

Module I

Spectroscopy

Spectroscopy deals with the interaction of atoms or molecules with electromagnetic radiation. Spectroscopic methods are reliable and accurate compared to classical methods of analysis.

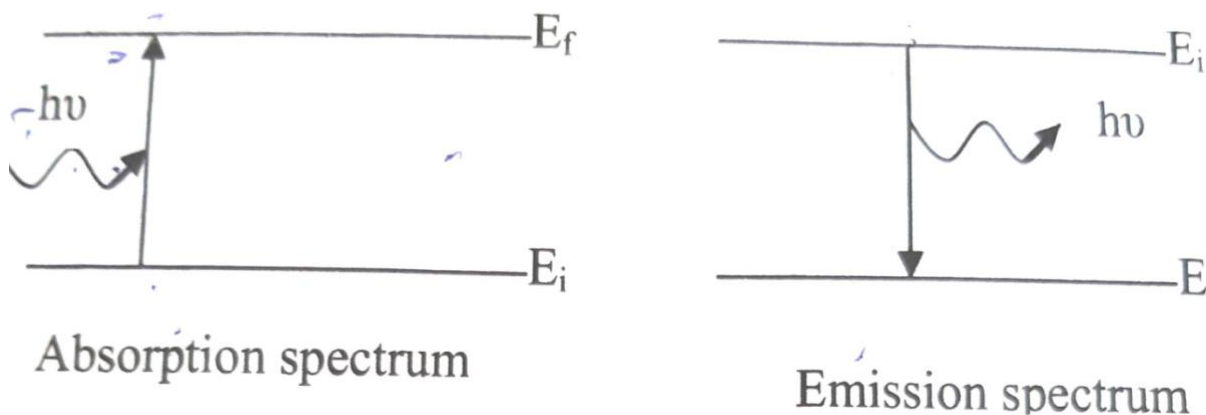
Main advantages of spectroscopic techniques are:

- 1.They require very less time for analysis.
 - 2.Less sample quantity is required.
 - 3.They give accurate result
 - 4.Sample materials remain unchanged during analysis and can be reused.
- Spectrum is graph of intensity of absorbed or emitted radiation by sample versus frequency or wavelength. It is the finger print or photograph of atoms or molecules.
 - Spectrophotometer or spectrometer is an instrument designed to measure the spectrum of a compound.

Types of spectra:

Based on the nature of interaction, the spectra can divided into two.

1. **Absorption spectra:**An atom or molecule undergo transition from the lower energy level (E_i) to high energy level (E_f) with the absorption of energy $h\nu$. The important spectral technique such as uv-Visible, IR, Microwave and NMR belongs to absorption spectrum.
2. **Emission spectra:** When an atom or molecule undergo transition from higher energy level (E_f) to lower energy level (E_i) with an emission of energy $h\nu$.Hydrogen and atomic emission spectrum are the examples of emission spectra.



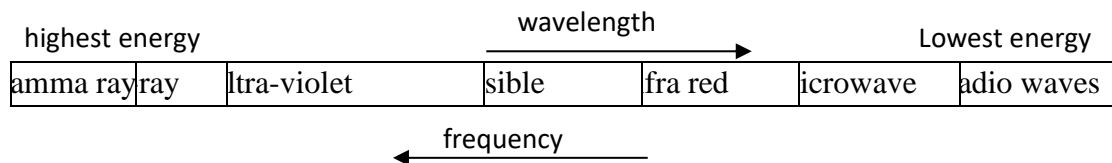
Based on the nature of interacting species, spectra can be divided into two:

1. Atomic spectra: It deals with the interaction of electromagnetic radiation with atoms, transition occurs between atomic energy levels. Eg: Atomic emission spectra, Hydrogen spectra etc

2. Molecular spectra: It deals with the interaction of electromagnetic radiation with molecules, transition occur between molecular energy levels. The important spectral technique such as UV-Visible, IR, Microwave and NMR belongs to this category.

Electromagnetic spectra

The arrangement of different types of electromagnetic radiation in the increasing order of their wavelength is known as electromagnetic spectra.



UNITS

Wavelength (λ): Distance between two adjacent crest or trough. Unit- Angstrom(\AA) or nanometer(nm)

Wavenumber: Total number of waves which can pass through a space of one centimetre.

Frequency(ν): Number of waves pass through a point in one second. $\nu = c/\lambda$

$$\text{Energy (E)} = h\nu = h \frac{c}{\lambda}$$

Molecular energy level

Molecule posses the four types of molecular energy levels.

1. Electronic energy level: It is associated with the transition of an electron from one energy state to other. Electronics energy level falls in the UV- visible region.

2. Vibrational energy level: Atoms in a molecule can vibrate by keeping the position of centre of mass constant. A vibrational level falls in the IR- visible region.

3. Rotational energy level: If a molecule rotate in space about an axis passing through its centre of mass. Rotational energy level falls in the microwave region.

4. Translational energy level: If the position of centre of mass changes with time, the molecule said to possess translational energy

Total energy of a molecule $E_{\text{total}} = E_{\text{Ele}} + E_{\text{Vib}} + E_{\text{Rot}} + E_{\text{Trans}}$ ($E_{\text{Ele}} \gg E_{\text{Vib}} \gg E_{\text{Rota}} \gg E_{\text{Trans}}$)

Beer-Lambert's Law

When a parallel beam of monochromatic radiation passed through an absorption solution of given concentration (c), the rate of decrease in intensity (-dI) with thickness (dx) is directly proportional to the intensity of the incident radiation (I) at that point and also to the concentration of the solution.

$$\text{i.e., } -\frac{dI}{dx} \propto IC$$

After integration, we get, $\log \frac{I_0}{I} = \epsilon c x$

Here I_0 = intensity of incident radiation

I = intensity of transmitted radiation

ϵ = Molar absorption co-efficient

C = Concentration of the solution

X = Thickness of a solution (Path length)

Here, $\log \frac{I_0}{I} = A$ (absorbance or optical density)

Absorbance (A) : It is the amount of light absorbed by solution at particular wavelength.

$$A = \epsilon c x$$

Transmittance (T): It is the amount of light passed through a solution. $T = \frac{I}{I_0}$

Absorbance (A) is related to Transmittance (T) by an equation

$$A = -\log T$$

Applications of Beer Lambert's Law

- To determine unknown concentration of the solution
- Used in colorimetric estimation

Limitations

- Beer Lambert's Law is applicable only for monochromatic radiation.
- It is applicable only for dilute solutions.
- If the solution containing impurities, deviation may occur.
- If the solution undergoes any dissociation, deviation may occur.

Example problem -1

1. The percentage transmittance of a 0.01M dye solution in ethanol is 20% IN A 2cm cell for light of wavelength 5000 Å. Find the absorbance (A) and molar absorption coefficient (ϵ)

Ans: $\log \frac{I_0}{I} = A = \epsilon c x$

$$A = \log \frac{I_0}{I} = \log \frac{100}{20} = 0.6989$$

$$X = 2\text{cm} = 0.2 \text{ dm}$$

$$\text{Molar absorption coefficient, } \epsilon = \frac{A}{x \times c} = \frac{0.6989}{0.2 \text{ dm} \times 0.01 \text{ mol dm}^{-3}} = \underline{\underline{349.4 \text{ mol}^{-1} \text{ dm}^2}}$$

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

$A = \epsilon c x$; Here ϵ and x are constants , therefore

$$\frac{A_1}{A_2} = \frac{C_1}{C_2}$$

$$\frac{0.045}{0.022} = \frac{0.04}{C_2}$$

$$C_2 = \underline{0.0195 \text{ M}}$$

3. A 50 ppm standard solution of Fe^{3+} after developing red colour with ammonium thiocyanate shows a transmittance of 0.2 at 620 nm while an unknown solution of Fe^{3+} after developing colour with the same amount of ammonium thiocyanate gives a transmittance of 0.4. Find the concentration of unknown Fe^{3+} solution.

$-\log T = \epsilon cx$; Here ϵ and x are constants, therefore

$$\frac{\log T_1}{\log T_2} = \frac{C_1}{C_2}$$

$$\frac{\log 0.2}{\log 0.4} = \frac{50}{C_2}$$

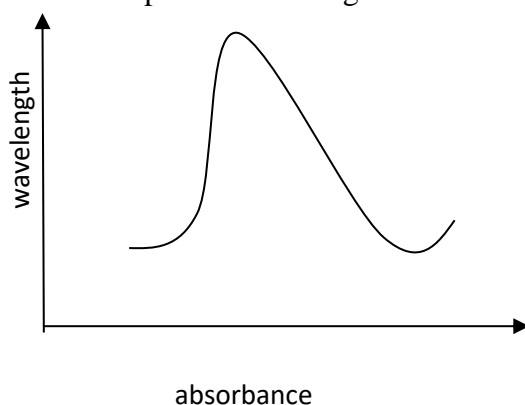
$$C_2 = \underline{28.4 \text{ ppm}}$$

UV-Visible Spectroscopy (Electronic Spectroscopy)

Principle

- Spectra obtained by the absorption of UV-Visible radiation.
- When a molecule absorbs UV-Visible radiation, the transition takes place in electronic energy levels.
- Electrons are promoted from bonding molecular orbital to anti-bonding molecular orbital.
- Different types of electrons are involved in electronic transitions. They are σ , π and non-bonding electrons (n).
- UV-Visible range is 200-800 nm

Spectra obtained is a plot of wavelength versus absorbance.

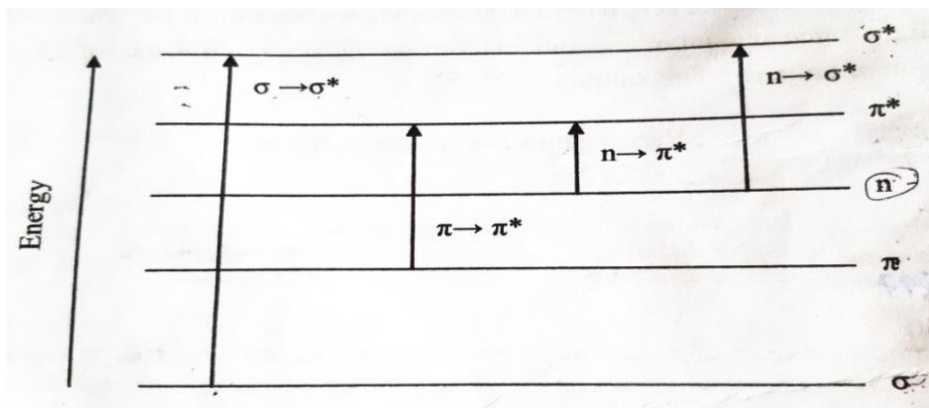


Classification of electronic transition

When a molecule absorbs UV-Visible radiation, electrons are promoted from bonding molecular orbital to anti-bonding molecular orbital. Different types of electrons are involved in electronic transitions. They are σ , π and non-bonding electrons (n). Electronic transitions are classified into four types. They are,

- σ - σ^* transition, π - π^* transition,

n - π^* transition, n - σ^* transition



σ - σ^* transition

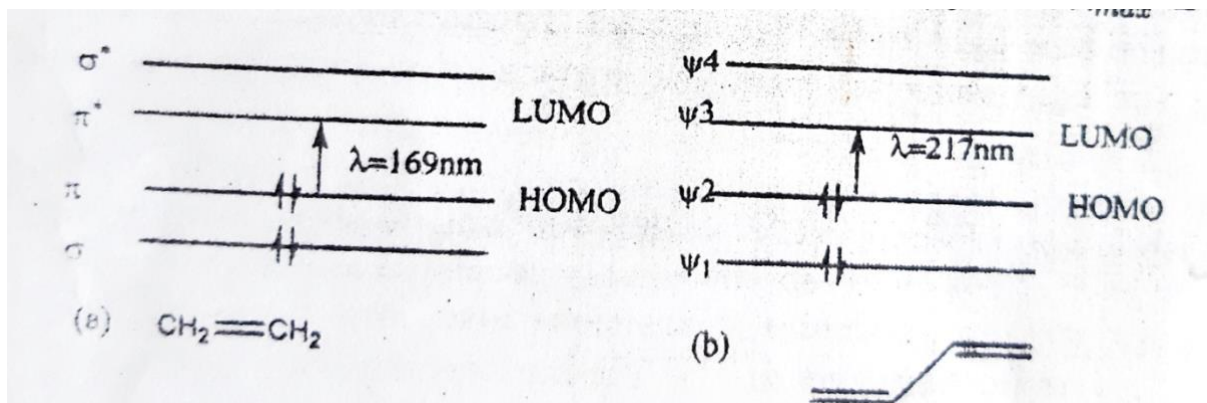
- Saturated hydrocarbon shows σ - σ^* transition
- This transition occurs at below 150 nm
- They are colourless compounds.

Eg: C-C and C-H bonds shows σ - σ^* transition. CH_4 , $\text{CH}_3\text{-CH}_3$ etc

π - π^* transition

- Unsaturated hydrocarbons containing double or triple bonds shows π - π^* transition.

For Eg. C=C of **ethylene** molecule gives an absorption maxima at 169 nm. So normal UV machines will not show such transitions. In the case of molecule containing conjugated double bonds, these transitions can be observed from highest occupied π molecular orbital (HOMO) to lowest unoccupied π molecular orbital (LUMO). In the case of **1,3-butadiene** these transitions are observed at 217 nm, 1,3-butadiene has four π molecular orbitals ($\Psi_1, \Psi_2, \Psi_3, \Psi_4$) formed by the linear combination of four atomic orbitals (p orbitals). Here Ψ_1 & Ψ_2 are bonding molecular orbitals and Ψ_3 & Ψ_4 are antibonding π molecular orbitals. Here the transition takes place from HOMO Ψ_2 to LUMO Ψ_3 with $\lambda_{\text{max}} = 217 \text{ nm}$

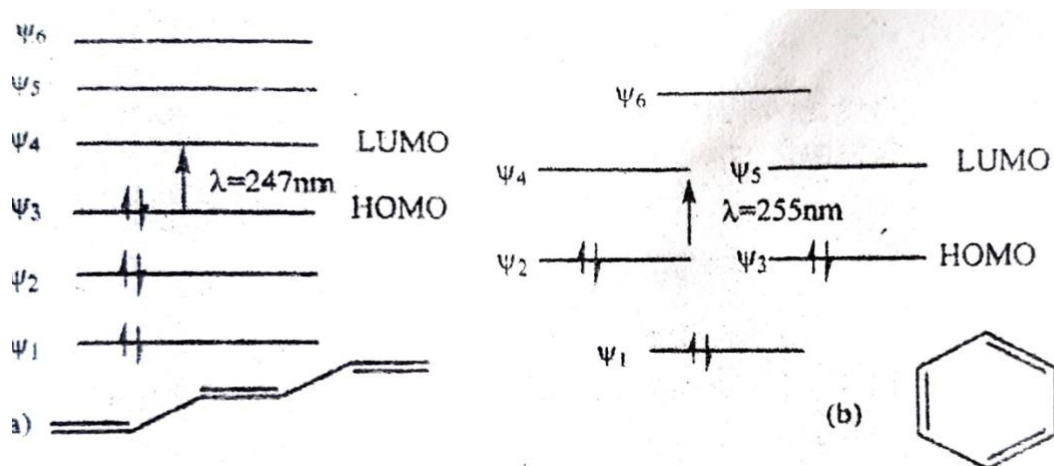


1,3,5-hexatriene:

There are three double bonds in conjugation. It has six π molecular orbitals ($\Psi_1, \Psi_2, \Psi_3, \Psi_4, \Psi_5, \Psi_6$) formed by the linear combination of six atomic orbitals (p orbitals). Here Ψ_1, Ψ_2 & Ψ_3 are bonding molecular orbitals and Ψ_4, Ψ_5 & Ψ_6 are antibonding π molecular orbitals. Here the transition takes place from HOMO Ψ_3 to LUMO Ψ_4 with $\lambda_{\text{max}} = 247 \text{ nm}$

Benzene:

There are three double bonds in conjugation. It has six π molecular orbitals ($\Psi_1, \Psi_2, \Psi_3, \Psi_4, \Psi_5, \Psi_6$) formed by the linear combination of six atomic orbitals (p orbitals). Here Ψ_1, Ψ_2 & Ψ_3 are bonding molecular orbitals and Ψ_4, Ψ_5 & Ψ_6 are antibonding π molecular orbitals. Here the transition takes place from HOMO to LUMO with $\lambda_{\text{max}} = 255 \text{ nm}$. Here Ψ_2 & Ψ_3 are degenerate orbitals (same energy) and Ψ_4 & Ψ_5 are also degenerate.



(a): Molecular energy level diagram of (a) 1,3,5-hexatriene (b) benzene

n- π^* transition

Such transitions are observed in aldehydes and ketones, which contain C=O group which has both π electrons and non bonding electrons (with oxygen atom). These transitions are generally observed with low intensity when compared with σ - σ^* & π - π^* transitions.

Eg. CH_3CHO , $\text{C}_6\text{H}_5\text{CONH}_2$

- Unsaturated aliphatic ketones show transitions at about 280 nm

n- σ^* transition

- Saturated compounds containing hetero atoms like O, N, S and Halogens (Cl, Br, I, F) show n- σ^* transition.

Eg: CH_3Cl , $(\text{CH}_3)_3\text{N}$

UNIVERSITY QUESTIONS

1. Most of the electronic spectrum appears as a broad band. Why?

Ans: Electronic transitions of a molecule are always accompanied by vibrational and rotational transitions. Therefore most of the electronic spectrum appears as a broad band.

2. List the electronic transition possible when UV light is absorbed by the following molecules.

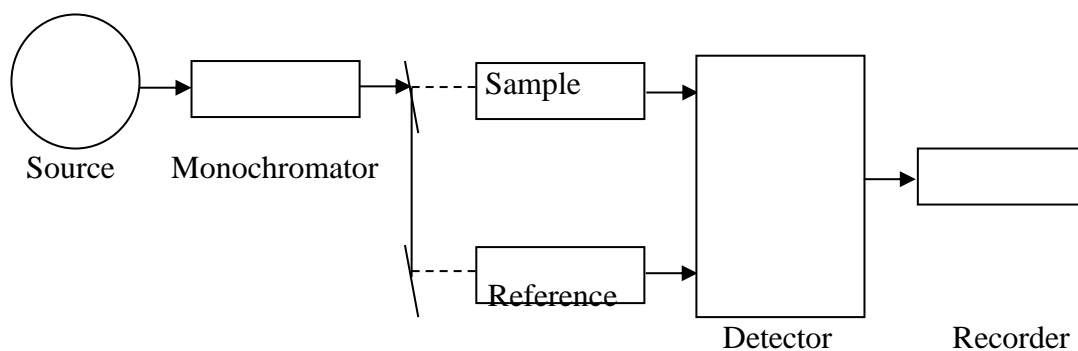
a) $\text{CH}_4 \rightarrow \sigma$ - σ^* transition

b) $\text{CH}_3\text{Cl} \rightarrow \sigma$ - σ^* transition, n- σ^* transition

c) $\text{HCHO} \rightarrow \sigma$ - σ^* transition, n- σ^* transition, π - π^* transition, n- π^* transition

Instrumentation

Spectrophotometer is a device which compares the intensity of the transmitted light with that of incident light.



- In uv-visible spectrophotometer, a beam of light is split into two equal halves.
- One half of the beam is passed through the sample and the other half is passed through the reference.
- A very dilute solution of sample is prepared using a suitable solvent, and is taken in a cuvet.
- The pure solvent is taken as the reference. Eg: -water, ethanol, hexane, cyclohexane.
- The intensities of light beams are then measured by electronic detector.
- If the sample does not absorb light of a given wavelength then, $I = I_0$
- If the sample absorbs light $I < I_0$.

- This difference is detected and recorded.
- Graph is plot with absorbance vs wavelength.

Applications of UV-Visible spectroscopy

- Detection of aromatic compounds and conjugated dienes.
- Determine the unknown concentration.
- Study of kinetics of chemical reaction.
- Determination of impurities.
- Determine the ozone present in the environment.

IR Spectroscopy (Vibrational spectroscopy)

Principle

- Vibrational spectroscopy arises due to the absorption of IR radiation.
- When a molecule absorbs IR radiation, vibrational transition takes place.
- The essential condition for a molecule to show IR spectrum is change in dipole moment during vibration.
- Homodiatomic molecules like H₂, N₂, Cl₂ etc does not show IR spectra.
- Heteroatomic molecules like CO₂, HCl etc show IR spectra.
- Molecules are made by atoms linked with a chemical bond. The movement of atoms and chemical bond are like a spring and ball. Its characteristic vibration is called natural frequency of vibration.
- When the applied IR frequency becomes equal to natural frequency of vibrations, absorption of IR takes place and we get a peak.

Number of vibrational modes in a molecule

A molecule can vibrate in many modes and each mode is called vibrational modes.

For a linear molecule, there will be two rotational 3 translational ie, for a linear molecule there will be $(3N - 5)$ modes of vibration where N is the number of atoms.

Eg: CO₂, HCl.

In a nonlinear molecule, there will be 3 rotational and 3 translational degrees of freedom ie ,for a non linear molecule there will be $(3N - 6)$ modes of vibration. Eg: H₂O

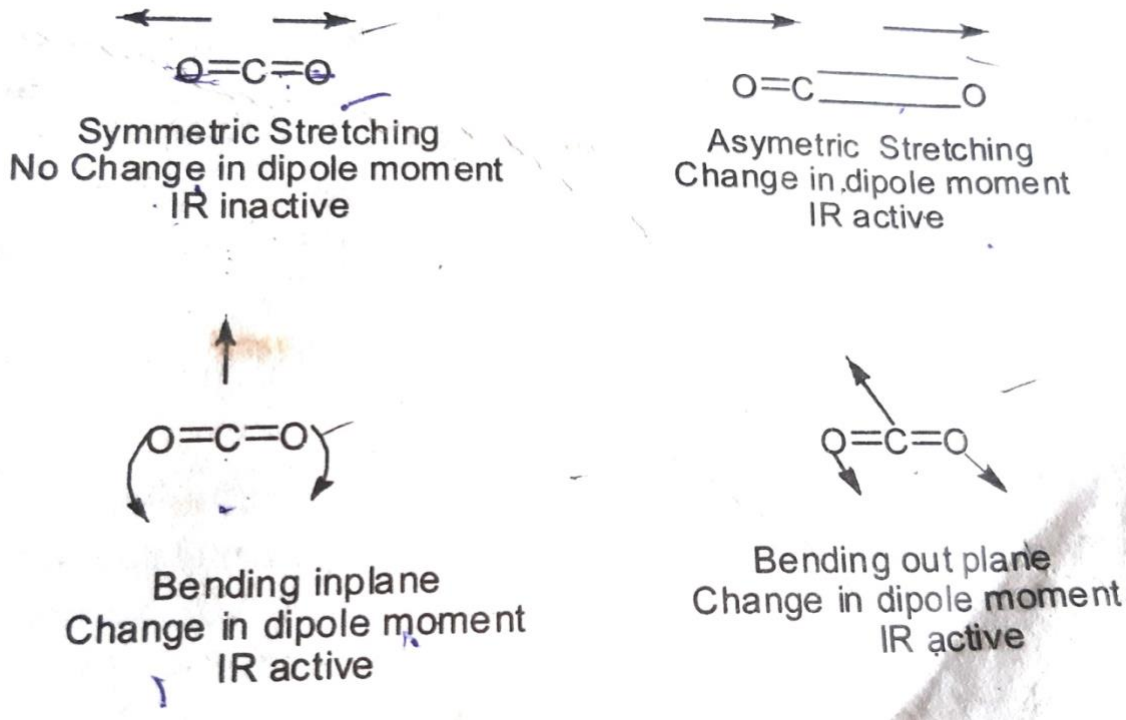
Linear molecule:

For a linear molecule there are 3 translational and 2 rotational degrees of freedom, therefore total number of vibrational Modes possible is equal to $3n - 5$

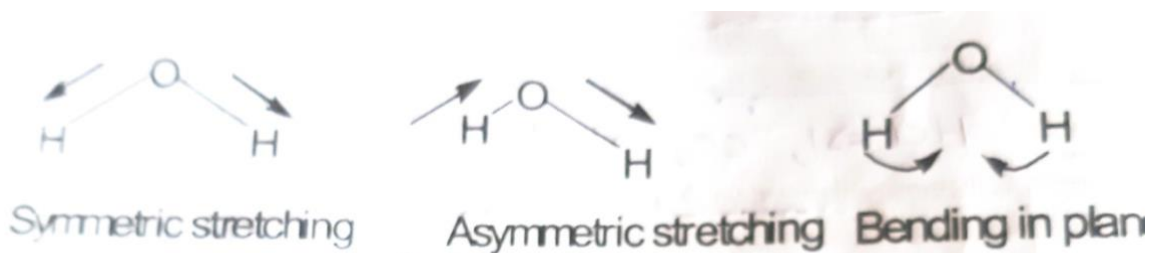
For a diatomic molecule there is only one $(3 \times 2 - 5 = 1)$ vibrational mode, i.e, stretching vibration. eg. HCl can undergo one stretching vibration.

Linear triatomic molecule like CO₂ has four $(3 \times 3 - 5 = 4)$ vibrational modes, symmetric stretching ,asymmetric stretching and two bending vibrations in two mutually perpendicular planes .out of the four vibrational modes, only three are IR active. the symmetric stretching does not involve the change of dipole moment and is not IR active .The two bending modes are equivalent(degenerate) therefore only two absorption frequencies observed in the case of CO₂ at 2349 cm⁻¹ for asymmetric

stretching and 667cm^{-1} for bending vibration. For Linear molecule like HCN, all the four modes are IR active



Non linear molecule : For a non linear molecule there are $3n-6$ vibrational degrees of freedom. For example H_2O molecule has three ($3 \times 3 - 6 = 3$) vibrational freedoms. They are ,symmetric stretching, asymmetric stretching and a bending Mode.unlike CO_2 here two bending modes are not possible for H_2O .



Vibrational energy States of diatomic molecule

A simple harmonic oscillator can be considered as a model for vibrating diatomic molecule . Consider two atoms of masses m_1 and m_2 connected by means of chemical bond of force constant 'k'. The system is analogous to the system of two masses connected by means of an ideal spring .According to classical mechanics the fundamental frequency of vibration (ν_0) is given by

The fundamental frequency of vibration (ν_0) of a diatomic molecule is given by

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

where K is the force constant, μ - reduced mass.

i.e., $\mu = \frac{m_1 \times m_2}{m_1 + m_2}$ where m_1 and m_2 are the masses of two atoms.

$$\text{Energy of vibration } E = \left(V + \frac{1}{2} \right) h\nu_0$$

Where V is called vibrational quantum number which has values 0,1,2,3,.....

In the ground state ($V=0$)

$E = \left(0 + \frac{1}{2} \right) h\nu_0 = \frac{1}{2} h\nu_0$, Which is called zero point energy, which implies that even at absolute zero (thermal death) there will be a vibration to satisfy Heisenberg's uncertainty principle. It is to be noted that a classical oscillator can have zero energy, but quantum systems like molecules can never be vibrationally at rest, but rotational energy of a molecule can have zero energy, as seen in rotational spectroscopy.

Let us consider a Molecule undergoing a transition from lower vibrational level v to up vibration level v' , then the difference in energy is equal to electromagnetic radiation of energy $h\nu$ absorbed.

$$\Delta E = h\nu$$

$$\left(V' + \frac{1}{2} \right) h\nu_0 - \left(V + \frac{1}{2} \right) h\nu_0 = h\nu$$

$$\text{OR } (V' - V) h\nu_0 = h\nu \dots\dots(1)$$

According to quantum mechanics, for the transition of vibration energy levels, the selection rule is given by $\Delta V = \pm 1$ i.e., $V' - V = \pm 1$

Therefore (1) becomes

$h\nu_0 = h\nu$ or $\nu_0 = \nu$, It implies that frequency of absorbed infrared radiation (ν) is equal to fundamental vibrational frequency of the molecule (ν_0). IR spectrum is a plot of %transmittable against wave number so it gives downward peak.

Problem 2.4.1. The CO molecule absorbs infrared frequency of 2140cm^{-1} . Calculate the force constant of the chemical bond, given that atomic masses of C = 12 amu and O = 16 amu.

Ans: From equation (1)

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

squaring and rearranging force constant (k) can be written as

$$k = 4\pi^2 \nu_0^2 \mu$$

Frequency of absorbed infrared radiation (ν) is equal to fundamental vibrational frequency

of the molecule (ν_0). Therefore

$$k = 4\pi^2\nu^2\mu$$

but $\nu = cD$ Therefore

$$k = 4\pi^2(cD)^2\mu$$

$$\mu = \frac{m_1m_2}{m_1 + m_2}$$

$$\mu = \frac{12 \times 16}{12 + 16} \times 1.66 \times 10^{-27} \text{ Kg} = 1.138 \times 10^{-26} \text{ Kg}$$

$$k = 4 \times 3.14^2 \times (3 \times 10^8 \text{ ms}^{-1} \times 214000 \text{ m}^{-1})^2 \times 1.138 \times 10^{-26} \text{ Kg}$$

$$k = 1849 \text{ Nm}^{-1}$$

Applications

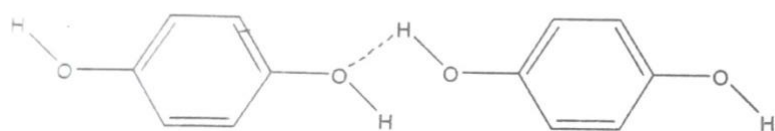
- To calculate the force constant of a diatomic molecule.
- Detection of functional groups in organic molecules.

The presence of functional groups can be readily detected from the stretching vibrations of the bonds present in the functional group. For example absorption range C=O group in saturated ketones is $1700-1725 \text{ cm}^{-1}$, -OH group in alcohol is at $3300-3500 \text{ cm}^{-1}$, NH_2 group is at $3200-3300 \text{ cm}^{-1}$, C=C in alkenes is $1620-1650 \text{ cm}^{-1}$ and C-H in organic compounds is at $2900-3000 \text{ cm}^{-1}$.

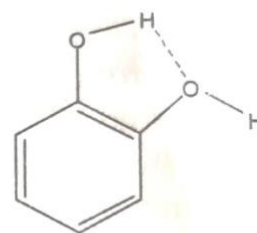
- To check the purity of a sample.
- Identification of unknown compounds.
- To study the progress of chemical reaction.
- To distinguish between intra and intermolecular hydrogen bonding in a molecule.

This is done by taking the IR spectra of compound at different dilution. As dilution increases, in case of intramolecular hydrogen bonding, stretching frequency ($3300-3500 \text{ cm}^{-1}$) remains unchanged. But in case of intermolecular hydrogen bonding stretching frequency decreases.

Eg. Ortho- hydroxy phenol, and para hydroxy phenol. In p-hydroxy phenol there exists inter molecular hydrogen bonding. The molecules get separated on dilution and intermolecular hydrogen bonding weakens and there is shift of absorption frequency with dilution. In o-hydroxy phenol the hydrogen bonding type is intramolecular which is not affected on dilution.



Inter molecular H-bonding in p-hydroxy phenol



intramolecular H-bonding in o-hydroxy phenol

University Questions

1. IR spectrum considered as molecular fingerprint. Why?

Ans: IR spectra arises due to the different types of vibration and rotation of the molecule. Different functional groups produce easily recognisable bands at definite positions in the spectrum. In addition to these bands, the spectrum shows a cluster of absorption bands. These are

characteristic of the molecule like finger print of an individual. Hence IR spectra considered as molecular fingerprint.

NMR Spectroscopy

NMR (Nuclear Magnetic Resonance) spectroscopy is a powerful tool for investigation of nuclear structure of atom or molecule.

Principle

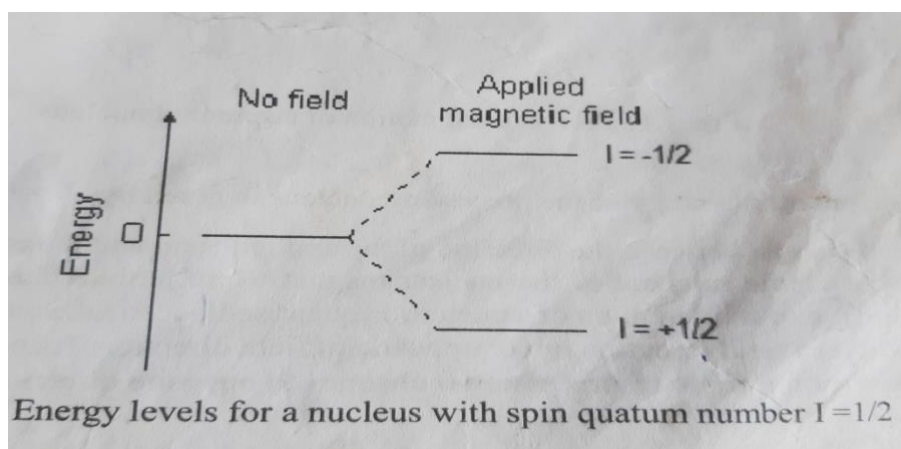
- NMR spectrum arises due to the absorption of radiofrequency radiation.
- When a molecule absorbs radiofrequency radiation transition takes place in nuclear energy levels.
- Nuclear energy levels created by keeping nuclei in a magnetic field.
- Nucleus with spin quantum number greater than zero exhibits NMR.
- A spectrum is a plot of strength of magnetic field versus intensity of radiation.

Rules for determining net spin of the nucleus

- If the number of neutrons and the number of protons are both even, then the nucleus has no spin, i.e., $I=0$. Eg: ${}^2\text{He}^4$, ${}^{12}\text{C}^{12}$, ${}^{16}\text{O}^{16}$
- If the number of neutrons plus the number of protons (mass number) is odd, then the nucleus has a half integral spin, i.e., $I=1/2$. Eg: ${}^{13}\text{C}^{13}$, ${}^{19}\text{F}^{19}$, ${}^{31}\text{P}^{31}$
- If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin, i.e., $I=1, 2, 3, \dots$. Eg: ${}^1\text{H}^2$, ${}^3\text{Li}^6$

Theory

- Consider the nucleus with spin $I=1/2$. According to quantum mechanism it has $(2I+1)$ possible orientations. i.e., $2 \times 1/2 + 1 = 2$ orientation.
- In the absence of an external magnetic field, these orientations are of equal energy.
- In the presence of an external magnetic field, the energy level splits into two.



Consider the nucleus in a magnetic field. The nucleus is in the lowest energy level aligned in the direction of the field.

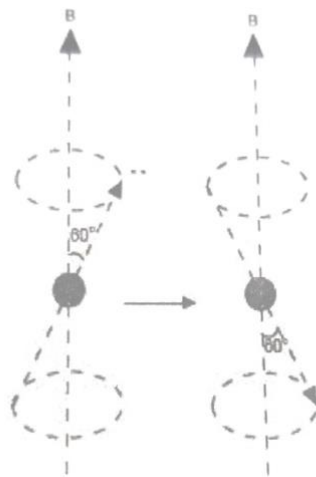
- When the nucleus is spinning on its axis in the presence of magnetic field the axis of spin will precess around the magnetic field just like a processional motion of a spinning top.
- The frequency of precession is termed as Larmor frequency or processional frequency.
- When this frequency become identical to radiofrequency resonance occurs.
- On irradiating the proton with a correct frequency from a radiofrequency source it will absorb energy & goes to excited state.
- Then it loses energy and return to ground state.
- Alternatively become excited and unexcited is said to be in a state of resonance.
- The emitted radiofrequency signal gives the NMR spectrum.

Flipping of spin

Larmor frequency becomes identical to the radio frequency, resonance occurs and flipping of proton takes place with the absorption of radiation .

The potential energy of the precessing nucleus is given by; $E = -\mu B \cos \theta$

Where θ is the angle between the direction of the applied field and the axis of nuclear spin and μ the dipole moment of the nuclear magnet. It can take only two orientations either 60° with the field direction or 60° opposite of field direction. If energy is absorbed by the nucleus , then the angle of procession θ changes to opposite direction. For a nucleus of Spin $I = \frac{1}{2}$ or $\cos 60^\circ$ absorption of radiation "flips" the magnetic moment to $I = -\frac{1}{2}$ or $-\cos 60^\circ$ that it opposes the applied field (the higher energy state).



Calculation of transition energy

The nucleus has a positive charge and its spinning. This generates a small magnetic field. The nucleus therefore possesses a magnetic dipole moment, μ which is proportional to its spin I .

$$\mu = \frac{\gamma I h}{2\pi}$$

the constant, γ is called the gyromagnetic ratio and is a fundamental nuclear constant which has a different value for every nucleus. h is the Planck's Constant. The energy of nucleus

$$E = -\frac{\gamma h B}{2\pi}$$

$$\text{Energy difference } \Delta E = -\frac{\gamma h B \Delta I}{2\pi} \text{ where } \Delta I = -\left(\frac{1}{2} - \frac{1}{2}\right) = -1$$

when an electromagnetic radiation of frequency (ν) comes in resonance ,

$$\Delta E = h\nu = \frac{\gamma h B}{2\pi} \text{ OR } \nu = \frac{\gamma B}{2\pi} = \text{Larmor frequency (}\nu_L\text{)}$$

At resonance, $\nu = \nu_L$

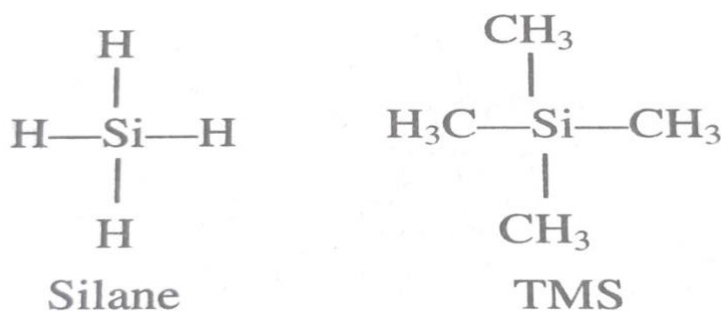
The energy difference between the two States is directly proportional to the strength of the applied field.

CHEMICAL SHIFT

Chemical shift is an important feature of NMR spectra. When a molecule is placed in a magnetic field, its electrons are caused to circulate and thus they produce secondary magnetic field. This induced magnetic field may oppose or reinforce the applied magnetic field. It depends upon the chemical environment of the proton.

In a given magnetic field, different set of protons require different frequencies to make absorption. This shift in frequency is called chemical shift. In other words it is the difference between the absorption positions of sample protons from that of standard (TMS).

Reference compound of NMR Spectroscopy



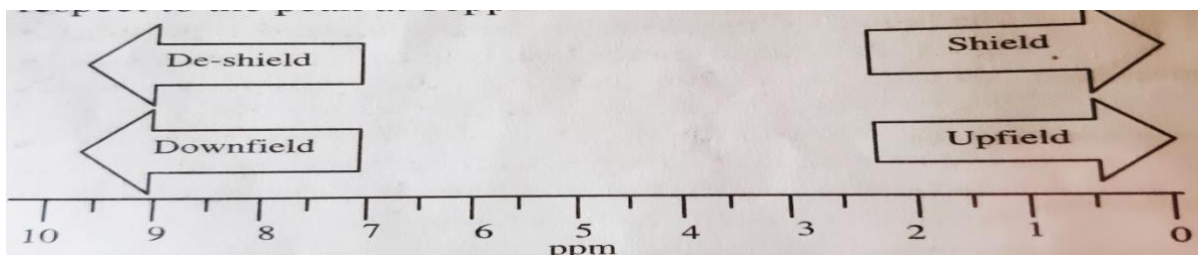
TMS[(CH₃)₄Si] is the most common reference compound used in NMR. Chemical shift value of TMS is 0ppm. It is used as reference because

- Chemically inert .So does not react with other samples.
- Volatile and easy to remove

- Low boiling point
- All protons are identical and gives a single signal

$$\text{Chemical Shift } (\delta) = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{Operating frequency in MHz}}$$

Chemical shift scale

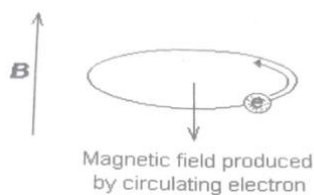


When ^1H NMR is taken using a 100 MHz instrument, For eg, the signal for the proton in chloroform (CHCl_3), appears at 728 Hz higher from the TMS signal. The chemical shift may also be defined as the shift in radio frequency from TMS per MHz radio frequency due to shielding or deshielding of hydrogen nuclei in different structural environment.

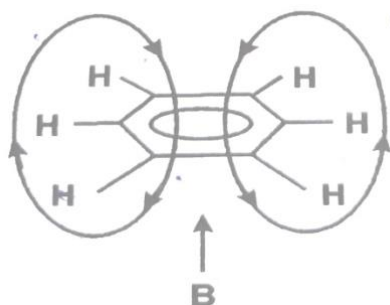
$$\begin{aligned} \text{Chemical Shift } (\delta) &= \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{Operating frequency in MHz}} \\ &= 728/100 = \underline{7.28 \text{ ppm}} \end{aligned}$$

Causes of chemical shift

1. Shielding : If the induced magnetic field opposes the applied field, the net field felt by a proton in a molecule will be less than the applied field, and the proton is said to be shielded. If the molecule contains more shielded protons, the greater must be the strength of the applied field in order to achieve resonance with radio frequency and produce an absorption signal. A more shielded proton absorbs RF radiation at low δ value.



2. Deshielding : The induced magnetic field reinforces the applied field, the net field felt by a proton in a molecule will be greater than the applied field, and the proton is said to be deshielded. eg: protons in an aromatic ring. Deshielded protons absorb RF radiation at high δ value.



Factors affecting chemical shift

1. Electronegativity.

Electronegative groups are attached to $-CH$ group decreases the electron density around the proton, there is deshielding and chemical shift increases.

Chemical shift increases with increase in electronegativity.



Chemical shift of CH_3 protons	CH_3F	CH_3-O-CH_3	$(CH_3)_3N$	CH_3-CH_3
	4.3	3.2	2.2	0.9

2. Cumulative effect of electronegative substituent's.

Cumulative effect of electronegative substituent's attached to $-CH$ groups decreases the shielding effect there for the chemical shift increases.

$CHCl_3$	CH_2Cl_2	CH_3-Cl	
Chemical shift(δ)	7.3	5.3	3.1

3. Distance from the electronegative atom.

When an electronegative atom is substituted in the hydrocarbon chain, the electronegativity around the proton decreases. As electronegativity around the proton decreases, shielding decreases and δ value increases.

$CH_3-CH_2-CH_2-Cl$			
$\delta =$	1	1.4	3.4

4. Hydrogen bonding

Presence of Hydrogen bonding changes chemical shift values. The more hydrogen bonding, more protons are deshielded and chemical shift increases.

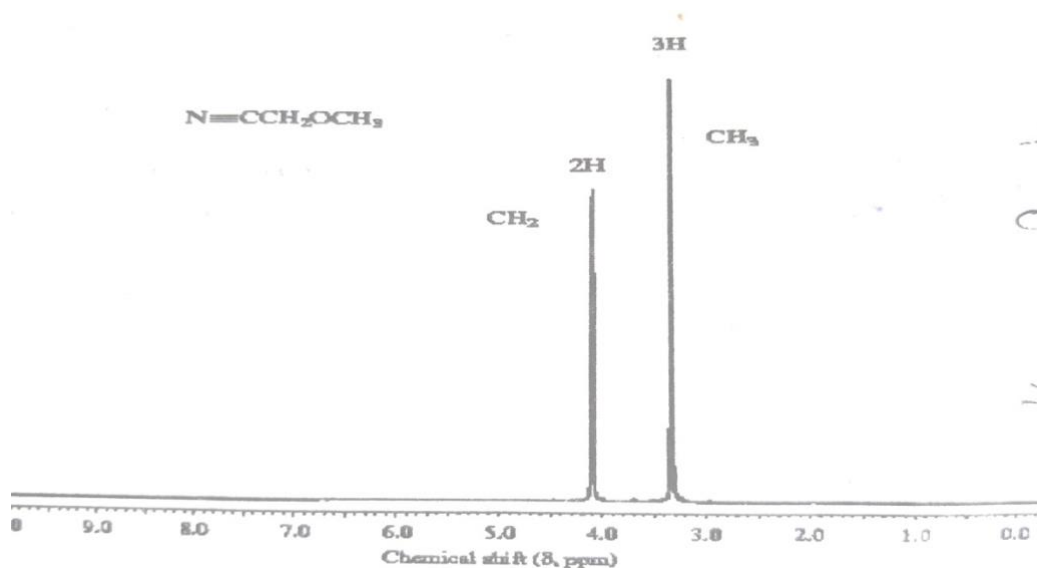
5. Magnetic anisotropic effect.

Electron present in the π system interact with the applied magnetic field causes anisotropy (non uniform magnetic field). It causes both shielding and deshielding effect.

Interpretation of chemical shift in a molecule

1. The number of signals, tells us how many different kinds of protons are present.
2. The position of the signals (values) gives information about the nature of protonic environment.
3. The intensity of the signals are measured by the area under each peak, which tells us the relative ratios of the different kinds of protons.

For example $\text{CH}_3\text{-O-CH}_2\text{CN}$, there are two kinds of protons, CH_3 protons and CH_2 protons. The CH_2 protons are less shielded (higher Delta Value) due to electron withdrawal from either side by the electronegative atoms. The peak area ratio is equal to 3:2, which is proportional to the number of H- atoms in each set.



Spin-Spin Splitting

NMR spectrum of any compounds at lower resolution gives broad signals. But the same at high resolution cause further splitting of NMR signal by Spin-Spin interaction.

Further splitting of NMR Spectrum due to the interaction between protons on adjacent atoms is referred to as a Spin-Spin splitting or coupling. Splitting arises due to the coupling interaction between neighbouring protons.

(n+1) rule

The multiplicity of a signal can be calculated by (n+1) rule, where n-is the number of protons on adjacent carbon atom.

If there are 'n' protons(H) in the neighbouring carbon atoms, the signal will split in to 'n+1'.

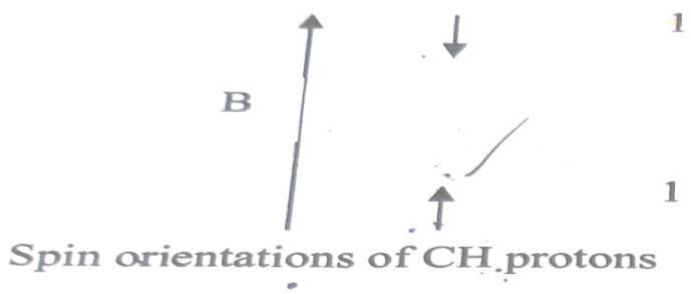
Coupling constant (J)

It is the distance between two adjacent peaks in a given NMR signal.

Eg:-NMR spectrum of $\text{CH}_3\text{-CH-Cl}_2$.

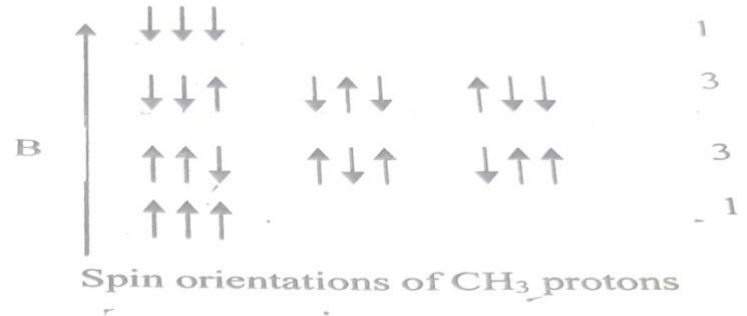
- Peak area ratio 3:1
- The -CH_3 protons split in to doublet (2) under the influence of -CH protons.
- Peak intensity ratio 1:1

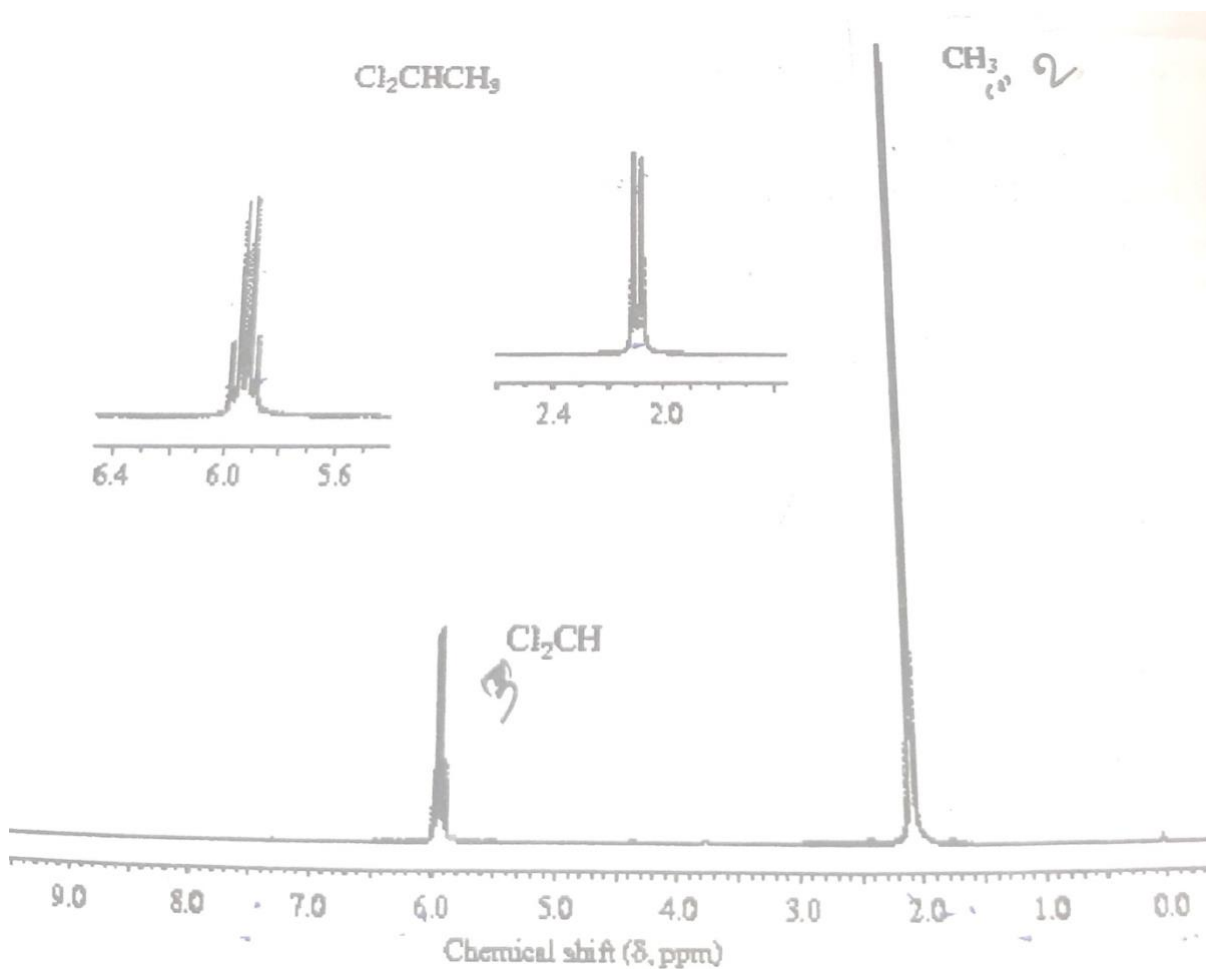
The spin of -CH protons can orient only in two ways



Similarly the -CH proton split in to quartet (4) with intensity ratio 1:3:3:1, under the influence of -CH₃ protons.

The spin of 3CH₃ protons can orient in 4 different ways.





Peak intensity ratio is given by pascals triangle

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      1 1
     1 2 1
    1 3 3 1
   1 4 6 4 1
  1 5 10 10 5 1

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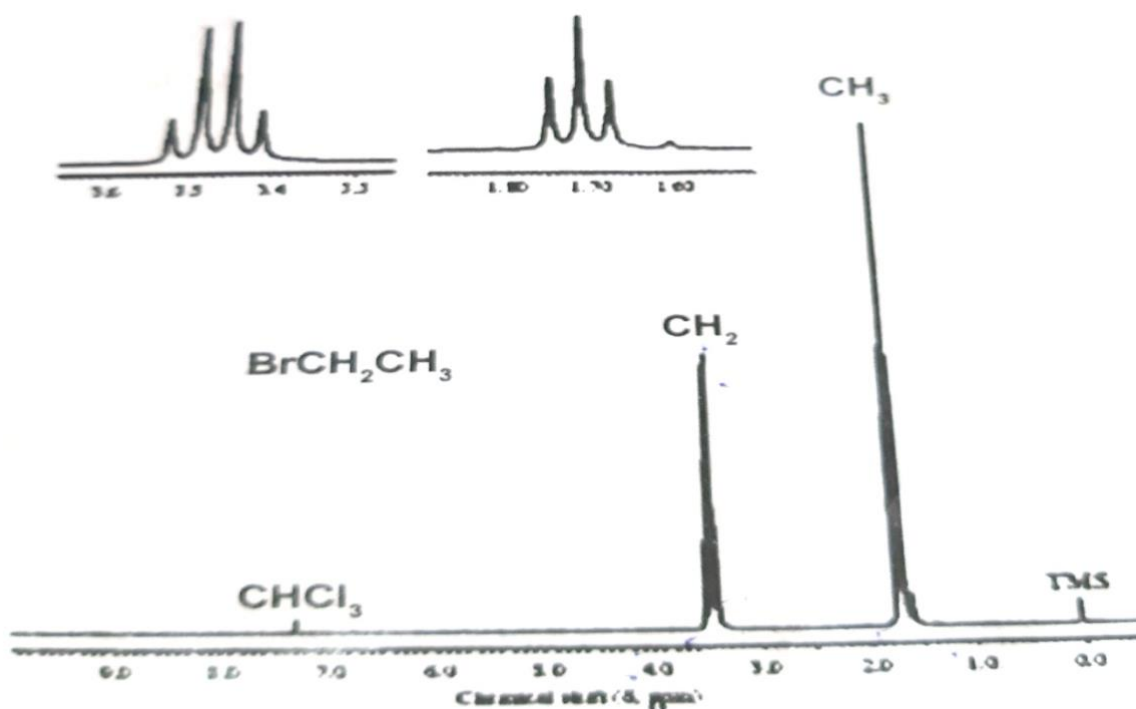
Eg:- Predict the NMR signal and splitting patterns of the NMR spectrum of Ethyl Bromide.



- Peak area ratio -3:2
- CH_3 split in to triplet(3)
- Peak intensity ratio – 1:2:1
- CH_2 split in to quartet(4)

- Peak intensity ratio 1:3:3:1

NMR spectrum



Applications of NMR

- Used for the structural elucidation of organic molecules.
- Used to study the hydrogen bonding.
- Study of isotopes other than protons.
- To study the keto-enol tautomerism.
- Used in quantitative analysis.
- MRI

MRI spectroscopy

It is a medical imaging technique used in radiology to visualise internal structure of body.

- Our body tissue contain lots of water and hence protons
- When the person is placed inside the powerful magnetic field of the machine, the protons align with the direction of the magnetic field. This external magnetic field, applied on the nuclei produce energy levels.
- Then a radio frequency, called resonance frequency is applied perpendicular to the magnetic field, causes transition between these levels. When such a radiation is absorbed, thenuclei are converted into excited state.
- If the RF radiations are removed, the nuclei will re-emit the absorbed radiation. This process is called *relaxation*.

- During relaxation a radiofrequency signal is generated from our body. This signal is called FID (Free induction decay response signal).
- The FID response signal is measured by a conductive field coil placed around the object being imaged.
- This measured and processed to obtain 3D images.

Application

- Used to diagnose the treatment in tumours of chest, brain, liver related diseases and heart problems.
- To determine fluorine concentration in body parts.
- To determine excessive fat deposition on different body organ and blood vessels.