

KSU CET UNIT

FIRST YEAR NOTES



14/01/2020
Tuesday

MODULE II

Spectroscopic Techniques and Applications

Introduction: Types of spectrum - electromagnetic spectrum - molecular energy levels - Beer Lambert's law (Numericals). UV-Visible Spectroscopy - Principle - Types of electronic transitions - Energy level diagram of ethane, butadiene, benzene and hexatriene.

Instrumentation of UV-Visible Spectrometer and applications. IR Spectroscopy - Principle - Number of vibrational modes - vibrational energy states of a diatomic molecule and Determination of force constant of diatomic molecule (Numericals) - Applications. ^1H NMR Spectroscopy - Principle - Relation b/w field strength and frequency - chemical shift - spin-spin splitting (Spectral problems) - coupling constant (definition) - applications of NMR - including MRI (brief).

Spectroscopy

> Spectroscopy deals with the interaction of atom, molecule or matter with electromagnetic radiation.

> It involves the production, measurement and interpretation of spectra arising by the absorption or emission of electromagnetic radiation by atom or molecule.

> This spectroscopic method is widely used today because ;

Advantages of spectroscopy :

- Requires very less time for analysis.
- Requires less sample quantity.
- Sample material remain unchanged during analysis.
- They give accurate results.

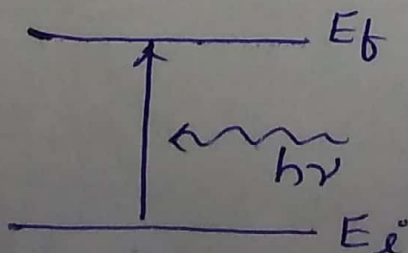
* Types of Spectra

(1) Based on the nature of interaction.

It is divided into two types :

(a) Absorption spectrum

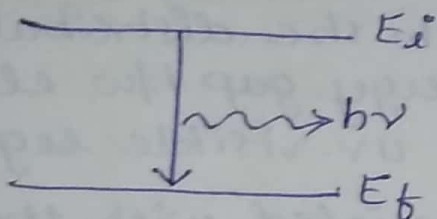
When an atom or molecule undergo a transition from lower energy level E_i to the higher energy level E_f by the absorption of photon of energy $h\nu$, the spectrum obtained is called absorption spectrum.



Examples: UV, visible spectrum, IR spectrum, NMR spectrum.

(b) Emission Spectrum

When an atom or molecule undergo a transition from higher energy level E_i to the lower energy level E_f by the emission of photon of energy $h\nu$, the spectrum obtained is called emission spectrum.



Example: Hydrogen spectrum.

(I) Based on the nature of interacting species.

(a) Atomic spectrum

Atomic spectrum arises by the transition b/w the atomic levels.

(b) Molecular spectrum

Molecular spectrum arises by the transition b/w the molecular energy levels.

eg: IR spectrum, NMR spectrum, UV-visible

* Electromagnetic spectrum

$$E = h\nu \quad h = 6.626 \times 10^{-34} \text{ Js}$$

Electromagnetic radiation contains mutually oscillating electric and magnetic waves.

$\nu = \frac{c}{\lambda}$ travels with a velocity of light.

$$\bar{\nu} = \frac{1}{\lambda}$$

$\bar{\nu} \rightarrow$ wave number (cm^{-1} or m^{-1})

Electromagnetic Spectrum is the arrangement of all electromagnetic radiation with increasing wavelength or decreasing frequency.

Molecular Energy Levels

1. Electronic Energy level
2. vibrational Energy level
3. Rotational Energy level
4. Translational Energy level.

(1) It is associated with the distribution of e^- s in various levels. Energy gap b/w electronic energy level falls in UV-visible region.

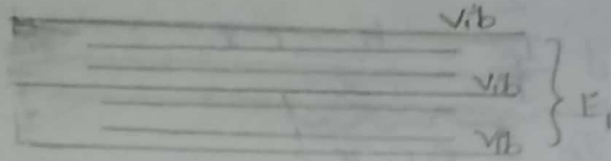
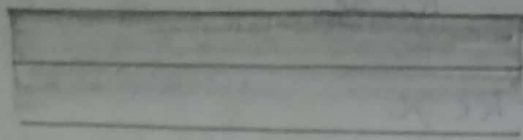
(2) It is the energy associated with the vibration of molecule. Energy gap b/w the vibration energy level falls in IR region. vibration may be either Bond stretching / Bond bending.

(3) It is associated with the spinning of the molecule about an axis passing through its centre of mass. The energy gap b/w rotational energy level falls in microwave region.

(4) It is concerned with the overall movement of the molecule along three axes.

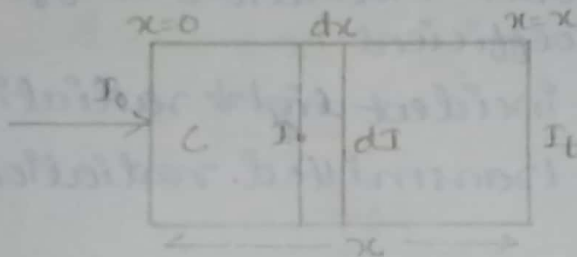
→ UV-visible spectrum appears as broad band. why?

Electronic energy levels are always associated with several vibrational and rotational energy levels. So, UV-visible spectrum appears as broad band.



Imp.
*
✓

Beer-Lambert's Law



"It states that, when a parallel beam of monochromatic electromagnetic radiation is passed through an absorbing solution of concentration 'c', the rate of decrease in intensity with the thickness of the solution is directly proportional to the intensity of incident radiation at that point and also to the concentration of the solution."

$$-\frac{dI}{dx} \propto IC$$

$$-\frac{dI}{dx} = KIC$$

$$-\frac{dI}{I} = Kc dx$$

$$-\int_{I_0}^I \frac{dI}{I} = Kc \int_0^x dx$$

$$-\ln I \Big|_{I_0}^I = Kc x \Big|_0^x$$

$$-\ln I + \ln I_0 = kcx$$

$$\ln a - \ln b = \ln \frac{a}{b}$$

$$\ln \frac{I_0}{I} = kcx$$

$$2.303 \log \frac{I_0}{I} = kcx$$

$$\log \frac{I_0}{I} = \frac{k}{2.303} cx$$

$$\log \frac{I_0}{I} = \epsilon cx$$

where ϵ is the molar extinction coefficient / molar absorption coefficient.

I_0 - Intensity of incident light radiations.

I - Intensity of transmitted radiation.

→ Absorbance (A)

It is the ratio of the logarithm of the ratio of incident light to the transmitted light.

$$\log \frac{I_0}{I} = A$$

$$\therefore A = \epsilon cx$$

→ Transmittance (T)

Ratio of intensity of transmitted light to the incident light.

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

$$A = -\log T$$

graph plotted b/w A and $\frac{1}{I}$ is a straight line.

$$A = -\log \left(\frac{I}{I_0} \right) = -\log \left(\frac{I_0}{I} \right)^{-1} = \log \left(\frac{I_0}{I} \right) = kcx$$

Problem.

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

→

$$T = 20\%$$

$$I_0 = 100, I = 20$$

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

$$A = \epsilon c x$$

$$\epsilon = \frac{A}{c x}$$

$$= \frac{0.6989}{0.01 \text{ mol dm}^{-3} \times 0.2 \text{ dm}}$$

$$\epsilon = \underline{\underline{349.45 \text{ mol}^{-1} \text{ dm}^2}}$$

Molar \Rightarrow Moles/litre
 \Rightarrow mol/dm³

10 cm = 1 decimetre

1 cm = 0.1 decimetre

M \Rightarrow mol/dm³

2 cm = 0.2 dm

State and explain the law governing absorption of electromagnetic radiation by matter.

* A dye solution of concentration 0.04 M shows absorbance of 0.045 at 530 nm. While a test solution of same dye shows absorbance of 0.022 under same condition. Find the concentration of test solution.

→ $A_1 = \epsilon c_1 x$ $A_2 = \epsilon c_2 x$

$$\frac{A_1}{A_2} = \frac{\epsilon c_1 x}{\epsilon c_2 x} = \frac{c_1}{c_2}$$

$$\frac{A_1}{A_2} = \frac{c_1}{c_2}$$

$$A_1 = 0.045, A_2 = 0.022$$

$$c_1 = 0.04$$

$$c_2 = \frac{c_1 A_2}{A_1} = \underline{\underline{0.0195 \text{ M}}}$$

* 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 the transmittance of 0.4. Find the concentration of unknown Fe^{3+} solution.

$$A = -\log T$$

$$A = \epsilon c x$$

$$\epsilon c x = -\log T$$

$$-\log T_1 = \epsilon c_1 x$$

$$-\log T_2 = \epsilon c_2 x$$

$$\frac{\log T_1}{\log T_2} = \frac{c_1}{c_2}$$

$$T_1 = 0.2$$

$$T_2 = 0.4$$

$$c_1 = 50$$

$$c_2 = ?$$

$$\frac{\log 0.2}{\log 0.4} = \frac{50}{c_2}$$

$$\therefore c_2 = \underline{\underline{28.46 \text{ ppm}}}$$

* UV-Visible Spectroscopy.

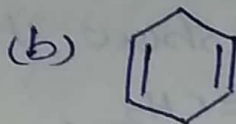
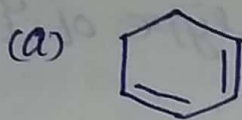
→ Principle: These are obtained by the transition of e^- s from lower electronic energy level to the higher electronic energy level by the absorption of UV-visible radiation. The e^- s may be σe^- s, πe^- s or non-bonding e^- s.

UV-visible spectroscopy is commonly used for identifying conjugated systems.

Conjugated system will absorb longest wavelength radiations.

Alternate single bond & double bond - conjugated system.

Which molecule will absorb at longest wavelength in U.V.



→ (a) since, (a) is a conjugated system. conjugated system will absorb UV-visible radiation at longer wavelength.

Range of U.V = 200 - 400 nm

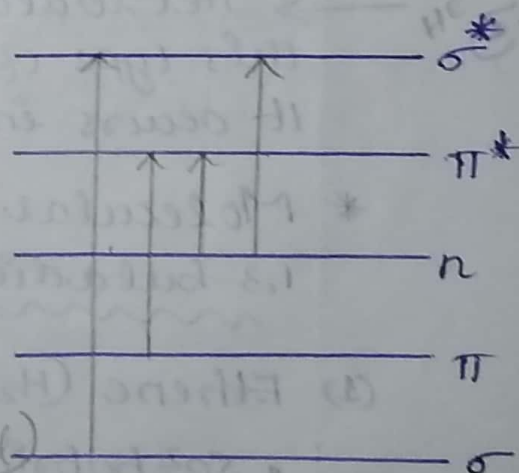
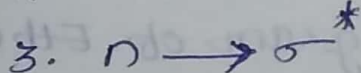
Visible = 400 - 800 nm

classification of electronic transitions

~~Imp~~

In UV-visible spectroscopy e^- s are promoted from bonding to antibonding molecular orbitals in three distinct types of e^- s; σ , π and n .

HOMO → LUMO
Highest Occupied Molecular Orbital → Lowest Unoccupied Molecular Orbital.



(1) σ to σ^* transition

→ Example = 1. Saturated (single bond)

hydrocarbon can give only $\sigma \rightarrow \sigma^*$ transition.

2. occurs below 150 nm. But an ordinary UV-visible spectrum is under the range 200-800 nm

So, saturated hydrocarbons cannot be detected using ordinary spectroscopy.

High frequency \Rightarrow low wavelength.

(2) π to π^* transition

→ Unsaturated hydrocarbon containing double bond / triple bond. show this type of transition.

eg: Ethene $\text{CH}_2=\text{CH}_2$,

Benzene

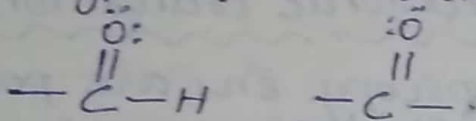


, 1,3,5-hexatriene,

1,3-butadiene molecules show $\pi \rightarrow \pi^*$ transition.

(3) n to π^* transition

→ Aldehydes ($-\text{CHO}$) and ketones ($-\text{CO}-$) shows this type of transition.



Lowest frequency
Highest wavelengths.

They ~~common~~ contain both π $\bar{\text{e}}$ s and non-bonding $\bar{\text{e}}$ s.

(Symmetrically forbidden)

(4) n to σ^* transition

→ Heteroatoms like N, O, S, halogens shows this type of transition.

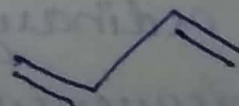
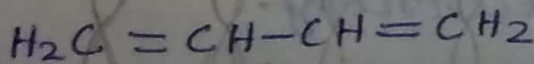
It occurs in low intensity.

* Molecular Energy Level Diagram of Ethene, 1,3-butadiene, 1,3,5-hexatriene, Benzene.

(1) Ethene ($\text{H}_2\text{C}=\text{CH}_2$)

- sp^2 hybridisation
- Atomic orbitals linearly combine to form molecular orbitals.

(2) 1,3-butadiene

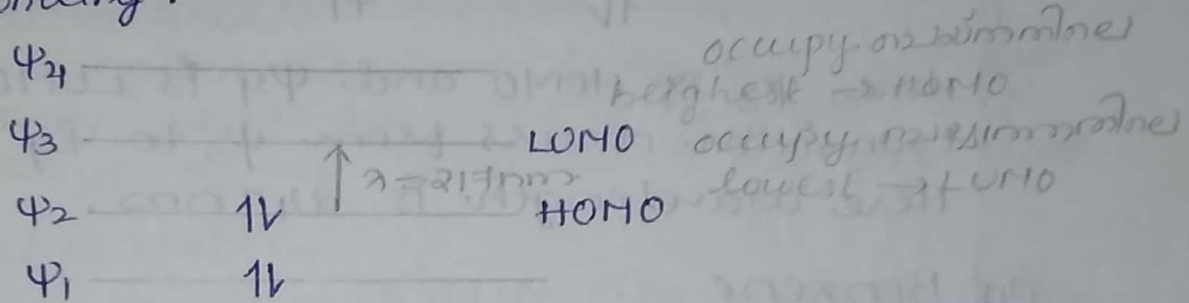


Here, there are four atomic orbitals and these atomic orbitals undergo linear combination to form four molecular orbitals $\psi_1, \psi_2, \psi_3, \psi_4$.

Two are bonding \rightarrow atomic orbital

Molecular orbitals $\left\{ \begin{array}{l} \rightarrow \text{Half are bonding} \\ \rightarrow \text{Half are antibonding} \end{array} \right.$

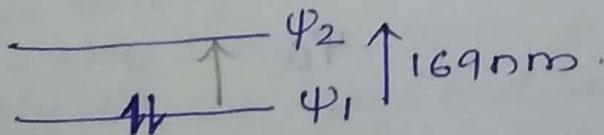
ψ_1 and ψ_2 are bonding & ψ_3 and ψ_4 are antibonding.



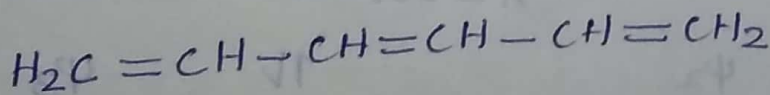
Electrons are excited from HOMO to LUMO.
In 1,3-butadiene electrons are excited from ψ_2 to ψ_3 .

Ethene

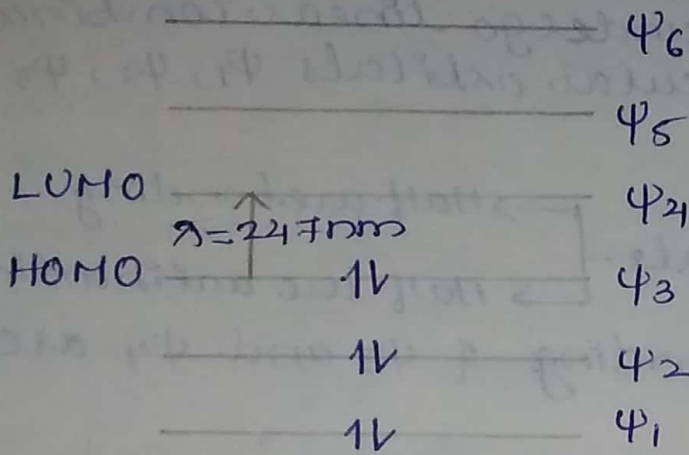
In ethene there are two atomic orbitals $H_2C=CH_2$. These two atomic orbitals combine to form two molecular orbitals ψ_1, ψ_2 .



(3) 1,3,5-hexatriene



Here there are 6 atomic orbitals. These undergo linear combination to form 6 molecular orbitals $\psi_1, \psi_2, \psi_3, \psi_4$ and ψ_5, ψ_6 . Here ψ_1, ψ_2, ψ_3 are bonding and ψ_4, ψ_5 and ψ_6 are antibonding molecular orbitals.

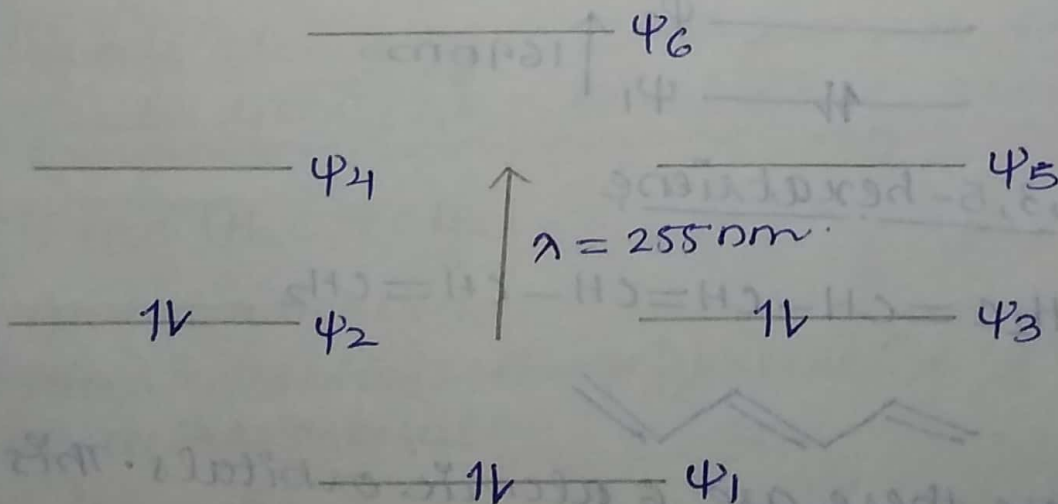


Here, ψ_3 is HOMO and ψ_4 is LUMO. Here transition occurs from ψ_3 to ψ_4 . Here wavelength is 247 nm.

(4) Benzene



Here there are 6 atomic orbitals and they undergo linear combination to form 6 molecular orbitals $\psi_1, \psi_2, \psi_3, \psi_4, \psi_5$ and ψ_6 . ψ_1, ψ_2, ψ_3 are bonding and ψ_4, ψ_5, ψ_6 are antibonding.



$\psi_1 \rightarrow$ Lowest energy, $\psi_6 \rightarrow$ Highest energy
 $\psi_2 \approx \psi_3 \rightarrow$ degenerate } same energy.
 $\psi_4 \approx \psi_5 \rightarrow$ degenerate }

Function of a monochromator is to isolate a narrow beam of radiation.

→ Instrumentation of UV-visible Spectroscopy.

Various components present are :

1. Radiation source
2. Monochromator
 - Entrance slit
 - Diffraction grating
 - Exit slit
3. Sample and reference cell
4. Detector
5. Recorder.

• Radiation source

→ Tungsten filament lamp and hydrogen discharge lamp are commonly used. But nowadays xenon flash lamps are also used.

• Monochromator

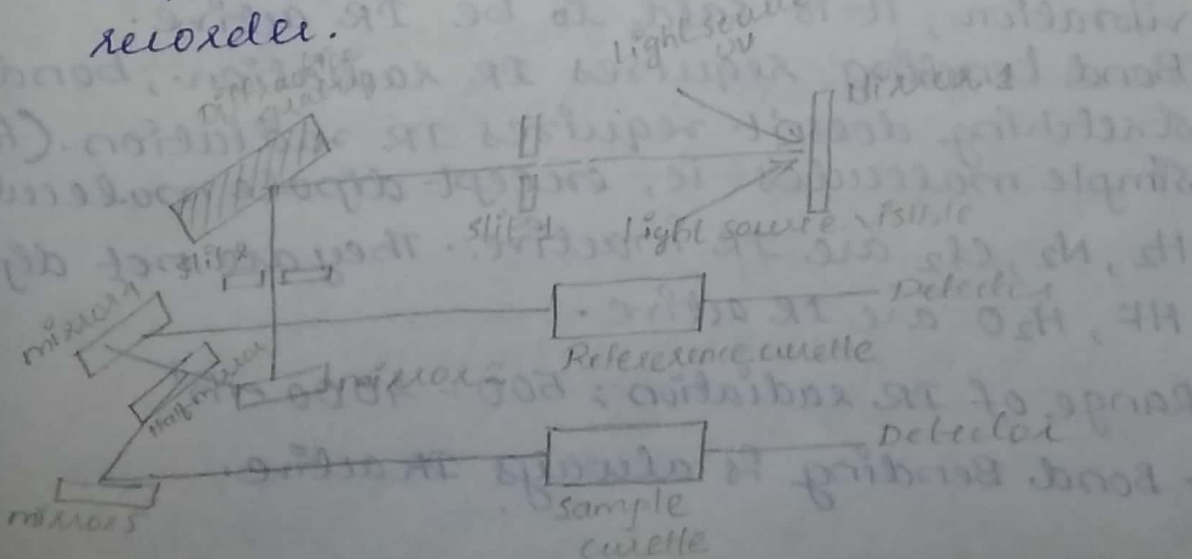
→ It has several parts like entrance slit, diffraction grating and exit slit.

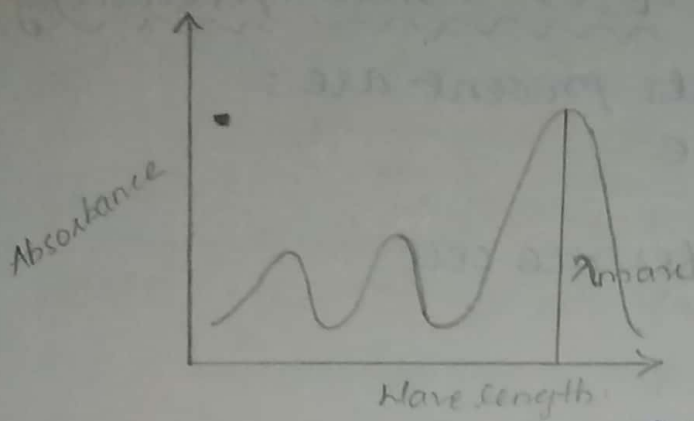
• Sample & reference cell

→ Sample is referred by dissolving it in suitable solvent and the pure solvent is the reference.

Radiation coming from monochromator split up into two halves → Double beam instrument. One half passes through sample and the other half passes through the reference. The light coming from the sample have some difference because it absorbs the rays and decreases the intensity.

• Detector, details and the output is given by recorder.





* Applications of U.V-visible spectroscopy

- (1) For the detection of aromatic compounds, conjugated dienes etc.
- (2) For the detection of impurities.
- (3) For the determination of unknown concentration.
- (4) Study of kinetics of chemical reaction.
- (5) Used in medical lab for the estimation of blood sugar, cholesterol etc.

* IR Spectroscopy

→ Also known as vibrational spectroscopy.

Principle = IR spectroscopy involves the transition b/w the vibrational energy levels of a molecule having a change in dipole moment during its vibration.

A molecule requires IR radiation for its vibration, it is said to be IR active.

Bond bending requires IR radiation, bond stretching doesn't require IR radiation. (for simple molecules it, except dipole molecules.)

H₂, N₂, Cl₂ are IR inactive. They are not dipole.

HF, H₂O are IR active. $\text{dipole moment} = \text{charge} \times \text{distance}$

Range of IR radiation: 500 - 4000 cm⁻¹

> Bond Bending is always IR active.

Homomolecules are IR inactive. $\text{dipole moment} = 0$ → IR active.
 Polar molecule → dipole moment → IR active.
 Electronegativity
 F > O > N
 Polar molecule → dipole moment → IR active.

> IR spectroscopy used to identify functional groups.

> Different functional groups give different stretching frequencies.

> HF is IR active, because its dipole moment changes during vibration.

> IR spectra is a plot of wave number and the percentage transmittance.

> Also known as vibrational-rotational spectrum. Because within vibrational levels there are several rotational levels.

> H_2, N_2, Cl_2, O_2 are IR inactive, because they have no change in their dipole moment during its vibration. Whereas HCl, H_2O, CO_2 etc. are IR active because there is a change in ~~the~~ dipole moment during vibration.

* Number of vibrational Modes in a molecule

For describing the position of a particle in space we require 3 degrees of freedom. Suppose, there are 'n' no: of particles then total no: of degrees of freedom = $3n$

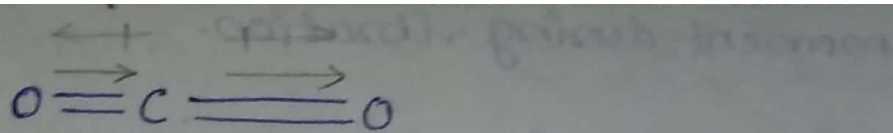
→ For a linear molecule,

translational degrees of freedom = 3
(even it is a linear or non-linear molecule)
No: of rotational degrees of freedom for a linear molecule = 2

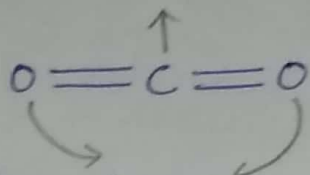
∴ No: of vibrational modes for a linear molecule = $3n - (2+3)$

= $3n - 5$ where n = no: of atoms present in that molecule.

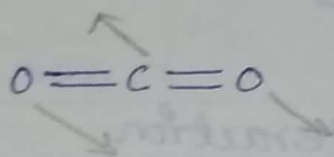
$$\begin{aligned} \text{Total degrees} &= \text{vib} + \text{rot} + \text{trans} \\ 3n &= \text{vib} + \text{rot} + \text{trans} \\ \text{vib} &= 3n - (\text{rot} + \text{trans}) \end{aligned}$$



- > Asymmetric stretching
- > IR active. Because, there is a change in dipole moment during vibration.



- > Bending in-plane
- > IR active. Because there is a change in dipole moment during vibration.



- > Bending out plane
- > IR active. Because there is a change in dipole moment during vibration.

* Vibrational Modes in Water (H₂O)

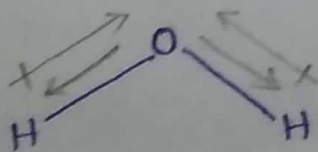
→ H₂O : Non linear molecule

$n = 3$

Total no. of vibrational modes
 $= 3n - 6 = 3 \times 3 - 6 = 9 - 6$
 $= \underline{3}$

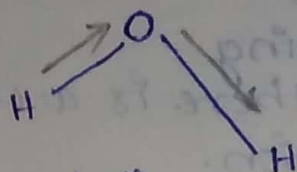
3 vibrational modes

- (1) symmetric stretching
- (2) asymmetric stretching
- (3) Bending.

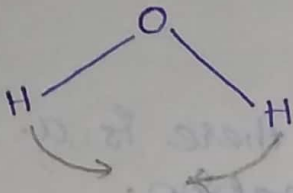


- > Symmetric stretching
- > IR active. Because there is a change in dipole

moment during vibration.



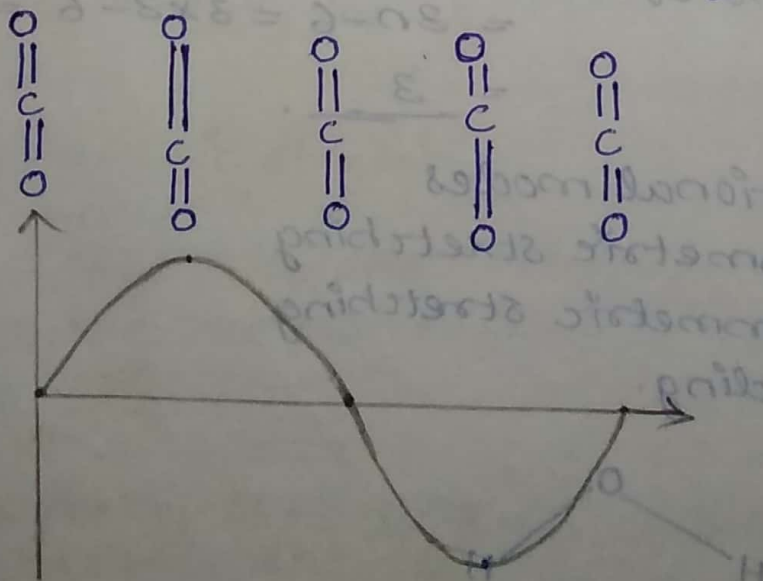
- > Asymmetric stretching
- > IR active.



- > Bending (in plane)
- > IR active.

* Mechanism of interaction

During the vibration of a chemical bond, it ~~in~~ changes there occurs a change in dipole moment, it will lead to the generation of an oscillating electric field. When a photon of frequency ^{come in} ~~coming~~ resonance with the frequency of vibration of a molecule, the absorption of photon takes place and the molecule starts oscillating with the frequency of radiation.



→ Mechanism of interaction of oscillating dipole of CO₂ in asymmetric stretching.

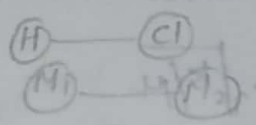
* Vibrational Energy and vibrational frequency

Fundamental vibrational frequency,

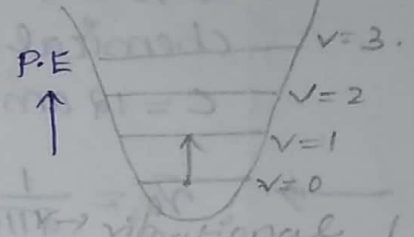
$$\nu_0 = \frac{1}{2\pi} \sqrt{k/\mu}$$

where, $k \rightarrow$ force constant
 $\mu \rightarrow$ reduced mass.

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



Interatomic distance.



(Potential energy level diagram)

Problem

$$\bar{\nu}_0 = \frac{1}{2\pi c} \sqrt{k/\mu} \text{ cm}^{-1}$$

Selection rule, $\Delta v = \pm 1$
 vibrational energy, $E = (v + 1/2) h\nu_0$
 Potential energy, $V = -1/2 kx^2$

$E = (v + 1/2) h\nu_0$ where, $v \rightarrow$ vibrational quantum number.

$v = 0, 1, 2, 3, \dots$

This equation is obtained by substituting $V = -1/2 kx^2$ in Schrodinger's equation.

For ground level,

$$E = (0 + 1/2) h\nu_0$$

$$E = \frac{1}{2} h\nu_0$$

This energy is called zero point energy.

Suppose, a particle is excited from the lower vibrational level 'v' to higher energy level 'v'.

$$\Delta E = h\nu$$

$$(v' + 1/2) h\nu_0 - [(v + 1/2) h\nu_0] = h\nu$$

$$(v' - v) h\nu_0 = h\nu \quad \text{where, } v' - v = 1$$

$$h\nu_0 = h\nu$$

$$\underline{\underline{\nu_0 = \nu}}$$

The frequency of absorbed IR radiation is equal to the fundamental vibrational frequency of a molecule.

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

$$\rightarrow \nu_0 = \frac{1}{2\pi c} \sqrt{k/\mu} \quad \begin{array}{l} \text{amu} \rightarrow \text{kg} \\ \times 1.66 \times 10^{-27} \end{array}$$

$$k = ? \quad \nu_0 = 2140$$

$$\mu = \frac{12 \times 16}{(12+16)} \times 1.66 \times 10^{-27} \quad \begin{array}{l} \text{cm} \rightarrow \text{m} \\ \times 10^2 \\ \text{cm}^{-1} \rightarrow \text{m}^{-1} \\ \times 10^2 \end{array}$$

$$\mu = 1.138 \times 10^{-26} \text{ kg}$$

$$c = 3 \times 10^8 \text{ m/s} = \underline{\underline{3 \times 10^{10} \text{ cm/s}}}$$

$$\nu_0^2 = \frac{1}{2^2 \times 3.14^2 \times (3 \times 10^8)^2} \times \frac{k}{1.138 \times 10^{-26}}$$

$$(2140 \times 10^2)^2 \times 2^2 \times 3.14^2 \times (3 \times 10^8)^2 = \frac{k}{1.138 \times 10^{-26}}$$

$$\underline{\underline{k = 1849.8 \text{ Nm}^{-1}}}$$

* calculate the force constant of HF molecule, if it shows IR absorption at 4138 cm^{-1} , given that atomic masses of H and F are 1u and 19u respectively. What would be the wavenumber if H atoms are replaced deuterium atom.

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

$$\mu = \frac{1 \times 19}{(1+19)} \times 1.66 \times 10^{-27} = \underline{\underline{1.577 \times 10^{-27} \text{ kg}}}$$

$$c = 3 \times 10^8 \text{ m/s}$$

$$(4138 \times 10^2)^2 = \frac{1}{2^2 \times 3.14^2 \times (3 \times 10^8)^2} \times \frac{k}{1.577 \times 10^{-27}}$$

$$\therefore k = 958.46 \text{ Nm}^{-1}$$

$$\bar{\nu}^2 \propto \frac{1}{\mu} \Rightarrow \bar{\nu}^2 \propto \frac{1}{M_1}$$

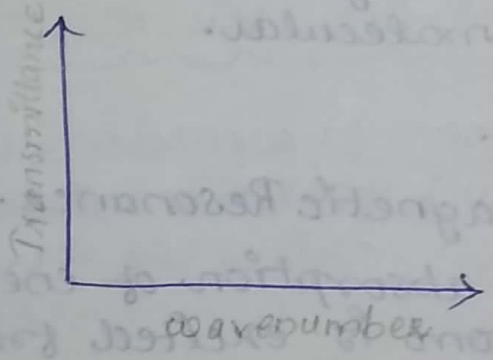
$$\bar{\nu}_2^2 \propto \frac{1}{M_2}$$

$$\frac{\bar{\nu}_1^2}{\bar{\nu}_2^2} = \frac{M_2}{M_1}$$

$$M_2 = \frac{2 \times 19}{2 + 19} \times 1.66 \times 10^{-27} = 3.003 \times 10^{-27}$$

$$\bar{\nu}_2 = 2998.27 \text{ cm}^{-1}$$

* Recording of IR spectrum



2.4.5 Recording of IR spectra

Earlier IR spectrometers operate in a continuous-sweep mode, whereas modern machines employ pulse Fourier-transform (FT-IR) technology. Infrared spectra can be recorded on a sample regardless of its physical state; solid, liquid and gas. For a solid, the sample is mixed with potassium bromide and the mixture is pressed into a thin wafer, which is placed in the path of the infrared beam. For liquids, a drop of liquid is placed between two sodium chloride disks, through which the infrared beam is passed. The transmittance percentage is plotted against wave number in cm^{-1} .

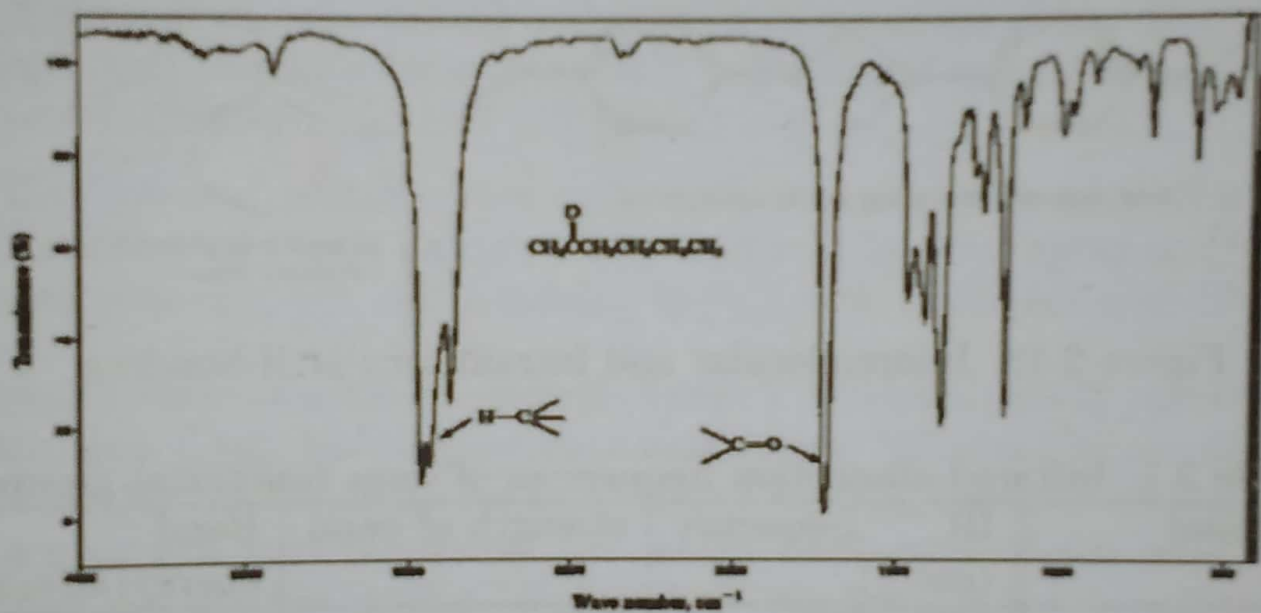


Figure 2.17: IR spectrum of 2-hexanone

* Applications of IR spectroscopy

(1) Determination of force constant of a diatomic molecule.

(2) Identification of functional group in organic molecule.

stretching frequency of $\overset{\text{(carbonyl)}}{\text{C}}=\text{O} = 1700 - 1725 \text{ cm}^{-1}$

O-H = $3300 \rightarrow 3500$

NH₂ = $3200 \rightarrow 3300$

C=C = $1620 \rightarrow 1650$

(3) Identification of unknown compounds.

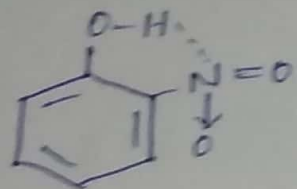
→ Fingerprint region
 $700 - 1500 \text{ cm}^{-1}$

It is done by comparison of IR spectrum of

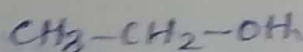
unknown compound with known compound. This comparison is especially made at the fingerprint region.

(4) Determination of purity.

(5) To distinguish between intermolecular and intramolecular hydrogen bonding.



ortho-nitrophenol \rightarrow intramolecular.
(ortho-hydroxyphenol)



\leftarrow H bond \rightarrow Intermolecular.

- > OH stretching frequency changes with diluting is intermolecular.
- > OH stretching frequency doesn't change with diluting is intramolecular.

* NMR Spectroscopy

NMR: Nuclear Magnetic Resonance.

- > It depends on absorption of energy when the nucleus of an atom is excited from its lower energy nuclear spin state to the higher energy.
- > In the absence of a magnetic field, the nuclear energy levels are degenerate.
- > Nuclear energy levels are produced only when the nucleus is placed in a magnetic field.
- > The energy required for transition falls in radiofrequency region.
- > NMR active: Nuclear spin quantum number, $I \neq 0$.

\rightarrow If no. of protons and no. of neutrons are even, then $I = 0$, i.e., nucleus has no net spin.

eg: He, C, O.

$${}^4_2\text{He} : \begin{matrix} P=2 \\ n=2 \end{matrix} \quad {}^{12}_6\text{C} : \begin{matrix} P=6 \\ n=6 \end{matrix} \quad {}^{16}_8\text{O} : \begin{matrix} P=8 \\ n=8 \end{matrix}$$

→ If the no. of neutrons and no. of protons are odd, then the nucleus has a half integral spin.
($n+p = \text{odd}$ Mass number = odd)

eg: ${}^1_1\text{H} : \begin{matrix} P=1 \\ n=0 \end{matrix}$, ${}^{13}_6\text{C} : \begin{matrix} P=6 \\ n=7 \end{matrix}$, ${}^{19}_9\text{F}$, ${}^{31}_{17}\text{Cl}$

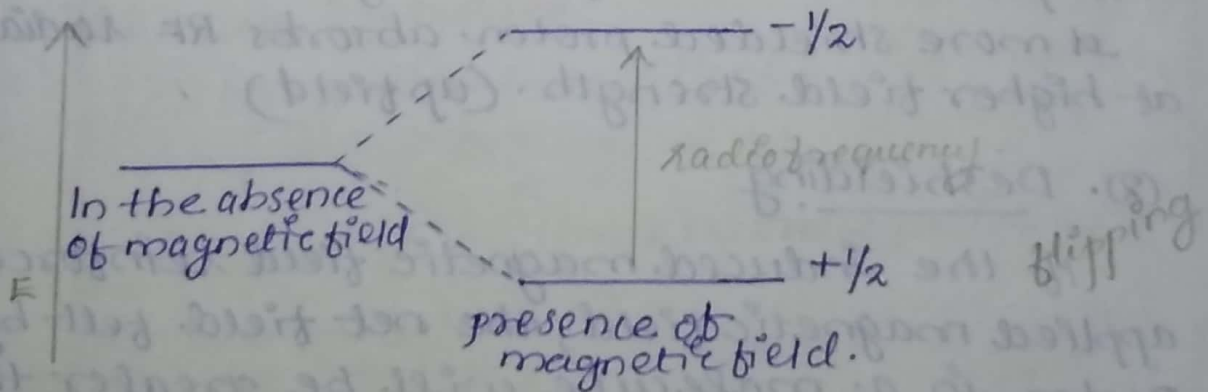
$I = +1/2$, $I = +1/2$, $P=17$, $3 \times 1/2 = 3/2$
 $n=20$, $I = 3/2$

→ If no. of neutrons and no. of protons are both odd, I value have integral spin (1, 2, 3)

eg: ${}^2_1\text{H} : \begin{matrix} P=1 \\ n=1 \end{matrix}$

→ A nucleus of spin quantum number 'I' can produce $(2I+1)$ possible orientation.

→ In the absence of magnetic field, there is only one nuclear energy. But in the presence of magnetic field there is two nuclear energy level.



Three energy levels: $-1, 0, +1$

Chemical shift (δ)

$\frac{\gamma_{\text{mp}}}{\nu}$

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\text{operating frequency in MHz}}$$

$$\delta = \frac{\Delta \nu \text{ in Hz}}{\text{operating frequency in MHz}}$$

chemical shift δ varies from $0 \rightarrow 10$.

Reference is TMS: Tetramethylsilane whose $\delta = 0$.

"chemical shift"

→ The dependence of resonance position of a nucleus that results from its molecular environment is called chemical shift.

> When a molecule is placed in a magnetic field, its π electrons are caused to circulate and it produces a secondary magnetic field or induced magnetic field. This induced magnetic field may oppose or reinforce the applied magnetic field. Thus two cases arise:

(1) Shielding

If the induced magnetic field opposes the applied magnetic field, the net field felt by the proton in a molecule will be less than the applied field and the molecule is said to be shielded.

The more shielded a proton is, the greater must be the strength of the applied field in order to achieve resonance with the radio frequency, and produce an absorption signal.

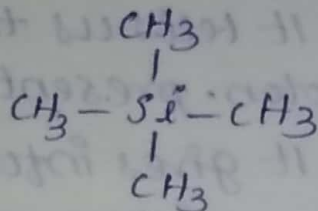
A more shielded proton absorbs RF radiation at higher field strength. (upfield)

(2) Desielding

If the induced magnetic field reinforces the applied magnetic field, the net field felt by the proton in a molecule will be greater than the applied field and the molecule is said to be deshielded.

A more deshielded proton absorbs RF radiation at lower field strength. (downfield)

Reference molecule: TMS \rightarrow TetraMethylsilane



• Shielding \uparrow δ value low

chemical shift, $\delta = 0$

- Deshielded: δ value high
- Proton nearer to electro-negative atom; deshielded

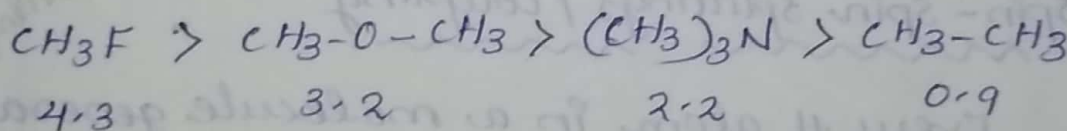
why

* Factors affecting chemical shift

(1) Electronegativity

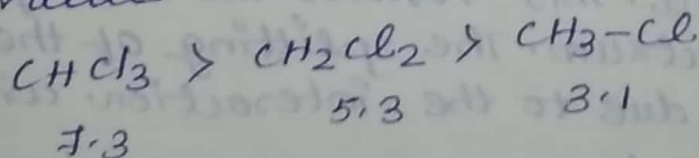
\rightarrow If an electronegative atom is present, then the electron density around the proton decreases. \therefore that proton is said to be the deshielded. Its chemical shift value is high.

\rightarrow shielded = right
 \rightarrow deshielded = left

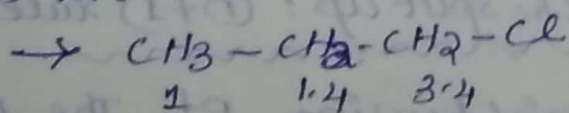


(2) Cumulative effect of electronegative substituent

\rightarrow If the no. of electronegative atom increases, δ value increases.



(3) Distance from the electronegative atom.



The distance from the electronegative atom increases, chemical shift value ~~increases~~ decreases

(4) Shielding

\rightarrow Greater the shielding, lower the δ value

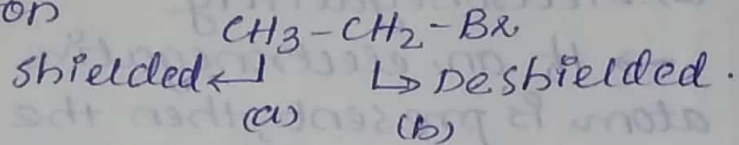
(5) Deshielding

\rightarrow Greater the deshielding, higher the δ value.

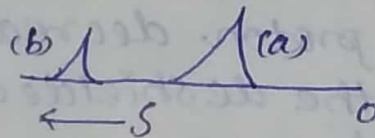
* Interpretation of chemical shift in a molecule

- (1) Number of signal : It tells us the no: of different types of proton, present in the molecule.
- (2) Position of signal : It gives information about nature of the protonic environment.
- (3) Intensity of signal : It is measured by the area under peak. It gives information about the ratio of different kinds of protons.

1. Type of Proton



2. Position



* Spin-spin splittings / coupling

Every H atom in a molecule generates magnetic field. Each H atom generates its own magnetic field whose magnetic moment will interact with the magnetic moment of external magnetic field. This results in the splitting of the NMR spectrum. The splitting of the NMR spectrum is due to the interaction with the neighbouring P^+ .

No: of peaks in which split up : $(n+1)$ rule

Let n be no: of neighbouring P^+ . The no: of peaks into which a particular signal split is desired by a rule.

i.e., $(n+1)$ rule

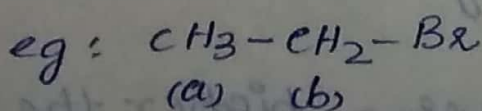


Figure 2.30. 1

Worked out examples

Problem 2.5.4. Predict the number of signal and splitting pattern of the nmr spectrum of 1-bromoethane ($\text{CH}_3 - \text{CH}_2 - \text{Br}$)

Ans: There are two types of protons CH_3 protons and CH_2 protons. The CH_3 protons are closer towards TMS and have low δ value (δ 1.6), CH_2 protons show a higher δ value (δ 3.3) due to the influence of electronegative atom Br. The peak area ratio of chemical shifts will be 3:2, which corresponds to the number of protons involved in producing a signal. Fig. 2.32

Splitting of signals: the CH_3 protons signal split into a triplet with intensity ratio 1:2:1

under the influence of CH_2 protons (fig. 2.31). Similarly CH_2 protons signal split into a quartet (with intensity ratio 1:3:3:1) under the influence of CH_3 protons (fig. 2.27).

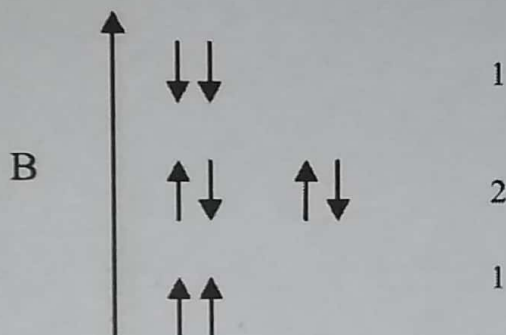


Figure 2.31: The spin orientations of CH_2 protons

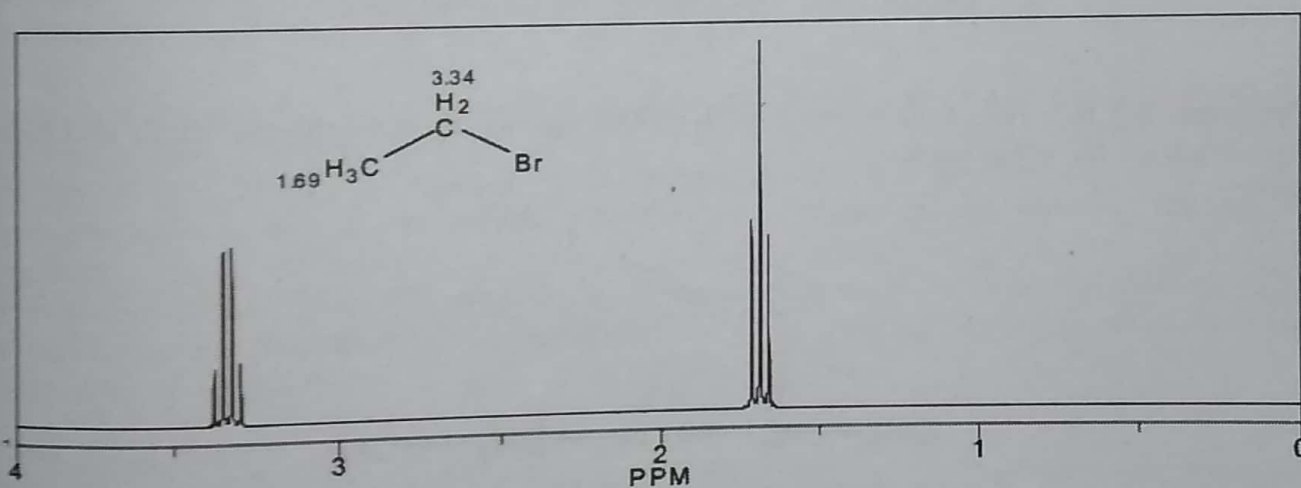
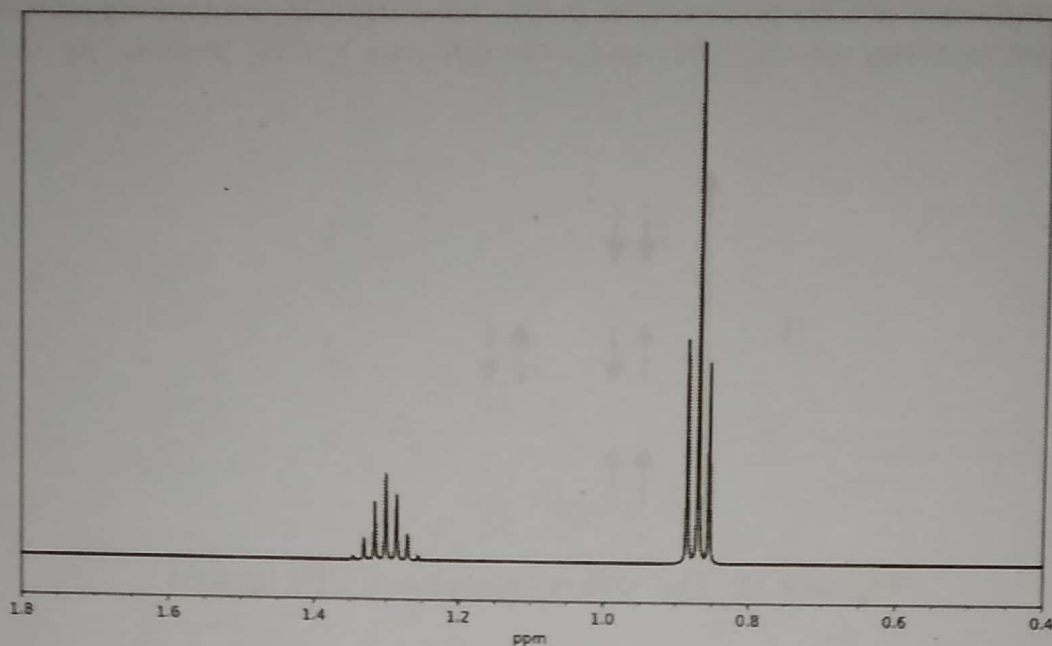


Figure 2.32: $^1\text{H-NMR}$ spectrum of $\text{CH}_3 - \text{CH}_2 - \text{Br}$

Problem 2.5.5. Predict the number of signal and splitting pattern of the nmr spectrum of propane ($\text{CH}_3 - \text{CH}_2 - \text{CH}_3$)

Ans: The compound propane, $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$ there are two different electronic environments. The two methyl groups on each end will generate one signal (a) and the CH_2 will generate a second NMR signal (b) at a different chemical shifts. The "a" signal, has two neighbouring protons (on the CH_2). According to the $n+1$ rule the "a" signal will be split in three ways called a triplet with intensity ratio 1:2:1. The "b" signal will have a total of 6 neighbouring protons (three from each neighbouring methyl) so that signal should be split in 6+1 or 7 ways called a septet, the intensity ratio will be 1:6:15:20:15:6:1 as given by Pascal's triangle (fig. 2.33)

Figure 2.33: $^1\text{H-NMR}$ spectrum of propane

Problem 2.5.6. Predict the number of $^1\text{H-NMR}$ signals, their relative positions and their multiplicities for ethyl acetate.

Ans:

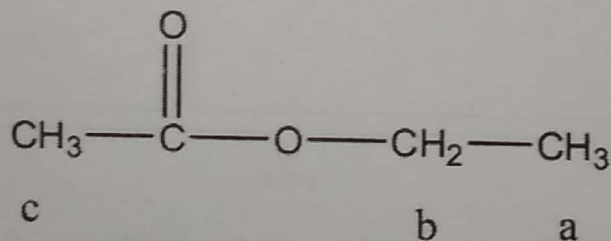
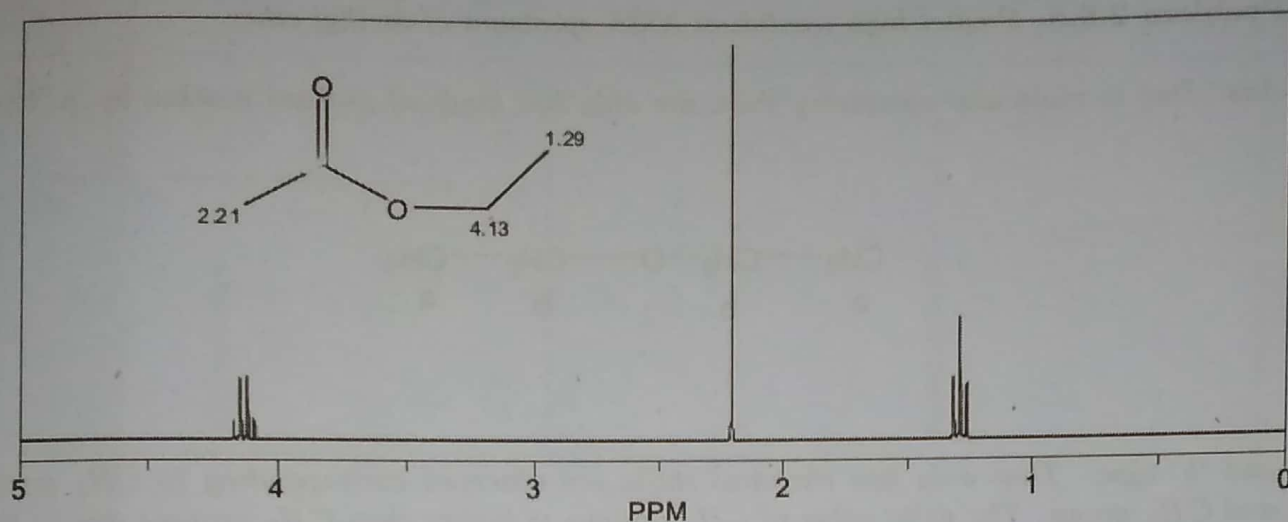


Figure 2.34: Ethyl acetate

There are three types of protons marked as a, b and c (fig. 2.34). The position of chemical shift of 'a' type ($-\text{CH}_3$) of protons are closer to TMS (low δ value), since the H atoms are far away from electronegative oxygen atom. The 'c' type of proton appears next and 'b' type protons appear last with high δ value. The relative peak areas of this chemical shift will be in the ratio 3:2:3 corresponding to number of protons in each set. (fig 2.35)

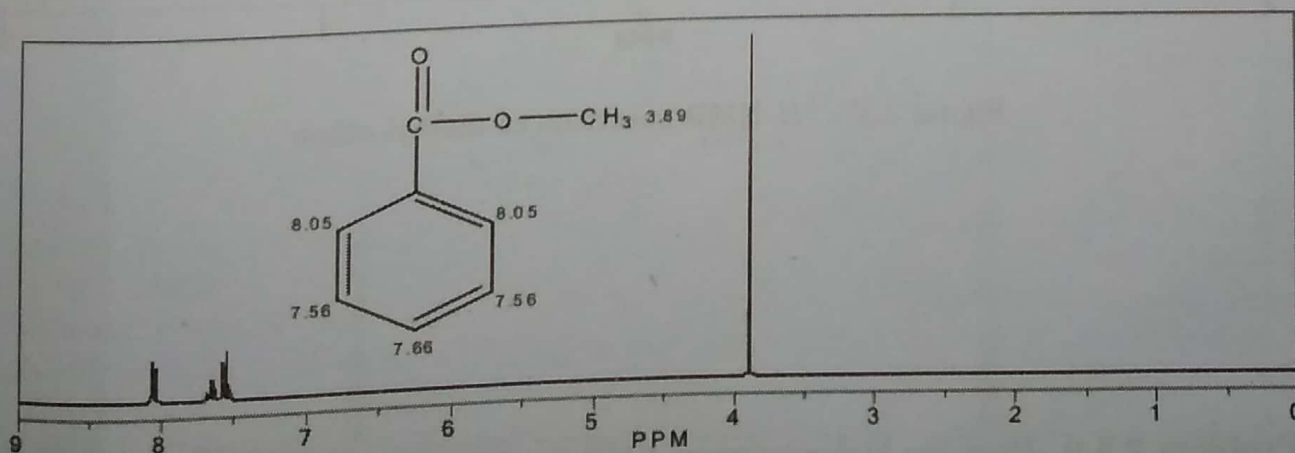
Splitting of signals: 'a' type CH_3 protons split into a triplet with intensity ratio 1:2:1 under the influence of CH_2 protons. Similarly CH_2 protons split into a quartet (with intensity ratio 1:3:3:1) under the influence of 'a' type CH_3 protons. 'c' type CH_3 protons has no neighbouring protons (separated by three bonds), hence 'c' type signal appears as singlet.

Figure 2.35: $^1\text{H-NMR}$ spectrum of ethyl acetate

Problem 2.5.7. Predict the number of $^1\text{H-NMR}$ signals, their relative positions and their multiplicities for methyl benzoate.

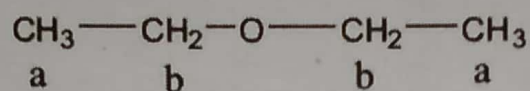
Ans: Here are only two types of protons for the molecule marked as a and b. The chemical shift of 'a' type (CH_3) protons are closer to TMS (δ between 3 and 4), whereas chemical shift of 'b' type (aromatic) protons are far away from TMS (δ between 6.5 and 8). The peak area ratio is 3:5, is corresponding to number of protons which produces the signal. (fig 2.36)

Spin-spin splitting: The CH_3 protons appear as singlet, as there is no neighbours. The aromatic protons (b-type) appear as multiplet due to the presence of ortho, meta and para substituted H- atoms.

Figure 2.36: $^1\text{H-NMR}$ spectrum of methyl benzoate

Problem 2.5.8. Predict high resolution NMR spectrum of diethyl ether

Ans: Due to molecular symmetry there are only two kinds of protons marked by 'a' type



and 'b' type. Thus only two chemical shifts are observed corresponding to CH_3 group and CH_2 group. The delta value of CH_2 protons is higher than CH_3 protons due to the presence of neighbouring oxygen atom. In high resolution spectrum the CH_3 group split into a triplet (1:2:1) under the influence of CH_2 group and CH_2 group split into a quartet (1:3:3:1) under the influence of CH_3 protons.

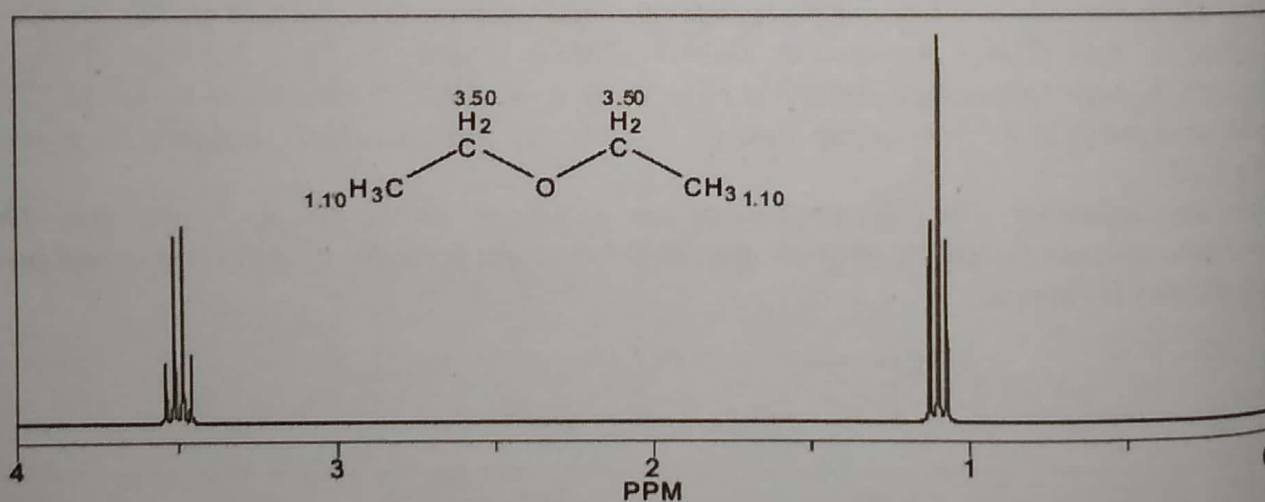
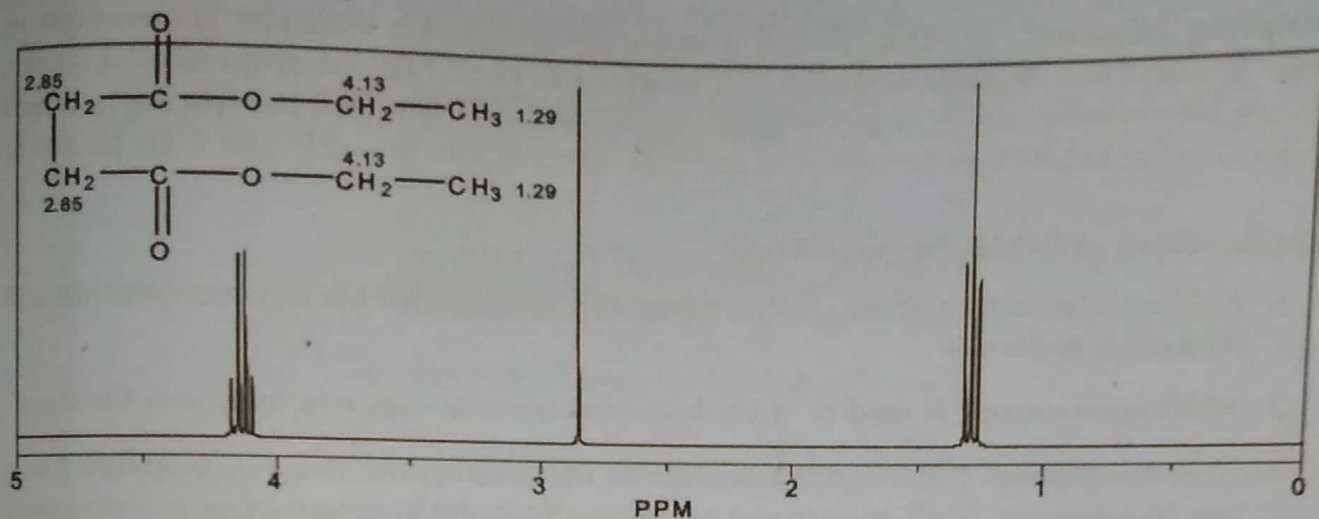


Figure 2.37: ^1H -NMR spectrum of diethyl ether

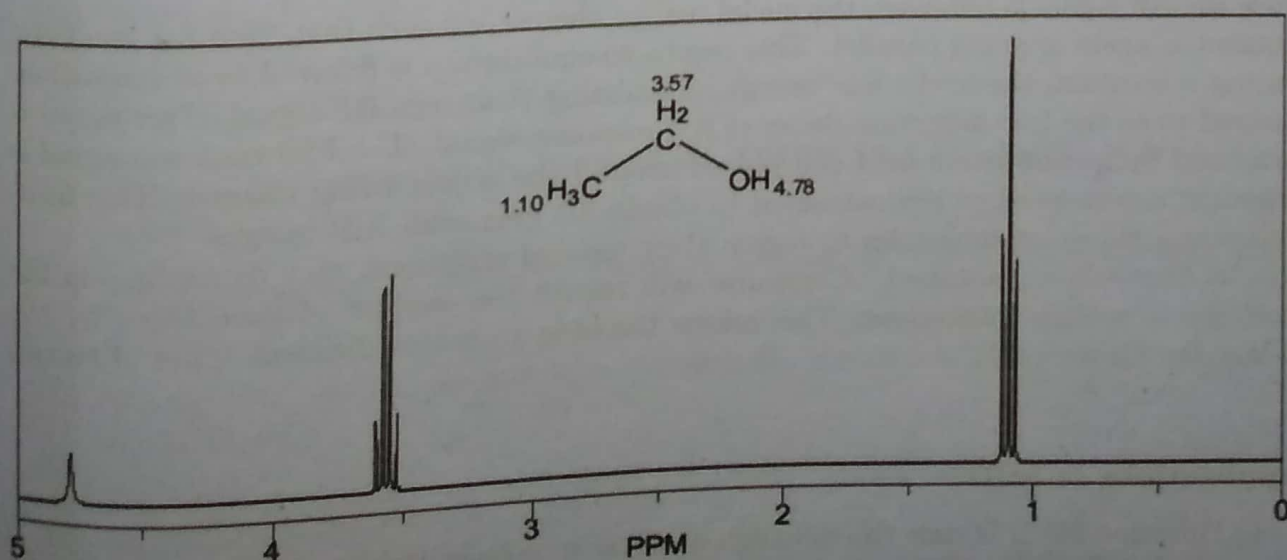
Problem 2.5.9. Draw the high resolution NMR spectrum of diethyl succinate.

Ans:

Figure 2.38: $^1\text{H-NMR}$ spectrum of diethyl succinate

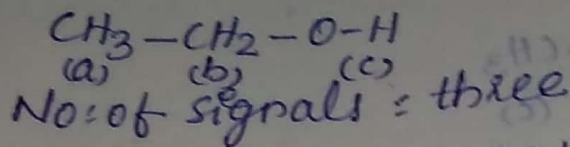
Problem 2.5.10. Explain the $^1\text{H NMR}$ spectrum of ethanol.

Ans: Consider the structure of ethanol; $\text{CH}_3-\text{CH}_2-\text{OH}$ There are three kinds of protons CH_3 protons, CH_2 protons and $-\text{OH}$ protons. The methyl peak has been split into three peaks (a triplet) under the influence of CH_2 protons. The methylene (CH_2) peak has been split into eight peaks (double quartet), under the influence of CH_3 and OH protons. The coupling constant of OH proton is different from CH_3 protons as the spin is transferred through oxygen atom in the former case. The OH protons get splitted into a triplet under the influence of CH_2 protons. This splitting pattern is observed only if ethyl alcohol is extremely pure. If traces of water is present in ethanol fast exchange of proton takes place between water and ethanol and splitting due to $-\text{OH}$ proton is not observed on CH_2 protons and vice versa.

Figure 2.39: $^1\text{H-NMR}$ spectrum of ethanol

Coupling constant, J The spacing between the peaks of a multiplet is measured in Hertz is called the coupling constant. For example in the NMR spectrum of ethanol the spacing between the methyl triplet is equal, In the case of CH_2 signal, the spacing between peaks is not constant due to difference in coupling constants of $-OH$ and CH_3 protons.

→ Ethanol

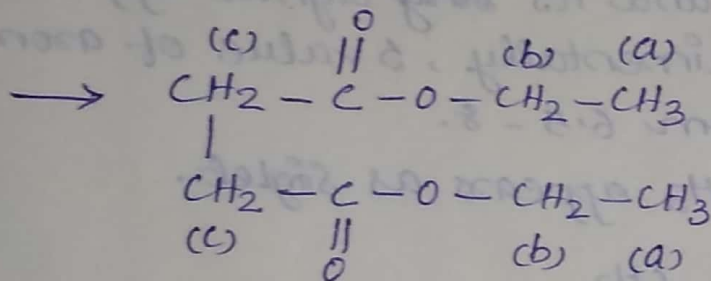
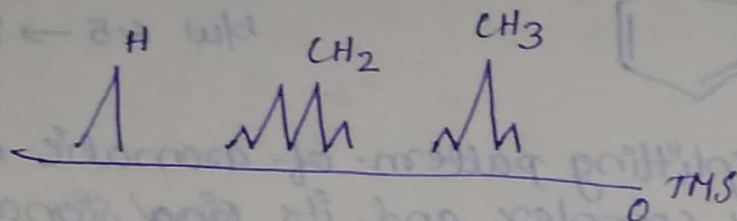


(a) = triplet 1:2:1

(b) = quartet 1:3:3:1

(c) = singlet

H in OH is more deshielded. Away from TMS value.



(a) : triplet → more shielded (extreme ~~left~~ right)

(b) : quartet → more deshielded (extreme left)

(c) : singlet (middle)

* Coupling constant (J)

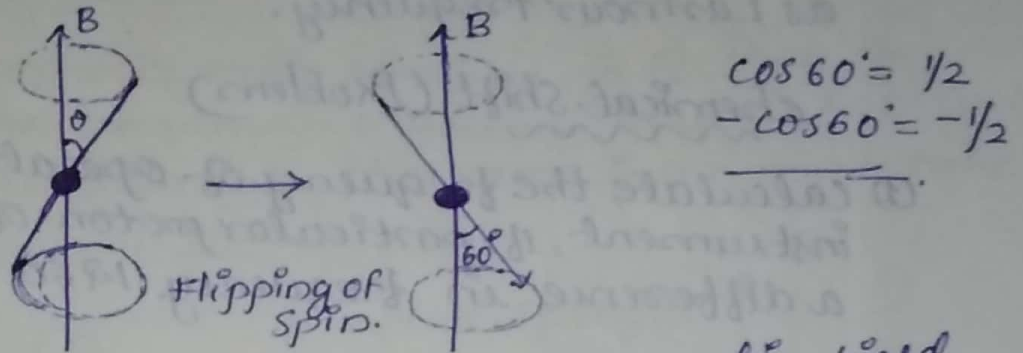
Spacing b/w the peaks of a multiplet is measured in Hz, is called coupling constant.

* Applications of NMR

- > structural elucidation of organic molecule
- > used to study keto-enol tautomerism, and H-bonding.

> Magnetic resonance imaging (MRI)
 (Free Induction Decay response: (FID) signal.)

* The precession of nucleus in a magnetic field.



When a nucleus is placed in a magnetic field, there occurs a precession.

θ is the angle between the direction of the applied magnetic field and axis of nuclear spin.

potential energy,

$$E = -\vec{\mu} \cdot \vec{B}$$

$$E = -\mu B \cos \theta \quad \text{--- ①}$$

The spin orientation of the nucleus is quantised. i.e., it can take only two orientations. Either 60° with the field direction or 60° opposite to the field direction.

We know that, $\mu = \frac{\gamma h}{2\pi}$ γ - gyromagnetic ratio.
 h - Planck's constant.

Substituting the value of μ in ①

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

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

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

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

But, $\Delta E = h\nu$

$$\therefore h\nu = \frac{\gamma h}{2\pi} B$$

$$\therefore \nu = \frac{\gamma B}{2\pi}$$

$\nu \propto B$

$$\cos \theta = 1$$

$$\Delta I = -1/2 - 1/2 = -1$$

$$h\nu = \Delta E$$

$$\nu = \frac{\Delta E}{h} = \frac{h\nu}{h} = \nu$$

∴ The energy difference b/w the two states is directly proportional to the strength of the applied magnetic field.

The frequency of the precessing nucleus is termed as Larmour frequency.

Chemical Shift (Problem)

(1) Calculate the frequency of operation of NMR instrument, if particular proton of δ value 4.2 shows a difference in frequency 1260 Hz from TMS.

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\text{operating frequency in MHz}}$$

$$\delta = \frac{\Delta\nu \text{ in Hz}}{\text{operating frequency in MHz}}$$

$$\rightarrow \delta = 4.2$$

$$\Delta\nu = 1260 \text{ Hz}$$

$$4.2 = \frac{1260}{\text{operating frequency in MHz}}$$

$$\therefore \text{operating frequency} = 300 \text{ MHz}$$

(2) CHCl_3 protons show a shift in frequency of 798 Hz from TMS signal in a 100 MHz NMR instrument, how much would be the shift in frequency for the same proton from TMS in a 300 MHz NMR instrument?

$$\rightarrow \delta = \frac{\Delta\nu}{\nu}$$

Same proton $\Rightarrow \delta$ constant.

$$\Delta\nu = \delta\nu$$

$$\Delta\nu \propto \nu$$

$$\Delta\nu_1 \propto \nu_1$$

$$\Delta\nu_2 \propto \nu_2$$

$$\left\{ \begin{array}{l} \Delta\nu_1 = \nu_1 \\ \Delta\nu_2 = \nu_2 \end{array} \right.$$

$$\frac{728}{\Delta\nu_2} = \frac{100}{300}$$

$$\Delta\nu_2 = 2184 \text{ Hz}$$

(3) IF gyromagnetic ratio of ^{13}C is $\frac{1}{4}$ of that of ^1H .
What is the frequency - must be irradiated to take ^{13}C NMR spectrum if, the same instrument take ^1H NMR spectrum at 300 MHz.

$$\rightarrow \nu = \frac{\gamma B}{2\pi} \quad B \rightarrow \text{field strength.}$$

Same instrument $\Rightarrow B$ constant.

$$\frac{\nu_1}{\nu_2} = \frac{\gamma_1}{\gamma_2}$$

$$\frac{\nu_{\text{C}}}{\nu_{\text{H}}} = \frac{\gamma_{\text{C}}}{\gamma_{\text{H}}}$$

$$\frac{\nu_{\text{C}}}{300} = \frac{1}{4}$$

$$\nu_{\text{C}} = \frac{300}{4} = 75 \text{ MHz}$$

2.5.5 Magnetic Resonance Imaging

Magnetic resonance imaging (MRI) is a medical imaging technique used in radiology to visualize internal structures of the body in detail. MRI makes use of the property of nuclear magnetic resonance (NMR) to image nuclei of atoms inside the body.

MRI machines make use of the fact that body tissue contains lots of water, and hence protons (1H nuclei), which get aligned in a large magnetic field. When a person is inside the powerful magnetic field of the scanner (0.2 to 3 Tesla depending on the scanner), average magnetic moment of many protons becomes aligned with the direction of the field. A radio frequency current is briefly turned on, producing radio waves of the right frequency, known as the resonance frequency. The radio waves are absorbed and thus flip the spins of the protons in the magnetic field. After the electromagnetic field is turned off, the spins of the protons return to thermodynamic equilibrium called relaxation. During this relaxation, a radio frequency signal is generated from the body, which can be measured with receiver coils and recorded and mapped.

Once the RF signal is removed, the nuclei realign themselves such that their net magnetic moment is again aligning parallel. This return to equilibrium is referred to as relaxation. During relaxation, the nuclei lose energy by emitting their own RF signal. This signal is referred to as the free-induction decay (FID) response signal. The FID response signal is measured by a conductive field coil placed around the object being imaged. This measurement is processed or reconstructed to obtain 3D grey-scale MR images.

Relaxation times for molecules to regain their natural alignment vary depending on the type of tissue being scanned. Computer will record the amount of time taken by the molecule to realign themselves. This allows the scan to detect different types of tissues as it make up the body.

Applications of MRI

1. Diffusion MRI: It uses the diffusion of water molecules in biological systems. Useful for diagnosis of neurological disorder and help in better understanding of connectivity of central nervous system.

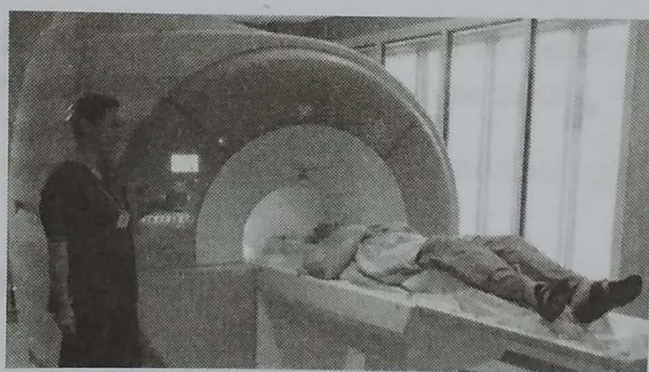


Figure 2.40: Magnetic Resonance Imaging

2. Magnetic resonance spectroscopy: Used to measure the levels of different metabolites in body tissues, particularly in brain.
3. Magnetic resonance angiography: It generates the pictures of the arteries.
4. Functional MRI: It measures signal changes in brain that are due to changing neural activity.