, Ge, etc.). By appropriate doping the intrinsic semiconductor may be increased by 10,000 times. Based on the nature added, the extrinsic semiconductors are of following two classes:

(1) n-type extrinsic semiconductor is an excess negatively charged electrons containing semiconductor and obtained by adding extremely small quantity of a pentavalent element impurities like, phosphorus, arsenic or antimony) to pure intrinsic semiconductor (like silicon, germanium, tellurium. etc.

Conduction Process: The doping agent atom (a 'donor atom') forms four the surrounding four atoms of intrinsic semiconductor (say of germanium, Ge) with four of its five valence electrons; while the fifth excess electron' remains loosely bound to the itself (see Figure 5.22 (a)). This loosely bound excess electron is easily excited from the valence band to the conduction band, when an electric field is applied. Thus, conduction is due to movement of present in an n-type semiconductor. In other words, the electrical conductivity of an n-type semiconductor is dependent only on the number of free or excess electrons present in the conduction band It may be noted that impurity atom donates the conduction-electron, without leaving a hole in the valence bands and the electrons are the only charge-carriers.

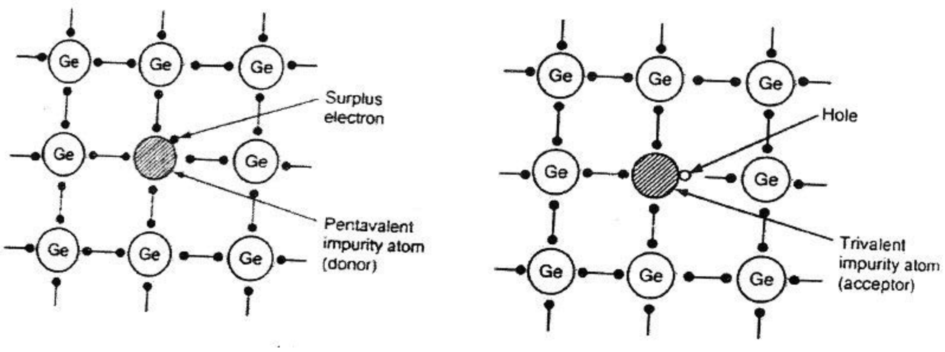

Fig. 5.22 Get crystal containing substitutional impurity: Doping of the impurity creates: (a) Surplus electrons, and (b) positive holes respectively in the Ge crystal lattice.

(II) p-type extrinsic semiconductor is an excess positively charged holes-containing semiconductor and is obtained by adding an extremely small quantity of trivalent element (like boron, aluminium) to the pure intrinsic semiconductor (like silicon, germanium, etc.) crystal lattice.

Conduction Process: All the three valence electrons present in the trivalent doping agent (an acceptor atom) form three covalent bonds with the surrounding three of the four atoms (say of germanium, Ge). One bond in one of the four surrounding Ge atoms is left incomplete. This gives rise to a positive hole Figure 5.22 (b)). The positive holes so-formed in the crystal lattice conduct current, when electric field is applied. In this type of conduction process, a hole travels to an adjacent atom by acquiring an electron and re-establishing covalent bond, by breaking an existing covalent bond in the adjacent atom and creating a new holes are filled by electrons from one atom to another and creating new holes in sequence in the movement of holes through the crystal of a p-type extrinsic semiconductor is nothing but movement of positive electric charge. Thus, in such a semiconductor, the positively charged holes are in excess and me during conduction.

Note: Positive holes are less mobile than free electrons, so the conductivity of a p-types semiconductors is less than that of an n-type semiconductor.

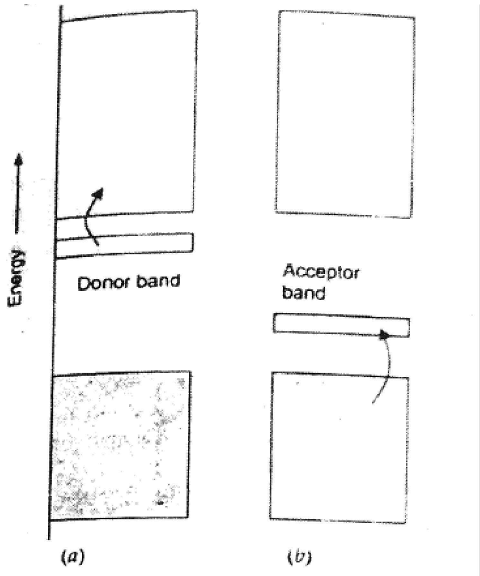

Fig. 5.23 Energy Level in Donor and Acceptor Bands

Preparation of Semiconductors: The basic materials used in the preparation of semiconductor devices are extremely pure Si and Ge (99.9999%). Various steps to be fallowed in preparation of these highly pure materials and are:

1. **Preparation of Pure Ge/Si:** This is achieved in following methods:

   Distillation: It involves separation of materials due to difference in boiling points. The material employed are germanium tetrachloride ($GeCl_4$) and trichlorosilane ($SiHCl_3$) for the preparation of Ge and Si respectively.

   For example, GeCl, (b.p. 83.1°C) is taken is a series of distillation stills and a layer of HCl is placed over the charge, which facilitates in the removal of As (usually pre as is then passed through the charge, which is heated electrically. The vapour witing column finally distils over in a receiver, kept in an ice bath. Pure GeCl, so obtained is then treated with extra pure water to get GeO_2, which is subsequently reduced in an atmosphere of hydrogen To get elemental germanium, which is subjected to further purification. Similarly, distilled $SiHCl_3$ is employed to get silicon of high purity

2. **Zone Refining:** This technique of purification involves recrystallization. It is based on the fact that iimpurities are more soluble in the melt than in the solid material. Zone refiner employed for the purifications of Ge is shown in figure 5.24.

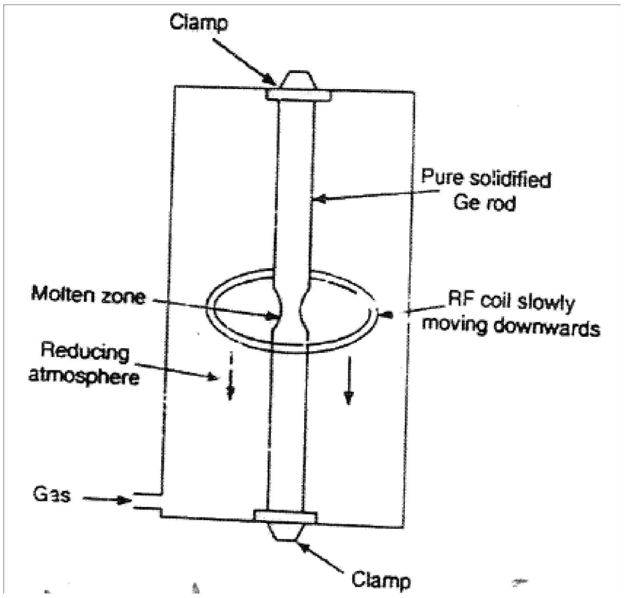

Fig. 5.24 *Zone refining of germanium.*

A rod of already purified Ge is clamped vertically by a RF coil to about 1,000°C in a reducing atmosphere. The heating coil is very slowly moved to bottom, when the impurities are sweft down with molten material; while pure Ge rod.solidifies at the upper portion. When the purification of upper portion of the rod is complete, the bottom portion of the rod is complete, the bottom portion of the rod (where impurities are concentrated) is separated. By using repeated zone refining, the impurity level can be reduced to 1 atom per 10^{12} atoms of Ge.

3. **Czochralski Crystal Pulling Technique** Ge and Si obtained four above two methods are polycrystalline, i.e., there is no regularity in crystal structure and contains crystals of different size. Preparation of & semiconductor devices require single crystal of semiconductor material. so they are grown in the form of single crystals. This method involves growing the crystal an a single crystal seed, thereby the atoms reproduce identical atomic arrangement as that of the seed crystal. In this process, solid polycrystalline semiconducting material (e.g., Ge taken in a quartz Chamber is heated (by using RF power source). till it melts. Then, the temperature is lowered to just above the m.p. of Ge. lowered to just above the mp. Of Ge. At this stage, properly oriented single seed crystal of Ge (attached to a puller rod) is carefully lowered into the melt, till it is in contact with the surface of the charge. Thereafter, the crystal is rotated slowly and then gradually pulled out. It will be noticed that the melt in contact with the seed crystal starts solidifying producing the orientation identical as that of the seed crystal. After this, the pull rate is kept at about 1.5 to 5 cm/minute and the rotation speed is maintained at about 100 rpm. Finally, an intrinsic crystal of Ge of 5 cm dia and 25 cm length is obtained. This crystal is then tested for its conductivity and cut into wafers (0.25 mm thick) with the help One side of each wafer is then lapped (rubbed against a metallic surface with an until it is flat and smooth.

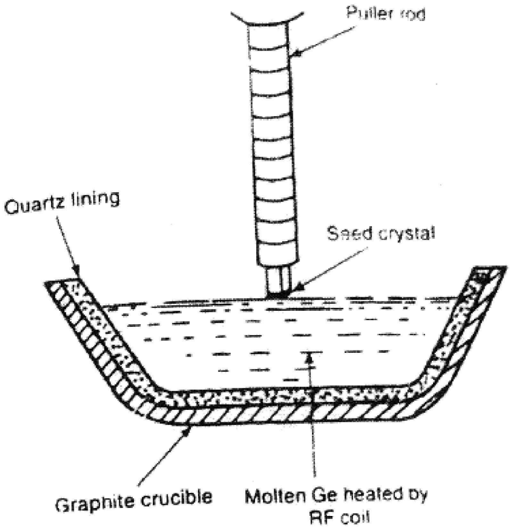

Fig. 5.25 Czochralski crystal pulling technique for purification of Ge

5.4.3 Doped Semiconductors

These are obtained by adding calculated amount of dopants (B or P) to the melt before crystal pulling stage. Usually, dopant atoms added are of the order of 1 atom of B or P per 108 atoms of Ge or Si. Some other methods of doping are:

1. **Epitaxy**: This method involves unified crystal growth on deposition of a thin crystal layer on another substrate, often with added dopants.

   The material in the epitaxial layer must have a lattice spacing and structure close to the substrate, e.g., Si on Ge or Ge on Si. The Si or Ge wafer (kept in a graphite boat) is placed in a lone cylindrical quartz tube reactor, which is then heated (by RF induction coil). Then, gases containing compound of Ge or Si mixed with calculated/appropriate quantities of dopant are introduced into the reactor. The process of heating is continued, till a thin film of dopant over the water results. The doped water so-obtained is ready for the fabrication of semiconductor devices. It may be pointed that for getting Si epitaxial film, SiC, H_2 and N_2 mixture is used. For carrying out n-type doping, this mixture is mixed with a calculated amount of phosphine (PH_3) and for p-type of doping, diborane (B_2H_6) is employed.

2. **Diffusion Technique:** This process involves conversion of a region of semiconductor material by solid or gaseous diffusion of impurity atoms into the crystalline lattice of semiconductor material without any melting. The process consists of heating say a p-type dopant (say Sb or P). This causes some of the impurity atoms to condense on the surface of wafer and diffuse, thereby resulting in a p-type semiconductor material. By this technique the extent of impurity to of impurity atoms penetration can be controlled, even less than a few millionths of a centimetre by controlling the concentration of dopant atoms and temperature. This technique is especially employed for preparing n or p-type semiconductors, used in very high frequency devices. This doping technique can also u to prepare n-p-n-type transistor with a base width of even 5 μ.
3. **Ion Implantion Technique**: It involves bombarding the semiconductor material with an electrical controlled beam of high energy ions of B or P of 10,000 eV. This causes implantation of some dopant atoms into the crystal lattice of semiconductor. This technique is especially employed for the fabrication of high frequency devices.

5.4.4 p-n Junction

When a junction on an interface or a boundary is made between two semiconductor material types, namely the p type or n-type inside a semiconductor, it is referred to as p-n junctions

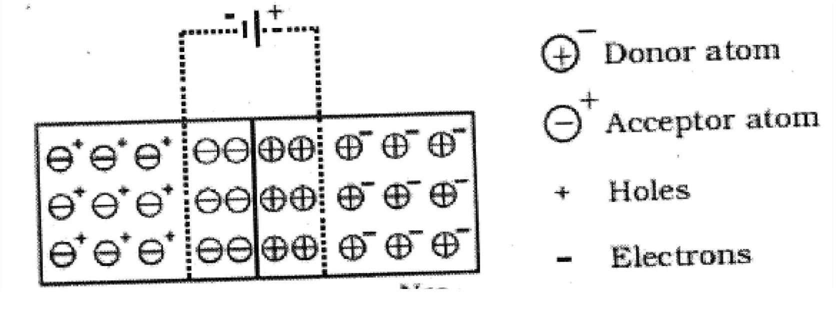

Fig. 5.26 A p-n Junction Dicode

P region has a high concentration of holes and n- region contains a large number of electrons. As soon as a the junction is formed, free electrons crossing the junction from n region into the p-region recombine with holes assumes the form as shown in the p-region very close to the junction. Similarly holes crossing the junction from p-region into the n-region, recombine with electrons in the n-region are very close to the junction. Thus a region is formed, which does not have any mobile changes very close to the region This region is called depletion region. In this region, on the left side of the junction, the acceptor atoms become negative ions and on the right side of the junction, the donor atoms become positive ions.

Forward Biased p-n Junction Diode:

When the positive terminal of the battery is connected to p-side and the negative terminal to then-side, so that the potential difference acts in opposite direction to the barrier potential, then the p-n junction diode is said to be forward biased. This can be understood in following points.

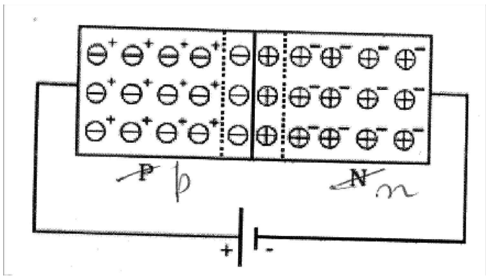

Fig. 5.27 *forward biased p-n functions diode.*

1. When the p-n junction is forward biased figure 5.27, the applied positive potential repels the holes in the p region, and the applied negative potential repels the electrons in the n-region, so the charges move towards the junction.
2. If the applied potential difference is more than the potential barrier, some holes and free electrons enter the depletion region.
3. Hence, the potential barrier, as well as the width of the depletion region, is reduced. The positive donor ions and negative acceptor ions within the depletion region regain electrons and holes respectively
4. As a result of this, the depletion region disappears and the potential barrier also disappears. Hence, under the action of the forward potential difference, the majority charge carriers flow across the junction in opposite direction and constitute current flow in the forward direction.

Reverse Biased p-n junction Diode:

When the positive terminal of battery is connected to the n-side and the negative terminal to the p-side, so that the applied potential difference is in the same direction as that of barrier potential, the function is said to be reverse biased This can be understood in follow up points:

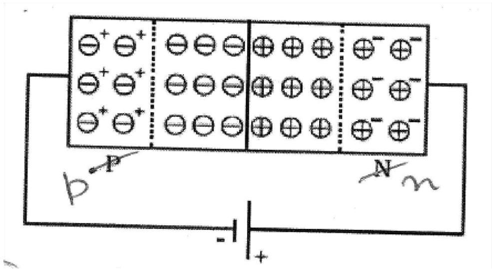

Fig 5.28 *Reverse Biased pn junction diode.*

1. When the PN junction is reverse biased (figure 5.28), electrons in the N region and holes in the P-region have attracted away from the junction.
2. Because of this, the number of negative ions in the P-region and positive ions in the N-region increases. Hence, the depletion region becomes wider and the potential barrier is increased.
3. Since, the depletion region does not contain majority charge carriers, it acts as an insulator. Therefore, no current should flow in the external circuit.
4. But, in practice, a very small current of the order of few microamperes flows in the reverse direction. This is due to the minority carriers flowing in the opposite direction.
5. This reverse current is small because the number of minority carriers in both regions is very small. Since the major source of minority carriers is, thermally broken covalent bonds, the reverse current mainly depends on the junction temperature.

The current voltage characteristics for forward bias as shown on the right hand half and for reverse bias is shown in left-hand half of the figure 5.29.

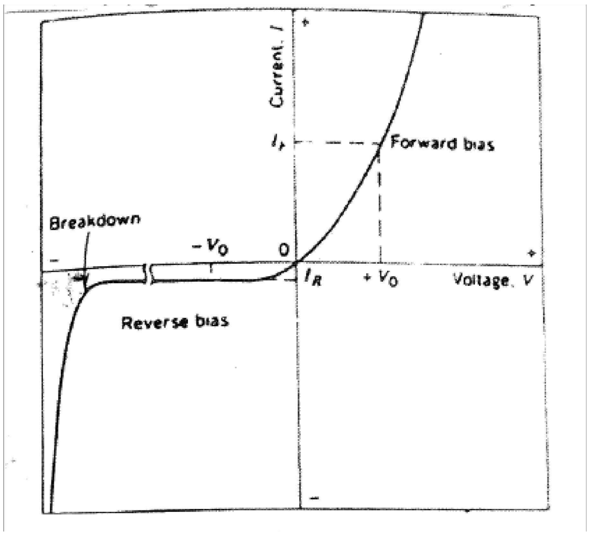

Fig. 5.29 The Current-Voltage Characteristics of p-n Junction for Forward and Reverse Biased Phenomenon of Breakdown is also Shown.

Symbol for a Semiconductor Diode: The diode symbol is shown in fig . The p-type and n-type regions are referred to as p-end and n-end respectively. The arrow on the diode points the direction of conventional current.

1. p-n Junction Diode as Rectifier:

A rectifier or diode is an electronic device that allows the current to flow in one direction only. For example, a rectifier transforms an alternating current into direct current. The p-n rectifying junction is constructed from a single piece of semiconductor, which is doped so as to be n-type on one side and p-type on the other as discussed earlier. The rectification process in terms of input input voltage and output current is demonstrated in figure 5.31. Whereas, voltage varies sinusodially with time (figure 5.31 a), maximum current flow for reversed voltage I_R is extremely small in comparison to that of the forward bias I_F (figure 5.31b).

Furthermore, coincidence between I_F and I_R and the maximum voltage (±vo) is noted in figure 5.31b.

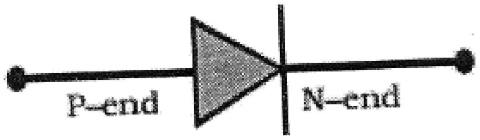

Fig. 5.30 *Circuit Symbol for a Semiconductor Diode*

(a) Voltage versus time for the input to a p-n rectifying junction (b) Current versus time showing rectification of voltage in (a) by a p-n rectifying junction having the voltage-current characteristics shown in Figure 5.30.

2. Junction Transistor:

Transistors are extremely important semiconducting devices in today's microelectronic circuitry capable of two primary types of functions. First, they can perform the same operation as their vacuum tube precursor (the triode), i.e., they can amplify an electrical signal. In addition, they serve as switching devices in computers for the processing and storage of information. The functions transistor is composed of two p-n junctions arranged back to back in either the n-p- n on p-n-p configuration.

5.4.5 Super Conductors

A super conductor is a substance that conducts electricity without resistance. The phenomenon of super conductivity was first observed by Kammerlingh Onnes in 1913, when they found that mercury because super conducting at around 4k. Ordinary metals conduct electricity and their specific conductivity is around 10^6 ohm ms^{-1}. Low temperature research has found that for a number of metals and alloys, the electrical resistance disappears abruptly and completely at temperatures, a few degrees above absolute temperature zero and the material starts behaving as super-conductors. The maximum temperature at which a superconduccting material exhibits superconductivity is called its critical temperature (Tc). Material in superconductivity state become diamagnetic and are repelled by magnets.

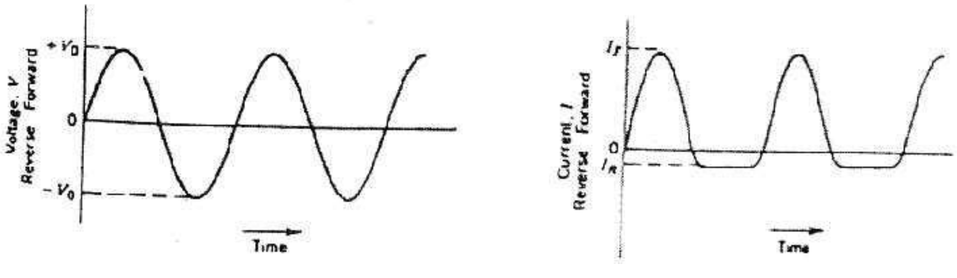

Fig. 5.31 *Rectification of Input Voltage and Output Current*

Properties of Super Conductors

1. They possess greater resistivity than other material at room temperature.
2. The transitions temperature for different isotopes of a superconductor element decreases with the atomic mass of the isotope.

3. On adding impurity to a superconducting element, the critical temperature is lowered.
4. Superconductivity is more concerned with the conduction of electrons than the atom of element.
5. During transition, neither thermal expansion nor elastic properties change.
6. In superconducting state, all electromagnetic effects disappear.
7. Application of a sufficient strong magnetic field to a superconductor below its critical temperature causes destruction of its superconducting property.
8. When a not too strong magnetic field is applied to a superconductor and this is cooler below its transition temperature, then the superconductor expels all magnetic flux from its interior. This is known as Meissner effect. In other words, if the magnetic field is applied after the superconductor has been cooled below its critical temperature, then the magnetic flux is excluded from the superconductor.

Applications of Super Conductivity

1. Superconducting magnets capable of generating high fields with low power consumptions are being employed in scientific tests and research equipments.
2. They are also used for magnetic resonance imaging (MRI) in the medical field as a diagnostic tool. On the basis of the production of cross-sectional images, any abnormalities in body tissues and organs can be corrected. Chemical analysis of body tissues is also possible by magnetic resonance spectroscopy (MRS)
3. Other numerous fields in which superconductivity is used are:
   - (i) Electrical power transmission through superconducting materials - power loss is extremely low and moment operates at low voltage levels.
   - (ii) Magnets for high-energy particle accelerators.
   - (iii) High-speed switch switching and signal transmission for computers.
   - (iv) High-speed magnetically levigated trains wherein the levigation results from magnetic repulsion.
   - (v) Memory or storage elements on computers.
   - (vi) For amplifying very small direct current and voltages.
   - (vii) In magneto-hydrodynamic (MHD) power generators to maintain plasma. These super conductors are smaller in size and consume less energy.

High Temperature Super Conductors:

In 1986, George Bednorz and Alex Muller (Zurich) noticed that an oxide of La, Ba, and Cu lost its resistance around 35k. In 1987, Paul Chu (Houston University) and Wu Jr (Alabama University) reported that a ceramic compound, $YBa_2Cu_3O_{7-y}$ (yd”0.5) is superconducting upto 100 K. This compound is also known as 1:2:3 compound, due to its Yi:Ba:Cu stoichiometry.

NOTES

Check Your Progress

13. What do you understand by conductors?
14. Define insulators.
15. State the band theory.
16. Define the valence bond.
17. What do you understand by a semi-conductor?
18. Define p-n junction.

5.5 ORGANIC SOLIDS

Organic chemistry concentrates on the structure, properties, preparation, reactions, and the synthesis of the various chemical compounds made up of carbon and hydrogen, which might contain quite a few different components as well; like nitrogen, oxygen and halogens also like; fluorine, chlorine, bromine and iodine. A few chemical compounds may likewise contain the elements like phosphorus or sulphur as well. Instances of organic solids incorporate wood, paraffin wax, naphthalene and a vast array of polymers and plastics.

The term 'organic solids' is normally used to explain the materials containing carbon as one of the other compounds. Carbon is the most commonly found compound, so there are an enormous number of materials that could really be mentioned as 'organic.' Both natural and synthesized organic solids are a vital element of our regular day to day life.

Organic solids are made up of molecules bonded by frail van der Waals forces (Pope and Swenberg, 1999; Aradhya, et al., 2012). This kind of bonding is responsible for its chemical and physical properties. Generally, organic solids are delicate with comparatively lower melting points and a relatively poor electrical conductivity.

Wood

Wood is a characteristic organic material comprising fundamentally cellulose fibres embedded in a lattice of lignin. If the mechanical properties are taken into consideration, the strands are solid in tension, and the lignin matrix opposes the pressure compression. In this way, wood has been a significant construction material as we started fabricating shelters and utilizing the boats. Wood to be utilized for construction purposes is generally known as timber or lumber. In construction, wood isn't just a primary material, but at the same time, it is also utilized to frame up the mould for the concrete base.

Wood-based materials are also broadly utilized for packaging (for example cardboard) and paper, which are both made from refined pulp. The chemical pulping processes utilize a mixture of high temperature and alkaline (kraft) or acidic (sulfite) chemicals to break the chemical bonds of the lignin prior to burning it out.

Polymers

One significant property of carbon in organic chemistry is that it can form specific compounds, the specific molecules of which are fit for appending themselves to each other, in this way shape up a chain or a network. This process is called polymerization and the chains or series of polymers, while the source compound is a monomer. Two principal groups of polymers exist: those made artificially are alluded to as synthetic polymers or industrial polymers (plastics) and those occurring naturally are known as biopolymers.

Monomers can have different chemical substituents, or functional groups, which can influence the chemical properties of organic compounds, like solvency and reactivity, along with the physical properties, like hardness, density, mechanical or tensile strength, abrasion resistance, thermal resistance, transparency, colour, and so on. In proteins, these distinctions enable the polymer to embrace biological active conformation in inclination to others.

We have been using natural organic polymers for a long time as waxes and shellac, which are called thermoplastic polymers. A plant-based polymer named cellulose gave rigidity to natural fibres and ropes, and by the early nineteenth century, naturally occurring rubber was widely used. Polymers are the unrefined or raw substances (the resins) used to make what are normally called plastics. Plastics are the end product, made after at least one polymer or other substances have been added to the resin during processing, which is then moulded into a final structure. Polymers that have been around, and that are being widely used, incorporate carbon-based polyethylene, polypropylene, polyvinyl chloride, polystyrene, nylons, polyesters, acrylics, polyurethane, polycarbonates, and silicon-based silicones. The process of forming a polymer is called polymerization.

Organic solids give electronic and optical materials whose properties can be customized to suit explicit applications. They additionally face difficulties with the basic concepts since they afford the unique system for laying out the limits to validate the conventional customary energy band models that have demonstrated so fruitfully in depicting the electronic properties of inorganic metals and semiconductors.

Structure Characteristics and Properties of Organic Solids

Any atom comprises a positively charged nucleus and at least one electron that is bound with the electric field of the nucleus. In a system having more than one atom, an electron isn't really bound to one nucleus yet it can be shared between different atoms, contingent upon the interatomic interactions and the energy state of the electron. In metals and inorganic semiconductors, the solid interatomic electronic interactions work with the delocalization of external shell electrons over an enormous number of atoms. Depending upon the basis of intermolecular and interatomic interactions, organic solids can be of two types:

Non-polar Organic Solids: The molecules are held intact by van der Waals forces, which are comparatively weaker contrasted with the covalent bonds. The physical properties of nonpolar organic solids are marginally changed compared with those of the free atoms since the intramolecular interactions are prevailing.

Polar Organic Solids: Organic slid materials where both ionic bonds and van der Waals forces exist. Instances of this are organic charge-transfer edifices and radical-ion salts, in which the positive and negative charges are isolated and situated on various molecules. However, the ionic holding in these ionic molecular crystals is more vulnerable than that in inorganic salts, as particles are bigger than atoms.

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Organic solids can also include photoconductive materials, conductive polymers, electroluminescent materials, and photovoltaic materials and the usefulness of which relies basically upon their atomic and molecular structures. However, a wide assortment of organic semiconductors and conductors have been demonstrated, they comprise a normal π - electron system in the structure of the constituent molecules.

5.5.1 Electrically Conducting Solids

Electrical property of solids is a reference to its conductivity. Electric conductivity is defined as its ability of a substance to transmit electric energy through it. So a good conductor of electricity is easily able to transmit the energy without boiling or melting or changing its composition in any way.

Solids have varying degrees of conductivity, i.e., all solids do not have uniform electrical properties. Electrical conductors allow electrons to flow between the atoms of that material with drift velocity in the conduction band. Electrical conductors may be metals, metal alloy, electrolyte, or some non-metals like graphite and a conductive polymer. These materials allow electricity (i.e., the flow of charge) to pass through them easily.

The outer electrons in the valence band are loosely attached to the atom. When an electron gets excited due to electromotive force or thermal effect, it moves from its valence band to the conduction band.

The conduction band is the band where this electron gets its freedom to move anywhere in the conductor. The conductor is formed of atoms. Thus as a whole, the conduction band is in the abundance of electrons.

In other words, it can be said that the metallic bonds are present in the conductors. These metallic bonds are based on the structure of positive metal ions. These structures are surrounded by an electron cloud.

5.5.2 Organic Charge Transfer Complex, Organic Metals and New Superconductors

A Charge-Transfer (CT) complex or electron-donor-acceptor complex is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor.

The charge-transfer association occurs in a chemical equilibrium with the independent donor (D) and acceptor (A) molecules

$$D + A \leftrightarrow DA$$

Electron Donor-Acceptor Complexes

A number of organic compounds form electron-donor-acceptor complexes (EDA complexes). Typical acceptors are nitrobenzenes or tetracyanoethylene. The strength of their interaction with electron donors correlates with the ionization potentials of the components. For TCNE, the stability constants (L/mol) for its complexes with benzene derivatives correlates with the number of methyl groups:

benzene (0.128), 1,3,5-trimethylbenzene (1.11), 1,2,4,5-tetramethylbenzene (3.4), and hexamethylbenzene.

1,3,5-Trinitrobenzene and related polynitrated aromatic compounds, being electron-deficient, form charge-transfer complexes with many arenes. Such complexes form upon crystallization, but often dissociate in solution to the components.

Dihalogen/Interhalogen CT complexes

Dihalogens X2 (X = Cl, Br, I) and interhalogens XY(X = I; Y = Cl, Br) are Lewis acid species capable of forming a variety of products when reacted with donor species. Among these species (including oxidation or protonated products), CT adducts D·XY have been largely investigated. The CT interaction has been quantified and is the basis of many schemes for parameterizing donor and acceptor properties.

Many organic species featuring chalcogen or pnicogen donor atoms form CT salts. The nature of the resulting adducts can be investigated both in solution and in the solid state.

Organic Metals

Organic metals are a class of chemical compounds that contain metals and organic ligands, which confer solubility in organic solvents or volatility. Compounds with these properties find applications in materials science for metal organic vapor deposition (MOCVD) or sol-gel processing. The distinct term “metal organic compound” refers to metal-containing compounds lacking direct metal-carbon bonds but which contain organic ligands. Metal β-diketonates, alkoxides, dialkylamides, and metal phosphine complexes are representative members of this class.

New Super Conductors

New superconductors are a variety of materials that are often artificially synthesized in laboratory and they cannot be described with the “classical” theory of superconductivity. The origin of their superconductivity is probably not the same as that of lead or mercury, especially as far as the process of two electrons forming a Cooper pair is concerned.

Check Your Progress

19. What do you mean by organic solids?
20. Define charge transfer complex.
21. What do you understand by organic metals?
22. What are new superconductors?

5.6 ANSWERS TO ‘CHECK YOUR PROGRESS’

1. Solid-state chemistry is the study of the synthesis, structure, and properties of solid phase materials, particularly, but not necessarily exclusively of, non-molecular solids.

2. Solid state reactions are the reactions which occurs among solids. The reactions where the product is solid and the two reactants must be solid are included in this type, but practically many reactions are categorized as solid state reactions even though both the reactants are not solid.
3. The temperature at which the reaction rate is maximum is generally taken as the reaction temperature.
4. Co-precipitations is a process in which normally soluble compounds are carried out of solution and precipitating them as hydroxides, citrates, oxalates, or formates.
5. This general term stands for combining the effect of one transformation in the solid with another reaction.
6. A perfect crystal is a crystal that contains no point, line, or planar defects. There are a wide variety of crystallographic defects.
7. A crystal in which the regular, periodic structure is interrupted by various defects is imperfect crystal.
8. The intrinsic defect is related to the presence of vacancies (missing atoms), interstitial atoms (added atoms), or anti-sites (exchanged atoms for polar material).
9. Extrinsic defects are caused by the presence of foreign atoms in the crystal structure. These foreign atoms can be either substitutional (replacing original lattice atoms) or interstitial.
10. Line defects are the lines along which whole rows of atoms in a solid are arranged anomalously.
11. On planes of single crystals, steps between atomically flat terraces can also be regarded as planar defects.
12. Colour centre is the defect in the regular spacing of atoms within a solid that absorbs the visible light of a particular colour or infrared or ultraviolet radiation, thus it lends a characteristic colour to the specific solid.
13. Conductors are the solids that allow easy passage of electric current through them.
14. These materials do not conduct electricity.
15. Band theory is based on the principle of molecular orbital theory of covalent bonds.
16. The band containing the outer or valence electrons, is called the valence bond.
17. Material having electrical conductivity in between those of insulators and conductors are called semi-conductors.
18. When a junction on an interface or a boundary is made between two semiconductor material types, namely the p type or n-type inside a semiconductor, it is referred to as p-n junctions.
19. Electric Conductivity is defined as its ability of a substance to transmit electric energy through it.

20. A charge-transfer (CT) complex or electron-donor-acceptor complex is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities.
21. Organic metals are a class of chemical compounds that contain metals and organic ligands, which confer solubility in organic solvents or volatility.
22. New superconductors are a variety of materials that are often artificially synthesized in laboratory and they cannot be described with the "classical" theory of superconductivity.

5.7 SUMMARY

- Solid-state chemistry is the study of the synthesis, structure, and properties of solid phase materials, particularly, but not necessarily exclusively of, non-molecular solids.
- Solid state reactions are the reactions which occurs among solids.
- Solid state reactions are diffusion controlled process (migration of ion).
- The decomposition product of some metal hydrates has a crystal lattice identical with that of the parent solid.
- Decomposition of the metal carbonates is another widely studied solid state reaction.
- A diverse array of methods are available to synthesize solid compounds and materials.
- In the preparation of solid care must be taken for stoichiometric quantities, pure starting materials and ensure that reaction has gone to completion.
- Co-precipitations is a process in which normally soluble compounds are carried out of solution and precipitating them as hydroxides, citrates, oxalates, or formates.
- Impurities may be introduced in a solid during crystallization deliberately or otherwise these impurities play an important role in determining the reactivity of solids.
- Counter diffusion of cations in solid state reactions and the formation of product at the interface as a result of migration of the magnesium ions and aluminium ions is popularly known as Wegner reaction mechanism.
- The study of solid-state reaction can be done in terms of thermodynamics and kinetics.
- In thermodynamics, the spontaneity of solid-state reactions is studied in terms of energy changes, whereas in kinetics, the growth of the product is studied with time.
- According to the definition of crystalline solids, an ideal crystal is one which has a regular repeating arrangement of unit cell throughout the crystal.
- The defect in crystals means that the perfect arrangement of the constituent ions is destroyed due to the presence of cationic and anionic vacancies in

the lattice points, dislocations of ions in the lattice, the presence of the same type of ions in the different oxidation states and the presence of impurities in the lattice points.

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- The point defects found in stoichiometric crystals are called stoichiometric defects while the point defects in non- stoichiometric crystals are known as non-stoichiometric defects.
- When the ratio of the cations and anions present in the imperfect ionic solid differs from that required by the ideal or perfect chemical formula of the compound, the defect is known as non-stoichiometric defect.
- Crystals having metal deficient defects are semiconductors. The conductivity is due to the movement of an electron from one cation to the other cation.
- The Schottky defect and Frankel defect are called thermodynamic defects because the number of these defects depends on the temperature.
- Electrical properties of solids are measured in terms of conductivity. Conductivity may be defined as the ease with which electric current can pass through a given substance.
- Band theory is based on the principle of molecular orbital theory of covalent bonds.
- A solid is a semi-conductor, i.e., a material having electrical conductivity in between those of insulators and conductors.
- A rectifier or diode is an electronic device that allows the current to flow in one direction only.
- Transistors are extremely important semiconducting devices in today’s microelectronic circuitry capable of two primary types of functions.
- A super conductor is a substance that conducts electricity without resistance.
- Electric conductivity is defined as its ability of a substance to transmit electric energy through it.
- The conduction band is the band where this electron gets its freedom to move anywhere in the conductor. The conductor is formed of atoms.
- A Charge-Transfer (CT) complex or electron-donor-acceptor complex is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities.
- Organic metals are a class of chemical compounds that contain metals and organic ligands, which confer solubility in organic solvents or volatility.
- New superconductors are a variety of materials that are often artificially synthesized in laboratory and they cannot be described with the “classical” theory of superconductivity.

5.8 KEY TERMS

- **Solid State Chemistry:** Solid-state chemistry is the study of the synthesis, structure, and properties of solid phase materials, particularly, but not necessarily exclusively of, non-molecular solids.

- **Solid State Reactions:** Solid state reactions are the reactions which occurs among solids. The reactions where the product is solid and the two reactants must be solid are included in this type.
- **Reaction Temperature:** The temperature at which the reaction rate is maximum is generally taken as the **reaction temperature**.
- **Co-Precipitation:** Co-precipitations is a process in which normally soluble compounds are carried out of solution and precipitating them as hydroxides, citrates, oxalates, or formates.
- **Surface Adsorption:** It is a common source of co-precipitation that causes significant contamination of precipitates with large specific surface areas.
- **Perfect Crystals:** A perfect crystal is a crystal that contains no point, line, or planar defects. There are a wide variety of crystallographic defects.
- **Imperfect Crystals:** A crystal in which the regular, periodic structure is interrupted by various defects is imperfect crystal.
- **Point Defect:** A point defect is an isolated distortion of the crystal lattice with intrinsic or extrinsic origin.
- **Intrinsic Defects:** The intrinsic defect is related to the presence of vacancies (missing atoms), interstitial atoms (added atoms), or anti-sites (exchanged atoms for polar material).
- **Extrinsic Defects:** Extrinsic defects are caused by the presence of foreign atoms in the crystal structure. These foreign atoms can be either substitutional (replacing original lattice atoms) or interstitial.
- **Line Defects:** Line defects are the lines along which whole rows of atoms in a solid are arranged anomalously.
- **Plane Defects:** On planes of single crystals, steps between atomically flat terraces can also be regarded as planar defects.
- **Colour Centre:** Colour centre is the defect in the regular spacing of atoms within a solid that absorbs the visible light of a particular colour or infrared or ultraviolet radiation, thus it lends a characteristic colour to the specific solid.
- **Conductivity:** Conductivity may be defined as the ease with which electric current can pass through a given substance.
- **Insulators:** These materials do not conduct electricity.
- **Doped Semiconductors:** These are obtained by adding calculated amount of dopants (B or P) to the melt before crystal pulling stage.
- **p-n Junction:** When a junction on an interface or a boundary is made between two semiconductor material types, namely the p type or n-type inside a semiconductor, it is referred to as p-n junctions
- **Organic Metals:** Organic metals are a class of chemical compounds that contain metals and organic ligands, which confer solubility in organic solvents or volatility.

- **New Super Conductors:** New superconductors are a variety of materials that are often artificially synthesized in laboratory and they cannot be described with the "classical" theory of superconductivity.

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5.9 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answers Questions

1. Define decomposition reactions.
2. What do you understand by laws governing nucleation?
3. Define the growth of nuclei.
4. What do yo9u understand by type 1 reactions?
5. State the exchange reactions.
6. Define kinetics of solid state reactions.
7. State the thermodynamics of the Schottky and Frenkel defect formation.
8. Define electrically conducting solids.

Long-Answers Questions

1. Explain the types of solid state reactions.
2. Differentiate between type 1 and type 2 reactions.
3. Describe the solid state ceramic method in detail.
4. Explain in detail the co-precipitation and precursor methods.
5. Describe the various types of crystal defects.
6. Explain the band theory in detail.
7. Describe the p-n diode in detail.
8. What do you understand by semi-conductor? Describe the various types of semiconductors.

5.10 FURTHER READING

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