

CHAPTER 2

SPECTROSCOPIC TECHNIQUES

2.1 INTRODUCTION

Spectroscopy is a branch of science dealing with the study of interaction of electromagnetic radiation with matter. It is one of the most important tools available for the study of atomic and molecular structure and used in the structural analysis of a wide range of substances. Atoms and molecules are infinitesimally small in dimensions, so it is not possible to see them. All information now we have about atoms and molecules are directly or indirectly are from spectroscopy. In fact spectrum is the finger print or photograph of atoms and molecules.

Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocities. Gamma rays, X-rays, ultraviolet, visible, infrared, microwaves and radio waves are all electromagnetic radiations of different wavelengths and energy. In the case of atoms and molecules, when an electron jumps from a lower energy level E_1 to a higher energy level E_2 the difference in energy is absorbed in the form of a quantum $h\nu$.

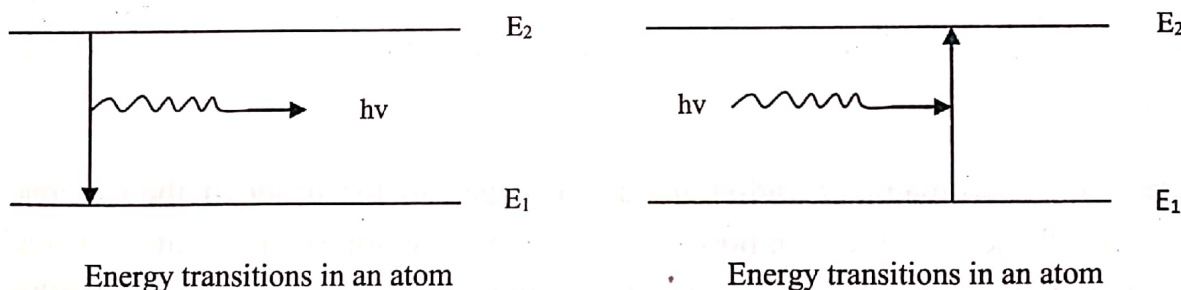


Fig. 2.1 Energy transitions in atoms

2.2 ATOMIC SPECTRUM AND MOLECULAR SPECTRUM

Atoms interact with electromagnetic radiations to give atomic spectra. Since atoms have limited number of energy levels, atomic spectrum consists of lines and it is called line spectra. Similarly molecules interact with electromagnetic radiations to give molecular spectra. Since molecules possess a number of energy levels, large numbers of such energy transitions are possible. The resulting spectrum consists of many lines which are close together making a band. Radiations have electric and magnetic components along

with them. It is made up of discrete wave like particles called photons. The energy corresponding to a photon is given by Planck's equation, $E = h\nu$

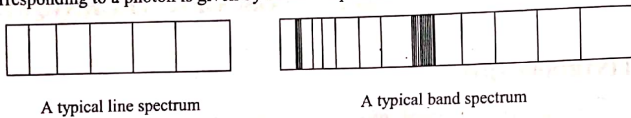


Fig.2.2 Fraunhofer lines

Electromagnetic radiations

$$E = h\nu \text{ or } E = hc/\lambda$$

Where h is the Planck's constant, ν is the frequency, λ is the wave length and c is the velocity of light. The arrangement of all types of electromagnetic radiations in the increasing order of their frequencies or decreasing order of their wavelengths are known as complete electromagnetic spectrum. The visible spectrum represents only a small portion of the electromagnetic spectrum and this portion is perceptible to human eye.

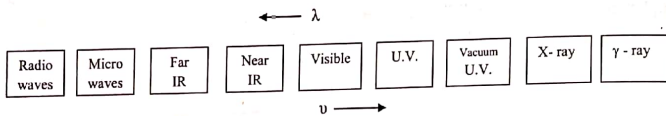


Fig. 2.3 Electromagnetic Spectrum

If all types of electromagnetic radiations are arranged in the order of their increasing frequency (see Table 2.1), then the portion above visible region is called ultraviolet while the region below it is the infrared region. Infrared radiations have longer wavelengths and are thus less energetic.

Table 2.1 Electromagnetic spectral regions

Region	Wave length	Frequency (hertz)
X-ray	$10^{-2} - 10$ nm	$3 \times 10^{19} - 3 \times 10^{16}$
Ultraviolet	10-400 nm	$3 \times 10^{16} - 7.5 \times 10^{14}$
Visible	400-800 nm	$7.5 \times 10^{14} - 3.8 \times 10^{14}$
Infrared	800 - 300,000 nm (0.8- 300 μ m)	$3.8 \times 10^{14} - 1 \times 10^{12}$
Microwave	$3 \times 10^5 - 5 \times 10^8$ nm (0.3 μ m -0.5 m)	$1 \times 10^{12} - 6 \times 10^8$
Radio waves	$5 \times 10^8 - 3 \times 10^{11}$ nm (0.5m - 300 m)	$6 \times 10^8 - 1 \times 10^6$

The wave length is usually expressed in nanometers, angstrom units etc.

2.3 DIFFERENT TYPES OF ENERGY PRESENT IN MOLECULES

Molecules possess different types of quantized energy levels such as rotational, vibrational, electronic etc.

- 1. Electronic energy (E_{elec}):** The molecule possesses electronic energy levels which is associated with the transition of an electron from the ground state energy level to the excited state by the absorption of photons of suitable energy. Electronic transitions give absorption or emission in the visible or UV region (UV- visible or electronic spectrum)
- 2. Vibrational energy (E_{vib}):** Vibrational energy is associated with vibrations within a molecule such as stretching and bending of bonds. The molecule is said to possess vibrational energy when the center of gravity does not change during to and fro motion of the nucleus of the molecule. Vibrational transitions give absorption or emission spectrum in the near IR region (IR spectrum or vibrational spectrum).
- 3. Rotational energy (E_{rot}):** When the molecule rotates about an axis perpendicular to the inter nuclear axis, passing through the center of gravity, it requires rotational energy. Rotational transitions give absorption or emission spectrum in the microwave region (microwave spectrum or rotational spectrum).
- 4. Translational energy (E_{trans}):** This is concerned with the overall movement of the molecules along the three axes. In other words, during the motion if the center of gravity changes, the molecule is said to possess translational energy. It is significant only in gases and to a lesser extent for liquids, but it is negligibly small.

The total energy of the molecule (E) is given by the sum of all these energies.

$$E = E_{elec} + E_{vib} + E_{rot} + E_{trans}$$

But the energy of translation is negligibly small, so as per Born-Oppenheimer approximation reduces to the following equation.

$$E = E_{elec} + E_{vib} + E_{rot}$$

It is to be noted that a series of rotational energy levels (designated by the rotational quantum number J) are associated with each vibrational energy level (designated by vibrational quantum number v). A series of vibrational energy levels are associated with each electronic state.

Table 2.2 Summary of the various types of molecular spectra

No	Spectra	Transitions between	Region of electromagnetic spectrum	Criteria (*)
1.	Rotational/Micro wave	Rotational energy levels	Microwave (1-100 cm ⁻¹)	Molecules must possess permanent dipole moment e.g.: HCl, H ₂ O etc.
2.	Vibrational rotational/ IR	Vibrational energy levels	Infrared (500-4000 cm ⁻¹)	Dipole moment of molecule must change during vibration.
3.	Electronic /UV-Visible	Electronic energy levels	Visible(12500-25000) and UV 25000-70000cm ⁻¹	All molecules.
4.	Raman	Vibrational and rotational levels.	Far and near infrared regions.	Periodic change in polarizability due to vibrational and rotational transitions.
5.	Nuclear Magnetic Resonance (NMR)	Magnetic energy levels of nuclei.	Radio frequency	Spin quantum number of nuclei $I > 0$
6.	Electron spin Resonance (ESR)	Magnetic energy levels of unpaired electron(s) (*)	Microwave	Presence of unpaired or odd electrons in a molecule

2.4 INSTRUMENTATION OF SPECTROPHOTOMETER

The instrument used to record the spectra of molecules, is called a spectrometer. The exact design of the instrument varies according to the spectral region being examined, but the basic features of all spectrometers are similar. A generalized schematic representation of spectrophotometer is shown in Fig.2.4. When radiations are passed through a transparent layer of the sample (solid, liquid or gas) certain specific wave lengths are removed by absorption. The absorbed energy is transferred to the atoms and molecules of the sample; thereby it gets excited from the ground state to the excited state. The measurement of decrease in the intensity of radiation is the basis of spectrophotometry. The spectrophotometer has the following components.

1. **A suitable source of electromagnetic radiation:** The source should be stable and provide continuous radiations. Generally, hydrogen discharge lamp and tungsten filament lamp sources are used in UV visible spectrometer but in IR spectrometers, electrically heated rod of rare earth oxides are used.

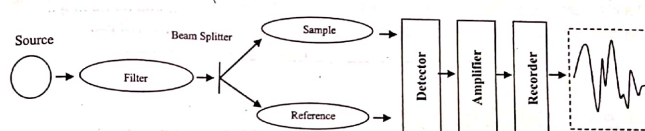


Fig. 2.4 Spectrophotometer

2. **Wavelength controller or filter or monochromator:** The filter unit consists of an entrance slit, a dispersing element and an exit slit. The dispersing element is generally a prism or grating. The function of the wavelength controller/ filter is to isolate a narrow band of wavelength from the radiation source.
3. **Sample holder/ cells:** Sample holder (cells) made up of silica or glass is used to contain sample solution as well as reference solution. Standard cells of rectangular form with one centimeter path length are generally used. The sample holder should satisfy the following requirements.
 - a) The cell should have uniform thickness.
 - b) They should be inert to the solvent.
 - c) They must transmit the light of wavelength used.
4. **Detectors:** Convert the transmitted radiation into electrical energy.
5. **Recording system:** The final absorption spectrum is displayed either on a video screen or, more generally, recorded on a chart paper. In this manner, we can measure the extent to which a substance absorbs radiation at each wavelength (or frequency or wave number).

2.5 BEER-LAMBERT'S LAW

In optics, the Beer-Lambert's law relates the absorption of light to the properties of the material through which the light is travelling. The Beer-Lambert's law (or Beer's law) is the linear relationship between absorbance and concentration of an absorbing species.

Lambert's law: States that when parallel, monochromatic radiation is passed through a solution, the logarithm of ratio of intensity of incident to transmitted light (I_0 / I) is proportional to the thickness of (l) of the solution.

$$\log \frac{I_0}{I} \propto l \quad A = \log \left(\frac{I_0}{I} \right)$$

Beer's Law: States that the absorbance ($\log I_0 / I$) of a solution is proportional to the concentration (c) of the absorbing solution when thickness (l) is kept constant.

$$\log \frac{I_0}{I} \propto c$$

The Beer-Lambert's law: It states that the proportion of light absorbed by a solute in a transparent solvent is independent of the intensity of the incident light and is proportional to the number of absorbing molecules in the light path. The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. If there are only a few molecules that absorb radiation, the total absorption of energy is less and consequently lower intensity peak is observed. This makes the basis of Beer - Lambert's law which states in other words, that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path.

Measure the intensity of the beam of light entering sample (I_0) and compare it with the intensity of the beam of light exiting sample (I). By taking the ratio I_0/I , we get an indication of what fraction of the light entering the sample was found exiting the sample. This ratio is called the transmittance

$$\text{Transmittance } T = \frac{I}{I_0}$$

Transmittance (T) is defined as the ratio of intensities of transmitted to incident light.

For our purposes it is mathematically convenient to define a new concept, Absorbance ($A = \log I_0 / I$) which gives a direct measure of how much light is absorbed by the sample.

When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore, by combining Beer's law and Lambert's Law, we can write,

$$\log \frac{I_0}{I} = \epsilon c l$$

Where
 I_0 = Intensity of incident radiation
 I = Intensity of light transmitted radiation.

c = concentration of the solution in mols/liter.

l = path length of the sample

ϵ = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation.

$$\log I_0 / I = A \text{ absorbance.}$$

The above relation is known as the Beer-Lambert's Law which is the fundamental equation for colorimetry and spectrophotometry.

Limitations of the Beer- Lambert's law

The Beer-Lambert's law is valid only in dilute solutions and the following are its main limitations.

1. The law is invalid at high concentrations due to electrostatic interactions between molecules in close proximity.
2. Turbid solutions cannot be measured due to scattering of light between particulates in the samples.
3. Beer- Lambert's law fails if the light is not monochromatic.
4. Deviations from the Beer- Lambert's law are frequently encountered as a consequence of association, dissociation, or reaction of the absorbing species with the solvent.
5. Beer- Lambert's law may not be obeyed when different forms of the absorbing molecules are in equilibrium.
6. A deviation from Beer- Lambert's law is observed when there is fluorescence or phosphorescence in the sample.

Problem 1: Calculate the frequency of radiations having wavelength 5000 \AA where $c = 2.996 \times 10^{10} \text{ cm/s}$

$$\text{Solution: Frequency } \nu = \frac{c}{\lambda} = \frac{2.996 \times 10^{10} \text{ cm s}^{-1}}{5000 \times 10^{-8} \text{ cm}} = 5.992 \times 10^{14} \text{ s}^{-1}$$

Problem 2: Calculate the absorbance if 10% of incident light is transmitted.

$$\text{Solution: Absorbance (A)} = \log \frac{I_0}{I} = \log \frac{100}{10} = \log 10 = 1$$

Problem 3: A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution, if $\epsilon = 6000 \text{ litre mol}^{-1} \text{ cm}^{-1}$

$$\text{Solution: } I_0 = 100, I = 40, \epsilon = 6000 \text{ litre mol}^{-1} \text{ cm}^{-1}, l = 2 \text{ cm}, c = ?$$

$$\log \frac{I_0}{I} = \epsilon c l \quad \text{i.e.} \quad \log \frac{100}{40} = 6000 \times c \times 2 \quad \text{or} \quad \log 2.5 = 12000 c$$

$$1200 c = 0.3979 \quad \text{or} \quad c = 0.3979/12000 = 3.316 \times 10^{-5} \text{ mol/liter}$$

Problem 4: A dye solution of concentration 0.04M shows absorbance of 0.045 at 530nm; while a test solution of same dye shows absorbance of 0.022 under same conditions. Find the concentration of the test solution.

From Beer-Lambert's law we have, $A = \epsilon c l$. When the molar absorptivity ϵ and l are constants, we have, $\frac{A_1}{A_2} = \frac{c_1}{c_2}$ i.e. $\frac{0.045}{0.022} = \frac{0.04}{c_2} \therefore c_2 = 0.0195 \text{ M}$

Problem 5: A monochromatic radiation is incident on a solution of 0.05 M concentration of an absorbing substance. The intensity of the radiation is reduced to one-fourth of the initial value after passing through 10 cm length of the solution. Calculate the molar absorption coefficient of the substance.

According to Beer-Lambert's law we have,

$$\log \frac{I_0}{I} = \epsilon c l, \quad \text{here } I_0/I = 4, c = 0.05 \text{ mol dm}^{-3}, l = 10 \text{ cm} = 0.1 \text{ m} \quad \epsilon = ?$$

$$\log 4 = \epsilon \times 0.05 \text{ mol dm}^{-3} \times 0.1 \text{ m} \therefore \epsilon = 0.6021/0.05 \times 0.1 \text{ mol}^{-1} \text{ dm}^3 \text{ m}^{-1}$$

$$\text{Molar absorption coefficient} = 120.42 \text{ mol}^{-1} \text{ dm}^3 \text{ m}^{-1}$$

2.6 ELECTRONIC SPECTROSCOPY (UV-VISIBLE SPECTROSCOPY)

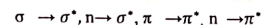
UV and visible or electronic spectra arise due to the transition of valence electrons from the lower energy level to the higher energy level by the absorption of energy. In some cases, the required energy can be supplied by radiation of visible wavelengths thus producing an absorption spectrum in the visible region (400-800 nm). In other cases, the transition occurs due to the absorption of ultraviolet radiations thus producing an ultraviolet spectrum in the region of (10-400 nm).

Principle: Ultraviolet absorption spectra occur due to the transition of electrons from lower electronic to higher electronic levels. Hence it is also called electronic spectroscopy. For a radiation to cause electronic excitation, it must be in the ultraviolet region of the electromagnetic spectrum.

Types of electronic transitions: The electrons involved in organic molecules can be classified in to different types

1. **Sigma (σ) electrons:** They are involved in saturated bonds and they are tightly bound. The electron density is concentrated along internuclear axis. Radiation of high energy is required to excite them.
2. **Pi(π) electrons:** They are involved in double or triple bonds. Here the electron density is concentrated above and below internuclear axis. They can be excited very easily.
3. **Nonbonding - n electrons:** Electrons attached to atoms such as chlorine, oxygen or nitrogen as lone pairs are called n electrons. (These non-bonding electrons can be excited at a lower energy.)

Absorption of UV and visible light by organic compounds will cause the promotion of electrons from the σ , π , and n (non-bonding) orbital in the ground state to σ^* and π^* orbitals in the excited state. Ultraviolet radiations promote the following electronic transitions:



1. $\sigma \rightarrow \sigma^*$ transitions: (sigma to sigma star transition)

In this, an electron is excited from the bonding σ orbital to corresponding σ^* orbital. These transitions occur in those compounds where all the electrons are involved in single bonds and no lone pairs of electrons are available. The transition energy required is very high, because σ electrons are held more firmly in the molecule. The absorption occurs in UV or far UV region. In saturated hydrocarbons such transitions occur.

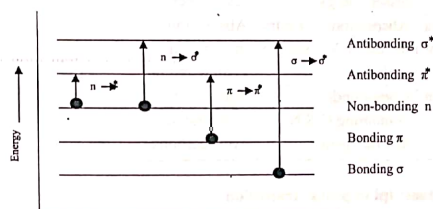


Fig. 2.5 Electronic transitions in UV-Visible spectrum

2. $n \rightarrow \sigma^*$ transitions: (n to sigma star transition)

Compounds containing non-bonding electrons on oxygen, sulphur, nitrogen or halogen atoms show absorption due to $n \rightarrow \sigma^*$ transitions. The energy required for $n \rightarrow \sigma^*$ transition

is less than that required for $\sigma \rightarrow \sigma^*$ transition. Therefore absorption corresponding to $n \rightarrow \sigma^*$ transitions occurs in ordinary UV, visible region. For example, methanol vapors show absorption band at 183 nm.

Table 2.3 Examples of Electronic Transitions

Transitions	Compound	λ_{\max} (nm)
$\sigma \rightarrow \sigma^*$	CH ₄	122
	CH ₃ -CH ₃	135
$\pi \rightarrow \pi^*$	CH ₂ =CH ₂	162
	CH≡CH	173
$n \rightarrow \sigma^*$	CH ₃ OH	183
	CH ₃ Cl	172
$n \rightarrow \pi^*$	(CH ₃) ₂ CO	279

Table 2.4 Comparison of various transitions.

$\sigma \rightarrow \sigma^*$ transitions	$n \rightarrow \sigma^*$ transitions	$\pi \rightarrow \pi^*$ transitions	$n \rightarrow \pi^*$ transitions
Transition of electrons from bonding σ to corresponding σ^* orbital	Transition of electrons from nonbonding σ orbital	Transition occurs in unsaturated compounds between π and π^* orbitals.	Transition occurs in compounds with O,S,N, halogens etc. Electrons transfer from n to π^* orbitals
Transition energy is very high	Transition requires lesser energy.	Transition requires lesser energy.	Transition energy is very low
Absorption occurs in the vacuum UV region.	Absorption occurs in the UV- visible region.	Absorption occurs in the near UV- visible region	Absorption occurs in the visible region (270-300 nm.)
Mainly observed in saturated hydrocarbons.	Compounds containing O,S,N and halogens.	Mainly observed in unsaturated hydrocarbons.	Hydrocarbons with O,S, Cl etc.

3. $\pi \rightarrow \pi^*$ transitions: (pi to pi star transition)

This occurs in molecules having a p electron. Unsaturated hydrocarbons exhibit this transition. The $\pi \rightarrow \pi^*$ bands appear at 180-190 nm in the case of aliphatic compounds and at 200-210 nm in the case of simple aromatic compounds.

4. $n \rightarrow \pi^*$ transitions: (n to pi star transition)

These are usually associated with groups such as carbonyl, thiocarbonyl, nitroso etc. which contain atoms having non-bonding electrons like oxygen, nitrogen, sulphur etc. These transitions are generally observed with low intensity when compared with other transitions. In aldehydes and ketones, transitions occur in the range of 270-300 nm. The following table shows some of the common electronic transitions with their corresponding wavelength.

Chromophores

The Greek word chromophore means "color carrier". In general chromophore is a group which is responsible for imparting color to a compound. The absorption of a given substance is greatly affected if it contains a chromophore. A chromophore is a functional group which has a characteristic absorption spectrum in the ultraviolet region. e.g. Nitro group is a chromophore because it gives yellow color to the compound. There are other functional groups such as -C=C-, -N=N- which absorb at wave lengths longer than 180 nm. By modern concept chromophore can be defined as an isolated covalently bonded group that shows a characteristic absorption in the UV or visible region irrespective of the fact whether color is produced or not. It may be noted that the part of the molecule having n or π electrons is responsible for absorption (e.g. Acetylene, ethylene, nitriles, carbonyls etc.)

Types of Chromophores

- Chromophores, which contain π electrons, can undergo $\pi \rightarrow \pi^*$ transition. For example, ethylene, acetylene etc...
- Chromophores, which contain both π and n electrons can undergo both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions e.g. carbonyls, nitriles etc.

Auxochromes

These are color enhancing groups. Polar groups such as -OH, -NH₂, -SH, -X (halogen) having unshared pair of electrons may show absorption above 190 nm. Such groupings are called auxochromes. These groups can extend the conjugation of the chromophore by sharing non-bonding electrons in order to shift the absorption band towards the longer wavelength. Thus, auxochromes are substituent which does not absorb ultraviolet radiations but their presence shifts the absorption maximum to longer wavelength.

2.7 ENERGY LEVEL DIAGRAM OF COMPOUNDS

In molecules with pi (π) bonds, the energy gap ΔE between electrons in the ground state (π) and excited state (π^*) corresponds to photons in the ultraviolet (UV) and visible part of the electromagnetic spectrum (180-700 nm wavelength or $E = 40-160$ kcal/mol). As the number of conjugated (consecutive) π bonds increases, the energy gap (ΔE) decreases, meaning that light of less energy (longer wavelength) is absorbed. The wavelength of maximum absorbance λ_{max} corresponds to ΔE . Therefore, λ_{max} will be in the UV part of the spectrum for molecules with fewer conjugated π bonds and more toward the visible for molecules with many conjugated π bonds. Therefore, using UV-Visible spectroscopy we can find out the λ_{max} of an unknown molecule. This in turn can tell us about the bonding present (if any). For example, let us consider what happens to λ_{max} when we increase the conjugation length from 0 (ethane) 1 (ethene) to 2 (butadiene) to 3 (hexatriene).

Table 2.5 Comparison of λ_{max} of various compounds

Compound	Formula	No. of conjugated pi bonds	λ_{max}
Ethane	$\text{CH}_3\text{-CH}_3$	0	150
Ethene	$\text{CH}_2=\text{CH}_2$	1	176
Butadiene	$\text{CH}_2=\text{CH-CH}=\text{CH}_2$	2	217
Hexatriene	$\text{CH}_2=\text{CH-CH}=\text{CH-CH}=\text{CH}_2$	3	258
Benzene	C_6H_6	3	255

It can be observed that, longer the conjugation, longer the absorption wavelength. In the case of Ethane we have σ to σ^* transition at λ_{max} of around 150 nm. As the number of conjugated pi (π) bonds increases, the λ_{max} increases. This means that the energy gap ΔE between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases as the number of conjugated pi (π) bonds increases.

For example, ethylene has one double bond and absorbs at 176 nm due to $\pi\text{-}\pi^*$ transition. Ethylene has two π orbitals, one ground state π bonding orbital and one excited state π^* antibonding orbital. When a molecule absorbs light at its longest-wavelength, an electron is excited from its highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In ethylene or simple alkenes, the HOMO orbital is π orbital and LUMO is π^* orbital. The energy difference between these two corresponds to a wavelength of 176 nm.

Butadiene however has four π electrons and has four π orbitals. Two bonding and two antibonding. The two bonding are designated as π_1 , π_2 and the two antibonding orbitals are designated as π_1^* and π_2^* . The π_1 orbital of butadiene is spread over four carbon atoms. The π_2 orbital of butadiene is less stable than π_1 orbital of ethylene. Similarly the two π_1^* and π_2^* orbital of butadiene are more stable and less stable respectively than π^* orbital of ethylene. On absorption of energy the electron jumps from π_2 bonding \rightarrow π_1^* antibonding (HOMO \rightarrow LUMO) orbital. Since the energy difference between π_2 to π_1^* in butadiene is less as compared to π to π^* in ethylene, butadiene absorbs at longer wavelengths. Hence, greater the number of π orbitals (conjugation) lower will be the energy difference between spectrum i.e. HOMO and LUMO and longer will be the absorption wavelength. Similarly, in the case of hexatriene, there are six π electrons and correspondingly six π orbitals, three bonding (π) and three antibonding (π^*) orbitals. On absorption of energy the electron jumps from π bonding \rightarrow π^* antibonding (HOMO \rightarrow LUMO) orbital. The energy gap ΔE between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is less due to more conjugation as shown in Fig.2.6

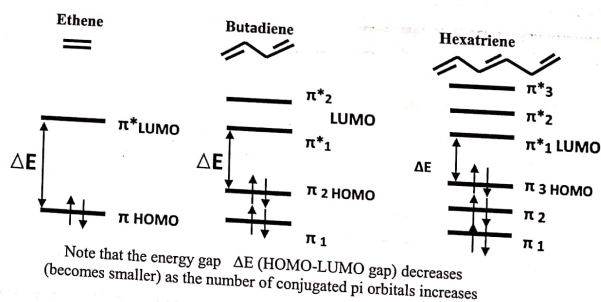
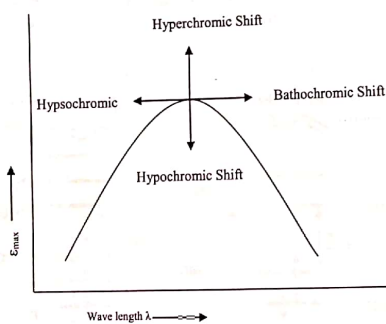


Fig.2.6 Energy level diagram of unsaturated compounds
As this trend continues past hexatriene toward molecules with longer conjugation length, λ_{max} starts to shift towards to visible region of the spectrum and color starts to appear. For example, tomatoes are red in colour because of the presence of lycopene, the compound having eleven conjugated double bonds. Thus it absorbs at λ_{max} value of 454 nm and tomatoes appear red.

Absorption and intensity shifts

- Hypsochromic Shift or Blue shift:** It is the shift in absorption maximum towards shorter wavelength or higher energy. This occurs either due to removal of conjugation or the change in polarity of the solvent. For example, absorption maximum of aniline shifts from $280 \mu\text{m}$ to $200 \mu\text{m}$ in acidic solutions.
- Bathochromic shift or Red shift:** It is the shift in absorption maximum towards longer wavelength or lower energy. This occurs either due to the presence of auxochromes or due to the change of solvent. For instance carbonyl compounds can undergo bathochromic shift due to $n \rightarrow \pi^*$ transitions when the polarity of solvent is lowered.
- Hyperchromic effect:** An effect that results in increased absorption intensity (optical density) of a compound. The introduction of an auxochrome usually causes hyperchromic shift.

Fig. 2.7 Various shifts in ϵ and λ

- Hypochromic effect:** An effect that results in decreased absorption intensity. This is caused by the introduction of a group which distorts the chromophore.

Instrumentation of UV- Visible Spectrophotometer

UV-Visible spectrometers have components similar to those of other spectrometers using electromagnetic radiation. The essential parts of a UV- Visible spectrophotometer are as follows (See Fig. 2.8)

a) Radiation source

The UV- Visible spectrophotometers usually covers the UV and visible regions. Their wavelength range extends from 200 nm to about 780 nm both high and low voltage hydrogen lamps give rise to continuous spectrum in the region between 200-370 nm, and a tungsten filament lamp for the region 325-750 nm.

b) Monochromator / filter

The filter unit consists of an entrance slit, a dispersing element and an exit slit. The dispersing element is generally a prism or grating. The function of the wavelength controller/ filter is to isolate a narrow band of wavelength from the radiation source.

c) Sample holder/ cells

Modern instruments are double- beam recording spectrophotometers in which the light beam from the source is divided in to two identical parallel beams of equal intensity. These beams are allowed to pass through the sample cell and reference cell containing the solvent. Cells used in UV-Visible spectroscopy are made entirely of quartz.

d) Detectors

The two beams, one emerging from the sample cell and the other from the reference cell, are then led to the detector system. The detectors convert the transmitted radiation in to electrical energy.

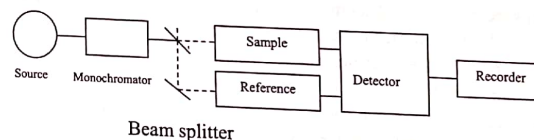


Fig. 2.8 Schematic diagram for UV- Visible spectrophotometer

e) Recording system

The detector transmits the signals to a recorder which gives the output displayed either on a video screen or, more generally, recorded on a chart paper. In this manner, we can measure the extent to which a substance absorbs radiation at each wavelength.

Applications of Electronic Spectroscopy (UV-Visible spectroscopy)

UV-Visible spectroscopy is used for

1. Identification of unknown compounds- An unknown compound can be identified by comparing its spectrum with the spectra of known compounds. If the two spectra coincide, then the two compounds must be identical. The rule governing this is known as Hartley's rule which states that compounds having similar structure would have similar absorption spectra.
2. For detecting impurities in organic compounds.
3. In the quantitative estimation of compounds.
4. Characterization of aromatic compounds and dienes.
5. Study of kinetics of chemical reactions.
6. Determination of structure of compounds.
7. For studying tautomeric equilibrium- The UV- Visible spectrophotometer can be used to determine the percentage of keto and enol forms present in compounds.
8. Determination of molecular weight of a compound.
9. Determination of unknown concentration.
10. To determine the ozone present in the environment by measuring its spectrum.

2.8 VIBRATIONAL (IR) SPECTROSCOPY

Vibrational spectroscopy is concerned with the study of mainly the vibrational motion of the molecules. It arises from the interaction of the fluctuating molecular dipole moment of the compound with the electromagnetic radiation. The vibrational spectra is given by the electromagnetic radiations in the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. The essential requirement for a molecule to show IR spectrum is the change in dipole moment of the molecule during the vibration (fluctuating dipole moment). This type of spectrum is given by molecules with permanent or fluctuating dipole moments. Therefore, H_2 , O_2 etc. will not give IR spectrum whereas HCl , H_2O etc. give the spectrum.

2.9 MODES OF VIBRATIONS IN A MOLECULE

When energy is absorbed by a molecule, the different bonds of constituent atoms exhibit the different modes of vibrations. They are as follows.

1. Stretching vibrations
2. Bending or deformation vibrations.

Stretching vibrations: In stretching vibrations, the atoms move along the bond axis. As a result, the bond length increases or decreases but bond angle remains unchanged. There are two types of stretching vibrations. These vibrations correspond to one dimensional movement.

- a) **Symmetric stretching:** In this type, the atoms of the molecule move in the same direction.
- b) **Asymmetric stretching:** In this type, the atoms of the molecule move in opposite direction.

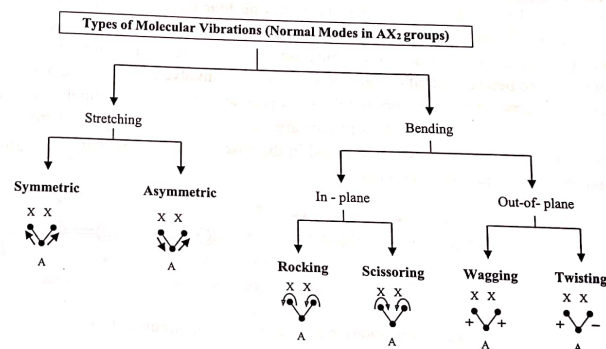


Fig. 2.9 Molecular vibration types

Bending or deformation vibrations

Bending or deformation vibrations involve a change in the bond angle whereas the bond length remains unchanged. There are four types of bending vibrations.

1. **Scissoring:** In this type, the atoms move away and come closer to each other in the same plane just like the blades of a scissors.
2. **Rocking:** In this type, the movement of atoms takes place in the same direction.
3. **Twisting:** In this type, one atom moves up and the other moves down the plane with respect to the central atom.
4. **Wagging:** In this type, both atoms move up and below the plane with respect to the central atom.

Number of vibrational modes in a molecule

For describing the position of an atom in a molecule, it requires three degrees of freedom, corresponding to three cartesian co-ordinates. The number of co-ordinates required to specify the position of all atoms in a molecule is called the number of degrees of freedom. Therefore, a molecule having "n" atoms, the degrees of freedom is equal to $3n$.

Linear molecule: For a linear molecule, there are three translational and two rotational degrees of freedom; hence, total number of vibrational mode possible is equal to $3n-5$. For example, CO_2 is a linear molecule, therefore, Vibrational degrees of freedom of $\text{CO}_2 = 3n - 5 = 3 \times 3 - 5 = 9 - 5 = 4$. So CO_2 is having four fundamental modes of vibrations such as symmetric stretching, asymmetric stretching, in plane bending and out of plane bending. Of the four normal modes, only the asymmetric stretching, in plane bending and out of plane bending vibrations are IR active as they involve a change in dipole moment. The symmetric stretching vibration does not produce any change in dipole moment, it is IR inactive. Also the two bending modes are equivalent (degenerate). Therefore, only two absorption frequencies are observed in the case of CO_2 at 2349cm^{-1} for asymmetric and 667cm^{-1} for bending vibration.

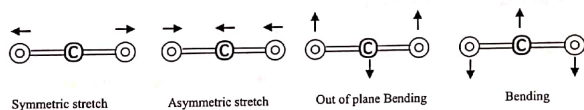


Fig.2.10 Vibrations in a linear triatomic molecule of CO_2

In the case of HCN , vibrational degrees of freedom of $\text{HCN} = 3n - 5 = 3 \times 3 - 5 = 9 - 5 = 4$. Here all the four modes are IR active.

Non Linear molecule

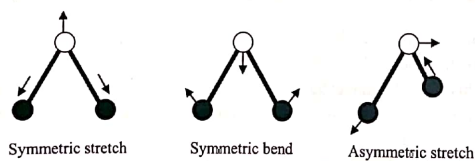


Fig.2. 11 Stretching in non-linear triatomic molecule

For a nonlinear molecule, there are $3n-6$ vibrational degrees of freedom. For example, H_2O , SO_2 , and NO_2 are non-linear triatomic molecules. The vibrational degrees of freedom = $3n - 6 = 3 \times 3 - 6 = 9 - 6 = 3$. Water is having three fundamental modes of vibration such as symmetric stretching, asymmetric stretching and bending vibration. All the three vibrations are IR active as there is a change in dipole moment during the vibration. So, IR spectrum of water exhibits three absorption bands.

Mechanism of interaction

For a vibrational mode to appear in the infrared spectrum for absorbing energy from the incident radiation, it is essential that a change in dipole moment occurs during vibration. Vibration of two similar atoms against each other (for example O_2 or N_2 molecules), will not result in a change of electric symmetry or dipole moment of the molecule, and hence such molecules will not absorb in the IR region. During the vibration of a molecule, such as CO_2 , there occurs a change in dipole moment; it will lead to the generation of an oscillating electric field. When a photon of a particular frequency comes in resonance with frequency of the vibration of a molecule, the absorption of photon takes place and molecules starts oscillating with the frequency of radiation.

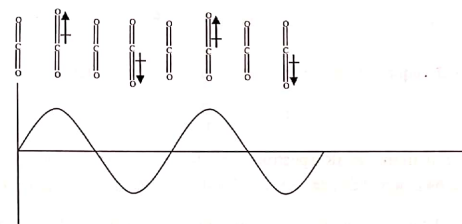


Fig. 2.12 Mechanism of interaction of oscillating dipole of CO_2 in asymmetric stretch

2.10 ENERGY OF VIBRATIONS

A simple harmonic oscillator can be considered as a model for a vibrating diatomic molecule. The vibrational energy is given by

$$E_{vib} = \left[v + \frac{1}{2} \right] x h\nu_0$$

Where v is the vibration quantum number and has values of 0,1,2,3..... and ν_0 is the fundamental vibrational frequency. The fundamental vibrational frequency ν_0 of such a molecule behaving like a simple harmonic oscillator is given by,

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Where k is the force constant (which relates the strength of the bond) and μ is the reduced mass of a diatomic molecule given by the equation, $\mu = \frac{m_1 m_2}{m_1 + m_2}$. When multiplying by Plank's constant (on both sides)

$$\Delta E_{vib} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

In spectroscopy, the unit commonly used is wave number $\bar{\nu}$. So we can write,

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

$$\sqrt{\frac{k}{\mu}} = \bar{\nu} 2\pi c \quad \text{i.e.} \quad k = 4 \mu \bar{\nu}^2 \pi^2 c^2$$

$$\text{or } k = 4 \bar{\nu}^2 \pi^2 c^2 \frac{m_1 m_2}{m_1 + m_2}$$

Since $c \bar{\nu} = \nu$, the equation for force constant may also be written as

$$k = 4 \nu^2 \pi^2 \frac{m_1 m_2}{m_1 + m_2}$$

Thus, knowing $\bar{\nu}$ from the IR spectrum, the force constant k for a given diatomic molecule (of known m_1 and m_2) can be calculated using the above equation.

Problem 6: CO molecule absorbs at 2140 cm^{-1} . Calculate the force constant of the molecule, given atomic masses of C and O are 12 amu and 16 amu respectively. (1 amu = $1.67 \times 10^{-27} \text{ kg}$).

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{Where, } \mu \text{ is the reduced mass of the system. } \sqrt{\frac{k}{\mu}} = \bar{\nu} 2\pi c \quad \text{or}$$

$$k = 4 \mu \bar{\nu}^2 \pi^2 c^2 \quad \text{----- (1)}$$

But reduced mass of the system is given by the equation, $\mu = \frac{m_1 m_2}{m_1 + m_2}$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 1.67 \times 10^{-27} \text{ kg} \times 16 \times 1.67 \times 10^{-27} \text{ kg}}{12 \times 1.67 \times 10^{-27} \text{ kg} + 16 \times 1.67 \times 10^{-27} \text{ kg}} = 1.14 \times 10^{-26} \text{ kg.}$$

But the velocity of light is $3 \times 10^8 \text{ m/s}$ and we have $\bar{\nu} = 2140 \text{ cm}^{-1} = 2140 \times 10^2 \text{ m}^{-1}$

Substituting the above values in equation (1) we have,

$$k = 4 \times 3.14^2 \times 1.14 \times 10^{-26} \text{ kg} \times (3 \times 10^8 \text{ ms}^{-1})^2 \times (2140 \times 10^2 \text{ m}^{-1})^2$$

$$k = 1853 \text{ kg/s}^2, \text{ but we know that } 1 \text{ N} = \text{kgm/s}^2$$

$$\text{i.e. } k = 1853 \frac{\text{kg s}^{-2} \text{ m}}{\text{m}} = 1853 \text{ Nm}^{-1}$$

Problem 7: If the fundamental vibrational frequency for HCl is $8.667 \times 10^{13} \text{ s}^{-1}$, calculate the force constant of HCl bond. [H = 1.008; Cl = 35.45].

$$\text{Force constant, } k = 4 \nu^2 \pi^2 \frac{m_1 m_2}{m_1 + m_2} \quad \text{----- (1)}$$

$$m_1 = \frac{1.008 \times 10^{-3}}{6.023 \times 10^{23}} = 1.6736 \times 10^{-27} \text{ kg;}$$

$$m_2 = \frac{35.45 \times 10^{-3}}{6.023 \times 10^{23}} = 58.8577 \times 10^{-27} \text{ kg;}$$

$$\frac{m_1 m_2}{m_1 + m_2} = \frac{(1.6736 \times 10^{-27})(58.8577 \times 10^{-27})}{(1.6736 \times 10^{-27}) + (58.8577 \times 10^{-27})} = 1.6273 \times 10^{-27} \text{ kg}$$

Frequency $\nu = 8.667 \times 10^{13} \text{ s}^{-1}$, substituting the values in eqn. (1)

$$K = 4 \times 3.14^2 \times (8.667 \times 10^{13})^2 \times (1.6273 \times 10^{-27}) = 482.086 \text{ kg S}^{-2}$$

$$= 482.086 \text{ Nm}^{-1} \quad (\text{Since } \text{kg S}^{-2} = \text{kg m S}^{-2} \text{m}^{-1})$$

Problem 8: Calculate the frequency (in Hz and cm^{-1}) of O-H bond, if the force constant and reduced mass of the atom pair are 770 Nm^{-1} and $1.563 \times 10^{-27} \text{ kg}$ respectively.

Solution:

$$\text{i) } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3.14} \sqrt{\frac{770 \text{ N m}^{-1}}{1.563 \times 10^{-27} \text{ kg}}} = \frac{1}{2 \times 3.14} \sqrt{\frac{770 \text{ kg m s}^{-2} \text{ m}^{-1}}{1.563 \times 10^{-27} \text{ kg}}} = 1.117 \times 10^{14} \text{ s}^{-1} \text{ or Hz}$$

$$\text{ii) } \bar{\nu} = \frac{\nu}{c} = \frac{1.117 \times 10^{14} \text{ s}^{-1}}{3 \times 10^8 \text{ m s}^{-1}} = 3723 \text{ cm}^{-1}$$

Instrumentation of IR Spectrophotometer

IR spectrometers have components similar to other spectrometers using electromagnetic radiation. The essential parts of an IR spectrometer are as follows.

- Radiation source:** The main sources of infrared radiation are (1) The Nernst glower, which is a filament containing oxides of zirconium, thorium and yttrium and cerium. (2) Globar is a bonded silicon carbide rod. (3) Nichrome wire wound on a ceramic support. When heated electrically at 1200 - 2000°C, they glow and produce IR radiation.
- Monochromator / filter:** The filter unit consists of prisms or gratings. The function of the wavelength controller/ filter is to isolate a narrow band of wavelength from the radiation source. The most commonly used prism materials are as follows.

Table. 2.6. Material wave number relation

Material	Wave number
Sodium chloride	4000 to 650 cm^{-1}
Potassium bromide	1000 to 400 cm^{-1}
Caesium iodide	1000 to 260 cm^{-1}
Calcium fluoride	50,000 to 1100 cm^{-1}

- Sample holder / cells:** Modern instruments are double-beam recording spectrophotometers in which the light beam emanating from the source is divided in to two identical parallel beams of equal intensity. These beams are allowed to pass through the sample cell and reference cell containing the solvent. Cells used in IR spectroscopy are generally made of sodium chloride or potassium bromide.

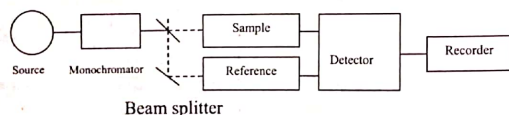


Fig.2.13 Schematic diagram for IR spectrometer

- Detectors:** The two beams, one emerging from the sample cell and the other from the reference cell, are then led to the detector system. The detectors convert the transmitted radiation in to electrical energy.

- Recording system:** The detector transmits the signals to a recorder which gives the output displayed either on a video screen or, more generally, recorded on a chart paper. In this manner, we can measure the extent to which a substance absorbs radiation at each frequency or wave number.

Interpretation of IR Spectrum

Interpretation of an IR Spectrum is not a simple matter. Some bands of weak intensity may occur at shorter wavelengths and these are called combination bands or overtone bands. The absorption bands of a particular group may be shifted by certain structural features – conjugation, angle strain or Van der Waals strain, hydrogen bonding. Overtone bands should not be confused with the intense fundamental bands originating from normal vibrational modes. IR spectrum is generally studied in two parts Fig.2.14.

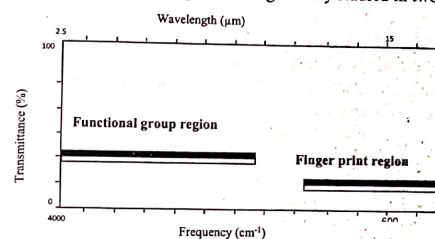


Fig.2.14 Functional group and finger print region

- Functional group region:** The bands in this region are particularly useful in identification of the type of functional groups present in the organic molecule. This region lies between 5000 cm^{-1} to 1300 cm^{-1} .
- Finger print region:** The area from 1300 cm^{-1} to 687 cm^{-1} is called the finger print region. The IR spectrum of an unknown substance is compared with the spectra of possible substances. It is associated with complex vibrational and rotational energy changes and is characteristic of the molecule as a whole. No two compounds can have identical bands in this region.

Applications of IR spectrometer

- The force constant for different bonds.
- To ascertain hydrogen bonding in a molecule.

3. For detecting impurities in a sample.
4. Shape and symmetry of molecules.
5. Determination of bond length.
6. Identification of unknown compounds.
7. Study of chemical reactions.
8. Structural elucidation of organic compounds.
9. Identification of functional groups in organic molecules.
10. Tautomeric equilibrium can be studied.
11. Study of co-ordination compounds.
12. Molecular symmetry and dipole moments.

2.11 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

NMR Spectroscopy is a powerful tool for investigating the structure of molecules. The technique is used to identify unknown compounds, to check for impurities and to study the shapes of molecules. In this branch of spectroscopy, radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule, which are created by keeping the nuclei in a magnetic field. The term 'nuclear' interprets the technique that detects nuclei of atoms such as hydrogen-1 (proton). The term magnetic interprets the nuclei that act like tiny magnets that can line up either in the same direction or in the opposite direction to an external magnetic field. The term "resonance" is the absorption of energy in the form of radio waves with the frequency corresponding to the size of energy jump as the nuclei flip from one alignment in a magnetic field to the other.

Theory of NMR spectroscopy

The matter part that interacts with electromagnetic radiation is the magnetic moment created by nuclear spin of atoms and molecules. Nucleus of an atom is positively charged, when it spins, it develops a magnetic field and act as a tiny bar magnet with a magnetic moment (μ). It has been found that any nucleus consisting of either an odd number of protons or an odd number of neutrons or both has the property of nuclear spin. For example,

1. Nuclei with odd atomic number (Z) and odd mass number (A) such as ${}^1_1\text{H}^1$, ${}^7_3\text{N}^{15}$ and ${}^{15}_7\text{P}^{31}$ etc.
2. Nuclei with odd atomic number (Z) and even mass number (A). ${}^2_1\text{H}^2$, ${}^3_1\text{H}^3$, ${}^{14}_6\text{C}^{14}$, ${}^{10}_5\text{B}^{10}$ etc.

3. Nuclei with even atomic number (Z) and odd mass number (A) ${}^{13}_6\text{C}^{13}$.
4. Nuclei with even atomic number (Z) and even mass number (A) have no magnetic moment, so they are NMR inactive. ${}^4_2\text{He}^4$, ${}^{12}_6\text{C}^{12}$, ${}^{16}_8\text{O}^{16}$ etc.

Nuclear spin and energy levels in magnetic field/ Quantum description of NMR

According to quantum theory, the spinning nucleus can have only those spin angular momentum values permitted by the equation

$$\text{Spin angular momentum} = I(1 + 1)^{\frac{1}{2}} \frac{h}{2\pi}$$

Where I, is the spin quantum number of the nuclei, which can have zero, integral or half integral values and h is the plank's constant. But the magnetic moment of the nucleus, μ can be equated to the gyromagnetic ratio and angular momentum, by the equation

$$\mu = \gamma \times \text{spin angular momentum.}$$

$$\mu = \gamma \times I(1 + 1)^{\frac{1}{2}} \frac{h}{2\pi}$$

On introducing a nucleus having a magnetic moment in to a magnetic field, H_0 , the two energy levels E_1 and E_2 separates corresponding to $m_1 = -\frac{1}{2}$ (antiparallel to the direction of magnetic field) and $m_1 = +\frac{1}{2}$ (parallel to the direction of magnetic field).

$$E_1 = -\frac{1}{2} \left(\frac{\gamma h}{2\pi} \right) H_0 \text{----- (1)}$$

$$E_2 = +\frac{1}{2} \left(\frac{\gamma h}{2\pi} \right) H_0 \text{----- (2)}$$

Thus when a nucleus absorbs energy (equal to the energy difference, $\Delta E = E_2 - E_1$), it gets promoted from the lower energy state E_1 to the higher energy state E_2 . In other words, magnetic moment of the nucleus changes from the parallel state to the anti-parallel state.

$$\Delta E = E_2 - E_1 \text{ (but } E = h\nu \text{)}$$

$$\nu = \frac{\Delta E}{h} \text{ on substituting the values of } E_1 \text{ and } E_2, \text{ we get}$$

$$\nu = \frac{\frac{1}{2} \left(\frac{\gamma h}{2\pi} \right) H_0 + \frac{1}{2} \left(\frac{\gamma h}{2\pi} \right) H_0}{h}$$

$$\text{or } \nu = \left(\frac{\gamma}{2\pi} \right) H_0 \text{----- (3)}$$

From the above equation it is clear that the frequency of absorbed or emitted by a nucleus in moving from one energy level to another is directly proportional to the applied magnetic field. Also it is clear that when the radio frequency is kept constant and the strength of magnetic field is varied, at some field strength, the energy required to flip proton matches the energy of the radiation. Then absorption occurs and a signal is produced. The resultant spectrum obtained is called NMR. Thus, nuclear magnetic resonance (NMR) is the study of the properties of molecules containing magnetic nuclei by means of the application of a magnetic field and the observation of the frequency at which they come in to resonance with a radiofrequency electromagnetic field.

Instrumentation of NMR Spectroscopy

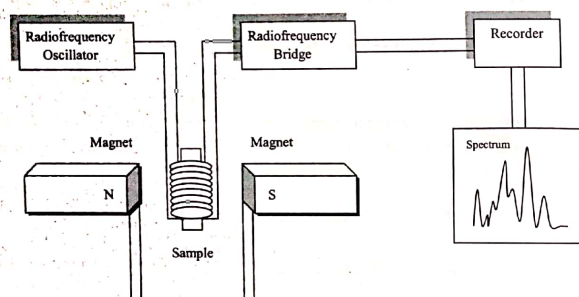


Fig. 2.15 Instrumentation -NMR

A typical NMR spectrometer consists of the following parts.

1. A radiofrequency source: In NMR, the frequency of radiation is kept constant, and the magnitude of the applied magnetic field is varied, till absorption of the radiation by proton occurs. The slight variation in the magnetic field is achieved by passing current through wire coils, wrapped round the two pole pieces of the magnet.
2. A transmitter to supply the desired radiofrequency (r.f) energy.
3. A detector- amplifier to pick-up and amplify the resonance signal.
4. A probe which serves to hold the sample between two pole pieces.
5. A device to receive and record the signal.

Procedure of NMR

For recording NMR spectra, the sample is placed between the poles of the strong magnet. The sample is then irradiated with radio waves to produce energy levels. Transition between these levels is induced by radiation from the radiofrequency transmitter. At certain value of the magnetic field, absorption of radiofrequency occurs. Absorption of radiation is detected on a radiofrequency bridge (a type of Wheatstone bridge arrangement), which goes out of balance, when absorption of radiation occurs. The resulting signal is amplified and recorded instantaneously on a chart.

Interpretation of NMR Spectra: The number of signals in NMR tells us how many different environments are there in a molecule. The area under each NMR signal is proportional to the number of hydrogen atoms in that environment. Thus various aspects of NMR can be interpreted as

1. The number of signals will give us how many different kinds of protons are there in a molecule.
2. The position of signals will give information about the electronic environment of each kind of proton.
3. The intensities of signals will give information about the number of protons of each kind.
4. Splitting of signals into several peaks will give information about the environment of proton with respect to other nearby protons.

2.12 CHEMICAL SHIFT

Chemical shift is an important feature of NMR spectra. In different chemical environments, the same type of nucleus will be shielded slightly from the applied field electrons. Chemical shift may be defined as a shift in position of a spectrum peak due to a small change in chemical environment. The separation in the positions of the spectral signals of hydrogen atoms in different chemical environments from that of some arbitrarily chosen standard is called the chemical shift. When a molecule is placed in a magnetic field, its electrons are caused to circulate, thereby producing an induced magnetic field, which may either

1. **Oppose the applied field / Shielding:** - Evidently, the effective field experienced by the protons is diminished. Under this state, the protons are shielded. The shielded protons in turn, shift the absorption position up field. Consequently, the value of the applied field necessary to bring the nucleus in resonance will be more. For example, acetylic protons exhibit this type of chemical shift

2. **Reinforces the applied field / Deshielding:** - Evidently, the effective field experienced by the protons is enhanced. Under this state, the proton is said to be deshielded. The deshielded protons in turn, shift the absorption position downfield in NMR spectrum. Consequently, the value of the applied field necessary to bring the nucleus in resonance will be less. For example, ethylenic and aldehydic protons exhibit this type of chemical shift.

Factors affecting Chemical Shift

1. **Shielding and deshielding:** Compared with a naked proton, a shielded (diminishing of applied magnetic field by the electrons of the atom) proton requires a higher applied field strength and a deshielded (increasing of applied magnetic field by the p electrons of the atom) proton requires a lower applied field strength. Thus Shielding and deshielding of protons by electrons causes chemical shift.
2. All aromatic protons differ widely because of the powerful deshielding due to the circulation of the p electrons.
3. **Electro negativity of attached atoms:** -The presence of certain electronegative compounds attached to aliphatic compounds can induce chemical shift.

Expression for Chemical Shift

Usually chemical shift is measured with respect to certain standard. Tetramethylsilane [TMS (CH₃)₄Si] is selected as the standard because of its conveniently located well defined absorption. Chemical shift positions are expressed in δ (delta) units, which is equal to the

$$\text{Chemical shift } \delta = \frac{\nu_s - \nu_{\text{reference}}}{\text{Operating frequency}} \times 10^6 \quad \text{or} \quad \delta = \frac{\nu_s - \nu_{\text{TMS}}}{\text{Operating frequency}} \times 10^6$$

In other words, Chemical shift $\delta = \frac{\Delta\nu}{\text{operational frequency in megacycles(per sec)}}$

Where, ν_s = frequency of the sample, $\nu_{\text{reference}}$ = frequency of the sample (TMS) and $\Delta\nu$ is the frequency shift. The value of δ is expressed in parts per million (ppm). Most chemical shift values have been found to lie between 0 and 10. TMS has been assigned δ value of 0. Previously, chemical shift was expressed in τ (tau) units, which are related to δ by the equation $\tau = 10 - \delta$.

Tetramethylsilane (CH₃)₄Si (TMS) is the most commonly used reference compound because of the following reasons.

1. Chemically inert and do not interfere with compounds under study.
2. It is volatile (b.p. 27°C) and samples may be recovered after recording spectra.
3. It gives single sharp absorption peak due to twelve equivalent protons.

4. It is soluble in most organic solvents.

Problem 9: what is the shift of the resonance from TMS of a group of nuclei with $\delta = 3.5$ and an operational frequency of 350 MHz?

Solution: We know that, $\delta = \frac{\nu_s - \nu_{\text{TMS}}}{\text{Operating frequency}} \times 10^6$

$$(\nu_s - \nu_{\text{TMS}}) = \frac{\delta \times \text{operating frequency}}{10^6} = \frac{3.5 \times 350 \times 10^6 \text{ Hz}}{10^6} = 1225 \text{ Hz} = 1.23 \text{ kHz}$$

Problem 10: Find the chemical shift in ppm(δ) for a proton that has resonance at 126Hz downfield from TMS on a spectrometer that operates at 60MHz.

$$\text{Solution: } \delta = \frac{\nu_s - \nu_{\text{TMS}}}{\text{Operating frequency}} \times 10^6 = \frac{126}{60 \times 10^6} \times 10^6 = 2.1$$

Thus chemical shift, $\delta = 2.1$ ppm

Problem 11: If the observed chemical shift of a proton is 200Hz from TMS and instrument frequency is 60 MHz, what is the chemical shift in terms of δ ? Express it in τ values.

$$\text{Solution: We know that, } \delta = \frac{\nu_s - \nu_{\text{TMS}}}{\text{Operating frequency}} \times 10^6 = \frac{200}{60 \times 10^6} \times 10^6 = 3.33$$

$$\text{But } \tau = 10 - \delta = 10 - 3.33 = 6.67$$

Problem 12: At what frequency shift from TMS would a group of nuclei with $\delta = 1.00$ resonate in spectrometer operating at 500 MHz?

$$\text{Solution: } \delta = \frac{\nu_s - \nu_{\text{TMS}}}{\text{Operating frequency}} \times 10^6 \quad \text{or} \quad \nu_s - \nu_{\text{TMS}} = \delta \times \text{operating frequency} \times 10^{-6}$$

$$\nu_s - \nu_{\text{TMS}} = 1.00 \times 500 \text{ MHz} \times 10^{-6} = 1.00 \times 500 \times 10^6 \text{ Hz} \times 10^{-6} = 500 \text{ Hz}$$

2.13 SPIN-SPIN COUPLING IN PROTON NMR SPECTRA

Each hydrogen in a molecule spins and generates their own magnetic field. Thus an NMR spectrum shows a signal for each kind of proton in a molecule. Each NMR-active nucleus has its own magnetic field as a result of its magnetic moment. Depending on the spin state of the nucleus, it will either add to or subtract from the external magnetic field. Splitting reflects the environment of the absorbing protons w.r.t. the nearby protons. Peaks are often split into multiple peaks due to magnetic interactions between nonequivalent protons on adjacent carbons; the process is called spin-spin splitting. In short fine splitting of the peaks in NMR spectrum due to the interaction between protons on adjacent atoms is referred to as spin-spin splitting or spin-spin coupling.

Rules for Spin-Spin Splitting

1. Chemically equivalent protons do not show spin-spin coupling.
2. Only nonequivalent protons couple.
3. Protons on adjacent carbons normally will couple.
4. Protons that are farther than two carbon atoms apart do not split each other.

The n+1 Rule

The number of lines (multiplicity) observed in the NMR signal for a group of protons is related to the number of protons in neighboring group. The multiplicity of a signal is calculated by using number of protons present in the nearby group. Count the number of neighbors (n) and add 1. This is known as "(n+1) rule." The (n+1) Rule, an empirical rule used to predict the multiplicity it states that if a given nucleus is coupled to n number of nuclei that are equivalent, the multiplicity of the peak is (n+1). In other words, if n number of protons is present in a nearby nucleus, the peak will split into (n+ 1) line.

It is important to keep straight two separate pieces of information:

1. The splitting pattern of a peak tells us how many nuclei are next to it.
2. The integral for a peak tells us how many nuclei are at that position.

Couplings are perhaps the most important parameter in NMR, as they allow us to elucidate chemical structure.

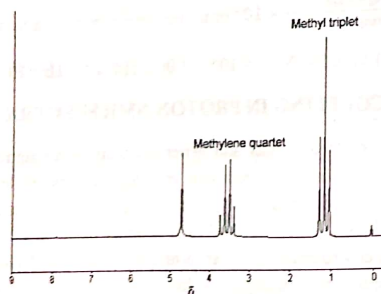
Structure of Ethanol

Fig. 2.16 NMR Spectrum of Ethanol

Fig.2.16 shows the ^1H NMR spectrum of ethanol ($\text{CH}_3\text{-CH}_2\text{-OH}$), which indicates three absorption peaks. This means that there are three different types of protons in ethanol, viz. CH_3 - protons, CH_2 - protons and OH protons. The methyl peak has been split into three peaks (a triplet) and the methylene peak has been split into four peaks (a quartet). This occurs because there is a small interaction (coupling) between the two groups of protons. The spacing between the peaks of the methyl triplet is equal to the spacing between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the coupling constant, J.

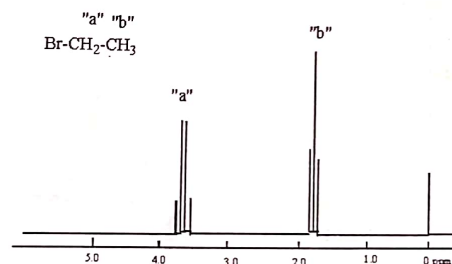
Structure of Ethyl Bromide

Fig.2.17 NMR Spectrum of Ethyl Bromide

Ethyl Bromide has two types of hydrogen. The downfield peak at about 3.5 ppm is the CH_2 shielded by the Br and appear as quartet due to the adjacent methyl group (n=3). The up field peak at about 1.7 ppm is the CH_3 and appears as a triplet due to the adjacent methylene (n=2)

Structure of Ethyl acetate

There are three types of protons marked as A, B and C.

1. Triplet $\delta \sim 1.3$ ppm; relative intensity 3; assigned to CH_3 part of ethyl group, triplet splitting due to neighboring CH_2 (H atoms are far away from electronegative O atom).
2. Singlet $\delta \sim 1.9$ ppm; relative intensity 3; assigned to CH_3 part of acetyl group, no splitting as no hydrogen attached to adjacent carbon
3. Quartet $\delta \sim 4.1$ ppm; relative intensity 2; assigned to CH_2 part of ethyl group, quartet splitting due to neighboring CH_3 .

The relative peak areas of these chemical shifts will be in the ratio 3:2:3 corresponding to the number of protons in each set.

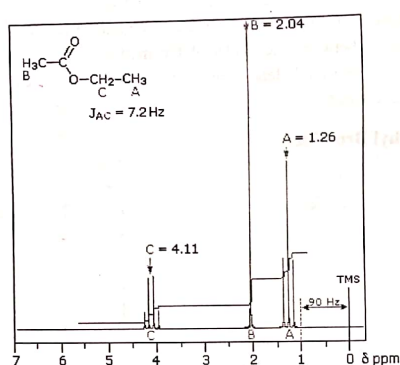


Fig.2.18 NMR spectrum of Ethyl acetate

Coupling Constants

Chemists quantify the spin-spin coupling effects using the term called the **coupling constant**, which is abbreviated with the capital letter J . Coupling constant is the distance between the centers of two adjacent peaks in a multiplet and usually it is a constant. The value of coupling constant is simply the difference, expressed in Hz, or in cps (cycles per second), between two adjacent sub-peaks in a split signal. It is a measure of the effectiveness of spin-spin coupling. The coupling constant is independent of the external field. In other words, we say that the value of J remains the same irrespective of the applied field. From the value of coupling constant, one can distinguish between 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 doublet. 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 same explanation can be given to distinguish a quartet from doublets.

Applications of NMR Spectroscopy

NMR Spectroscopy is a technique used by most modern chemical laboratories. It has applications in a wide range of disciplines, and development of new applied methods for NMR is an active area of research. Methods in NMR spectroscopy have particular relevance to the following applications:

1. The application of nuclear magnetic resonance best known to the general public is magnetic resonance imaging for medical diagnosis.
2. It is used for the identification of atomic configurations in molecules.
3. It is used for quantitative analysis of materials for particular isotope content from integrated area under NMR absorption band.
4. It is a rapid, non-destructive method for analyzing proton content of oils and fats.
5. It is used for the determination of water (H_2O) in liquid N_2O_4 and in heavy water- D_2O
6. It is used in structural diagnosis and study of keto-enol tautomerism.
7. It is used in the investigation of intra-molecular conversions.
8. It is used in the study of inorganic complexes and their structural determinations.
9. In the study of hydrogen bonding
10. It is used in the study of reaction kinetics.
11. Sample purity determination
12. Another use for nuclear magnetic resonance is data acquisition in the petroleum industry for petroleum and natural gas exploration and recovery.

2.14 MAGNETIC RESONANCE IMAGING (MRI)

Magnetic resonance imaging (MRI), is a medical imaging technique used in radiology to investigate the anatomy and function of the body in both health and in disease. MRI scanners use strong magnetic fields and radio waves to form images of the body. The technique is widely used in hospitals for medical diagnosis, staging of disease and for follow-up without exposure to ionizing radiations. Reflecting the fundamental importance and applicability of MRI in medicine, Paul Lauterbur and Sir Peter Mansfield were awarded the 2003 Nobel Prize in Medicine for their "discoveries concerning magnetic resonance imaging"

Principle: Magnetic resonance imaging employs nuclear magnetic resonance protons to produce proton density maps (or images) of the human body. Thus, MRI can be utilized to differentiate between healthy and diseased tissues of the body. It is based on the fact that the protons present within water, lipids, fats etc. resonate at a given frequency. Since human body contains about 75% water (H_2O) having two hydrogen nuclei, images of the

different parts of the body can easily be taken. In a diseased condition of body part, the distribution of water, fats, lipids etc. alters, and hence by using MRI, one can detect the diseased part(s) of the body.

Procedure: For taking the image in MRI, a varying magnetic field is applied across the body part under consideration. The protons in various regions of body come to resonate at different radio frequencies and the intensity of signal is proportional to the number of protons at that magnetic field. The body part is then rotated into a different orientation and another projection is made. Finally, the data obtained from different projections are combined by a computer to get a three-dimensional image of the body part. MRI requires very small time for scanning a particular body part.

Applications

1. For investigating the functioning of myocardium, heart etc.
2. For identifying the regions of excessive fat deposition in different organs, blood vessels etc.
3. For estimating fluorine concentration in body parts.
4. For the analysis of blood.

Advantages

1. MRI can create more detailed images of the human body than are possible with X-rays.
2. MRI provides good contrast between the different soft tissues of the body, which makes it especially useful in imaging the brain, muscles, the heart and cancers compared with other medical imaging techniques such as computed tomography (CT) or X-rays.
3. Unlike CT scans X-rays, MRI does not use ionizing radiations.
4. MRI is used to distinguish pathologic tissue (such as brain tumor) from normal tissue.

SOLVED EXAMPLES

Example 1: A solution shows a transmittance of 20% when taken in a cell of 2.5cm thickness. Calculate its concentration, if the molar absorption coefficient is $12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

$$I_0 = 100, I = 20, \epsilon = 12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

$$\log \frac{I_0}{I} = \epsilon c l \text{ in this case } l = 2.5 \text{ cm and } c = ?$$

$$\log \frac{100}{20} = 12000 \times c \times 2.5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \times \text{cm}$$

$$\log 5 = \epsilon c \times 30000 \text{ dm}^3 \text{ mol}^{-1} \text{ or } 30000 c = 0.6989$$

$$c = 0.6989/30000 = 2.3296 \times 10^{-5} \text{ mol dm}^{-3}$$

Example 2: $^1\text{H}^{35}\text{Cl}$ has a force constant (k) value of 480 Nm^{-1} . Calculate the fundamental frequency and its wave number.

Solution:

$$\text{Reduced mass } (\mu) \text{ of } ^1\text{H}^{35}\text{Cl} = \frac{m_1 m_2}{m_1 + m_2}$$

$$\text{Here, } m_1 = \frac{1.0 \times 10^{-3}}{6.023 \times 10^{23}} = 1.66 \times 10^{-27} \text{ kg and } m_2 = \frac{35 \times 10^{-3}}{6.023 \times 10^{23}} = 58.11 \times 10^{-27} \text{ kg}$$

$$\mu = \frac{(1.66 \times 58.11)}{(1.66 + 58.11)} \times 10^{-27} \text{ kg} = \frac{96.4626}{59.77} \times 10^{-27} \text{ kg} = 1.614 \times 10^{-27} \text{ kg}$$

$$\text{i) } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3.14} \sqrt{\frac{480 \text{ N m}^{-1}}{1.614 \times 10^{-27} \text{ kg}}} = \frac{1}{2 \times 3.14} \sqrt{\frac{480 \text{ kg m s}^{-2} \text{ m}^{-1}}{1.614 \times 10^{-27} \text{ kg}}} = 8.683 \times 10^{13} \text{ s}^{-1} \text{ or Hz}$$

$$\text{ii) } \bar{\nu} = \frac{\nu}{c} = \frac{8.683 \times 10^{13} \text{ s}^{-1}}{3 \times 10^8 \text{ m s}^{-1}} = 2.894 \times 10^5 \text{ m}^{-1} = 2894 \text{ cm}^{-1}$$

IMPORTANT QUESTIONS

1. What do you mean by electromagnetic radiation and electromagnetic spectrum?
2. Define the term frequency and wave number.
3. Give the energy of an electromagnetic radiation.
4. State the types of spectroscopy.
5. The spectrum arising from electronic transition occurs as a broad band. Justify.
6. Beer-Lambert's Law (RGPV, June 02, Dec. 02, 03, 04, June 05)
7. Write notes on UV-Visible spectroscopy
8. Write notes on IR spectroscopy (RGPV, June 07)
9. What is chemical shift in NMR spectroscopy (K.U.2014)
10. Write the expression for vibrational energy and fundamental vibrational frequency. Explain the different types of vibrational frequencies and the applications of vibrational spectroscopy to structural studies. (K.U.2014)
11. The absorbance of a 0.01M dye solution in ethanol is 0.62 in a 2 cm cell for light of wavelength 5000 \AA . If the path length of light through the sample is doubled and the concentration is made half, what will be the value of absorbance? KTU 2016
12. CHCl_3 protons show a shift in frequency of 728Hz from TMS signal in a 100 MHz instrument, how much would be the shift in frequency for the same proton from TMS in a 300 MHz NMR instrument? (2019 May/ June)
13. What interpretations are obtained from chemical shifts in molecule? (KTU 2019June)

14. Discuss the factors affecting chemical shift. (KTU 2019 June)
15. Calculate the force constant of HF molecule, if it shows IR absorption at 4138 cm^{-1} . Given that the atomic masses of hydrogen and fluorine are 1 a.m.u and 19 a.m.u respectively. What would be the wave number if hydrogen atoms are replaced by deuterium atoms? (KTU 2019 June).
16. How will you distinguish the isomers of C_4H_{10} using NMR spectroscopy?(KTU 2019)
17. Write three points of comparison between UV and IR spectrum. (KTU 2016 Jan)
18. Why is TMS taken as reference to determine chemical shift values in NMR spectroscopy? (KTU 2016 Aug)
19. What is MRI? How is it useful in the field of medicine? (KTU 2016 Aug)
20. Explain the principle of NMR spectroscopy. Which of the following nuclei can have a presence in NMR spectrum?(i) $^{16}_8\text{O}$ (ii) $^{13}_6\text{C}$ (iii) ^2_1H . Explain reason. (KTU 2016)