

SPECTROSCOPY

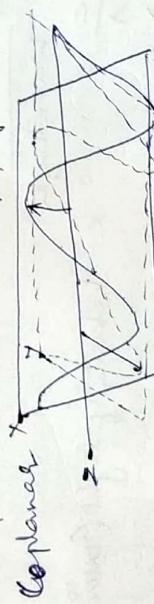
Spectroscopy is modern tool for recognizing the unknown compound using electromagnetic radiation.

Electromagnetic radiation:

According to the wave theory, light travels in the form of waves. It was believed that radiant energy is emitted by fluctuation of electric charge and magnetic field. Like light, there are various forms of electromagnetic radiations such as UV-visible, Infrared, X-rays, Radiowaves etc.

Some of the important characteristics of electromagnetic radiation are;

- (i) These are produced by the oscillation of electric charge and magnetic field residing on the atom. The electric and magnetic components are mutually perpendicular to each other and are



- (ii) These are characterized by their wavelengths or frequencies (or) wave numbers.
- (iii) Emission or absorption of radiation is quantised and each quantum of radiation is called a photon

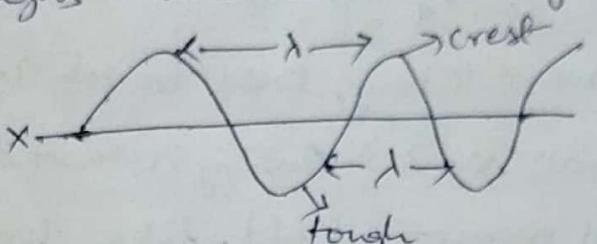
The study of Spectroscopy deals with the emission as well as absorption spectra.

Emission spectra is produced by the emission of radiant energy by an excited atom.

Absorption spectra is produced, when white light is passed through a substance and transmitted light is analysed by a spectrophotograph.

When visible light is passed through a prism, it is split up into seven colors with definite wave lengths.

a) Wavelength (λ): It is the distance between any two successive crests (or) troughs are called wavelength.



Wavelength is measured by \AA° , cm, nm and pm

Visible light range is 3800\AA° to 7600\AA°

$$\begin{aligned} 1\text{\AA}^\circ &= 10^{-8} \text{ cm} \\ &= 10^{-9} \text{ nm} \\ &= 10^{-10} \text{ pm} \end{aligned}$$

b) Frequency (ν): The number of waves which can pass through a point in one second is called frequency.

(ν) Frequency expressed in (ν) cycle per second (or) Hz

$$1 \text{ Hz} = 1 \text{ cycle/sec.}$$

$$\text{Frequency} \propto \frac{1}{\text{wavelength}}$$

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

c = Velocity of light ($3 \times 10^10 \text{ cm/sec}$)

c) Wave number ($\bar{\nu}$): The total number of waves which can pass through a space in one cm.

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

Units = cm^{-1}

$$E = h\nu$$

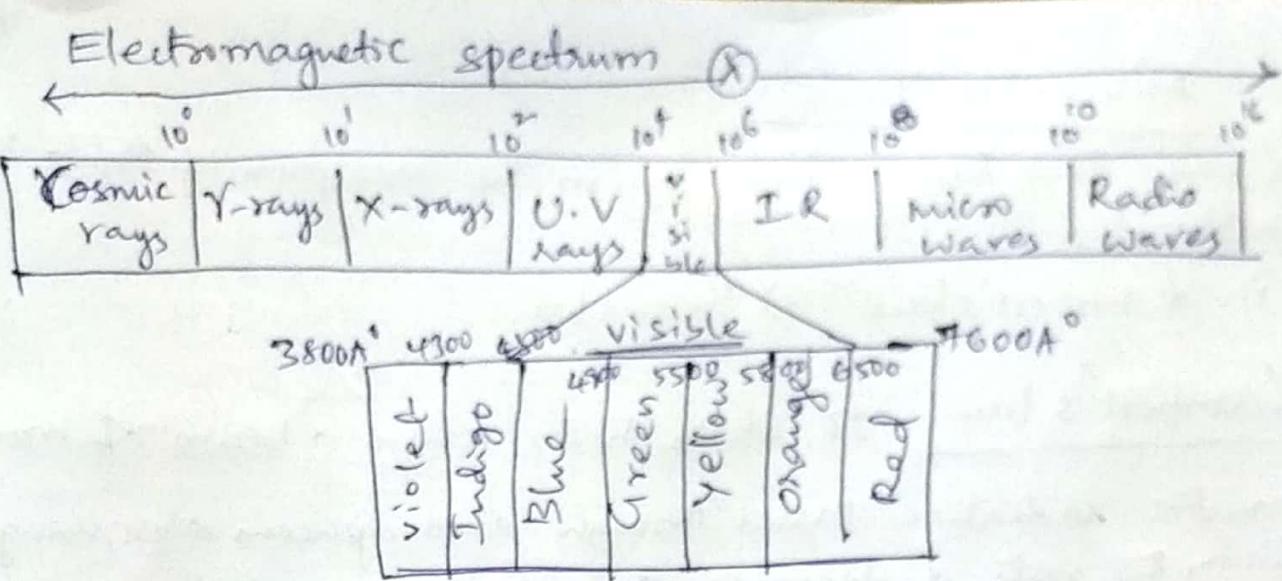
$$= \frac{hc}{\lambda}$$

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

h = plank's constant ($6.626 \times 10^{-27} \text{ ergs/sec}$)

$$E \propto \frac{1}{\lambda}$$

2020/4/26 10:56



→ U.V - range - 190 - 400 nm

→ visible " - 400 - 800 nm

→ Infra-Red " 667 - 4000 cm⁻¹

→ Radio frequency 60 - 300 MHz

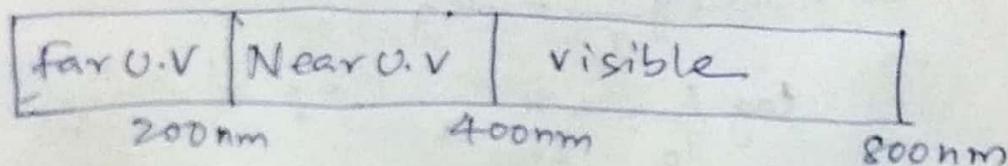
Ultra-violet and visible spectroscopy

Spectroscopy involves the interaction between matter and Electromagnetic radiation.

U.V spectroscopy is also called electronic spectroscopy since it involves the promotion of electrons (σ , π , n) from ground state to higher energy state.

→ This spectra is useful in predicting the number of conjugated double bonds also aromatic conjugation, α, β unsaturated Carbonyl compounds and ~~homo-nuclear~~ homoanular and heteroannular conjugated dienes.

→ U.V Spectrum, electronic excitations occur in the range 200 - 800 nm and involves the promotion of electrons to the higher energy molecular orbitals.

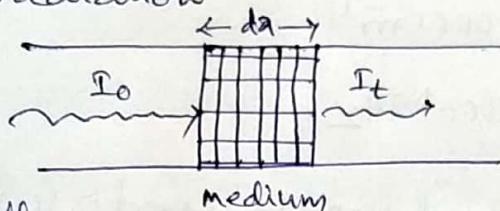


Absorption laws:

There are two laws which govern the absorption of light by the molecules

- (i) Lambert's law (ii) Beer's law

(i) Lambert's law; It states that, when a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of incident radiation



Mathematically, the law is expressed as

$$-\frac{dI}{da} \propto I \quad \because k = \text{proportionality constant}$$

$$-\frac{dI}{da} = kI \quad \because -dI = \text{decreasing the intensity of light}$$

Let I_0 be the

$$\frac{dI}{I} = -k \cdot da \rightarrow \textcircled{1} \quad I = \text{Intensity of light after passing through the medium}$$

Integrating above eq \textcircled{1} with limits

$$\int_{I_0}^I \frac{dI}{I} = - \int_{a=0}^{a=x} k \cdot da$$

$$\begin{aligned} (\text{or}) \quad & \left[\ln \frac{I}{I_0} = -ka \right] \quad (\text{or}) \quad \left[\frac{I}{I_0} = e^{-ka} \right] - \textcircled{2} \\ & \boxed{I = I_0 \cdot e^{-ka}} - \textcircled{3} \end{aligned}$$

From eqn \textcircled{2} $2.303 \log \frac{I}{I_0} = -ka$

$$\log \frac{I}{I_0} = -\frac{k}{2.303} \cdot a \quad \therefore k' = \frac{k}{2.303}$$

cont - 4:

$$\log \frac{I}{I_0} = -k' \cdot \lambda$$

∴ k' = extinction coefficient of absorbing medium (5)

$$\log \frac{I_0}{I} = k' \cdot \lambda$$

∴ $\log \frac{I_0}{I} = A$ ∵ A = Absorption

$$A = k' \cdot \lambda$$

$$A \propto \lambda$$

Units k' :

$$A = k' \cdot \lambda$$

$$k' = \frac{A}{\lambda}$$

$$\therefore A = l$$

$$\lambda = \text{cm}$$

$$k' = \text{cm}^{-1}$$

Beer's law: It states that "when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of Intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of solution"

Mathematically, this law is stated as

$$-\frac{dI}{d\lambda} \propto I \cdot c \quad \because C = \text{Molar absorption coefficient}$$

$$-\frac{dI}{d\lambda} = \epsilon \cdot I \cdot c \quad \text{--- (1)} \quad c = \text{conc of solution}$$

Integrating eq (1) I

$$\int_{I_0}^I \frac{dI}{I} = - \int_{\lambda=0}^{\lambda=\lambda} \epsilon \cdot c \cdot d\lambda$$

$$\ln \frac{I}{I_0} = -\epsilon \cdot c \cdot \lambda$$

(or)

$$\frac{I}{I_0} = e^{-\epsilon \cdot c \cdot \lambda}$$

--- (2)

$$I = I_0 \cdot e^{-\epsilon \cdot c \cdot \lambda}$$

From eq (2) $2.303 \log \frac{I}{I_0} = -\epsilon \cdot c \cdot \lambda$

$$\log \frac{I}{I_0} = \frac{-\epsilon}{2.303} \cdot c \cdot \lambda \quad \therefore \epsilon' = \frac{\epsilon}{2.303}$$

$$\log \frac{I_0}{I} = -\epsilon' \cdot c \cdot \lambda$$

$\therefore \epsilon'$ = Molar Extinction coefficient
of absorbing solution.

$$\log \frac{I_0}{I} = \epsilon' \cdot c \cdot \lambda$$

$$A = \epsilon' \cdot c \cdot \lambda$$

$$A \propto C \cdot \lambda$$

units of ϵ' :

$$A = \epsilon' \cdot c \cdot \lambda$$

$$\epsilon' = \frac{A}{c \cdot \lambda}$$

$$\therefore A = 1 \\ c = \text{concentration (moles/litre)} \\ \lambda = \text{cm}$$

$$\epsilon' = \frac{1}{\text{moles/lit. cm}} \quad (\text{or}) \quad \epsilon' = \frac{\text{mole}^{-1} \text{lit. cm}^{-1}}{\text{}}$$

Theory of Electronic Spectroscopy:

When a molecule absorbs U.V-visible light, its electrons get promoted from ground state to higher energy state. In ground state the spins of the electrons in each molecular orbital are essentially paired. In the higher energy state, if the electrons are paired, then it's called an excited singlet state. On other hand, if the spins of the electrons in the excited state are parallel, it is called an excited triplet state.

Normally the absorption of visible light results in singlet ground state to excited singlet state transition. i.e. excitation proceeds with the retention of spin. An excited singlet state is converted into excited triplet state with the emission of energy as light.

Types of Electronic transitions

According to MOT, when a molecule is excited by absorption of Energy (Visible), its electrons are promoted from the bonding to an antibonding orbital.

- i) The antibonding orbital which is associated with the excitation of σ -electron is called σ^* antibonding orbital. It is represented as $\sigma \rightarrow \sigma^*$ transition
- ii) When a non-bonding electron (n) gets promoted to an antibonding sigma orbital (σ^*) then it represents $n \rightarrow \sigma^*$ transition
- iii) Similarly $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions

The Energy required for various transitions obey the following order:

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi - \pi^* > n \rightarrow \pi^*$$

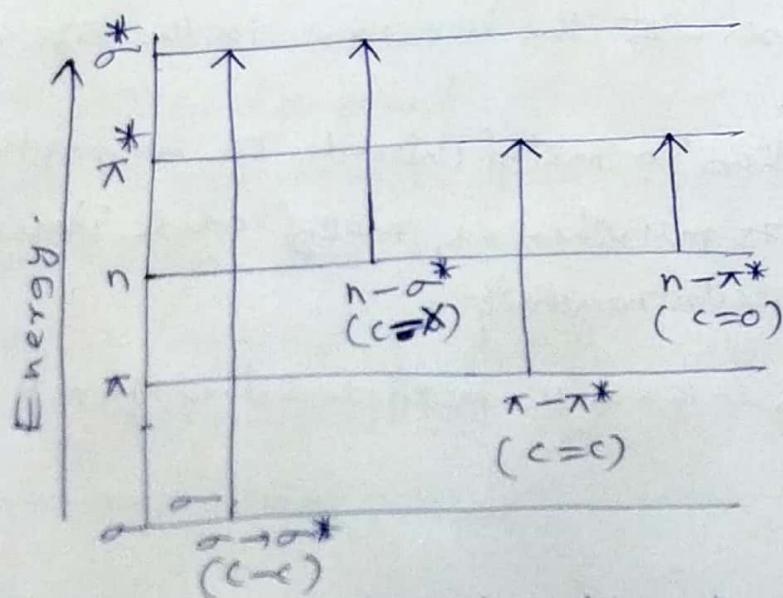
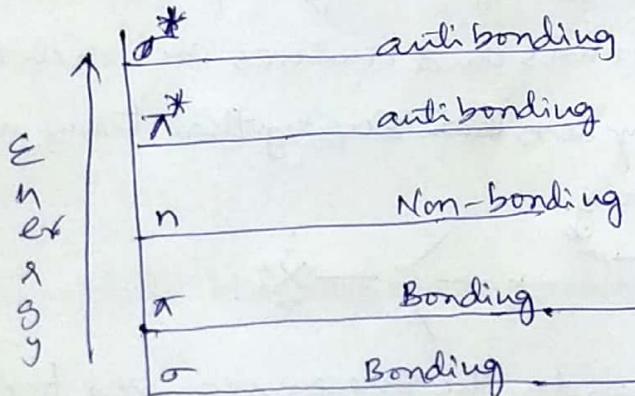
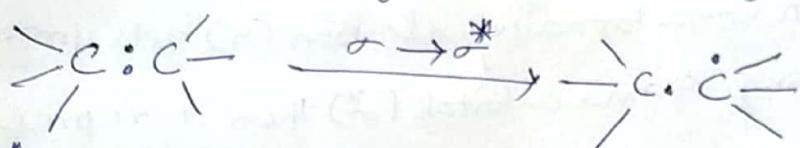


Fig: Various transitions involved in Electronic Spectroscopy.

① $\sigma \rightarrow \sigma^*$ transition; It is a very high energy process since σ bonds are, in general, very strong. In the organic compounds in which all the valence shell electrons are involved in the formation of σ bonds do not show absorption in the normal U.V.-region ($180-400$ m μ)

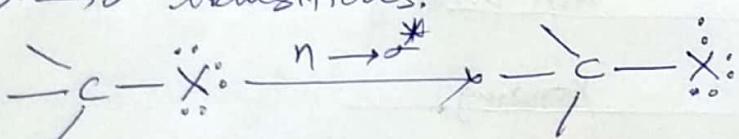
for saturated hydrocarbons like methane, propane etc. absorption occurs near 50 m μ (high energy). Such transition requires radiation of very short wavelength (high energy)



② $n \rightarrow \sigma^*$ transition;

This type of transition takes place in saturated compounds containing one heteroatom with unshared pair of electrons.

Some compounds undergoing this type of transitions are saturated halides, alcohols and amines etc. Such transition require comparatively less ~~less~~ energy than required for $\sigma \rightarrow \sigma^*$ transitions.



③ In ~~saturated~~ alkyl halides, the energy required for such a transition decreases with the increase in the size of the halogen atom.

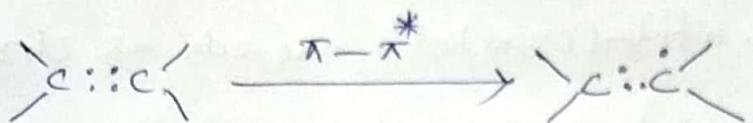
Eg ① In $n \rightarrow \sigma^*$ transition in methyl chloride, the absorption maximum is 172-175 m μ , whereas, methyl iodide λ_{max} is 238 m μ due to electronegativity

Eg ② water absorbs at 167 m μ , methyl alcohol at 174 m μ .

c) $\pi \rightarrow \pi^*$ transition:

This type of transition occurs in the unsaturated centres of molecules like $C=C$ or $C\equiv C$ and also in aromatics.

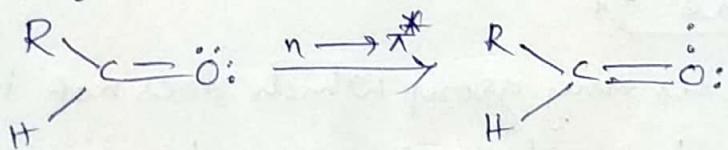
The excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelength.



E.g. alkenes, alkynes, Benzenoid compounds, cyanide, and azo-compounds show this transition.

d) $n \rightarrow \pi^*$ transition:

In this type of transition, an electron of unsaturated electron pair on hetero atom gets excited to π^* antibonding orbital. This type of transition requires least amount of energy out of all the transitions.



Saturated aldehydes ($R-CHO$) show this transition at 180nm

The chromophore concept

All those compounds which absorb light of wavelength between $400-800\text{nm}$ appear coloured to the human eye.

Exact color depends upon the wavelength of light observed by the compound. Originally, a chromophore was considered. Any system which is responsible for imparting color to the compound. Nitro compounds are generally yellow in colour.

Similarly any conjugated group is a chromophore for providing colour to dyes.

definition: It is defined as any isolated covalently bonded group that shows characteristic absorption in UV or visible light.

Eg: Ethylene ($C=C$), Acetylene ($C\equiv C$), Carbonyls ($>C=O$), Alkyl (-COOH) Esters ($-C-O-R'$), nitro ($C\equiv N$) etc, are all as chromophores.

→ chromophore which contains both π electrons and nonbonding electrons, such chromophores undergo two types of transitions i.e $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$

Eg: $>C=O$, $C\equiv N$, $N\equiv N$, $-N\overset{<}O$ compounds etc.

→ chromophores which contains π electrons and they undergo $\pi \rightarrow \pi^*$ transitions

Eg: $>C=C'$, $-C\equiv C-$ etc.

Anaechrome :

It is defined as any group which does not itself act as a chromophore but whose presence brings about a shift of absorption band towards the red end of the spectrum (longer wavelength (λ_{max}))).

The absorption of longer wavelength is due to the combination of a chromophore and an anaechrome to give rise to another chromophore.

Anaechromic groups do not show characteristic absorption above 200m μ .

Eg: Anaechrome, $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, $-SH$ etc.

Eg: Benzene shows an λ_{max} at 255m μ whereas aniline absorbs at 280m μ . Hence, amino ($-NH_2$) group is an anaechrome.

Absorption and Intensity shifts

a) Bathochromic effect (Red-shift): It is an effect by virtue of which the absorption maximum is shifted towards longer wavelength due to the presence of an auxochrome or by the change of solvent.

The $\pi \rightarrow \pi^*$ transition for carbonyl compounds experiences red shift when the polarity of solvent is decreased.

b) Hypsochromic shift (Blue shift): It is an effect by virtue of which the absorption maximum is shifted towards shorter wavelength.

It may be caused by the removal of conjugated and also by changing the polarity of the solvent-

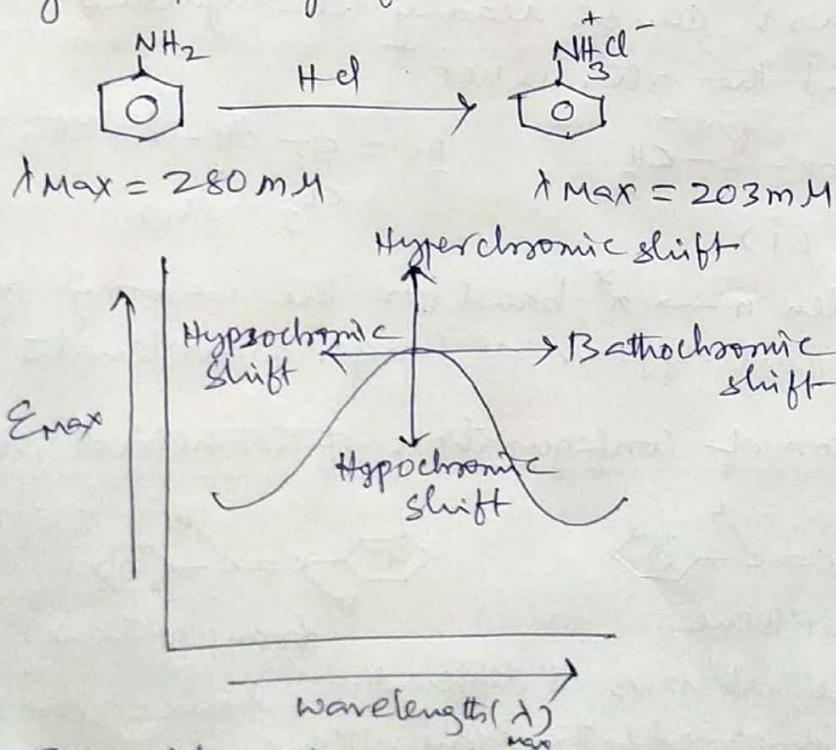


Table: Absorption and Intensity shifts .

c) Hyperchromic shift: It is an effect due to which the intensity of absorption maximum increases. Introduction of auxochrome usually increases intensity of absorption.

pyridine



$\lambda_{\text{MAX}} = 257 \text{ m}\mu$

$E_{\text{MAX}} = 2750$

2-methylpyridine



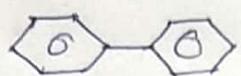
$\lambda_{\text{MAX}} = 262 \text{ m}\mu$

$E_{\text{MAX}} = 3560$

(12)

d) Hypochromic shift: It is an effect due to which the intensity of absorption maximum decreases.

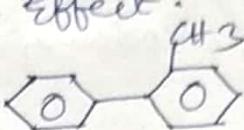
The introduction of group which distorts the geometry of the molecule causes hypochromic effect.



Biphenyl

$\lambda_{\text{MAX}} = 250 \text{ m}\mu$

$E_{\text{MAX}} = 19000$



2-methyl biphenyl

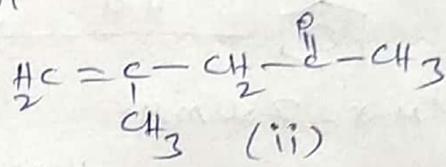
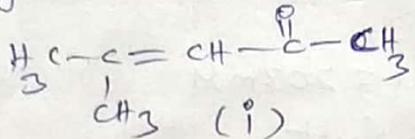
$\lambda_{\text{MAX}} = 237 \text{ m}\mu$

$E_{\text{MAX}} = 10250$

Applications: UV-visible spectroscopy is used to detect the following

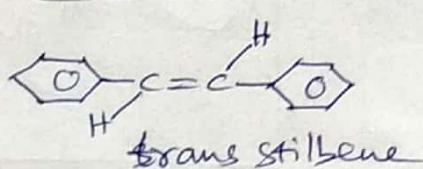
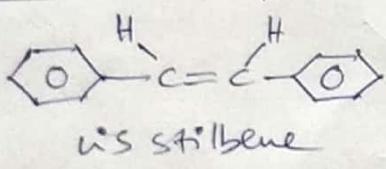
① Detection of conjugated and Non-conjugated compounds.

It is used to distinguish conjugated and nonconjugated. The following isomers can be readily distinguished since one is conjugated and the other is not.



The forbidden $n \rightarrow \pi^*$ band for the carbonyl group in the compound (i) will appear at longer wavelength.

② Determination of configuration of Geometrical isomers:



The cis alkene absorbs at different wavelengths as compared to the trans alkene.

The distinction becomes possible when one of the isomer is forced to be non-coplanar by steric hindrance, thus cis alkene is suffered distortion and absorption occurs at lower wavelength.

3) Identification of a compound in different solvents:

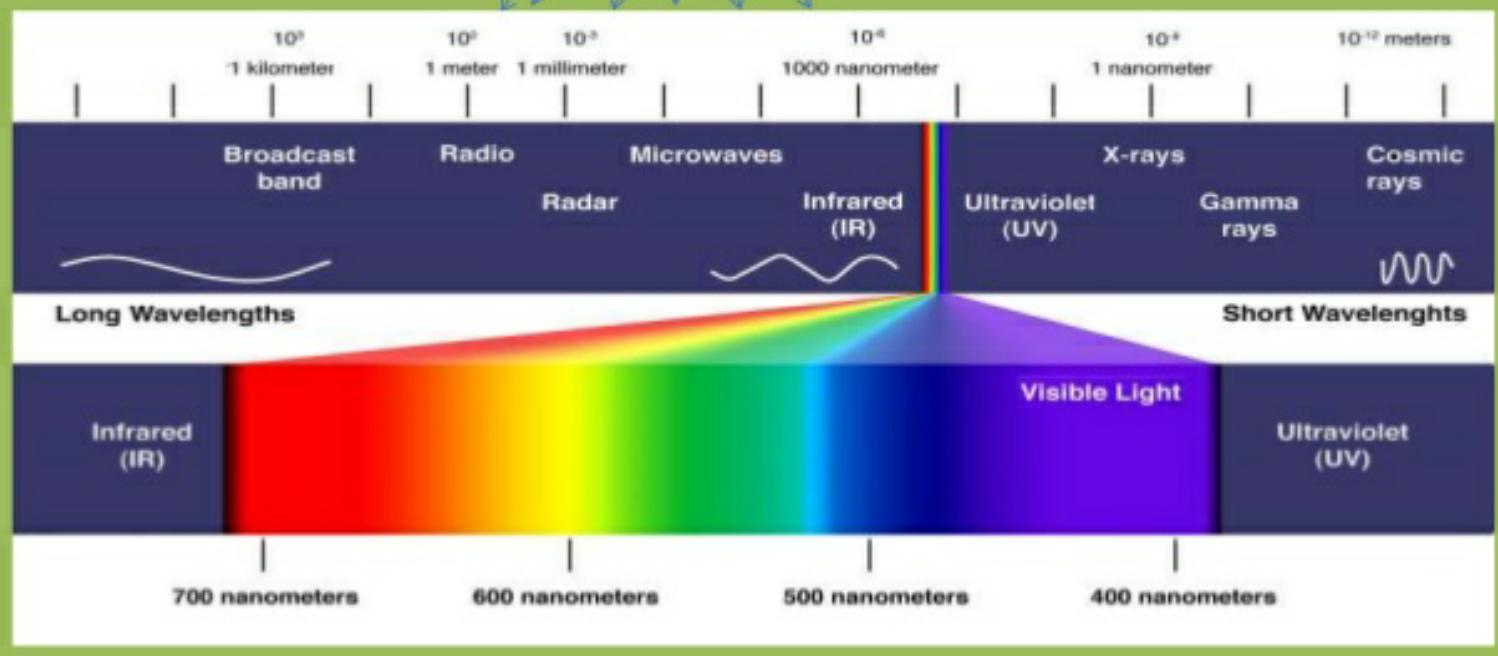
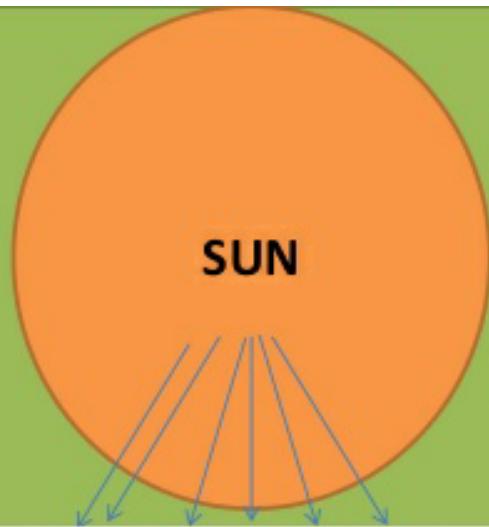
Sometimes, the structure of the compound changes with the change in the solvent. Chloral hydrate shows an absorption maximum at $290\text{m}\mu$ in hexane while absorption disappears in the aqueous solution. Clearly, the compound contains a carbonyl group in hexane solution and its structure is $\text{CH}_2\text{COCl} \cdot \frac{1}{2}\text{H}_2\text{O}$ whereas in aqueous solution it is present as $\text{CH}_2\text{CO(OH)}_2$.

4) Examination of polynuclear hydrocarbons:

Benzene and polynuclear hydrocarbons have characteristic spectra in ultra-violet and visible region. Thus, the identification of the polynuclear hydrocarbons can be made by comparison with the spectra of known polynuclear compounds. The presence of substituents on the ring, generally, shifts the absorption maximum to longer wavelength.

(d)

IR & NMR SPECTRA

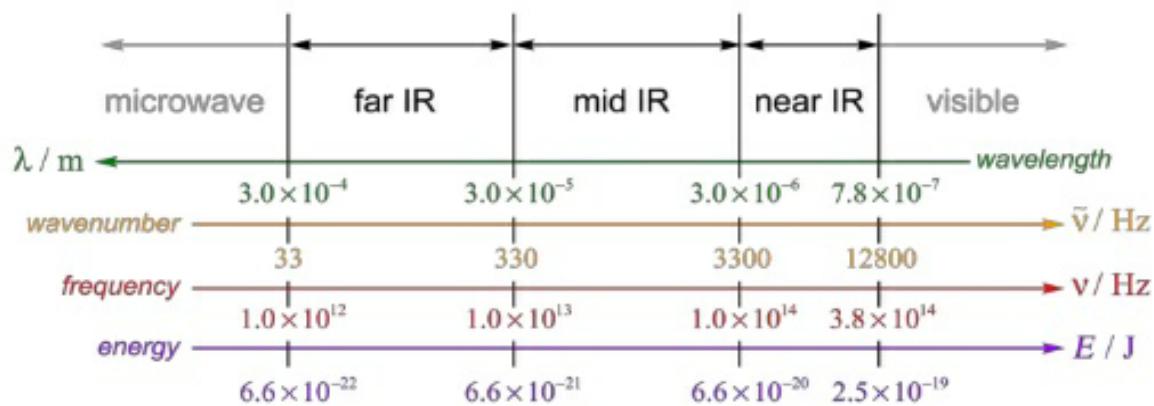


Infrared spectroscopy

It is a very powerful technique which uses electromagnetic radiation in the infrared region for the determination and identification of molecular structure as well as having various quantitative applications within analytical chemistry

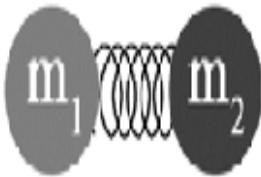
1. **Near infrared** ($12820\text{-}4000\text{ cm}^{-1}$): poor in specific absorptions, consists of overtones and combination bands resulting from vibrations in the mid-infrared region of the spectrum.
2. **Mid-infrared** ($4000\text{-}400\text{ cm}^{-1}$): provides structural information for most organic molecules
3. **Far Infrared** ($400\text{-}33\text{ cm}^{-1}$): has been less investigated than the other two regions; however, it has been used with inorganic molecules.

Regions of IR Radiation



Principle of IR Spectroscopy:

Hooke's law and frequency of vibration -We have seen that the bonds are not static but vibrating in different ways. A vibrating bond can therefore be considered a spring with its ends tethered to two atoms



If the masses of the atoms are m_1 and m_2 , the frequency of stretching vibration of the diatomic molecule can be given by the Hooke's law:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

where, ν is the frequency of vibration, k is the spring constant, and μ is the reduced mass i.e. $m_1 m_2 / (m_1 + m_2)$

The spring constant, k is the measure of the bond strength. The stronger the bond, the higher the k , and consequently the higher is the frequency of vibration.

Selection Rules

A molecular vibration is IR active i.e. it absorbs IR radiation if the vibration results in a change in the dipole moment .

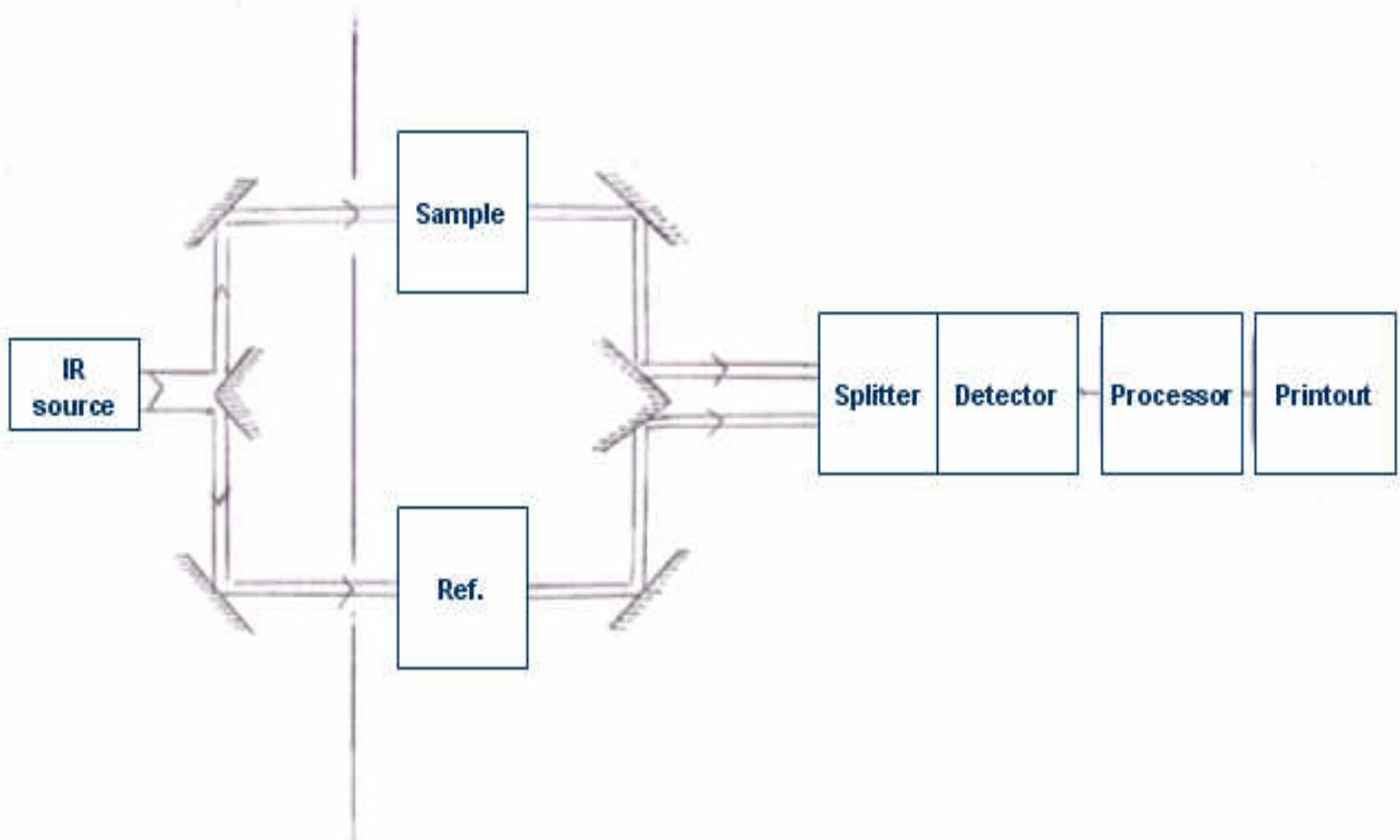
➤ A diatomic molecule, that has one mode of vibration, may not absorb an IR radiation if the vibration does not accompany a change in the dipole moment.

ex: H₂, N₂, O₂, etc.

➤ Vibration of carbon monoxide (C=O), on the other hand, causes a change in dipole moment and is therefore IR active.

➤ Vibration of a bond involving two atoms that have large electro negativity difference is usually IR active.

Instrumentation:



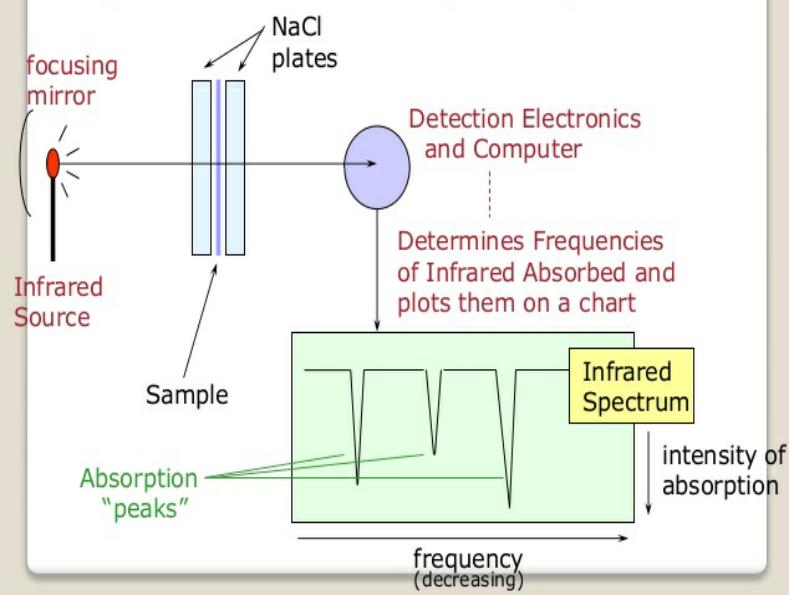
Thermo Nicolet

FT-IR System

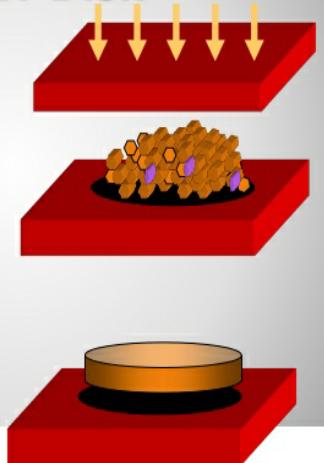


Optical Bench

Simplified Infrared Spectrophotometer



Preparing a KBr Disk



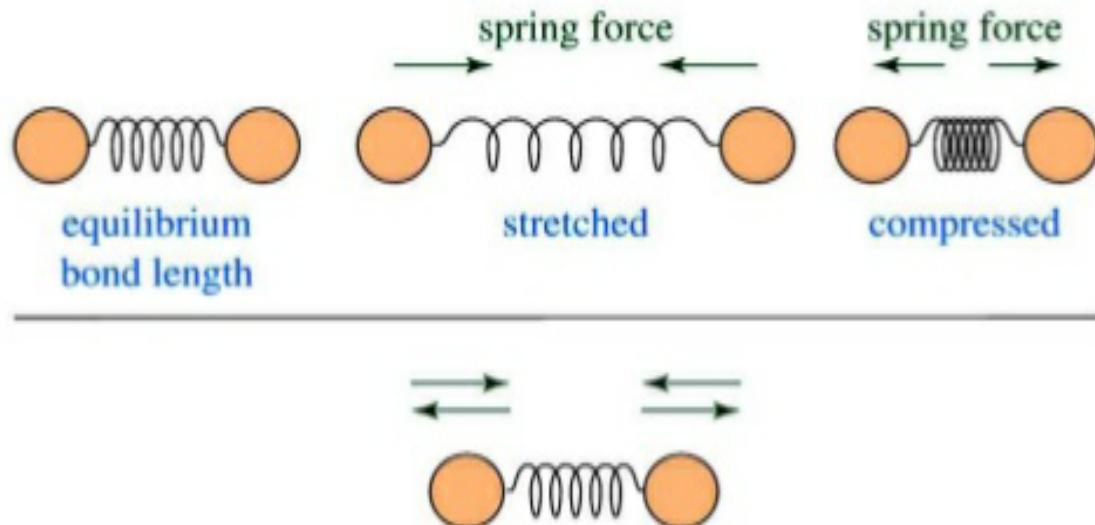
Apparatus for KBr Disk



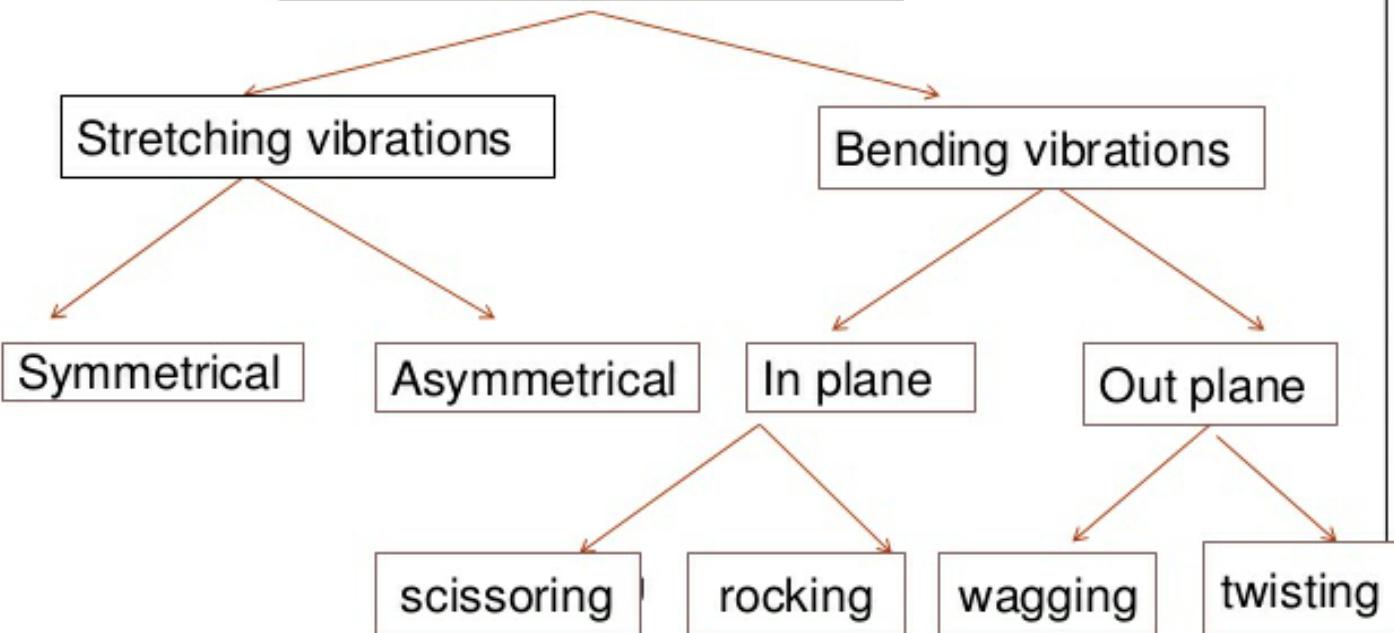
VIBRATIONAL MODES

- Infrared radiation induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two atoms.
- Infrared (IR) spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group.

Specific bonds respond to (absorb) specific frequencies

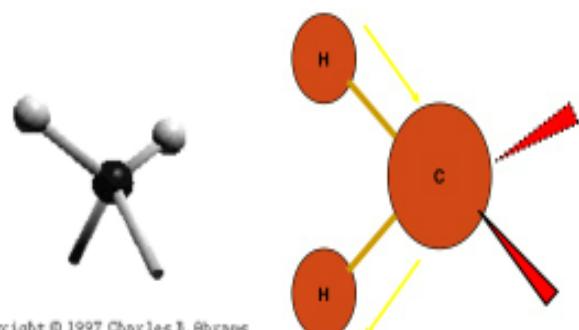


Molecular vibrations



b) Asymmetrical stretching

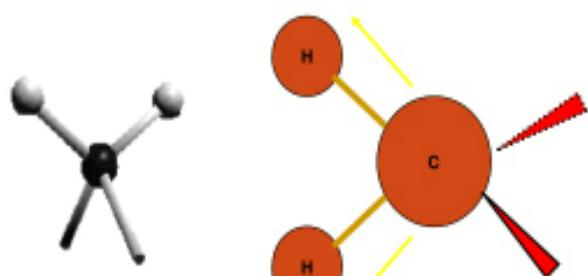
- one bond length is increased and other is decreased.



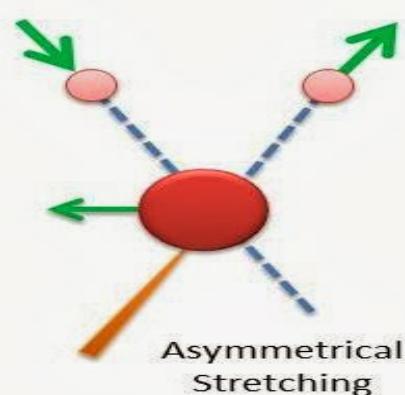
Copyright © 1997 Charles E. Abrams

a) Symmetrical stretching:

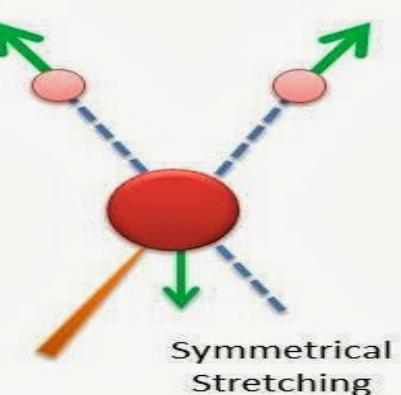
- Two bonds increase or decrease in length simultaneously.



Copyright © 1997 Charles E. Abrams



Stretching Vibrations



Namrata Heda

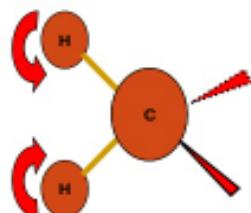
A) In plane bending

i. Scissoring:

- 2 atoms approach each other
- Bond angles are decrease

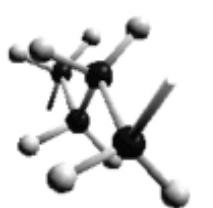


Copyright © 1997 Charles S. Johnson

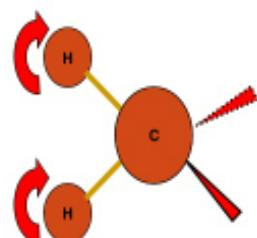


ii. Rocking:

- Movement of atoms take place in the same direction.



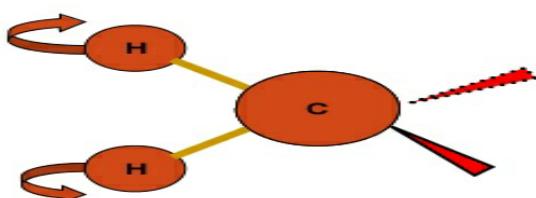
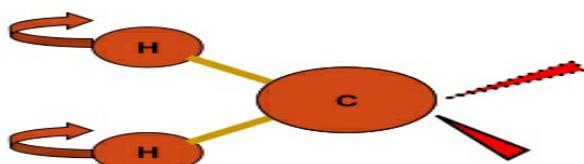
Copyright © 1997 Charles S. Johnson



B) Out plane bending

i. Wagging:

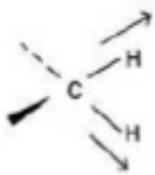
Two atoms move to one side of the plane. They move up and down the plane.



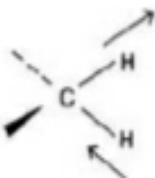
ii. Twisting:

One atom moves above the plane and another atom moves below the plane.

The two primary modes of vibration are *stretching* and *bending*. Stretching modes are typically of higher energy than bending modes. Stretching modes are often divided into two: a symmetric and asymmetric stretch; the asymmetric stretch is usually of higher energy.

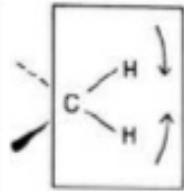


Symmetric stretch
(~2853 cm⁻¹)

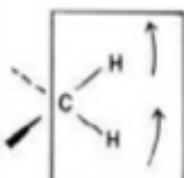


Asymmetric stretch
(~2925 cm⁻¹)

STRETCHING VIBRATIONS

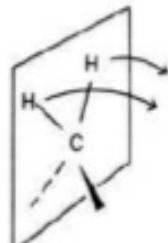


Scissoring
(~1450 cm⁻¹)

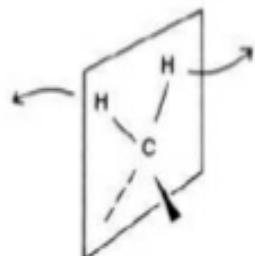


Rocking
(~720 cm⁻¹)

IN-PLANE



Wagging
(~1250 cm⁻¹)



Twisting
(~1250 cm⁻¹)

BENDING VIBRATIONS

Number of Fundamental Vibrations

The IR spectra of polyatomic molecules may exhibit more than one Vibrational absorption bands. The number of these bands corresponds to the number of fundamental vibrations in the molecule which can be calculated from the degrees of freedom of the molecule.

In case of a nonlinear molecule : $(3n - 3 - 3) = 3n - 6$
Total degrees of freedom ($3n$) = Translational + Rotational + Vibrational degrees of freedom
Infrared (IR) Spectroscopy

In case of a linear molecule : $(3n - 2 - 3) = 3n - 5$ degrees of freedom are Vibrational degrees of freedom or fundamental vibrations.

1. Ex CO₂:

Number of atoms (n) = 3

Total degrees of freedom (3n) = 3 x 3 = 9

Rotational degrees of freedom = 2

Translational degrees of freedom = 3

Therefore, Vibrational degrees of freedom (3n - 5) = 9 - 2 - 3 = 4

2. Ex: Benzene (C₆H₆):

Number of atoms (n) = 12

Total degrees of freedom (3n) = 3 x 12 = 36

Rotational degrees of freedom = 3

Translational degrees of freedom = 3

Therefore, Vibrational degrees of freedom (3n - 6) = 36 - 3 - 3 = 30

Ex3: Ethane (C₂H₆):

Number of atoms (n) = 8

Total degrees of freedom (3n) = 3 x 8 = 24

Rotational degrees of freedom = 3

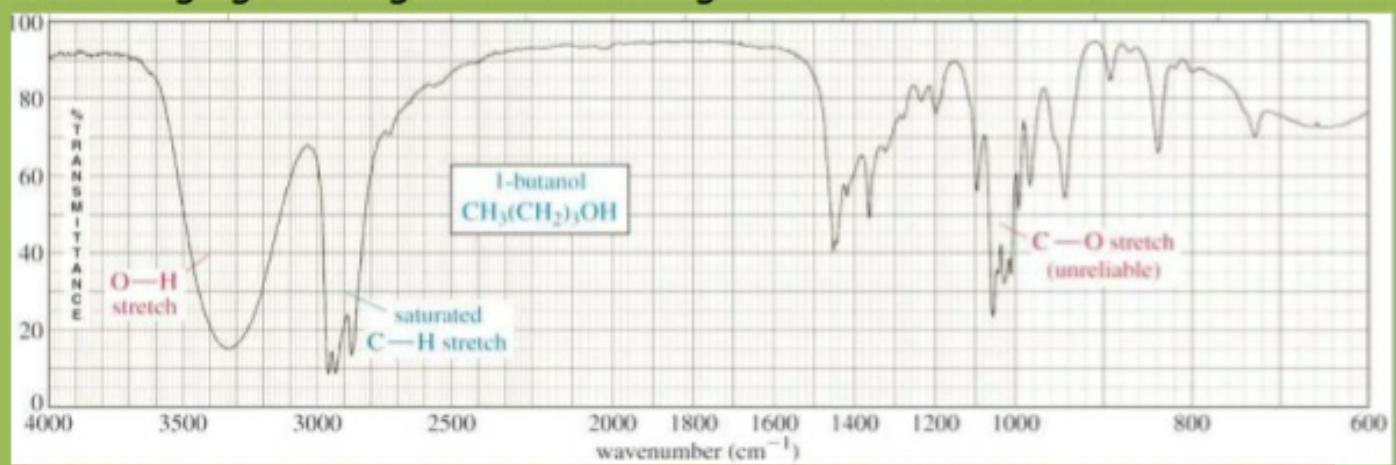
Translational degrees of freedom = 3

Hence, Vibrational degrees of freedom (3n - 6) = 24 - 3 - 3 = 18

• The IR Spectrum

→ There are two type of IR Spectra from which we can obtained the information about the quality of molecule .

1. The Functional Group region: Identifies the functional group with the consequence of changing stretching vibrations. Ranges from 4000 to 1600 cm^{-1} .
2. The Fingerprint region: Identifies the exact molecule with the consequence of changing bending vibrations. Ranges from 1600 to 625 cm^{-1} .



Focus your analysis on this region. This is where most stretching frequencies appear

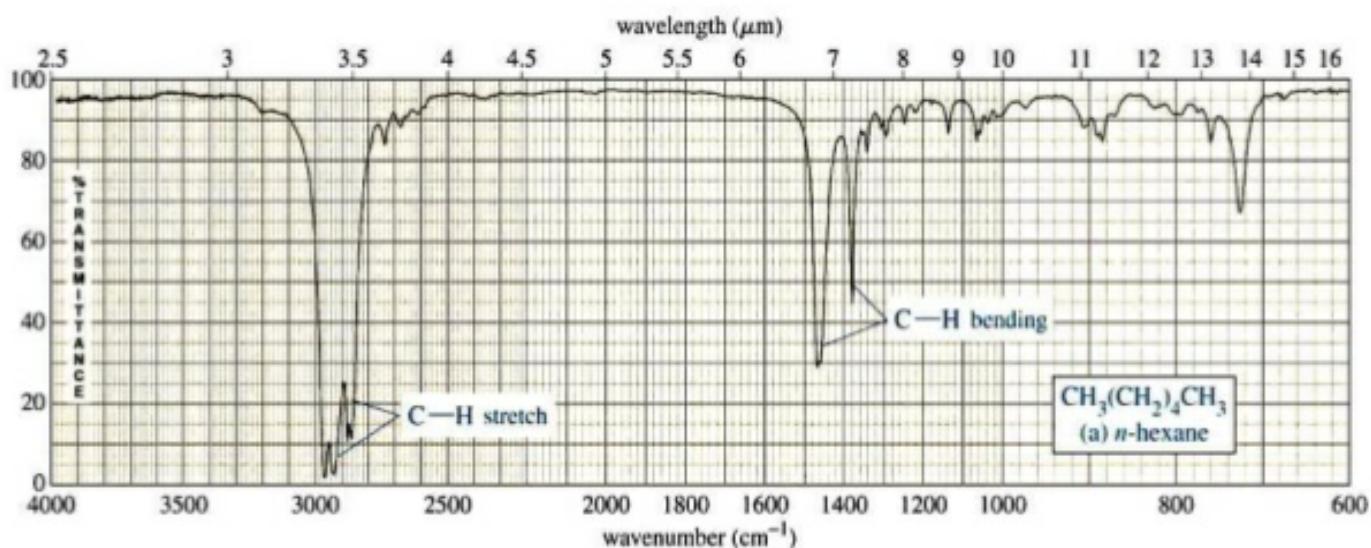
Fingerprint region: complex and difficult to interpret reliably

<i>Functional Group</i>	<i>Characteristic Absorption(s) (cm⁻¹)</i>
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C≡N Stretch	2260 - 2220 (m)
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)

s=strong, m=medium, w=weak, v=variable.

IR SPECTRUM OF ALKANES

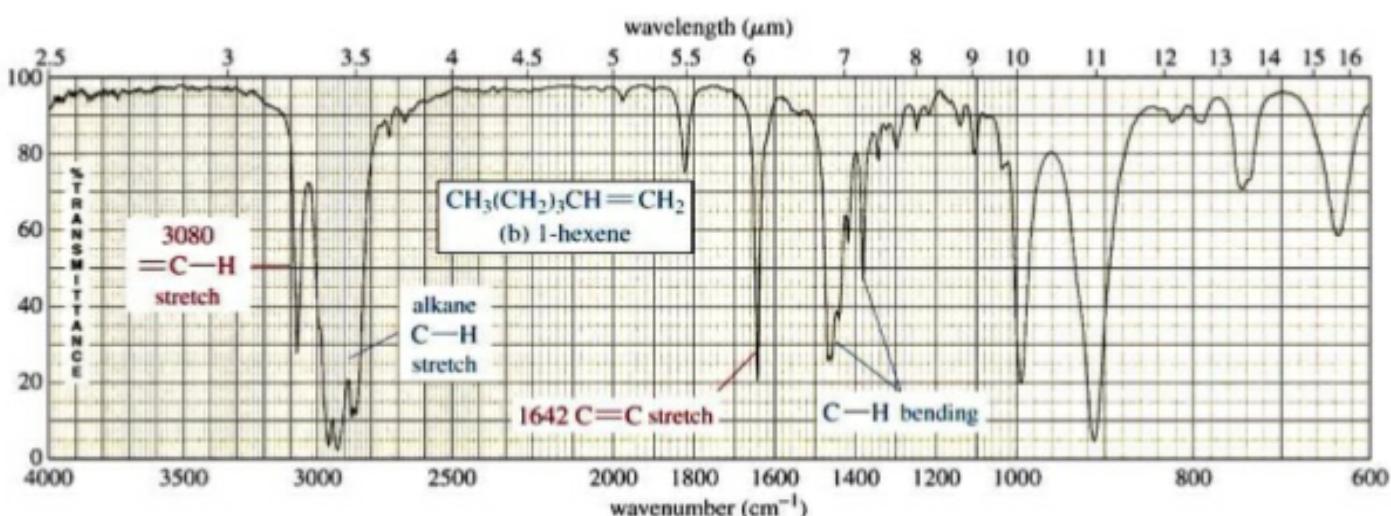
Alkanes have no functional groups. Their IR spectrum displays only C-C and C-H bond vibrations. Of these the most useful are the **C-H bands**, which appear around **3000 cm⁻¹**. Since most organic molecules have such bonds, most organic molecules will display those bands in their spectrum.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

IR SPECTRUM OF ALKENES

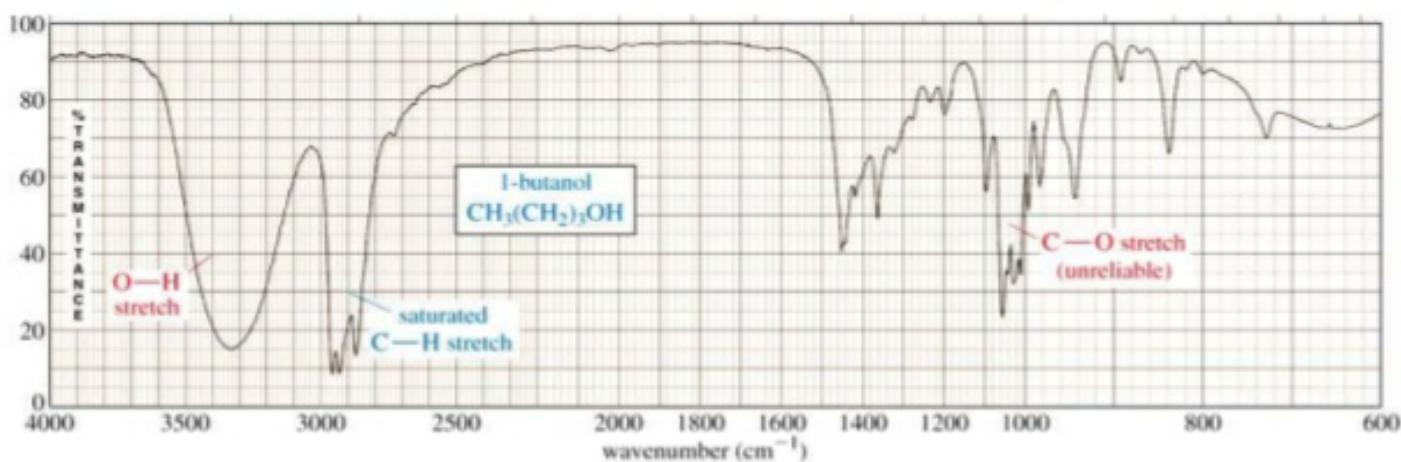
Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm⁻¹**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm⁻¹** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm⁻¹ (see next slide)



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

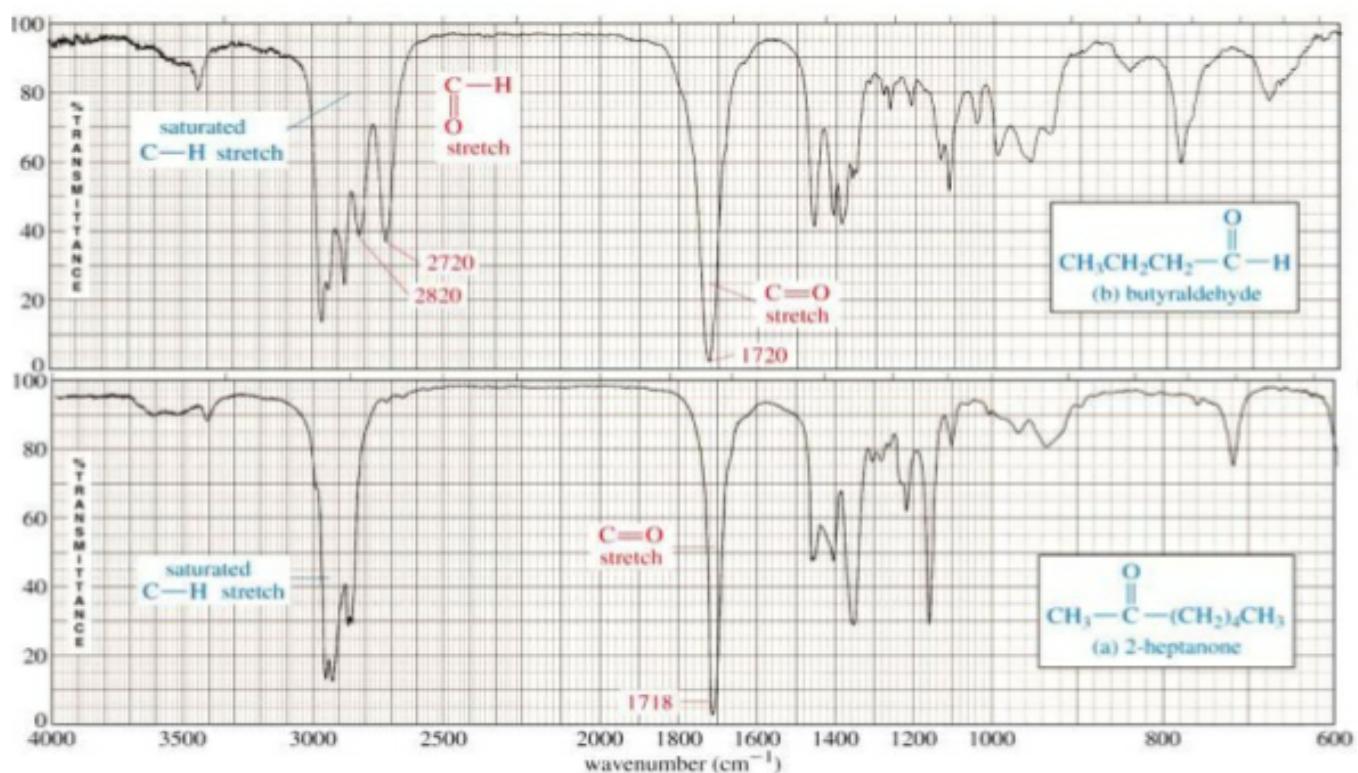
IR SPECTRUM OF AN ALCOHOL

The most prominent band in alcohols is due to the **O-H bond**, and it appears as a strong, broad band covering the range of about **3000 - 3700 cm⁻¹**. The sheer size and broad shape of the band dominate the IR spectrum and make it hard to miss.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR SPECTRUM OF ALDEHYDES AND KETONES

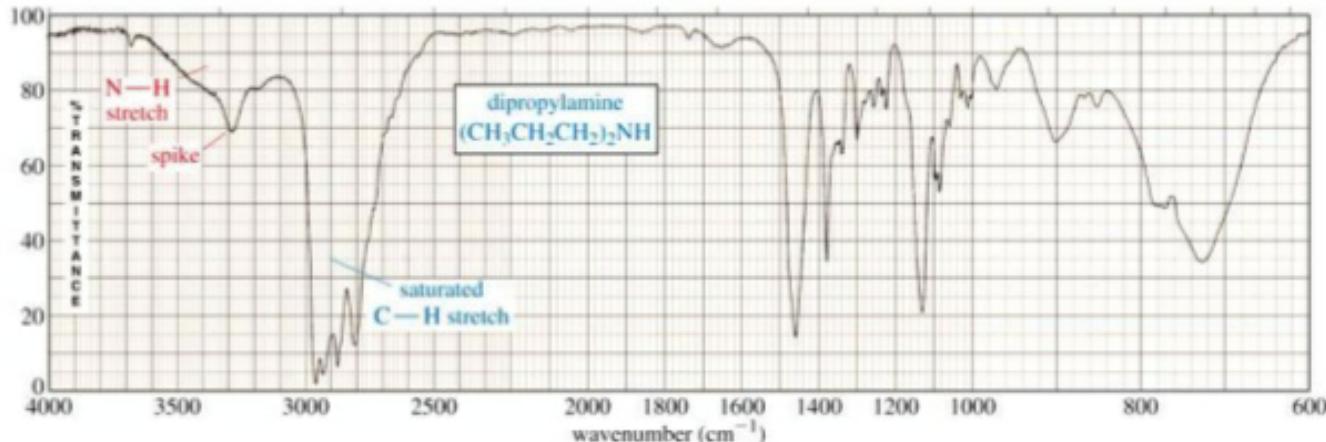


Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

IR SPECTRA OF AMINES

The most characteristic band in amines is due to the **N-H bond stretch**, and it appears as a weak to medium, somewhat broad band (but not as broad as the O-H band of alcohols). This band is positioned at the left end of the spectrum, in the range of about **3200 - 3600 cm⁻¹**.

Primary amines have two N-H bonds, therefore they typically show two spikes that make this band resemble a molar tooth. Secondary amines have only one N-H bond, which makes them show only one spike, resembling a canine tooth. Finally, tertiary amines have no N-H bonds, and therefore this band is absent from the IR spectrum altogether. The spectrum below shows a secondary amine.



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

1. Identification of Substances

- To compare spectrums.
- No two samples will have identical IR spectrum.
- Criteria: Sample and reference must be tested in identical conditions, like physical state, temperature, solvent, etc.
- Disadvt: Enantiomers cannot be distinguished (spectrum are identical).

6. Functional Group Isomerism

- Isomerism shown by compounds having same molecular formula but different functional groups.

$$\text{OH} = 3500-3100 \text{ cm}^{-1}$$

4. Detection of Impurities

- Determined by comparing sample spectrum with the spectrum of pure reference compound.
- Eg.: ketone impurity in alcohols.
- Detection is favoured when impurity possess a strong band in IR region where the main substance do not possess a band.

5. Isomerism in Organic Chemistry

(i) Geometrical Isomerism:

- *trans* isomers give a simpler spectrum than *cis* due to symmetry.

(ii) Conformers (Rotational Isomers):

- Identified with the help of high resolution IR spectrometers.

14. Analysis of Petroleum HCs, Oil & Grease contents

- These contain C–H bonds.
Absorption at $3100\text{--}2700\text{ cm}^{-1}$.
- ‘Freons’—Fluorocarbon-113; do not contain C–H bond.
- Thus, quantity of HCs, oil & grease in freons is determined by measuring C–H absorption at 2930 cm^{-1} .

OTHER APPLICATIONS

1. Determination of unknown contaminants in industry using FTIR.
2. Determination of cell walls of mutant & wild type plant varieties using FTIR.
3. Biomedical studies of human hair to identify disease states (recent approach).
4. Identify odor & taste components of food.
5. Determine atmospheric pollutants from atmosphere itself.
6. Examination of old paintings

Introduction:-

Nuclear Magnetic Resonance (NMR) is a spectroscopy technique which is based on the absorption of electromagnetic radiation in the **radio frequency region 4 to 900 MHz** by nuclei of the atoms.

Proton Nuclear magnetic resonance spectroscopy is one of the most powerful tools for elucidating the number of hydrogen or proton in the compound.

It is used to study a wide variety of nuclei:

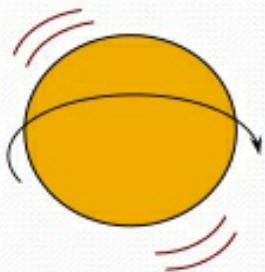
- ^1H ^{15}N
- ^{19}F ^{19}F
- ^{13}C ^{31}P

3. PROTON NMR

- It is a technique which is based on the absorption of electromagnetic radiation in the radio frequency region **4 to 900 MHz** by nuclei of the atoms.
- It is used to study a wide variety of nuclei: ^1H , ^{15}N , ^{19}F , ^{13}C , ^{31}P .
- The most common form of NMR is based on the hydrogen-1 (^1H), nucleus or proton.
- It can give information about the structure of any molecule containing hydrogen atoms.

NUCLEAR SPIN

The nuclei of some atoms have a property called “**SPIN**”.

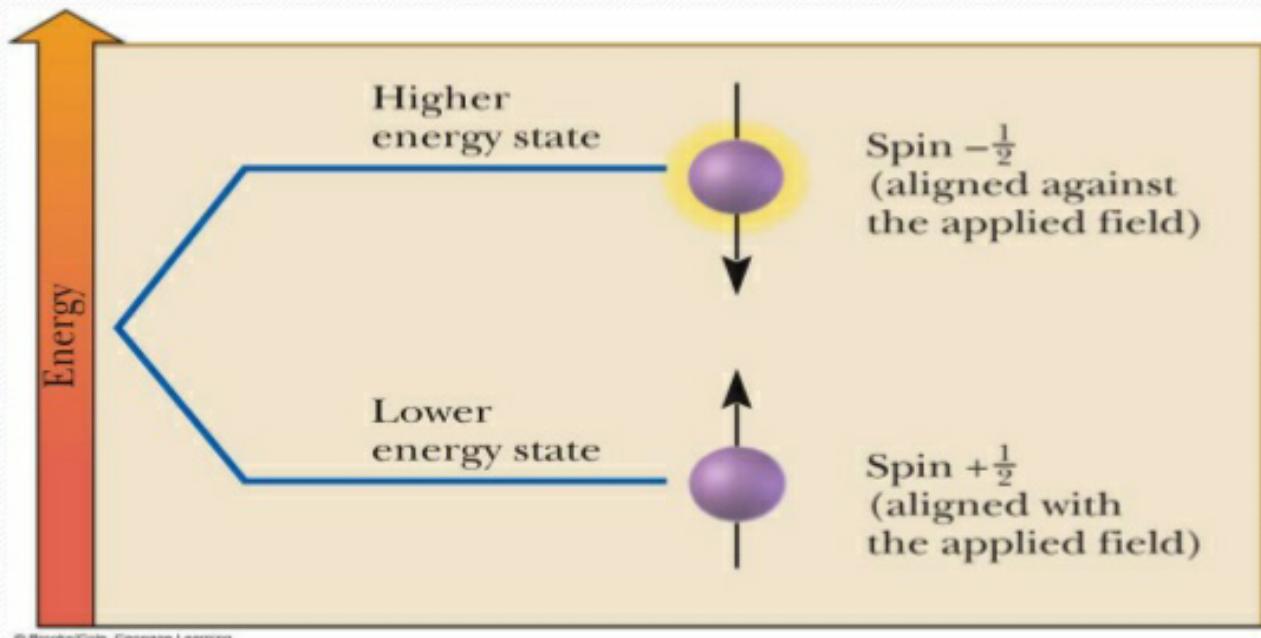


These nuclei behave as if they were spinning.

This is like the spin property of an electron, which can have two spins: **+1/2** and **-1/2**.

Each spin-active nucleus has a number of spins defined by its spin quantum number, **I**.

The number of Spin states = $2I + 1$

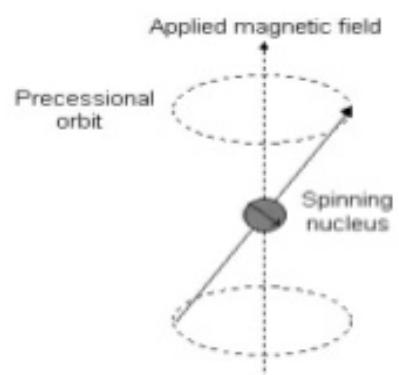
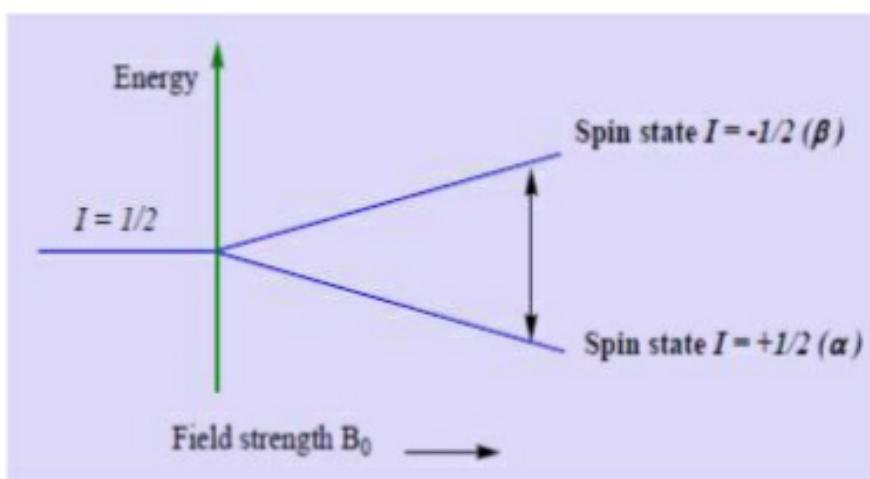


© Brooks/Cole, Cengage Learning

Change in spin state energy separation with increase by applied magnetic field , B_0

If an external magnetic field is applied, the number of possible orientations calculated by $(2I+1)$.

Hydrogen has spin quantum number $I=1/2$ and possible orientation is $(2 \cdot 1/2 + 1 = 2)$ two $+1/2$ and $-1/2$.



Theory of NMR:-

Spin quantum number (I) is related to the atomic and mass number of the nucleus.

I	Atomic Mass	Atomic Number	Examples
Half-integer	Odd	Odd	^1H ($1/2$)
Half-integer	Odd	Even	^{13}C ($1/2$)
Integer	Even	Odd	^2H (1)
Zero	Even	Even	^{12}C (0)

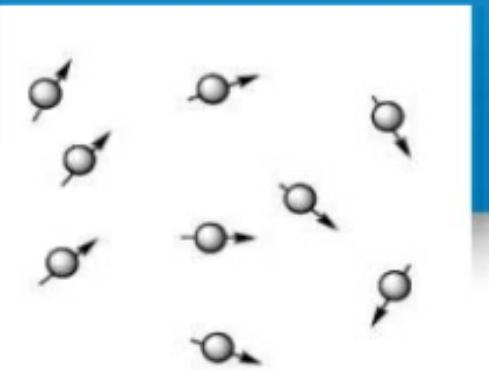
NMR active Not NMR active

Elements with either odd mass or odd atomic number have the property of nuclear “spin”.

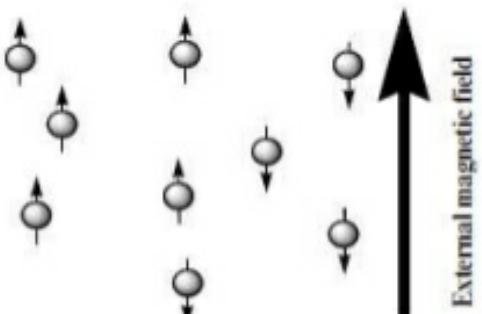
Principles of NMR

The theory behind NMR comes from the spin of a nucleus and it generates a magnetic field. Without an external applied magnetic field, the nuclear spins are random in directions.

But when an external magnetic field(B_0), is present the nuclei align themselves either with or against the field of the external magnet.



No external magnetic field

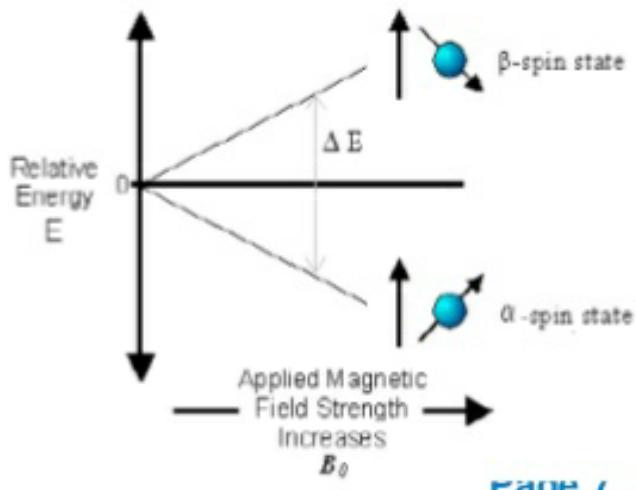
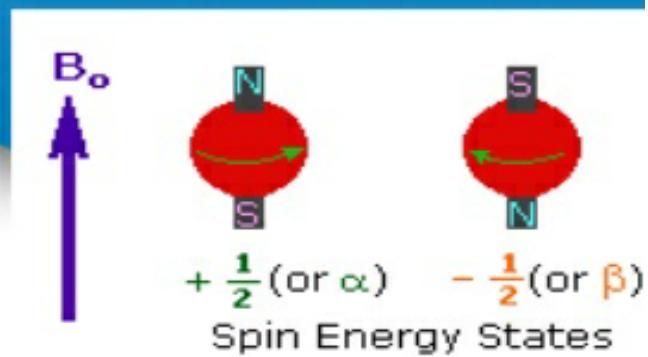


With external magnetic field

If an external magnetic field is applied, an energy transfer (ΔE) is possible between ground state to excited state.

when the spin returns to its ground state level, the absorbed radiofrequency energy is emitted at the same frequency level.

The emitted radiofrequency signal that give the NMR spectrum of the concerned nucleus.



The emitted radio frequency is directly proportional to the strength of the applied field.

$$v = \frac{\gamma B_o}{2\pi}$$

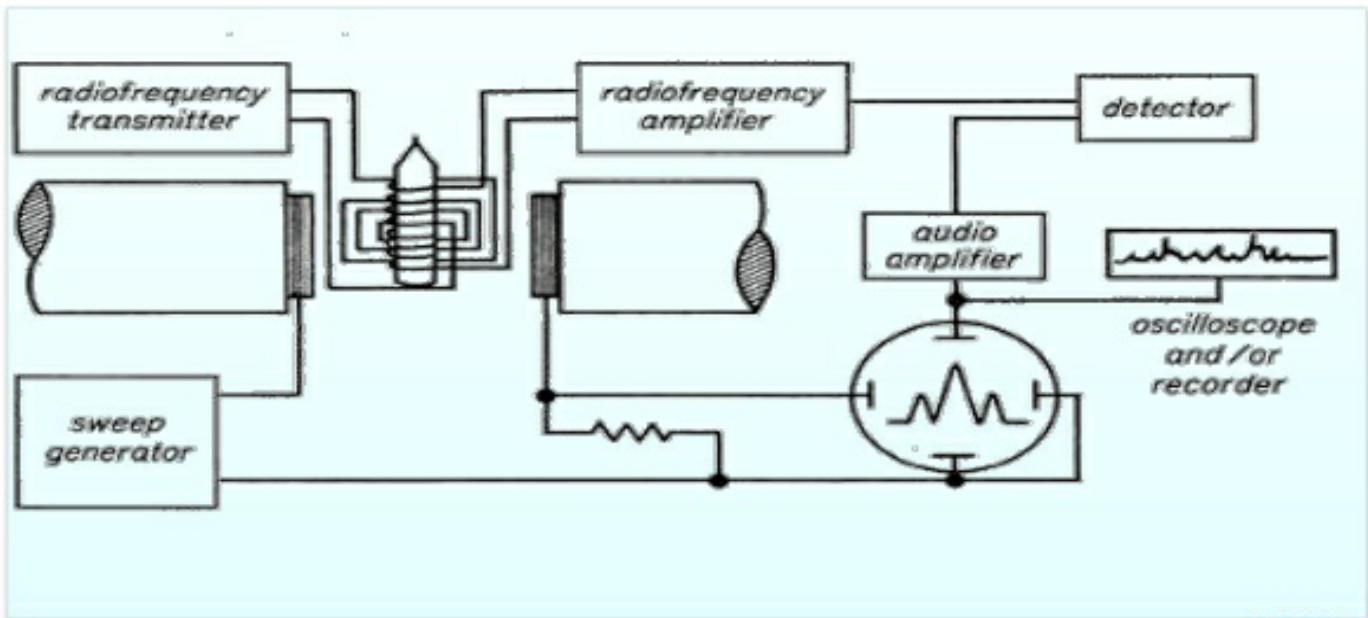
B_o = External magnetic field experienced by proton

γ = Magnetogyric ratio (The ratio between the nuclear magnetic moment and angular moment)

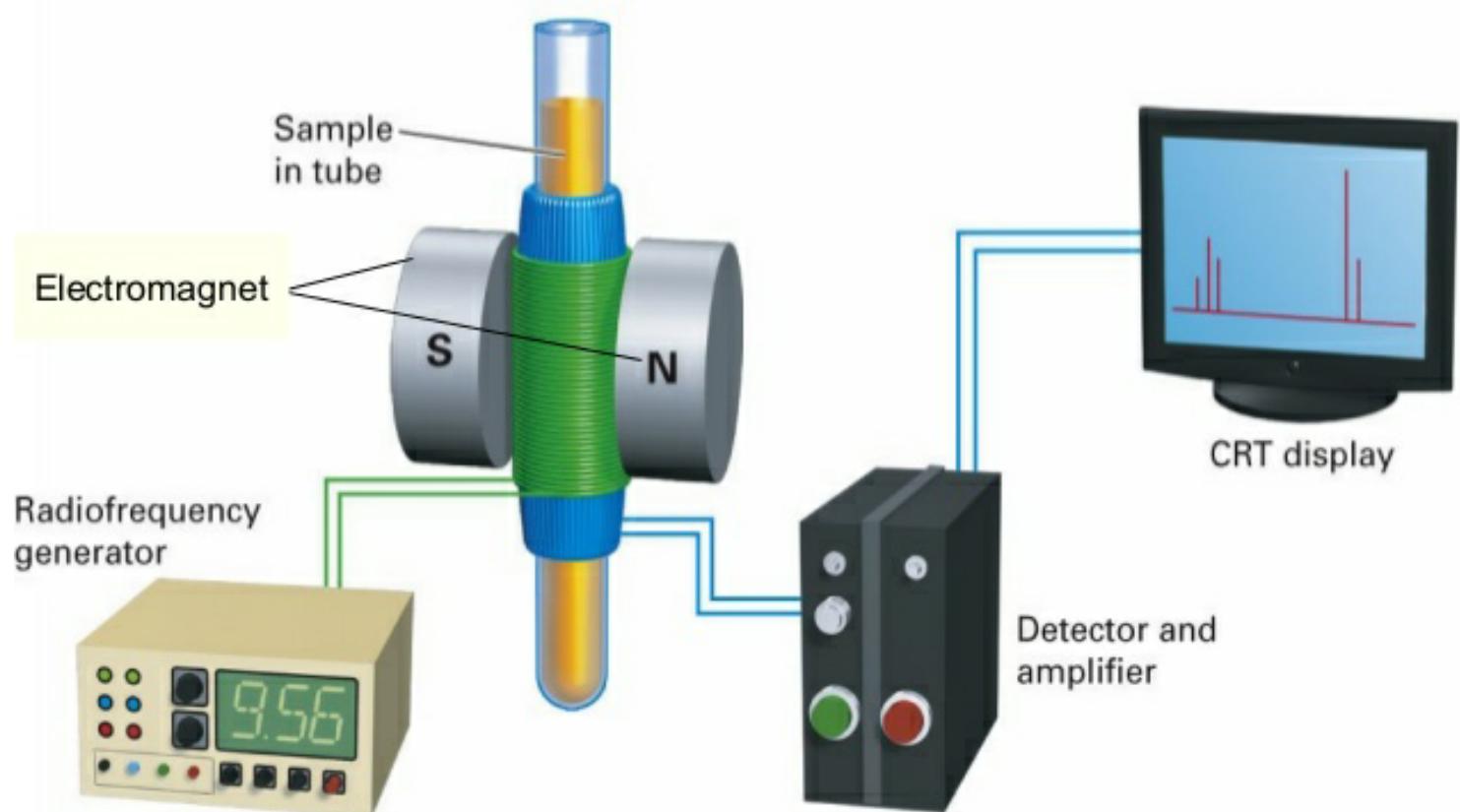
NMR instrumentation

- 1. Sample holder
- 2. Permanent magnet
- 3. Magnetic coils
- 4. Sweep generator
- 5. Radio frequency transmitter
- 6. Radio frequency receiver

7. Read out systems



Schematic diagram of NMR set-up



Chemical shift

A **chemical shift** is defined as the difference in parts per million (ppm) between the resonance frequency of the observed proton and tetramethylsilane (TMS) hydrogens.

TMS is the most common reference compound in NMR, it is set at $\delta=0$ ppm

$$\text{Chemical shift, } \delta = \frac{\text{frequency of signal} - \text{frequency of reference}}{\text{spectrometer frequency}} \times 10^6$$

τ scale

- The alternative system which is generally used for defining the position of resonance relative to the reference is assigned tau (**τ**) scale.

$$\tau = 10 - \delta$$

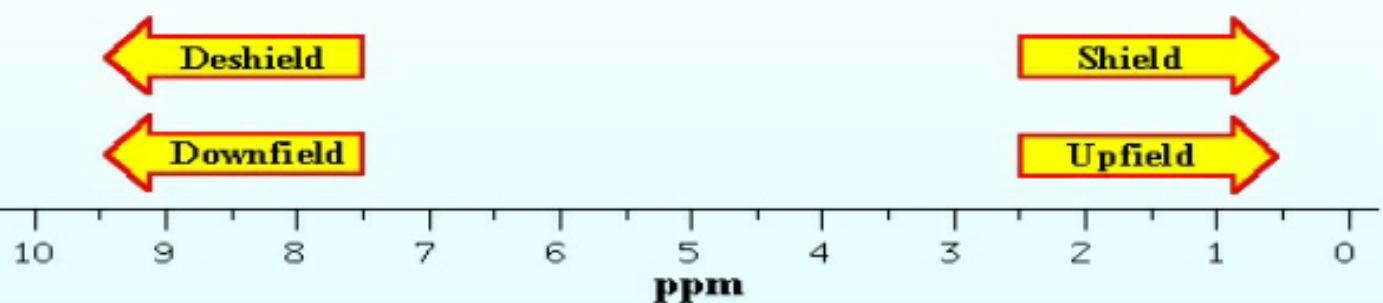
- A small numerically value of **δ** indicates a small downfield shift while large value indicates a large downfield shift.
- A small value of **τ** represents a low field absorption and a high value indicates a high field absorption.

Shielding of protons:-

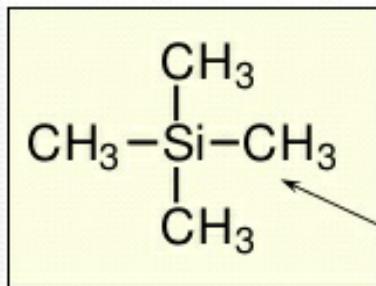
High electron density around a nucleus **shields** the nucleus from the external magnetic field and the signals are **upfield** in the NMR spectrum

Deshielding of protons:-

Lower electron density around a nucleus **deshields** the nucleus from the external magnetic field and the signals are **downfield** in the NMR spectrum

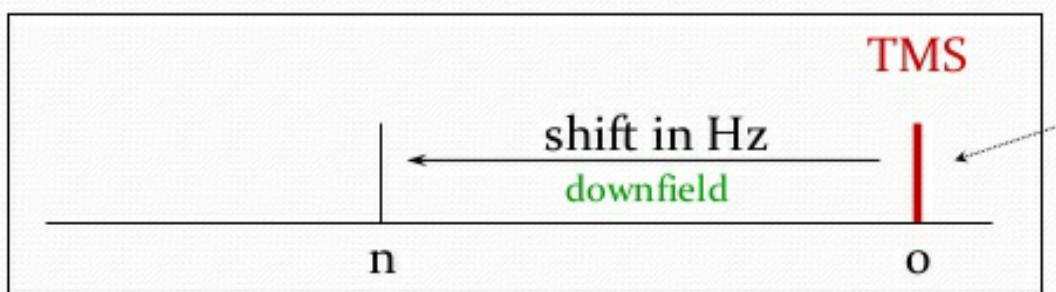


Rather than measure the exact resonance position of a peak, we measure how far downfield it is shifted from TMS.



reference compound
tetramethylsilane
“TMS”

Highly shielded
protons appear
way upfield.



Chemists originally thought no other compound would come at a higher field than TMS.

- TMS (Tetra methyl silane) is most commonly used as IS in NMR spectroscopy. Due to following reasons;
 - It is chemically inert and miscible with a large range of solvents.
 - Its twelve protons are all magnetically equivalent.
 - Its protons are highly shielded and gives a strong peak even small quantity.
 - It is less electronegative than carbon.
 - It is highly volatile and can be easily removed to get back sample.

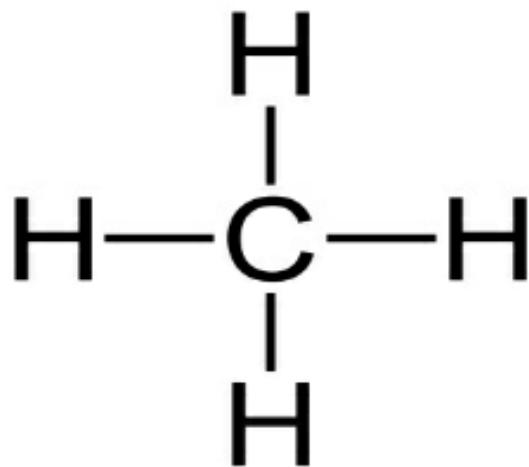
◎ Shielding and Deshielding:-

- The circulation of electron around the protons itself generates field in a such way that , it oppose the applied field.
- The field felt by the protons is thus diminished and the proton is said to be **shielded** and the absorption said to be **upfield**.
- If the induced magnetic field reinforced the applied magnetic field ,then the field felt by the proton is augmented and the proton is said to be **deshielded** and the absorption is known as **downfield**.

- ⦿ NMR spectrum of a substance gives very valuable information about its molecular structure.
- ⦿ Hydrogen atoms in different environments respond differently to the field
- ⦿ Each different environment of protons produce signal in a different positions
- ⦿ Protons can classified as
 1. Equivalent Protons
 2. Non-Equivalent protons
- ⦿ Equivalent protons will shows single signal
- ⦿ Non - equivalent protons will shows more than one signal.

◎ Equivalent Protons

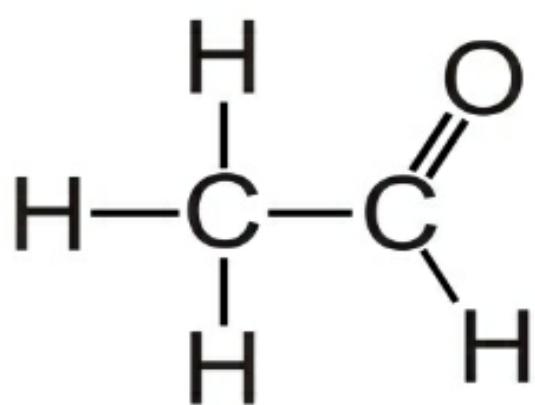
EX. methane



Non-Equivalent

PROTONS

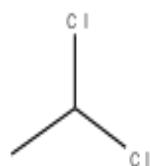
Ex.acetaldehyde



- (a) $\text{CH}_3\text{CHClCH}_3$ - 2-Chloropropane - 2 signals
 (b) CH_3COCH_3 - Acetone - 1 signal
 (c) $\text{CH}_3\text{CH}_2\text{OH}$ Ethyl alcohol - 3 signals
 (d) $\text{CH}_3\text{CH}_2\text{Cl}$ Ethyl chloride - 2 signals
 (e) CH_3-CH_3 Ethane - 1 signal



1, 2- D ichloroethane 1 signal

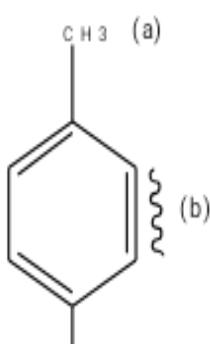


1, 1- D ichloroethane 2signals

a b a

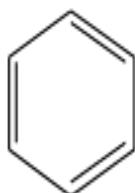
$\text{CH}_3\text{CHClCH}_3$ - 2 signals

2-Chloropropane

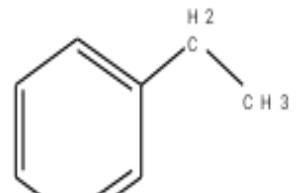


p-xylene

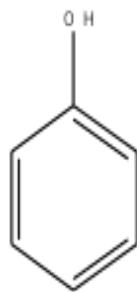
2 signals



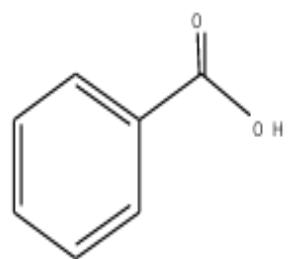
Benzene 1 signal



Ethyl benzene 3 signals



Phenol 2 signals



Benzoic acid - 2 signals

^1H NMR chemical shift

Type of proton	Approximate chemical shift (ppm)	Type of proton	Approximate chemical shift (ppm)
$(\text{CH}_3)_2\text{Si}$	0		6.5–8
$-\text{CH}_3$	0.9		9.0–10
$-\text{CH}_2-$	1.3		2.5–4
$-\overset{\text{l}}{\underset{\text{l}}{\text{CH}}}-$	1.4		2.5–4
$\begin{array}{c} \text{C}=\text{C}-\text{CH}_3 \\ \\ \text{I} \end{array}$	1.7		3–4
	2.1		4–4.5
	2.3	RNH_2	Variable, 1.5–4
$-\text{C}\equiv\text{C}-\text{H}$	2.4	ROH	Variable, 2–5
$\text{R}-\text{O}-\text{CH}_3$	3.3	ArOH	Variable, 4–7
$\begin{array}{c} \text{R}-\text{C}=\text{CH}_2 \\ \\ \text{R} \end{array}$	4.7		Variable, 10–12
$\begin{array}{c} \text{R}-\text{C}=\text{C}-\text{H} \\ \\ \text{R} \quad \text{R} \end{array}$	5.3		Variable, 5–8

^aThe values are approximate because they are affected by neighboring substituents.

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(\text{CH}_3)_2\text{Si}$	0	$\text{C}-\text{I}$	0–40
$\text{R}-\text{CH}_3$	8–35	$\text{C}-\text{Br}$	25–65
$\text{R}-\text{CH}_2-\text{R}$	15–50	$\begin{array}{c} \text{C}-\text{Cl} \\ \text{C}-\text{N} \\ \text{C}-\text{O} \end{array}$	35–80 40–60 50–80
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{CH}-\text{R} \end{array}$	20–60		165–175
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	30–40		165–175
$\equiv\text{C}$	65–85		175–185
$=\text{C}$	100–150		190–200
	110–170		205–220

n+1 rule:-

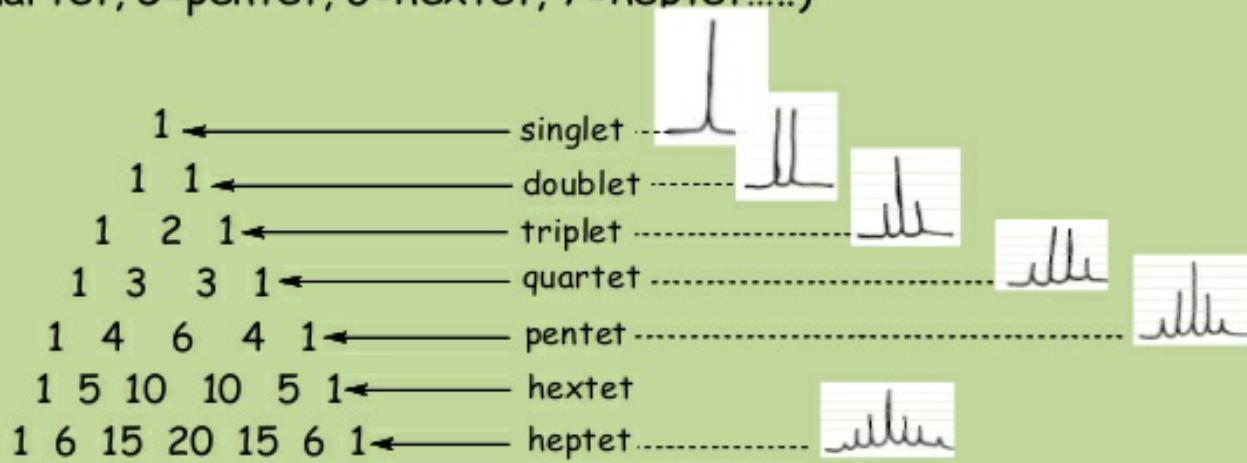
- ❖ The multiplicity of signal is calculated by using n+1 rule.
- ❖ This is one of the rule to predict the splitting of proton signals. This is considered by the nearby hydrogen nuclei.

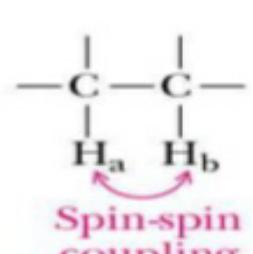
Therefore, n= Number of protons in nearby nuclei

- Zero H atom as neighbour $n+1=0+1=1$ (singlet)
- One H atom as neighbour $n+1=1+1 = 2$ (doublet)
- Two H atom as neighbour $n+1=2+1 =3$ (triplet)

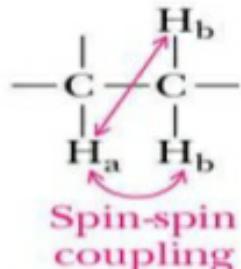
Spin-Spin Splitting in ^1H NMR Spectra

- Peaks are often split into multiple peaks due to **magnetic interactions** between nonequivalent protons on adjacent carbons. The process is called **spin-spin splitting**
- The splitting is into one more peak than the number of H's on the adjacent carbon(s). This is the "**n+1 rule**"
- The relative intensities are in proportion of a binomial distribution given by Pascal's Triangle
- The set of peaks is a **multiplet** (2 = doublet, 3 = triplet, 4 = quartet, 5=pentet, 6=hextet, 7=heptet.....)

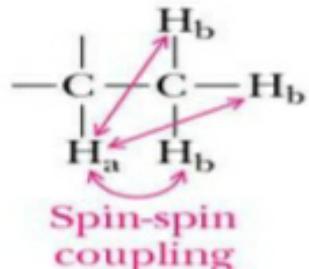




One H_b atom

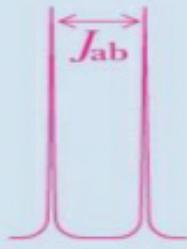


Two equivalent H_b atoms

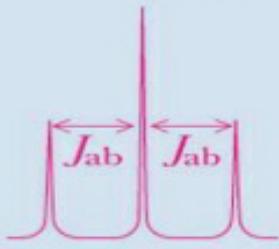


Three equivalent H_b atoms

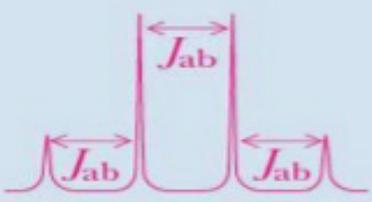
$\uparrow \quad \downarrow$
1 : 1



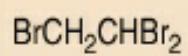
$\uparrow\uparrow \quad \uparrow\downarrow \quad \downarrow\downarrow$
1 : 2 : 1



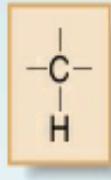
$\uparrow\uparrow\downarrow \quad \uparrow\downarrow\downarrow$
 $\uparrow\downarrow\uparrow \quad \downarrow\uparrow\downarrow$
 $\uparrow\uparrow\uparrow \quad \downarrow\uparrow\uparrow \quad \downarrow\downarrow\uparrow \quad \downarrow\downarrow\downarrow$
1 : 3 : 3 : 1



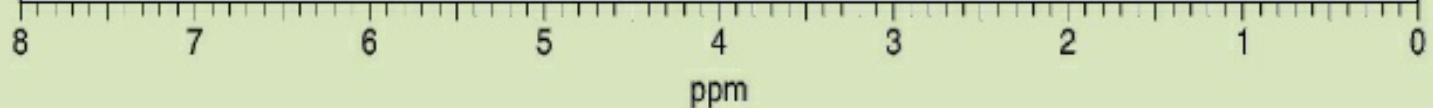
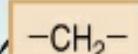
Observed splitting in signal of H_a

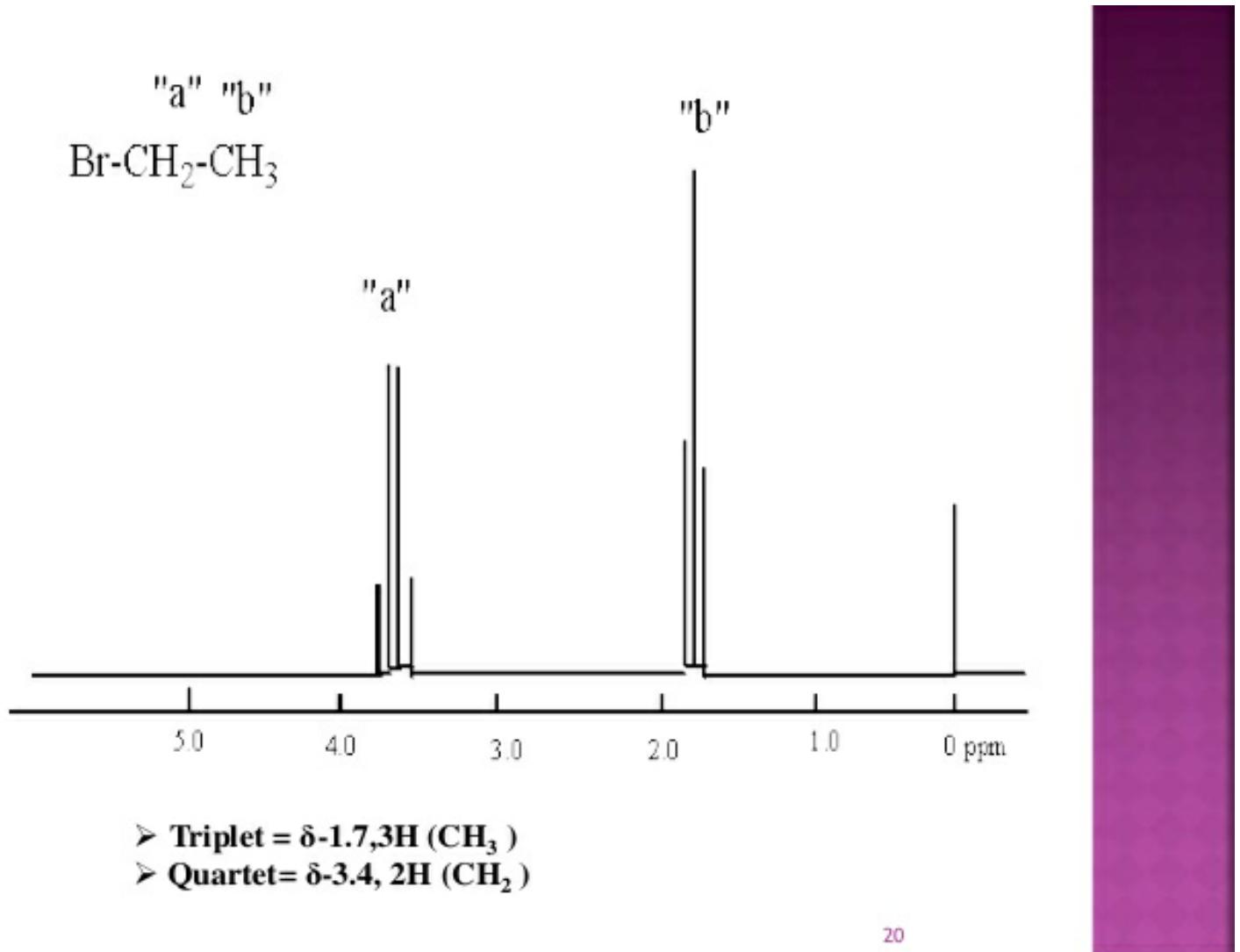


three peaks
triplet

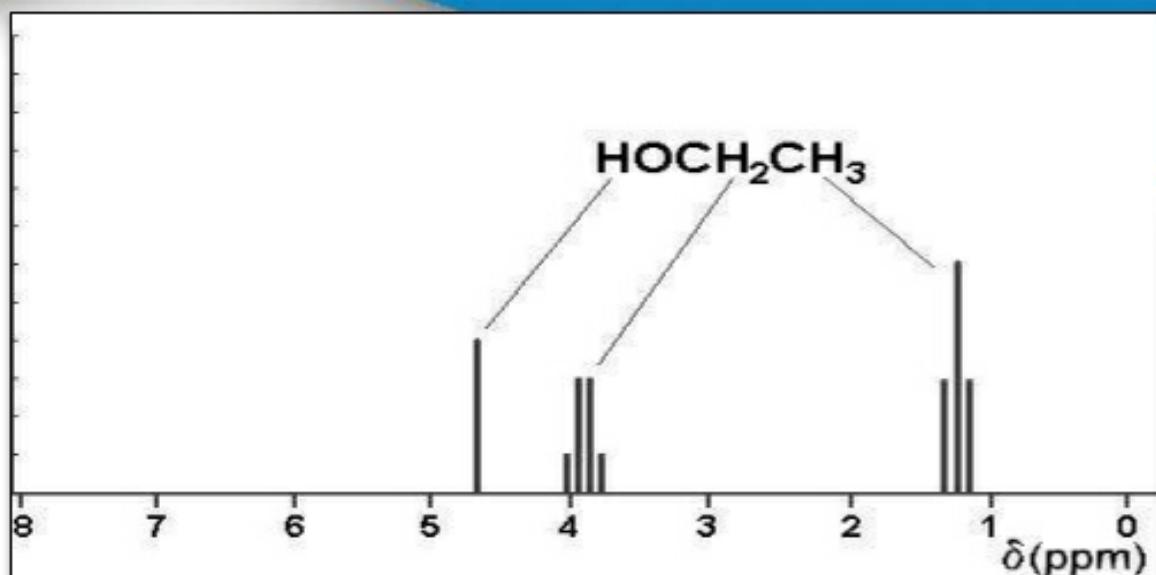


two peaks
doublet





Proton NMR spectra of Ethanol:-



^1H spectrum of Ethanol:-

3 types of proton





MRI

- MRI is a radiology technique
- That uses magnetism, radio waves, and a computer to produce images of body structures.
- MRI is based on the principles of NMR
- In 1997 the first MRI exam was performed on a human being.
- It took 5 hours to produce one image.

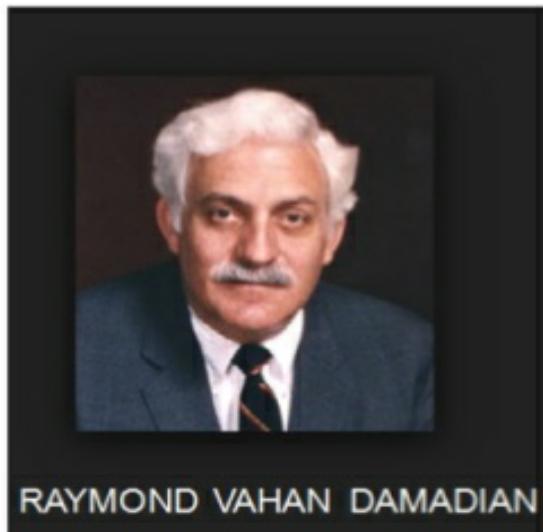
Niranjan Ultrasound India pvt.Ltd

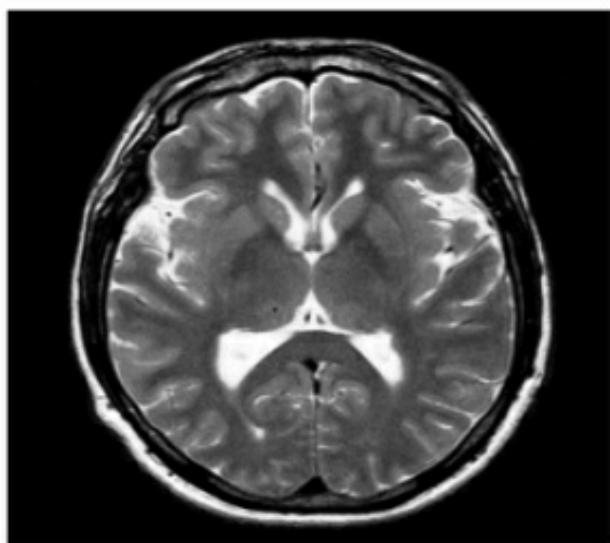




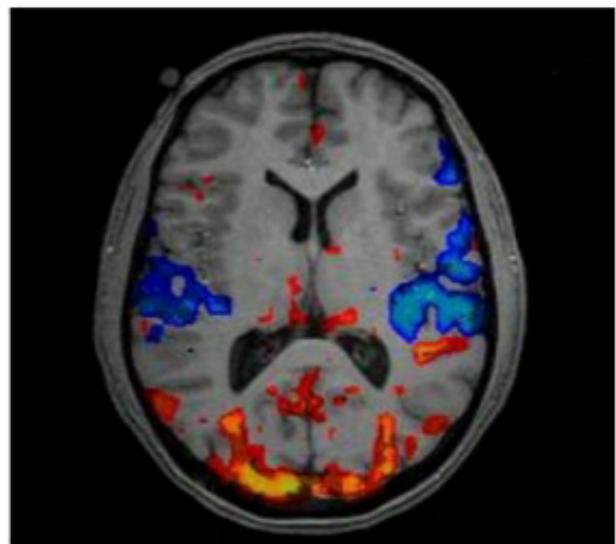
FATHER OF MRI

- Magnetic resonance imaging inventor





MRI scan



fMRI scan



WHAT CAN BE DIAGNOSED BY AN MRI SCAN?

- Most ailments of the brain, including tumours
- Sport injuries
- Musculoskeletal problems
- Most spinal conditions/injuries
- Vascular abnormalities
- Female pelvic problems
- Prostate problems
- Some gastrointestinal tract conditions
- Certain ear, nose and throat (ENT) conditions
- Soft tissue and bone pathology/conditions



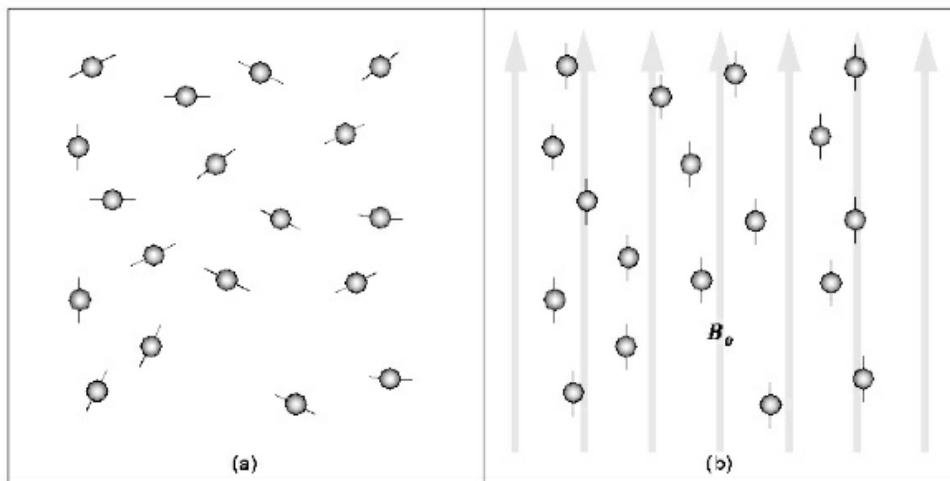
PRINCIPLE

- MRI makes use of the magnetic properties of certain atomic nuclei.
- Hydrogen nucleus (single proton) present in water molecules, and therefore in all body tissues.
- The hydrogen nuclei partially aligned by a strong magnetic field in the scanner.



CONTI..

- The nuclei can be rotated using radio waves, and they subsequently oscillate in the magnetic field while returning to equilibrium.
- Simultaneously they emit a radio signal.
- This is detected using antennas (coils)
- Very detailed images can be made of soft tissues.



**Randomly arranged
hydrogen atom**

**After the strong magnetic
field applied**



MAIN COMPONENTS OF MRI

- Scanner
- Computers
- Recording hardware

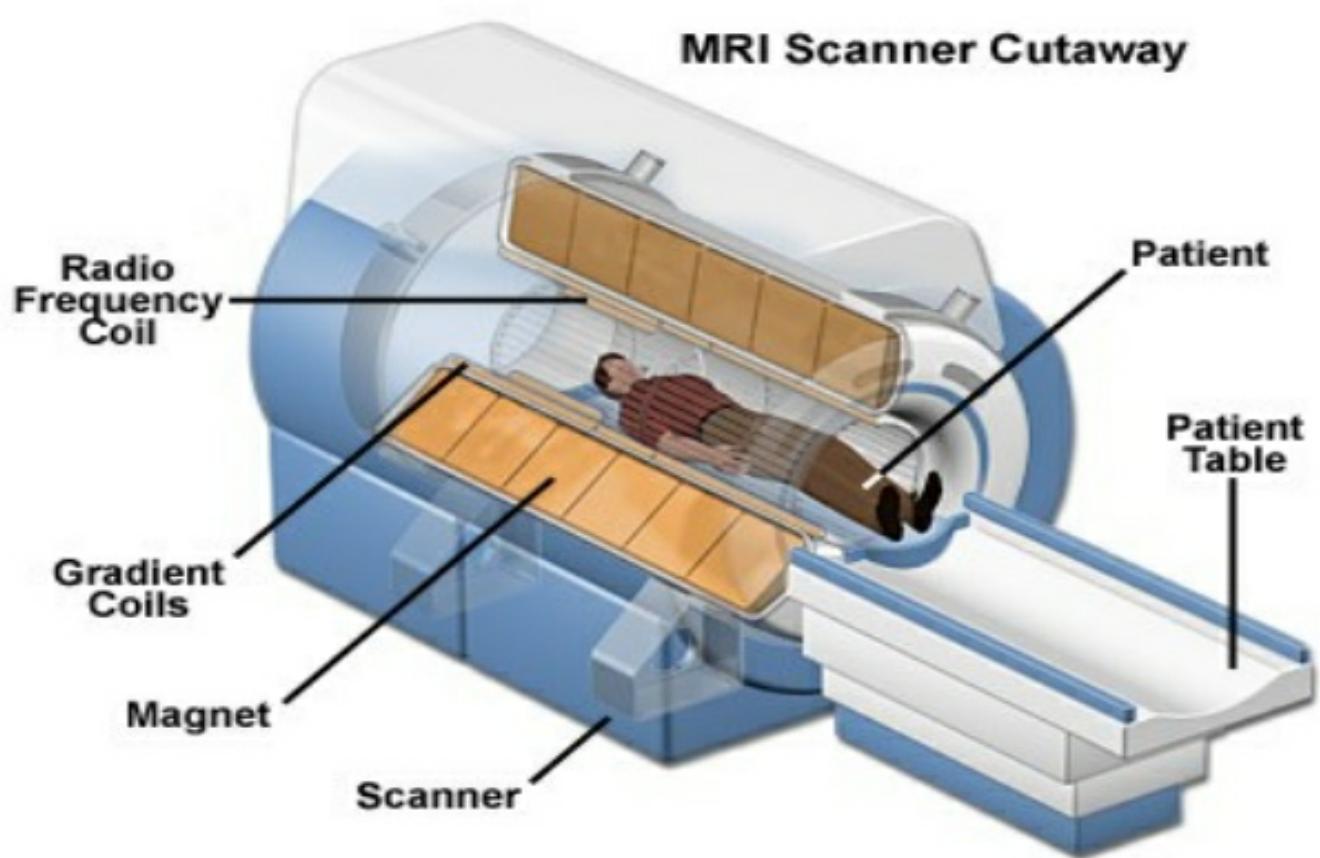


SCANNER

- An MRI scanner is a large tube that contains powerful magnets.
- Main components of scanner
 - Static magnetic field coils
 - Gradient coils
 - RF (radiofrequency) coils



MRI Scanner Cutaway





Static Magnetic Field Coils

- Three methods to generate magnetic field
 1. **Fixed magnet**
 2. **Resistive magnet**
 3. **Super conducting magnet**
- Fixed magnets and resistive magnets are generally restricted to field strengths below 0.4t
- High-resolution imaging systems use super conducting magnets.
- The super-conducting magnets are large and complex
- They need the coils to be soaked in liquid helium to reduce their temperature to a value close to absolute zero.



GRADIENT COILS

- Gradient coils are used to produce deliberate variations in the main magnetic field
- There are usually three sets of gradient coils, one for each direction.
- The variation in the magnetic field permits localization of image slices as well as phase encoding and frequency encoding.
- The set of gradient coils for the z axis are helmholtz pairs, and for the x and y axis paired saddle coils.



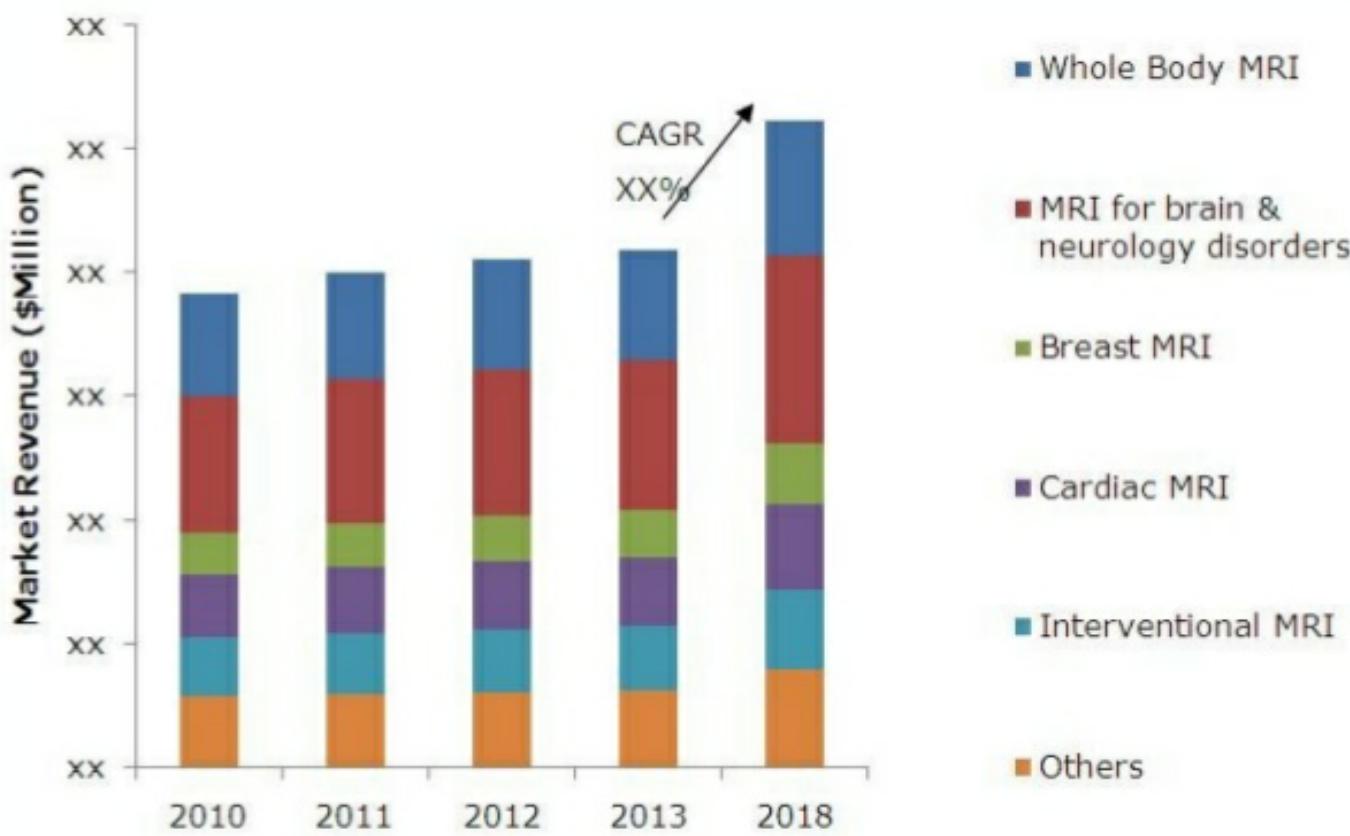
RADIOFREQUENCY COIL

- RF coils act as transmitter and receiver
- RF coils are the "antenna" of the MRI system
- That transmit the RF signal and receives the return signal.
- They are simply a loop of wire either circular or rectangular
- Helmholtz pair coils consist of two circular coils parallel to each other.
- They are used as the z gradient coils in MRI scanners
- Paired saddle coils are also used for the x and y gradient coils.



ADVANTAGES OF MRI

- No ionizing radiation
- Variable thickness in any plane
- Better contrast resolution
- Many details without iv contrast



GENERAL APPLICATIONS OF NMR SPECTROSCOPY

- ✓ NMR is used in biology to study the Biofluids, Cells, Per fused organs and biomacromolecules such as Nucleic acids(DNA, RNA), carbohydrates Proteins and peptides. And also Labeling studies in biochemistry.
- ✓ NMR is used in physics and physical chemistry to study High pressure Diffusion ,Liquid crystals ,liquid Crystal solutions , Membranes, Rigid solids.
- ✓ NMR is used in food science.

¹H-NMR SPECTROSCOPY applications

¹H widely used for structure elucidation.

Inorganic solids- In organic compounds are investigated by solid state ¹H-NMR.eg CaSO₄.H₂O.

Organic solids- Solid-state ¹H NMR constitutes a powerful approach to investigate the hydrogen-bonding and ionization states of small organic compounds.

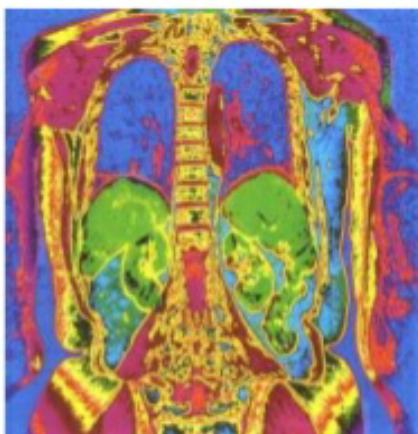
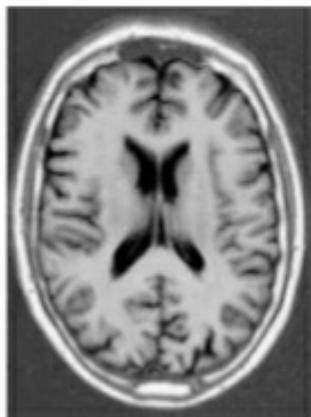
- Direct correlation with hydrogen-bonding lengths could be demonstrated, e.g. for amino acid carboxyl groups.

Contd...

- ✓ NMR is used in pharmaceutical science to study Pharmaceuticals and Drug metabolism.
- ✓ NMR is used in chemistry to ;
 - Determine the Enantiomeric purity.
 - Elucidate Chemical structure of organic and inorganic compounds.
 - Macromolecules –ligand interaction.

Application of NMR in medicine

MRI is specialist application of multi dimensional Fourier transformation NMR



- ✓ Anatomical imaging.
- ✓ Measuring physiological functions
- ✓ Flow measurements and angiography.
- ✓ Tissue perfusion studies.
- ✓ Tumors



Thank You

IR SPECTROSCOPY

1. Introduction to IR Spectroscopy

2.1 Introduction: Spectroscopy can be defined as the interaction between matter and light. Infrared spectroscopy is a very powerful technique which uses electromagnetic radiation in the infrared region for the determination and identification of molecular structure as well as having various quantitative applications within analytical chemistry Figure 1:

Infrared spectrometers use optical devices for dispersing and focusing electromagnetic radiation of IR frequency which is passed through the sample and any changes in absorbance measured against a reference beam.

There are three well defined IR regions (near, mid and far). The boundaries between them are not clearly defined and debate still persists, but broadly they are defined as:

- **Near infrared (12820-4000 cm⁻¹):** poor in specific absorptions, consists of overtones and combination bands resulting from vibrations in the mid-infrared region of the spectrum.
- **Mid-infrared (4000-400 cm⁻¹):** provides structural information for most organic molecules.
- **Far Infrared (400-33 cm⁻¹):** has been less investigated than the other two regions; however, it has been used with inorganic molecules.

The low energies, typically encountered within the infrared region, are not sufficient to cause electronic transitions; however, they are large enough to cause changes in the frequency and amplitude of molecular vibrations.

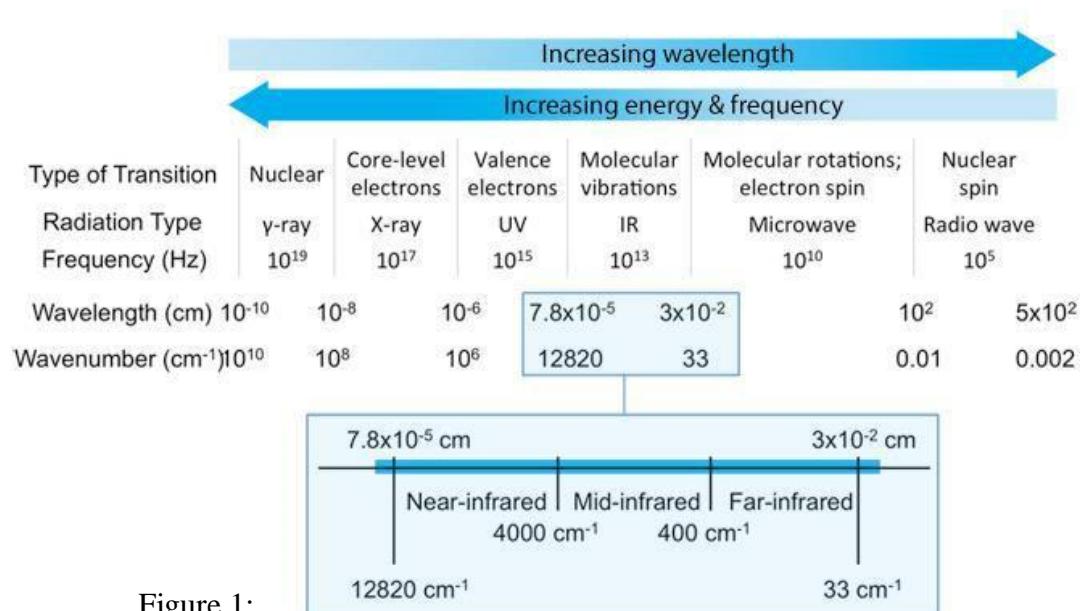


Figure 1:

2.2 Principle of IR Spectroscopy:

Hooke's law and frequency of vibration -We have seen that the bonds are not static but vibrating in different ways. A vibrating bond can therefore be considered a spring with its ends tethered to two atoms



Figure : Spring analogy of a bond vibration

If the masses of the atoms are m_1 and m_2 , the frequency of stretching vibration of the diatomic molecule can be given by the Hooke's law:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \text{-----(1)}$$

where, ν is the frequency of vibration, k is the spring constant, and μ is the reduced mass i.e. $m_1 m_2 / (m_1 + m_2)$

The spring constant, k is the measure of the bond strength. The stronger the bond, the higher the k , and consequently the higher is the frequency of vibration. This treatment implies that the diatomic molecule is a simple harmonic oscillator. The energy of a quantum harmonic oscillator is given by:

$$E = (n + 1/2)hv \quad \text{-----(2)}$$

where, $n = 0, 1, 2, \dots$ and h is the Planck's constant

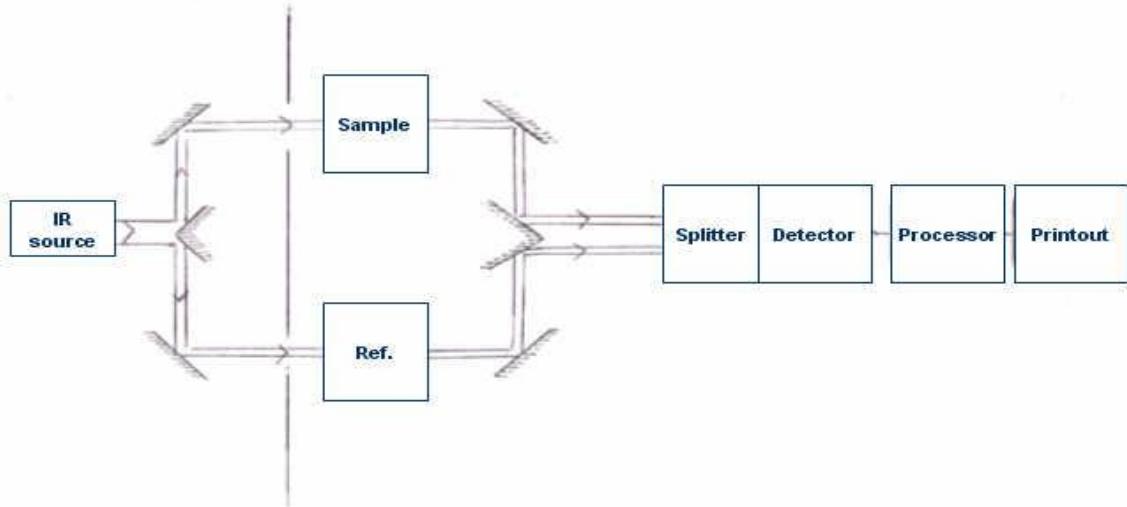
2.3 Selection Rule: A molecular vibration is IR active i.e. it absorbs IR radiation if the vibration results in a change in the dipole moment. A diatomic molecule, that has one mode of vibration, may not absorb an IR radiation if the vibration does not accompany a change in the dipole moment. This is true for all the homo nuclear diatomic molecules such as H₂, N₂, O₂, etc. Vibration of carbon monoxide (C=O), on the other hand, causes a change in dipole moment and is therefore IR active. Vibration of a bond involving two atoms that have large electronegativity difference is usually IR active.

2.4 Instrumentation:

Most IR spectrophotometers are double-beam instruments consisting of the following main parts:

- (i) Radiation source
- (ii) Sample and reference cells
- (iii) Attenuator and comb (photometer)

- (iv) Monochromator
- (v) Detector and amplifier
- (vi) Recorder



(i) Radiation Source: Infrared radiation is usually produced by electrically heating a N(frst filament

(mainly composed of oxides of zirconium, thorium and cerium) or a globar (rod of silicon carbide) to 1000-1800°C. The infrared radiation of successively increasing wavelength is used. The radiation from the source is divided into sample and reference beams of equal intensity by beam divider.

(ii) Sample and Reference Cells: Reference and sample beams pass through the reference cell and sample cell, respectively. Glass and quartz cannot be used as windows of cells and optical prisms, etc. because they absorb strongly in most of the IR region. Thus, alkali metal halides such as NaCl, NaBr, KCl and KBr are most commonly used as these are transparent to most of the IR region.

(iii) Attenuator and Comb (Photometer): The reference beam passes through the attenuator and the sample beam through the comb. Then the two beams can be alternately reflected out of the optical system and to the entrance slit of the monochromator with the help of several mirrors. Thus, the photometer combines the reference and sample beams into a single beam of alternating segments. The comb allows balancing of the two beams.

(iv) Monochromator: The combined beam passes through the prism or grating of the monochromator which disperses the beam into various frequencies. Since the prism or grating rotates slowly, it sends individual frequency bands to the detector, thus allowing a

scan of frequency bands. Gratings that give better resolutions than prisms consist of a series of parallel and straight thin lines on a smooth reflecting surface; the spacing between lines is of the order of few angstrom (\AA) depending on the desired wavelength range.

(v) Detector and Amplifier: The detector is a thermocouple which measures radiant energy by means of its

heating effect that produces current. Due to difference in the intensity of the two beams falling on the detector, an alternating current starts flowing from the detector to the amplifier where it is amplified and relayed to the recorder.

(vi) Recorder: It records IR spectra as a plot of wavelengths λ or wave numbers of absorbed radiations against the intensity of absorption in terms of transmittance T or absorbance(A).

$$T = \frac{I}{I_0} \quad \text{and} \quad T\% \text{ (percent transmittance)} = \frac{I}{I_0} \times 100 \quad \text{or} \quad A = \log(1/T)$$

where, I_0 is the intensity of the incident radiation and I the intensity of the radiation emerging from the sample.

2.5 Types of vibrations

When a molecule absorbs IR radiation in the range 100-10,000 cm⁻¹, the absorbed radiation causes transitions in its vibrational energy levels. These energy levels are also quantized, but vibrational spectra appear as bands rather than discrete lines. The energy differences between various rotational energy levels of a molecule are far less than that between its vibrational energy levels. Thus, a single transition in vibrational energy levels is accompanied by a large number of transitions in rotational energy levels and so the vibrational spectra appear as vibrational-rotational bands instead of discrete lines. Organic chemists are mainly concerned with these vibrational-rotational bands, especially with those occurring in the region 4000-667 cm⁻¹.

Various atoms in a molecule may be regarded as balls of different masses and the covalent bonds between them as weightless tiny springs holding such balls together. Atoms in a molecule are not still but they vibrate.

The two types (modes) of fundamental molecular vibrations known are: (a) stretching and (b) bending vibrations (deformations).

(i) Stretching Vibrations: In stretching vibrations, the distance between two atoms increases or decreases, but

the atoms remain in the same bond axis. Stretching vibrations are of two types: **(a) Symmetrical stretching.** In this mode of vibration, the movement of atoms with respect to the common (or central) atom is simultaneously in the same direction along the same bond axis.

(b) Asymmetrical Stretching. In this vibration, one atom approaches the common atom while the other departs from it.

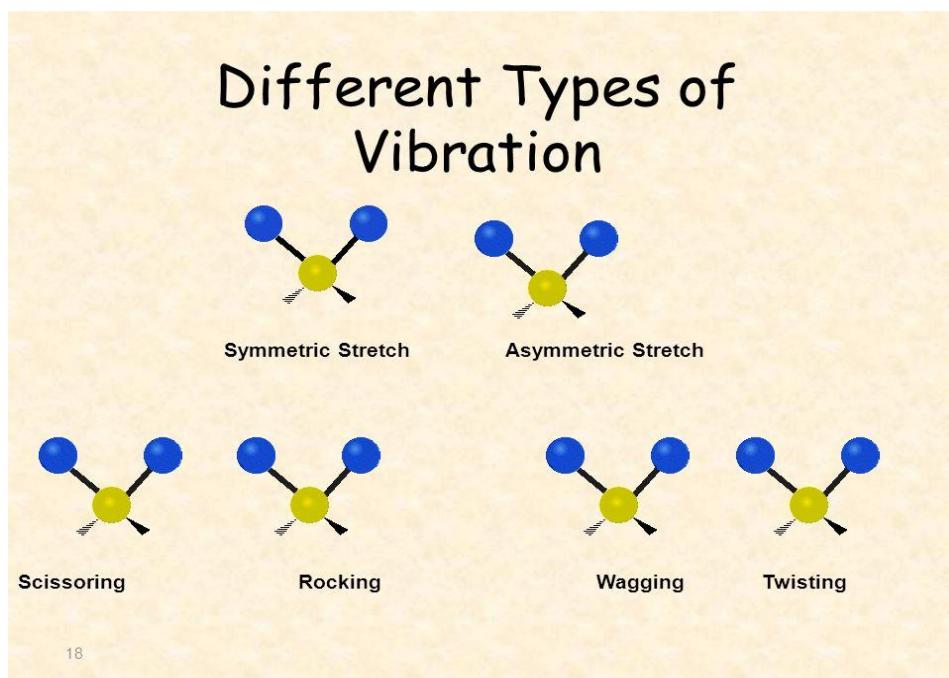
(ii) Bending Vibrations (Deformations): In such vibrations, the positions of the atoms change with respect to their original bond axes. Bending vibrations are of four types:

(a) Scissoring. In this mode of vibration, the movement of atoms is in the opposite direction with change in their bond axes as well as in the bond angle they form with the central atom .

(b) Rocking. In this vibration, the movement of atoms takes place in the same direction with change in their bond axes. Scissoring and rocking are in-plane bending Vibrations

(c) Wagging. In this vibration, two atoms simultaneously move above and below the plane with respect to the common atom.

(d) Twisting. In this mode of vibration, one of the atom moves up and the other moves down the plane with respect to the common atom. Wagging. and Twisting. are out-plane bending Vibrations



2.6 Number of Fundamental Vibrations

The IR spectra of polyatomic molecules may exhibit more than one vibrational absorption bands. The number of these bands corresponds to the number of fundamental vibrations in the molecule which can be calculated from the degrees of freedom of the molecule. Each atom has three degrees of freedom corresponding to the three Cartesian Coordinates (x , y and z) necessary to describe its position relative to other atoms in the molecule. Therefore, a molecule having n atoms will have $3n$ degrees of freedom.

In case of a nonlinear molecule, three of the degrees of freedom describe rotation and three describe translation. Thus, the remaining $(3n - 3 - 3) = 3n - 6$ degrees of freedom are its vibrational degrees of freedom or fundamental vibrations, because Total degrees of freedom $(3n)$ = Translational + Rotational + Vibrational degrees of freedom *Infrared (IR) Spectroscopy*

In case of a linear molecule, only two degrees of freedom describe rotation (because rotation about its axis of linearity does not change the positions of the atom) and three describe translation. Thus, the remaining

$(3n - 2 - 3) = 3n - 5$ degrees of freedom are vibrational degrees of freedom or fundamental vibrations.

Examples: i) CO_2 : Number of atoms (n) = 3

$$\text{Total degrees of freedom } (3n) = 3 \times 3 = 9$$

$$\text{Rotational degrees of freedom} = 2$$

$$\text{Translational degrees of freedom} = 3$$

$$\text{Therefore, vibrational degrees of freedom } (3n - 5) = 9 - 2 - 3 = 4$$

ii) Ethane (C_2H_6): Number of atoms (n) = 8

$$\text{Total degrees of freedom } (3n) = 3 \times 8 = 24$$

$$\text{Rotational degrees of freedom} = 3$$

$$\text{Translational degrees of freedom} = 3$$

$$\text{Hence, vibrational degrees of freedom } (3n - 6) = 24 - 3 - 3 = 18$$

iii) Benzene (C_6H_6): Number of atoms (n) = 12

$$\text{Total degrees of freedom } (3n) = 3 \times 12 = 36$$

$$\text{Rotational degrees of freedom} = 3$$

$$\text{Translational degrees of freedom} = 3$$

$$\text{Therefore, vibrational degrees of freedom } (3n - 6) = 36 - 3 - 3 = 30$$

2.7 Concept of group vibrations

The complexity of infrared spectra in the 1450 to 600 cm^{-1} region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region. Absorption bands in the 4000 to 1450 cm^{-1} region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.

Group Frequencies: More detailed descriptions for certain groups (e.g. alkenes, arenes, alcohols, amines & carbonyl compounds) may be viewed by clicking on the functional class name. Since most organic compounds have C-H bonds, a useful rule is that absorption in the 2850 to 3000 cm⁻¹ is due to sp³ C-H stretching; whereas, absorption above 3000 cm⁻¹ is from sp² C-H stretching or sp C-H stretching if it is near 3300 cm⁻¹.

Typical Infrared Absorption Frequencies

Functional Group	Type		Frequencies cm-1
C-H	sp ³ hybridized	R ₃ C-H	2850-3000
	sp ² hybridized	=CR-H	3000-3250
	sp hybridized	C-H	3300
	aldehyde C-H	H-(C=O)R	2750, 2850
N-H	primary amine, amide	RN-H ₂ , RCON-H ₂	3300, 3340
	secondary amine, amide	RNR-H, RCON-HR	3300-3500
	tertiary amine, amide	RN(R ₃), RCONR ₂	None
O-H	alcohols, phenols	free O-H	3620-3580
		hydrogen bonded	3600-3650
	carboxylic acids	R(C=O)O-H	3500-2400
CN	Nitriles	RCN	2280-2200
CC	Acetylenes	R-CC-R	2260-2180
C=O	Aldehydes	R(C=O)H	1740-1720
	Ketones	R(C=O)R	1730-1710
	Esters	R(CO ₂)R	1750-1735
	Anhydrides	R(CO ₂ CO)R	1820, 1750
	Carboxylates	R(CO ₂)H	1600, 1400
C=C	Olefins	R ₂ C=CR ₂	1680-1640
-NO ₂	nitro groups	RNO ₂	1550, 1370

2.8 APPLICATIONS OF IR SPECTROSCOPY

Infrared spectroscopy is widely used in industry as well as in research. It is a simple and reliable technique for measurement and quality control. It is also employed in forensic analysis in civil and criminal analysis. Some of the major applications of IR spectroscopy are as follows:

1. Identification of functional group and structure elucidation:

Entire IR region is divided into group frequency region and fingerprint region. Range of group frequency is $4000\text{-}1500\text{ cm}^{-1}$ while that of finger print region is $1500\text{-}400\text{ cm}^{-1}$. In group frequency region, the peaks corresponding to different functional groups can be observed. According to corresponding peaks, functional group can be determined.

Each atom of the molecule is connected by bond and each bond requires different IR region so characteristic peaks are observed. This region of IR spectrum is called as finger print region of the molecule. It can be determined by characteristic peak

2. Identification of substances

IR spectroscopy is used to establish whether a given sample of an organic substance is identical with another or not. This is because large number of absorption bands is observed in the IR spectra of organic molecules and the probability that any two compounds will produce identical spectra is almost zero. So if two compounds have identical IR spectra then both of them must be samples of the same substances.

3. Studying the progress of the reaction

Progress of chemical reaction can be determined by examining the small portion of the reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of the reactant group and/or the rate of appearance of the characteristic absorption band of the product group due to formation of product is observed.

4. Detection of impurities

IR spectrum of the test sample to be determined is compared with the standard compound. If any additional peaks are observed in the IR spectrum, then it is due to impurities present in the compound.

5. Quantitative analysis

The quantity of the substance can be determined either in pure form or as a mixture of two or more compounds. In this, characteristic peak corresponding to the drug substance is chosen and $\log I_0/I_t$ of peaks for standard and test sample is compared. This is called base line technique to determine the quantity of the substance.

NMR SPECTROSCOPY

Nuclear Magnetic Resonance (PMR or ^1H NMR) Spectroscopy

4.1 Introduction:

Similar to the UV and IR spectroscopy, nuclear magnetic resonance (NMR) spectroscopy is also an absorption spectroscopy in which samples absorb electromagnetic radiation in the radio-frequency region (3 MHz to 30,000 MHz) at frequencies governed by the characteristics of the sample. As the name itself implies, NMR spectroscopy involves nuclear magnetic resonances which depend on the magnetic property of atomic nuclei. Thus, NMR spectroscopy deals with nuclear magnetic transitions between magnetic energy levels of the nuclei in molecules. NMR signals were first observed in 1945 independently by Prucell at Harvard and Bloch at Stanford. In 1952, Prucell and Bloch won the Nobel Prize in Physics for their discovery.

There are approximately 100 isotopes for which NMR spectroscopy is possible, but the most commonly used by organic chemists are proton nuclear magnetic resonance (PMR or ^1H NMR) spectroscopy and carbon-13 nuclear magnetic resonance (^{13}C - NMR) spectroscopy. This chapter deals with PMR spectroscopy.

4.2 Theory:

Nuclei of some isotopes possess a mechanical spin, i.e. they have angular momentum. The total angular momentum of a spinning nucleus depends on its spin, or spin number I (nuclear spin quantum number). Each proton and neutron has its own spin and I is a resultant of these spins. The spin number I may have values $0, \frac{1}{2}, 1, \frac{3}{2}, \frac{5}{2}, \dots$ etc. depending on the mass number and atomic number of the atom as shown in Table -1. Nuclei composed of even number of protons and neutrons have no net spin ($I=0$) because their spins are paired off.

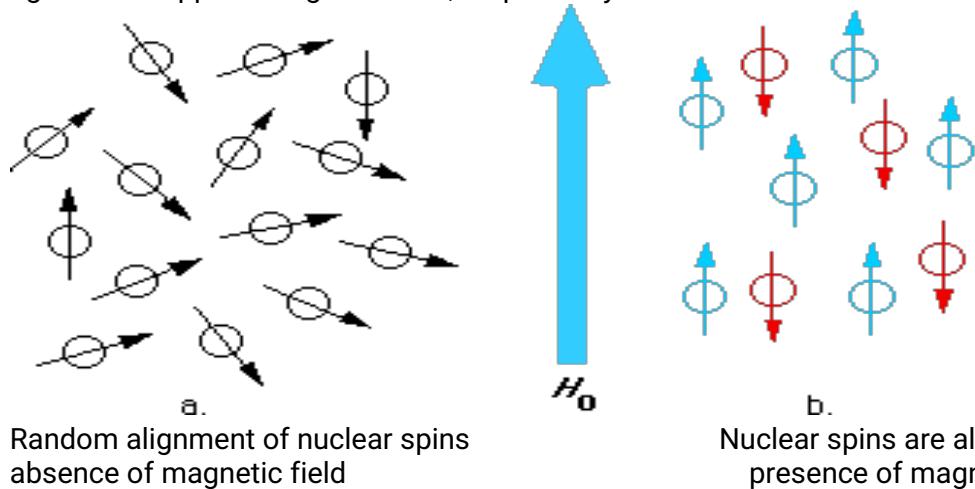
The isotopes with either odd mass number or odd atomic number possess a mechanical spin and only such isotopes can exhibit a nuclear magnetic resonance spectrum.

Mass number (A)	Atomic Number (Z)	Spin number (I)	Examples
Odd	Odd or even	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$	^1H , ^{13}C , ^{15}N , ^{19}K , ^{31}P ^{11}B , ^{35}Cl , ^{37}Cl , ^{79}Br ^{127}I , ^{17}O
Even	Even	0 (no spin)	^{12}C , ^{16}O , ^{32}S , ^{34}S
Even	Odd	$\frac{1}{2}$	^{14}N , ^2H ^{10}B

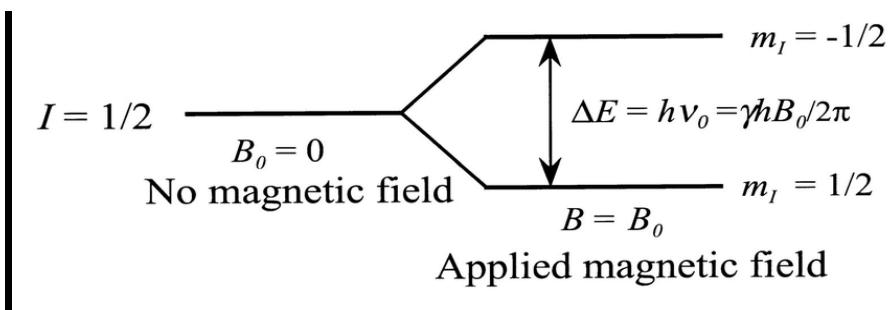
Table -1: Spin number of some isotopes

When a magnetic nucleus with spin number I is placed in a uniform magnetic field H_0 , its magnetic dipole or magnetic moment may assume any one of $2I + 1$ orientations with respect to the direction of the applied magnetic field H_0 and the system is said to be quantized. The most important nuclei for organic chemists are ^1H and ^{13}C . For both of these $I = 1/2$. Hence, number of orientations for their magnetic dipoles will be $2 \times 1/2 + 1 = 2$ (because number of orientations = $2I + 1$). Thus, the magnetic dipoles of nuclei with $I = 1/2$,

e.g. ^1H and ^{13}C , will align parallel or antiparallel to the applied magnetic field, i.e. with or against the applied magnetic field, respectively.



The alignment with the applied magnetic field is of lower energy and I corresponds to the α -spin state ($+1/2$) of the nucleus, and the alignment against the applied magnetic field is of higher energy and corresponds to the β -spin state ($-1/2$) of the nucleus.



Orientation of nuclear magnetic dipoles in an external magnetic field
 H_0

The energy difference ΔE (i.e. the energy required for a transition) has been shown to be a function of the applied magnetic field H_0 . The following fundamental NMR equation correlates the electromagnetic frequency ν for the transition in a given field H_0

$$\Delta E = h\nu = \frac{-\gamma h B_0}{2\pi} \quad \text{or} \quad \nu = \frac{\gamma H_0}{2\pi} \quad \text{or} \quad \nu \propto H_0$$

Where, h = plank constant; $H_0 = B_0$ = applied magnetic field; ν = frequency of emr

The nuclei aligned in such a way that their magnetic axes make an angle with the axis of the applied magnetic field H_0 are responsible for the process of absorption or emission of energy, i.e. for the NMR phenomenon. When the frequency of the rotating magnetic field and the precessional frequency of the nucleus become equal, they are said to be in resonance, and absorption or emission of energy by the nucleus can occur.

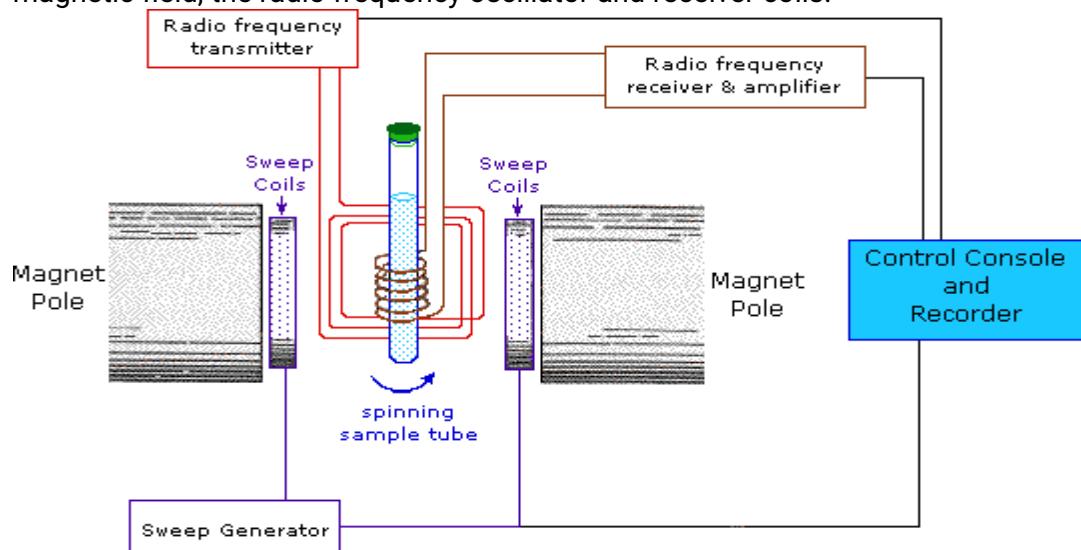
4.3 Instrumentation

The schematic diagram of a NMR spectrometer containing the following components is given in Figer

(i) *A strong magnet with homogeneaus field:* The strength of its field can be varied

continuously and precisely over a relatively narrow range with the help of the sweep generator.

- (ii) A radio-frequency oscillator.
- (iii) A radio-frequency receiver and detector.
- (iv) A recorder, calibrator and integrator.
- (v) A *sample holder*: It spins the sample to increase the homogeneity of the magnetic field on the sample, and keeps the sample in the proper position with respect to the main magnetic field, the radio frequency oscillator and receiver coils.



The sample under investigation is taken in a glass tube and placed in the sample holder. Most commonly, NMR spectrometers irradiate the sample with a beam of constant radio frequency obtained from the radio-frequency oscillator, while the magnetic field strength is varied with the help of the sweep generator. ΔE varies as the H_0 varies. At the field strength, when ΔE becomes equal to the energy of the incident radio frequency, absorption of energy takes place and transition from a lower spin state to a higher spin state occurs. This causes a tiny electric current to flow in the coil of the radio frequency receiver which is amplified and recorded as a signal on the chart paper by the recorder.

A NMR spectrum is recorded as a plot of a series of peaks (signals) corresponding to different applied field strengths against their intensities. Each peak represents a set of protons. The areas under the peaks are directly proportional to the number of protons they represent.

PMR spectra are usually run at 60 MHz, 100 MHz and 500 MHz are available. By measuring frequency shifts from a reference marker (usually Tetramethylsilane, TMS), an accuracy of ± 1 Hz can be achieved.

4.4 Internal Reference: Tetramethylsilane Si (CH_3)₄ (TMS) is the most commonly used reference compound because of the following advantages:

- (i) It is chemically inert, hence does not react with compounds under study.
- (ii) It is volatile (b.p. 27°C), hence precious samples may be easily recovered after recording the spectra.
- (iii) It gives a single, sharp and intense absorption peak because all its twelve protons are equivalent. Thus, very small quantity (1-2 drops) is needed.
- (iv) Its protons absorb at higher field than that of almost all organic compounds, hence overlapping of signals does not occur.
- (v) It is not involved in intermolecular association with the sample or solvent, hence the absorption positions of its protons remain unchanged.

(vi) It is soluble in most of the organic liquids.

Sometimes the DSS (sodium 2,2-dimethyl-2-silapentane-5-sulphonate, $\text{CH}_3\text{JSiCH}_2\text{CH}_2\text{CH}_2\text{S}(\text{O})_3\text{Na}$), is used as an internal reference in aqueous solutions.

4.5 Chemical Shift:

The chemical shift is expressed as the difference between the absorption position of a particular proton and the absorption position of a reference proton. Due to varying electronic environment of the proton or group of protons, their absorption signals appear at different field values. Thus, signals in PMR spectra give information about the different kinds of protons and their environments in molecules.

We can express the chemical shifts in terms of Hz by setting the TMS peak at 0 Hz at the right-hand edge. The chemical shifts are commonly expressed in δ unit which is a proportionality and thus dimensionless. It is independent of the field strength. Chemical shift values in Hz, i.e. ν are converted into δ units as follows:

$$\delta \text{ (or ppm)} = \frac{\text{Chemical shift in Hz}}{\text{Oscillator frequency in Hz}} \times 10^6$$

Oscillator frequency is characteristic of the instrument, e.g. a 60 MHz instrument has an oscillator frequency 60×10^6 Hz. The factor 10^6 is included in the above equation simply for convenience, i.e. to avoid fractional values. Since δ , which is dimensionless, is expressed in parts per million, expression ppm is often used. Thus, a peak at 60 Hz ($\nu 60$) from TMS at an applied frequency 60 MHz would be at $\delta 1.00$ or 1.00 ppm

$$\delta \text{ (or ppm)} = \frac{60}{60 \times 10^6} \times 10^6 = 1.00$$

The same peak at an applied frequency of 100 MHz would be at 100 Hz ($\nu 100$) but would still be at $\delta 1.00$ or 1.00 ppm

$$\delta \text{ (or ppm)} = \frac{100}{100 \times 10^6} \times 10^6 = 1.00$$

The δ unit has been criticized because δ values increase in the downfield direction; the reply is that these are really negative numbers. In the other commonly used unit, a value of 10.00 is assigned to TMS peak. This unit expresses chemical shifts in τ values as $\tau = 10.00 - \delta$

Example 1. Protons of a compound exhibit a NMR signal at $\delta 2.5$. What will be the value of chemical shift of these protons in Hz if the spectrum is recorded on a 60 MHz spectrometer?

Solution: $\delta = \frac{\text{Chemical shift in Hz}}{\text{Oscillator frequency in Hz}} \times 10^6$

Suppose the chemical shift in Hz is x . Therefore, $2.5 = \frac{x}{60 \times 10^6} \times 10^6$

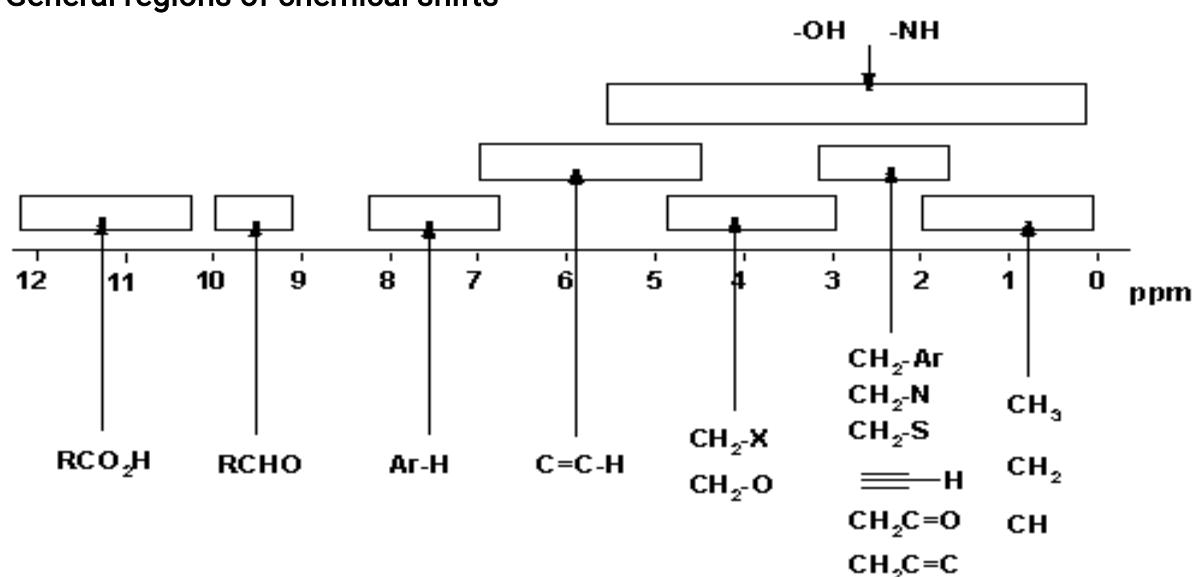
Hence, $x = 2.5 \times 60 = 150$ Hz

Example 2. If the observed chemical shift of a proton is 200 Hz from TMS and instrument frequency is 60 MHz, what is the chemical shift in terms of δ ? Express it in τ value.

Solution : $\delta = \frac{200}{60 \times 10^6} \times 10^6 = 3.33$

$$\tau = 10.00 - \delta = 10.00 - 3.33 = 6.67$$

General regions of chemical shifts



4.6 Factors Affecting Chemical Shift: Any factor which is responsible for shielding or deshielding of a proton will affect its chemical shift. The following factors affect the chemical shift:

(i) **Electronegativity-inductive effect:** The degree of shielding depends on the electron density around the proton. The higher the electron density around a proton, the higher the shielding and higher is the field (lower the δ value) at which the proton absorbs. Thus, the electron density around a proton successfully correlates with its chemical shift. Thus, the greater the electronegativity of the atom, the greater is the deshielding of the proton. For example, the chemical shifts (in δ unit) of protons of methyl halides (CH_3F , CH_3Cl , CH_3Br , CH_3I : 4.26, 3.05, 2.68, 2.16, respectively) are in accordance with the electronegativity of the halogen attached to the methyl group, i.e. the greater the electronegativity of the halogen attached to the methyl group, the lower is the field (higher δ values) at which the PMR signal of its protons appears.

(ii) **Anisotropic effects:** The carbon atom in acetylene is more electronegative than that in ethylene but the acetylenic protons are more shielded than the ethylenic protons, thus acetylenic protons absorb at 82.35, whereas ethylenic absorbs at 84.60. Such anomalies are explained on the basis of anisotropic (direction dependent) effects produced by circulation of π electrons under the influence of the applied magnetic field. These effects depend on the orientation of the molecule with respect to the applied field. Anisotropic effects are in

addition to the induced magnetic field generated by the circulation of α electrons. Generally, the induced magnetic field generated by circulating π electrons is stronger than that generated by α electrons.

(iii) **Hydrogen bonding:** Hydrogen bonded protons absorb at a lower field than the non-hydrogen bonded protons. Due to high electronegativity of the atom to which the proton is hydrogen bonded, the electron density around it is decreased as compared to that around the non-hydrogen bonded proton. Thus, the hydrogen bonded protons are highly deshielded and absorb at a lower field than the non-hydrogen bonded protons. This downfield shift of the absorption depends on the strength of the hydrogen bonding. The stronger the hydrogen bonding, the lower will be the field at which the proton absorbs.

(iv) **van der Waals deshielding:** In crowded molecules, some protons may occupy sterically hindered position resulting in van der Waals repulsion. In such a case, electron cloud of a bulky group (hindering group) will tend to repel the electron cloud surrounding the proton. Thus, the proton will be deshielded and will absorb at slightly lower field than expected in the absence of this effect.

4.7 Number of PMR Signals: Equivalent and Nonequivalent Protons:

The number of signals in a PMR spectrum shows how many kinds of protons are present in a molecule. This is because protons with the same chemical environment absorb at the same field strength, whereas protons with different chemical environments absorb at different field strengths. The protons with the same chemical environment are said to be chemically equivalent. Chemically equivalent protons occupy chemically equivalent positions, i.e. they are in identical chemical environments. Chemically equivalent protons are chemical shift equivalent, i.e. they have the same chemical shift.

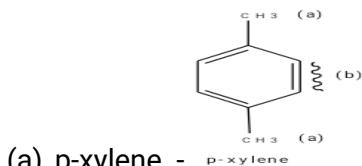
Example 1. Indicate the kinds of protons and number of PMR signals in the following compounds:

Solution. (a) The compound has three kinds of protons labeled as *a*, *b* and *c*, hence it will exhibit 3 PMR signals. *a* *b* *c*

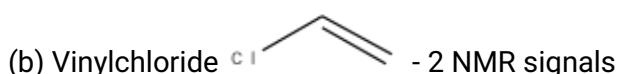
CH₃CH₂CH₂Cl Protons *c* are enantiotopic, hence equivalent 3 PMR signals
1-Chloropropane

- a* *b* *a*
(b) CH₃CHClCH₃ - 2-Chloropropane - 2 PMR signals
a *a*
(c) CH₃COCH₃ - Acetone - 1 PMR signal

Example 2. How many NMR signals do you expect from each of these compounds?



(b) 2 NMR signals





Example 4. Indicate the expected number of NMR signals.

(a) Methylcyclopropane - 4 NMR signals

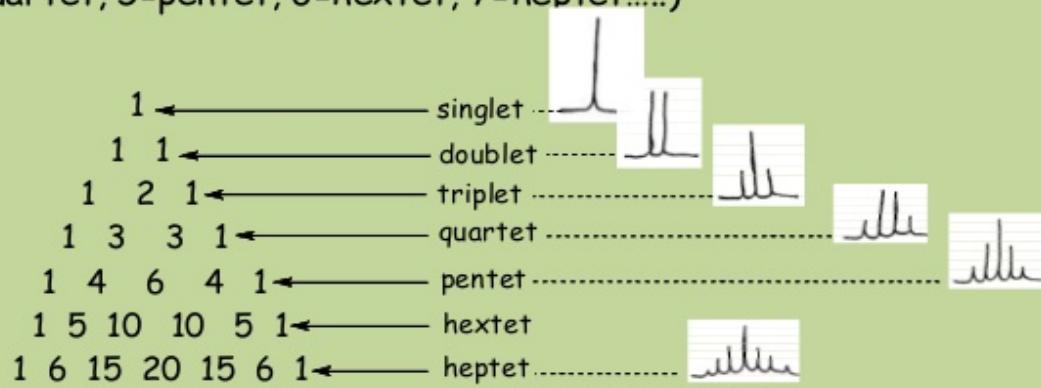
(b) Mesitylene - 2 NMR signals

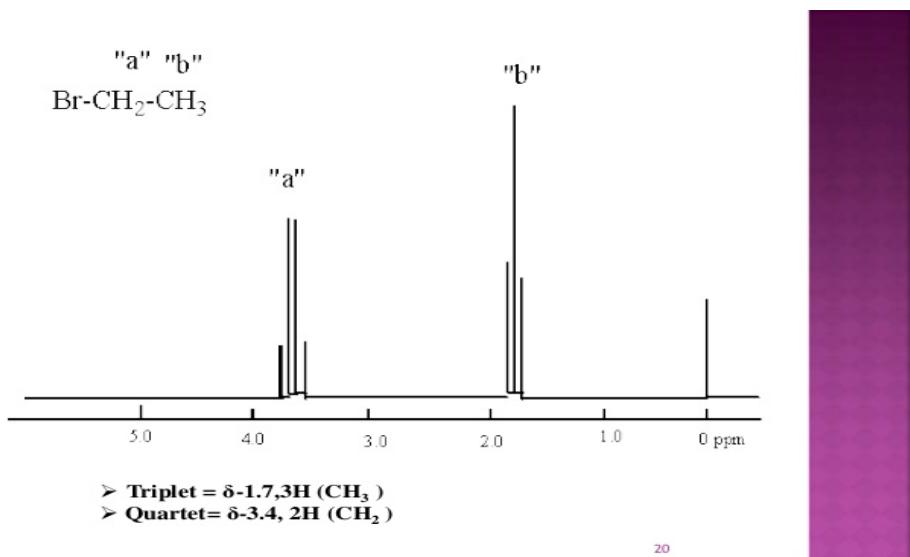
(c) Ethyl succinate - 3 NMR signals

(d) 2,3-Dichloropropanoic acid - 4 NMR signals

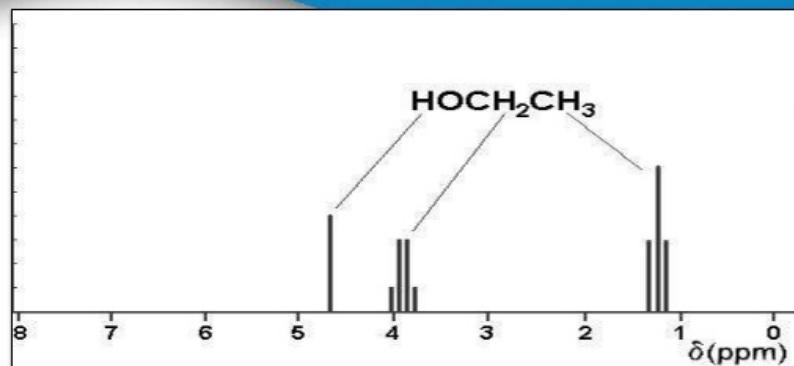
Spin-Spin Splitting in 1H NMR Spectra

- Peaks are often split into multiple peaks due to **magnetic interactions** between nonequivalent protons on adjacent carbons, The process is called **spin-spin splitting**
- The splitting is into one more peak than the number of H's on the adjacent carbon(s), This is the "**n+1 rule**"
- The relative intensities are in proportion of a binomial distribution given by Pascal's Triangle
- The set of peaks is a **multiplet** (2 = doublet, 3 = triplet, 4 = quartet, 5=pentet, 6=hextet, 7=heptet.....)





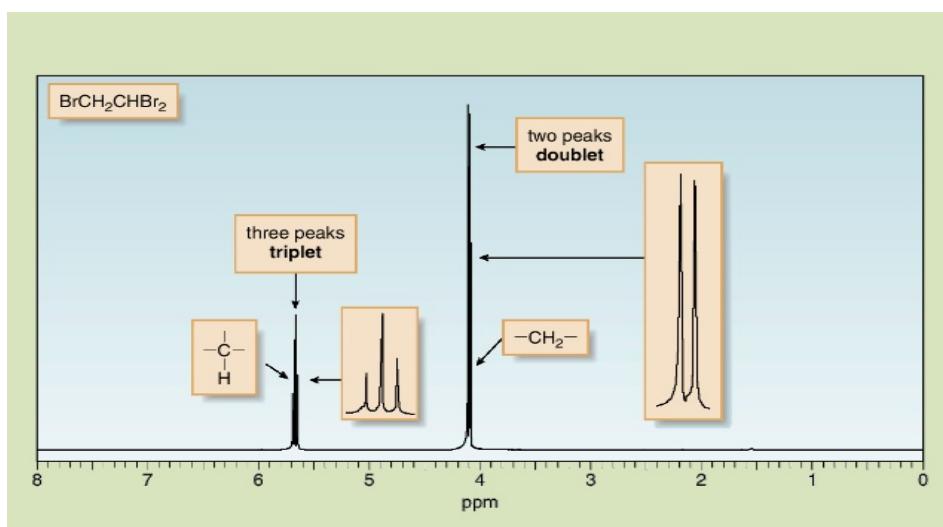
Proton NMR spectra of Ethanol:-



^1H spectrum of Ethanol:-

3 types of proton
 $\text{CH}_3, \text{CH}_2, \text{OH}$

Page 21



1.8 Applications of NMR Spectroscopy:

The important applications of PMR spectroscopy, besides obtaining routine structural information, are summarized as follows.

- i) PMR spectroscopy is an important tool in the hands of organic chemists for getting structural information.
- ii) It is also useful in stereo chemical studies.
- iii) An organic molecule consists of carbon-hydrogen skeleton, and thus NMR spectroscopy is especially useful in the study of this structural feature of the molecule.
- iv) **Identification of Structural Isomers:** Structural isomers can easily be distinguished by PMR spectroscopy.

For example (i) CH_3OCH_3 and $\text{CH}_3\text{CH}_2\text{OH}$

In dimethyl ether, all the six protons are equivalent. Hence, its PMR spectrum will show only one singlet. In ethanol, there are three kinds of protons. Thus, its PMR spectrum will exhibit three signals.

(v) **Detection of Aromaticity:** Aromatic protons are highly deshielded due to the circulating π electrons and appear at very low field ($\delta = 6-8.5$). From this, the aromatic character of a compound under study can be predicted.

(vi) **Detection of Hydrogen Bonding:** Intermolecular and intramolecular hydrogen bonding can be detected by PMR spectroscopy because both shift the absorption position of the hydrogen-bonded proton to downfield. Besides, both types of hydrogen bonding can also be distinguished, as the intermolecular hydrogen bonding is concentration-dependent, while the intramolecular hydrogen bonding is not concentration-dependent.

(vii) **Distinction Between *cis-trans* Isomers and Conformers:** PMR spectroscopy can easily distinguish *cis* and *trans* isomers because the concerned protons have different values of chemical shifts. Similarly, the axial and equatorial positions of protons or groups carrying protons and various conformations of a molecule can be distinguished on the basis of different values of their coupling constants, chemical shifts and peak areas.

(viii) **Quantitative Analysis:** The fact that areas under the peaks are directly proportional to the number of protons causing the respective peaks is the basis for the quantitative analysis by NMR spectroscopy. Impure samples may be determined by the addition of a known pure compound as an internal standard. If the reactants and products are known, then the rate of the reaction may be determined.

MRI: MAGNETIC RESONANCE IMAGING:

MRI is a radiology technique was introduced by Raymond vahan damadian in 1997. It is based on the principles of NMR.

MRI is used to detect the following

- Alignment of brain including tumors
- Musculoskeletal properties
- Spinal conditions and injuries
- Gastrointestinal tract conditions

- It can also be used to look at other internal organs. MRI scans can be used to find blood clots as well.
-

- In 1997 the first MRI exam was performed on a human being.
- It took 5 hours to produce one image technique.

UV PPT

CHROMOPHORE

❖ It is a Greek word.

Chroma = “color” & phoros = “bearer”

❖ Defined as any isolated covalently bonded group that shows a characteristic absorption of Electromagnetic radiation in the UV or visible region.

❖ Compound containing chromophore is **CHROMOGEN**

Eg: C=C, C=O, NO₂



TYPES OF CHROMOPHORES

1. INDEPENDENT CHROMOPHORES

If one chromophore is required to impart colour

Eg: Azo group –N=N-, Nitroso group –NO-

2. DEPENDENT CHROMOPHORES

If more than one chromophore is required to impart colour

Eg: Acetone having one ketone group is colorless whereas diacetyl having two ketone groups is yellow.

SIMPLE CHROMOPHORIC GROUPS

Groups	λ_{max}
C - C	1350
C = C	1900
C = O	1900 2800
O - H	1850
NO ₂	2800
C ₆ H ₅ (PHENYL)	1950 2500



Auxochrome

A saturated/ unsaturated group with non bonding electrons when attached to chromophore altering both wavelength as well as intensity of absorption.

Eg: OH, NH₂, NHR, COOH, CN, Cl etc..



Two types:

1) Basic/positive auxochromic groups

Effective in acid solutions

Eg: OH, OR, NHR etc.

2) Acidic/negative auxochromic groups

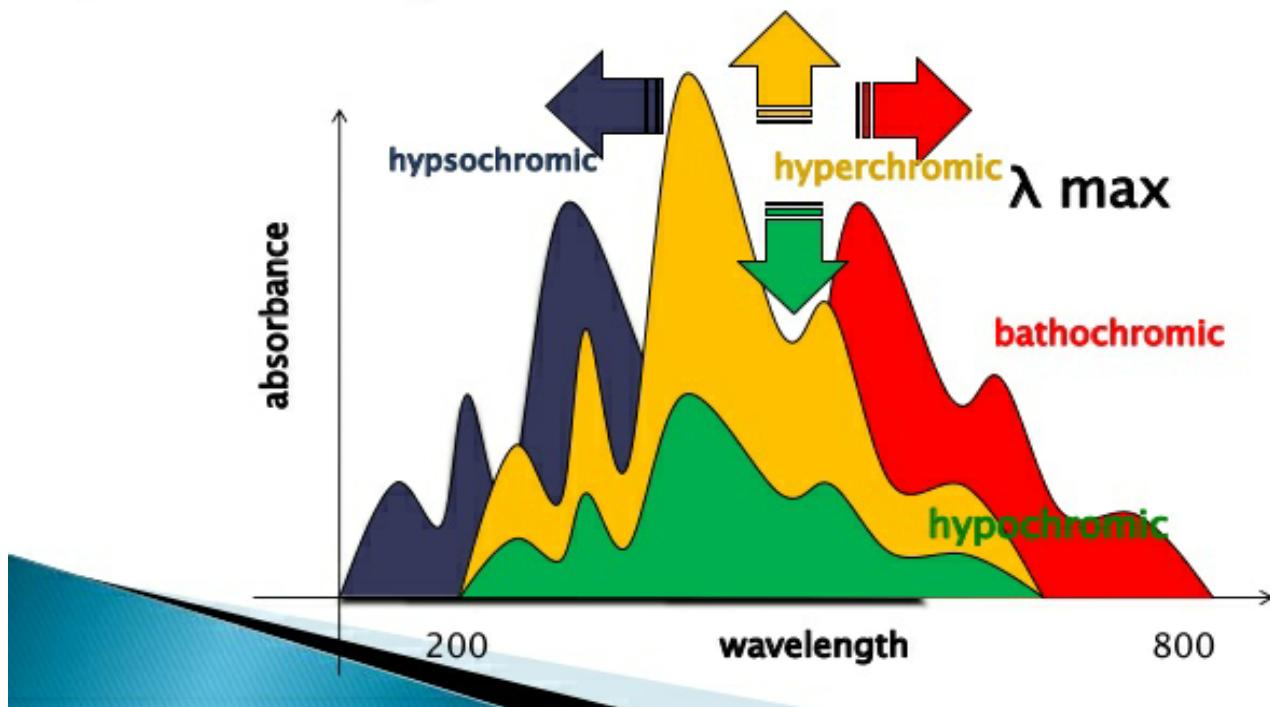
Effective in alkaline solutions

Eg: NO, CO, CN etc.



CHANGES IN POSITION & INTENSITY OF ABSORPTION

For isolated chromophore groups such as $-C=C-$ absorption takes place at far UV which cannot be easily studied but the position & intensity can be modified:



BATHOCHROMIC SHIFT/ RED SHIFT

- Shift of absorption maximum towards longer wavelength
- Due to presence of groups like OH, NH₂ etc.
(auxochromes)

Eg: ethylene shows absorption at **170nm** whereas 1,3-butadiene shows at **217nm**.



HYPSOCHROMIC SHIFT / BLUE SHIFT

- Shift of absorption maximum towards shorter wavelength
- May be caused by removal of conjugation

Eg: In Aniline, absorption takes place at **280nm**.
In acidic solutions, absorption takes place at **200nm**

HYPERCHROMIC SHIFT

- Increase in intensity of absorption
- By introduction of ‘auxochrome’

Eg: introduction of methyl group in position 2 of pyridine increases intensity of absorption from **2750** to **3560**

HYPOCHROMIC SHIFT

- Decrease in intensity of absorption

Eg: introduction of methyl group in position 2 of biphenyl group causes hypochromic effect because of distortion



Name of the Student:

GAMARNATH

Admin. No.: 19261A0470

Branch: ECE 2

Subject: CHEMISTRY

ASSIGNMENT

(UNIT 5)

College: MAHATMA GANDHI
INSTITUTE OF
TECHNOLOGY



Chemistry Assignment

unit - V : Spectroscopic techniques and applications

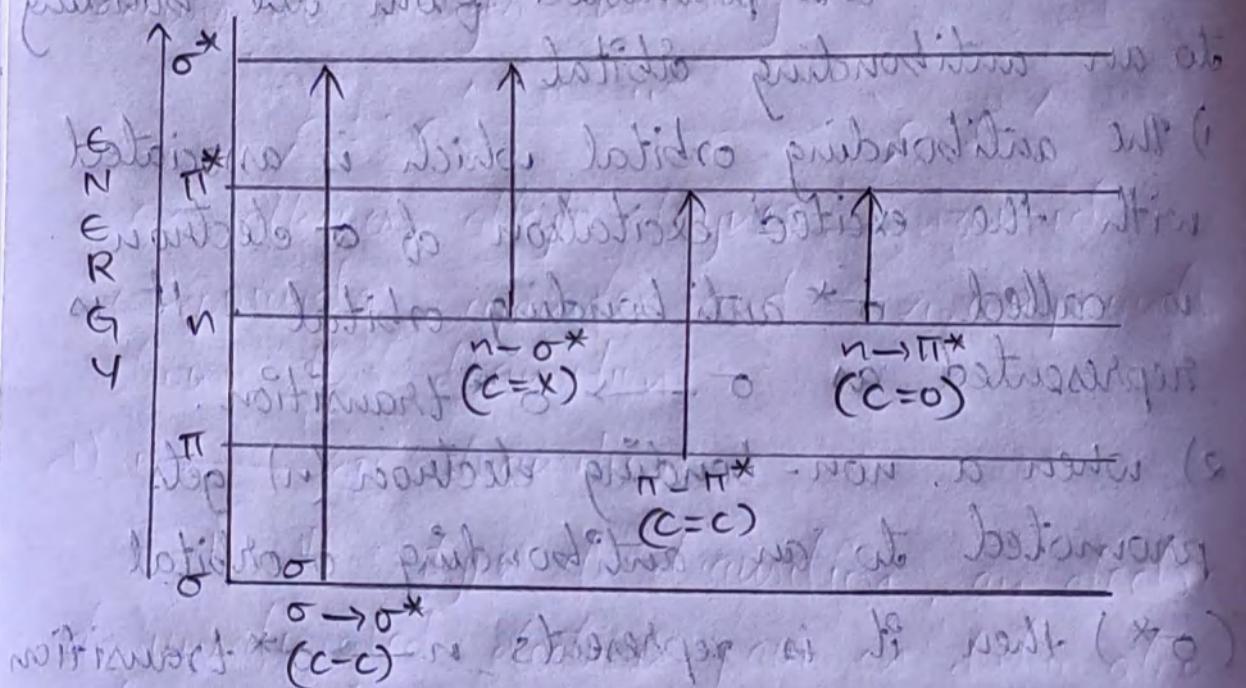
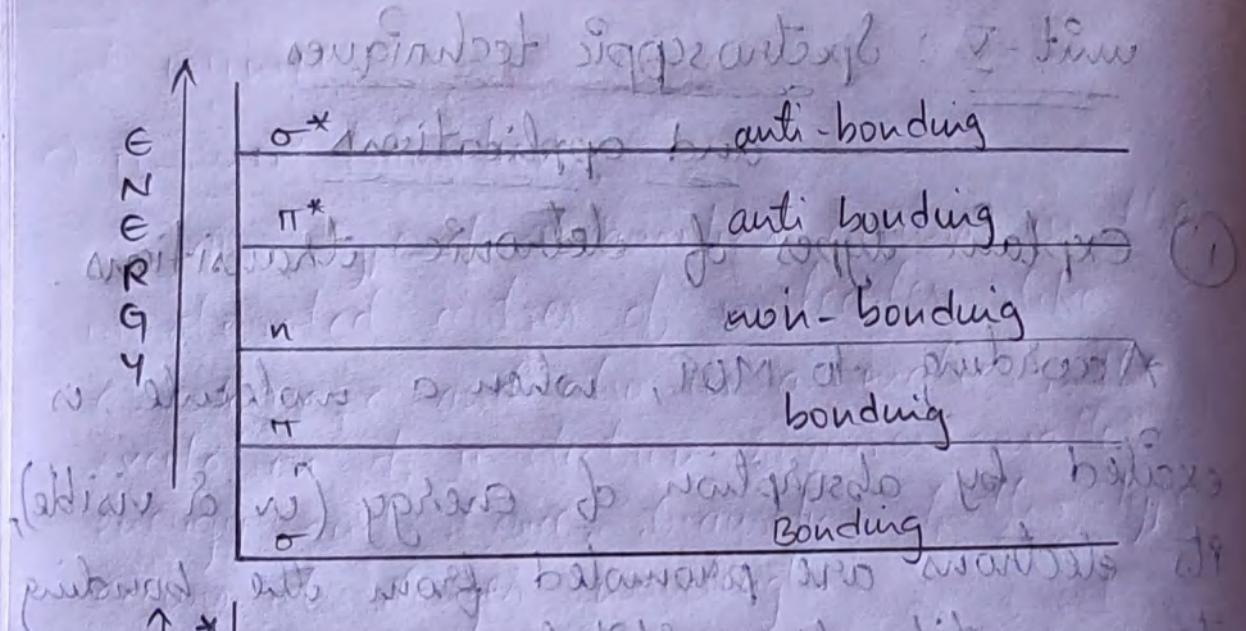
① Explain types of electronic transitions.

According to MOT, when a molecule is excited by absorption of energy (Uv & visible), its electrons are promoted from the bonding to an antibonding orbital.

- 1) The antibonding orbital which is associated with the ~~excited~~ excitation of σ electron is called σ^* anti bonding orbital. It is represented as $\sigma \rightarrow \sigma^*$ transition.
- 2) When a non-bonding electron (n) gets promoted to an antibonding σ orbital (σ^*) then it is represents $n \rightarrow \sigma^*$ transition.
- 3) Similarly: $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition

The energy required for various transitions obey the following order:



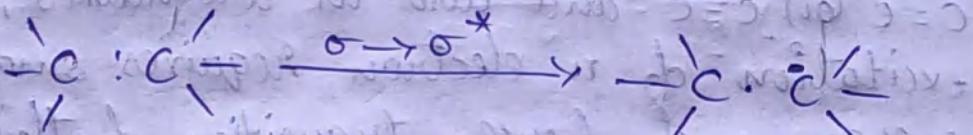


various transitions involved in electronic Spectroscopy

a) $\sigma \rightarrow \sigma^*$ transition : It is a very high energy process since σ bonds are, in general, very strong. The organic compounds in which all the valence shell electrons are involved in the formation of σ bonds, do not show

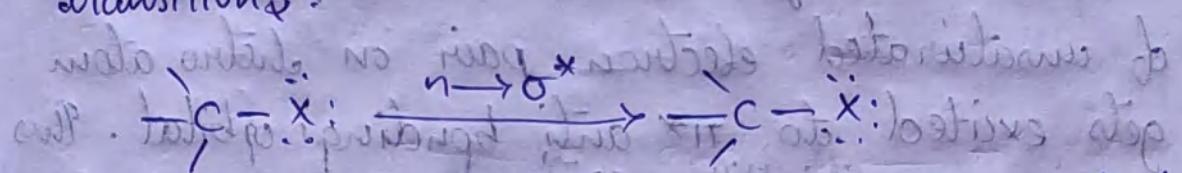
absorption in the normal UV region (180-400) $\text{m}\mu$.

for saturated hydrocarbons like methane, propane etc, absorption occurs near 300 $\text{m}\mu$ (high energy); such transition requires radiation of very short wavelength (high energy).



b) $n \rightarrow \sigma^*$ transition:

This type of transition takes place in saturated compounds containing one hetero atom with unshared pair of electrons. Some compounds undergoing this type of transitions are saturated halides, alcohols and amines etc. such transition require comparatively less energy than required for $\sigma \rightarrow \sigma^*$ transitions.



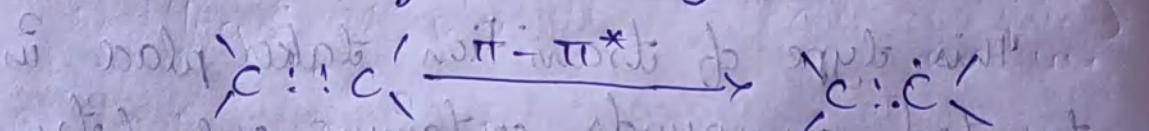
In alkyl halides, the energy required for such a transition decreases with the increase in the size of the halogen atom.

Ex ①: $n \rightarrow \sigma^*$ transition in methyl chloride, the absorption maximum is 172-175 $\text{m}\mu$ whereas, methyl iodide, wavelength maximum is 258 $\text{m}\mu$ due to electronegativity.

(Ex②) water absorbs at $167\text{ m}\mu$, methyl alcohol at $174\text{ m}\mu$.

c) $\pi \rightarrow \pi^*$ transition : nitriles, etc.

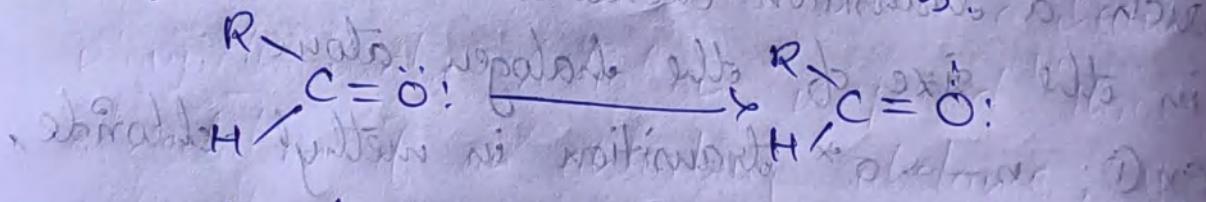
This type of transition occurs in the unsaturated centres of molecules like $\text{C}=\text{C}$ (or) $\text{C}\equiv\text{C}$ and also in aromatics, the excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelength.



Ex: alkenes, alkyl alkynes, benzoid compounds, cyanides and azo-compounds show this transition.

d) $n \rightarrow \pi^*$ transition :

In this type of transition, an electron of unsaturated electron pair on hetero atom gets excited to π^* anti bonding orbital. This type of transition requires least amount of energy out of all the transitions.



Saturated aldehydes ($\text{R}-\text{CHO}$) show this transition at $180\text{ m}\mu$.

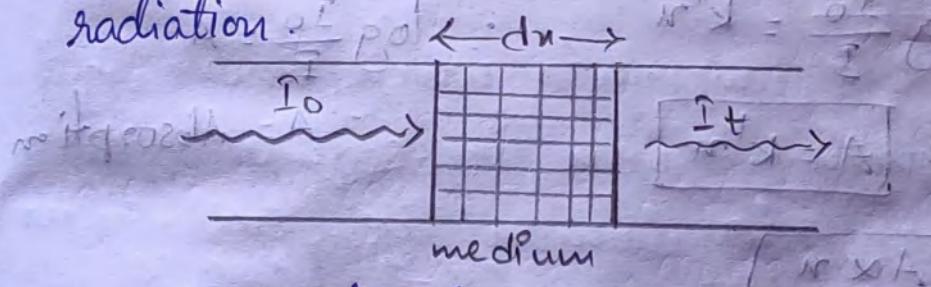
(2) Derive Beer's - Lambert law of absorption.

Absorption laws:

There are two laws which govern the absorption of light by the molecules.

(1) Lambert's law (2) Beer's law.

(i) Lambert's law: It states that, when a beam of mono chromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of incident radiation.



Mathematically, the law is expressed as

$$-\frac{dI}{dn} \propto I \quad \because k = \text{proportionality const.}$$

$\therefore dI = \text{decreasing the intensity of light.}$

$$-\frac{dI}{dn} = kI \quad \because dn = \text{thickness of the medium}$$

$$\frac{dI}{I} = -kdn \quad I_0 = \text{Intensity of incident light}$$

Let I_0 be the, $I = \text{intensity of light after passing through the medium}$

Integration above eq. ① with limits

$$\int_{I_0}^I \frac{dI}{I} = - \int_{n=0}^m k \cdot dn \quad I_0 \rightarrow I \quad 0 \rightarrow n$$

$$\left[\ln \frac{I}{I_0} = -kn \right] \Rightarrow \frac{I}{I_0} = e^{-kn} \Rightarrow \boxed{I = I_0 e^{-kn}} \quad ②$$

$$\frac{I}{I_0} = e^{-kn}$$

$\ln \frac{I}{I_0} = -kn$ comes out and short
with help of logarithms

$$2.303 \log \frac{I}{I_0} = -kn$$

$$\log \frac{I}{I_0} = -\frac{k}{2.303} n \quad \left[\because k' = \frac{k}{2.303} \right]$$

$$\log \frac{I}{I_0} = -k'n \quad \text{so } k' = \text{extinction coeff.}$$

$\log \frac{I}{I_0} = -k'n$ of absorbing medium

$$\log \frac{I_0}{I} = k'n \rightarrow \log \frac{I_0}{I} = A$$

$$\therefore A = k'n \quad \therefore A = \text{Absorption}$$

$$A \propto n$$

no changes in units. Absorptions law.

$$\text{units, } k' := A = k'n$$

$$\text{units of extinction coefficient} = k' = \frac{A}{n} \quad \therefore A = 1 \quad n = \text{cm}$$

$$k' = \text{cm}^{-1}$$

② Beer's law: It states that when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident

radiation as well as the concentration of solution.

Mathematically this law is stated as

$$-\frac{dI}{dn} \propto I \cdot c \quad : \epsilon = \text{molar absorption coefficient}$$

$$-\frac{dI}{dn} = \epsilon \cdot I \cdot c \rightarrow ① \quad : c = \text{conc. of solution}$$

integrating eq. ①

$$\int \frac{dI}{I} = - \int \epsilon \cdot c \, dn \quad : n = 0 \text{ to } u$$

$$I_0 = I e^{-\epsilon \cdot c \cdot u}$$

$$\ln \frac{I}{I_0} = -\epsilon \cdot c \cdot u \quad : \text{Molar extinction coefficient}$$

$$\frac{I}{I_0} = e^{-\epsilon \cdot c \cdot u} \quad : \text{Molar extinction coefficient}$$

$$\log \frac{I}{I_0} = -\epsilon \cdot c \cdot u \quad : \text{Molar extinction coefficient}$$

From eq. ②, $\ln \frac{I}{I_0} = -\epsilon \cdot c \cdot u$

$$2.303 \log \frac{I}{I_0} = -\epsilon \cdot c \cdot u$$

$$\log \frac{I}{I_0} = \frac{-\epsilon}{2.303} \cdot c \cdot u$$

$$\therefore \epsilon' = \frac{\epsilon}{2.303}$$

$$\log \frac{I}{I_0} = -\epsilon' \cdot c \cdot u \quad : \epsilon' = \text{molar extinction coefficient}$$

$$\log \frac{I_0}{I} = \epsilon' \cdot c \cdot u \quad : \epsilon' = \text{molar extinction coefficient}$$

$$A = \epsilon' \cdot c \cdot u \quad : A = \text{absorbance}$$

$$A \propto c \cdot u$$

units of ϵ' :

$$A = \epsilon' \cdot c \cdot n$$

as A is molar absorptivity
 c is conc.
 n is cm

$$\epsilon' = \frac{A}{c \cdot n}$$

moles/litre \cdot cm⁻¹

molar absorptivity

$$[\epsilon' = \text{mole}^{-1} \cdot \text{litr}^{-1} \cdot \text{cm}^{-1}]$$

- ③ Define the terms with suitable examples.
- Chromophore
 - Aurochrome
 - Hypsochromic shift
 - Bathochromic shift.

a) Chromophore:

All those compounds which absorb light of wavelength between 400-800 nm appear coloured to the human eye. Exact colour depends upon the wavelength of light observed by the compound. Originally, a chromophore was considered any system which is responsible for improving color to the compound. Nitro compounds are generally yellow in colour. Similarly aryl conjugated azo group is a chromophore for providing colour to the azo dyes.

definition: It is defined as any isolated covalently bonded group that shows a characteristic absorption in UV (or) visible light.

Ex:- Ethylene ($C=C$), Acetylene ($C\equiv C$), carbonyl ($>C=O$), acids ($-COOH$), ethers ($-C^{\ddot{O}}-OR$), nitriles ($C\equiv N$) etc, are such acts as chromophores.

chromophores which contains both π electrons and non-bonding electrons, such chromophores undergo two types of transitions i.e. $\pi-\pi^*$ and $n-\pi^*$.

Ex: $>C=O$, $C\equiv N$, $N\equiv N$, $-N\overset{O}{\equiv}O$ compounds etc.

chromophores which contains π electrons and ethyl, undergo $\pi-\pi^*$ transitions.

Ex: $C=C$, $-C\equiv C-$ etc.

b) Auxochrome:

It is defined as any group which does not itself acts as a chromophore but whose presence brings about a shift of absorption bond towards the red end of the spectrum (longer wavelength λ_{max}).

The absorption of longer wavelength is due to the combination of a chromophore and an auxochrome do give rise to another chromophore.

Auxochromic groups do not show characteristics absorption above $200m\mu$.

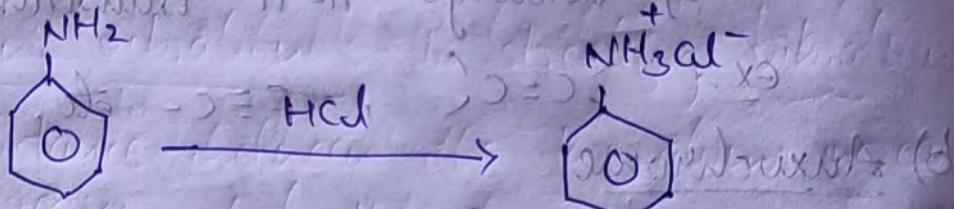
Ex: Auxochrome. $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, SH etc.

Ex: Benzene shows an λ_{max} at 255 nm whereas aniline absorbs at 280 nm. Hence amino (-NH₂) group is an auxochromine.

c) Hypsochromic Shift (Blue shift):

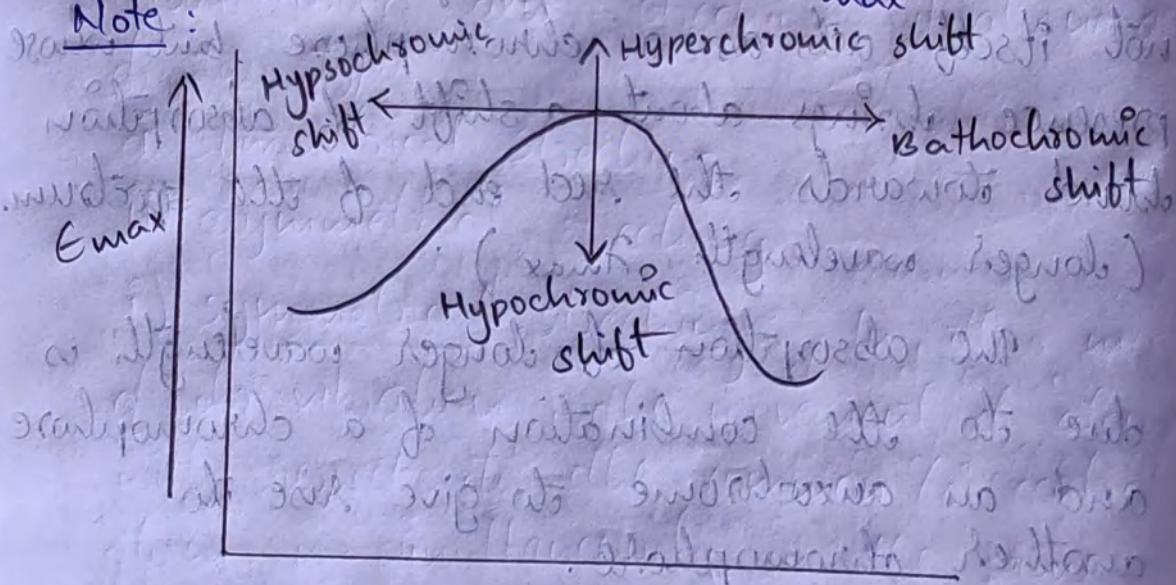
It is an effect by virtue of which the absorption maximum is shifted towards shorter wavelength.

It may be caused by the removal of conjugated and also by changing the polarity of the solvent.



$$\lambda_{\text{max}} = 280 \text{ nm} \quad \lambda_{\text{max}} = 255 \text{ nm}$$

Note:



wavelength \rightarrow
wavelength (λ)

Absorption and Intensity shift

d) Bathochromic shift (Red shift):

It is an effect by virtue of which the absorption maximum is shifted towards longer wavelength due to the presence of an auxochrome (or) by the change of solvent.

The $n \rightarrow \pi^*$ transition for carbonyl compound experiences red shift when the polarity of solvent is decreased.

④ Discuss and explain the molecular vibrations of IR spectra.

When a molecule absorbs IR radiation in the range 100-10,000 cm^{-1} , the absorbed radiation causes transitions in its vibrational energy levels. These energy levels are also quantized, but vibrational spectra appear as bands rather than discrete lines. The energy differences between various rotational energy levels of a molecule are far less than that between its vibrational energy levels. Thus, a single transition in vibrational energy levels is accompanied by a large number of transitions in rotational energy levels and so the vibrational spectra appear as vibrational-rotational bands instead of discrete lines.

various atoms in a molecule may be regarded as balls of different masses and the covalent bonds between them as weightless tiny springs holding such balls together. Atoms in a molecule are not still but they vibrate.

The two types (modes) of fundamental molecular vibrations known are

a) Stretching vibrations

b) bending vibrations.

a) Stretching vibrations: In stretching vibrations,

the distance between the two atoms increases or decreases, but the atoms remain in the same bond axis. Stretching vibrations are of two types

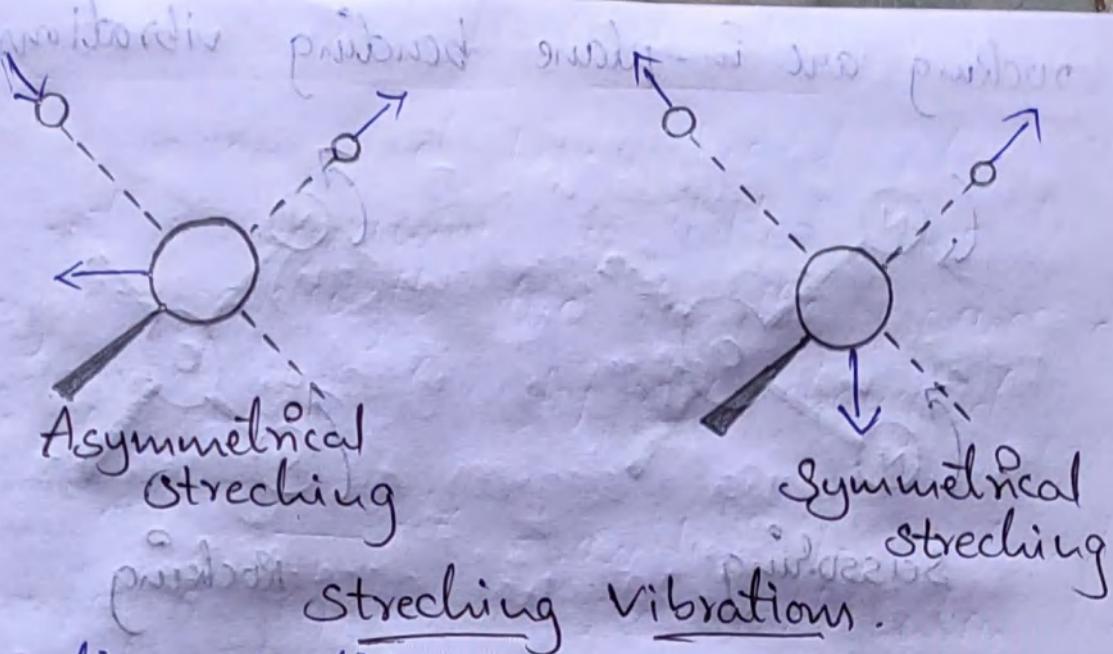
i) Symmetrical stretching

ii) Asymmetrical stretching.

i) Symmetrical stretching: In this mode of vibration, the movement of atoms with respect to the common (or central) atom is simultaneously in the same direction along the same bond axis.

ii) Asymmetrical stretching: In this vibration,

one atom approaches the common atom while the other departs from it.



b) Bending Vibrations : In such vibrations, the positions of the atoms change with respect to their original bond axes. Bending vibrations are of two types.

i) In plane and ii) Out plane.
i) In plane : In plane bending vibrations are of two types.

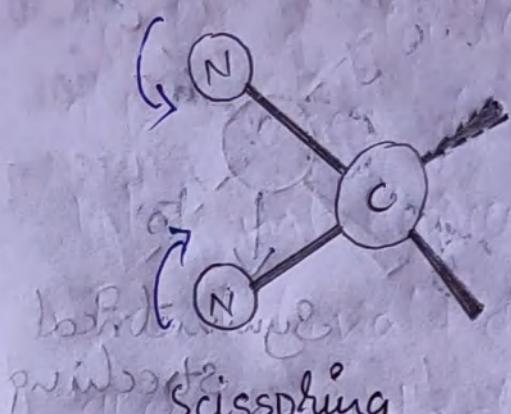
i) Scissoring

ii) Rocking

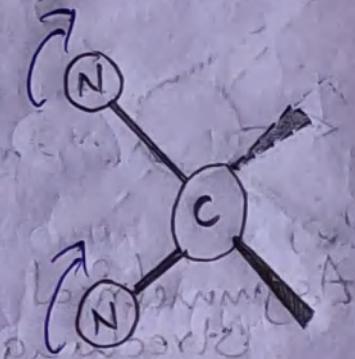
i) Scissoring : In this mode of vibration, the movement of atoms (with respect to the common) is in the bond angle they form is in the opposite direction with change in their bond axes as well as in the bond angle they form with their central atom.

ii) Rocking : In this vibration, the movement of atoms takes place in the same direction with change in their bond axis. Scissoring and

rocking are in-plane bending vibrations.



Scissoring



Rocking

in-plane bending vibrations

Out plane bending vibrations

2) Out plane : Out plane bending vibrations

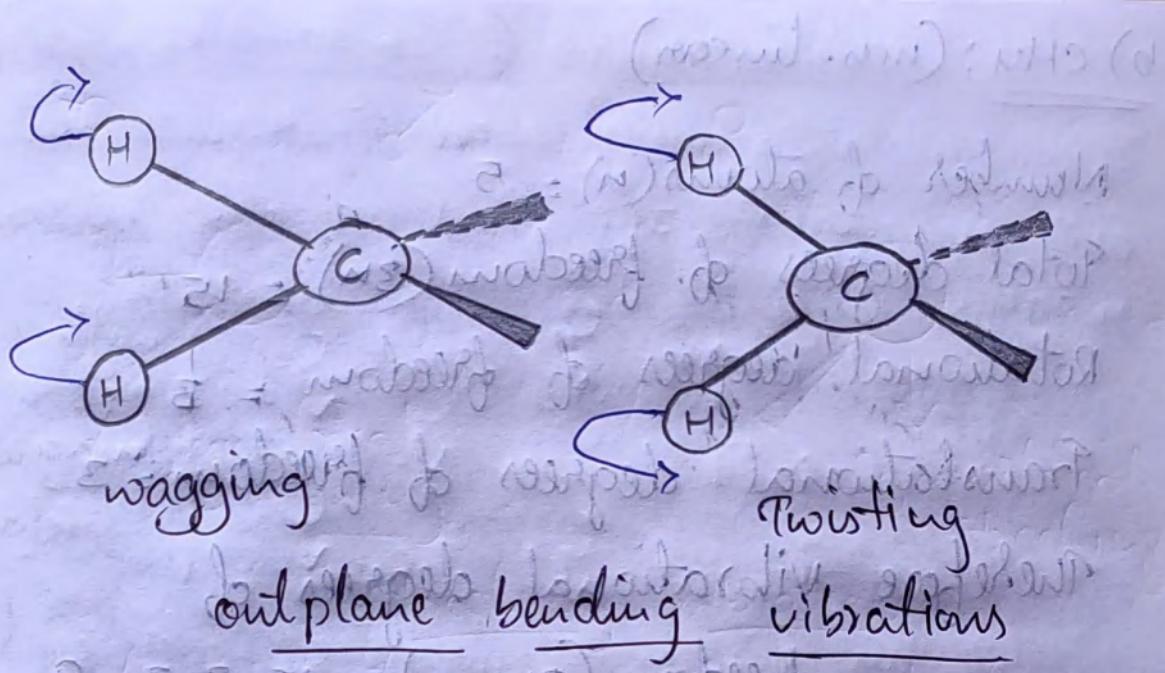
are of two types. i) wagging ii) twisting

i) wagging

i) wagging : In this vibrations, two atoms simultaneously move above and below the plane with respect to the common atom.

ii) Twisting . In this mode of vibration,

one of the atom moves up and the other moves down the plane with respect to the common atom. Wagging and twisting are out-plane bending vibrations.



⑤ Calculate the no. of fundamental vibrations of following.

a) CO_2 b) CH_4 c) Benzene d) HCN .

e) H_2O f) SO_2

a) CO_2 : (linear)

Number of atoms (n) = 3

Total degrees of freedom ($3n$) = $3 \times 3 = 9$

Rotational degrees of freedom = 2

Translational degrees of freedom = 3

Therefore, vibrational degrees of

$P = (3n - 5)$ freedom = $9 - 2 - 3 = 4$

s = wagging
e = twisting
o = out-of-plane bending

$A = s + e + o = (3 - n) + 5$

b) CH₄: (non-linear)

Number of atoms (n) = 5

Total degrees of freedom ($3n$) = 15

Rotational degrees of freedom = 3

Translational degrees of freedom = 3

Therefore vibrational degrees of

$$\text{freedom } (3n-6) = 15 - 3 - 3 = 9$$

c) Benzene (C₆H₆): (non-linear)

Number of atoms (n) = 12

Total degrees of freedom ($3n$) = 36

Rotational degrees of freedom = 3

Translational degrees of freedom = 3

Therefore vibrational degrees of
freedom ($3n-6$) = 36 - 6 = 30

d) HCN: (linear)

Number of atoms (n) = 3

Total degrees of freedom ($3n$) = 9

Rotational degrees of freedom = 2

Translational degrees of freedom = 3

Therefore vibrational degrees of

$$\text{freedom } (3n-5) = 9 - 2 - 3 = 4$$

e) H_2O : (non-linear)

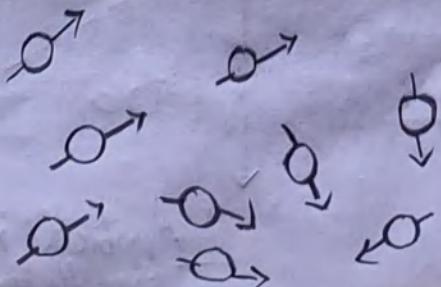
Number of atoms (n) = 3
Total degrees of freedom ($3n$) = 9
Rotational degrees of freedom = 3
Translational degrees of freedom = 3
Therefore vibrational degrees of freedom ($3n-6$) = $9-3-3=3$

f) SO_2 : (non-linear)

Number of atoms (n) = 3
Total degrees of freedom ($3n$) = $3 \times 3 = 9$
Rotational degrees of freedom = 3
Translational degrees of freedom = 3
Therefore vibrational degrees of freedom ($3n-6$) = $9-3-3 = 3$

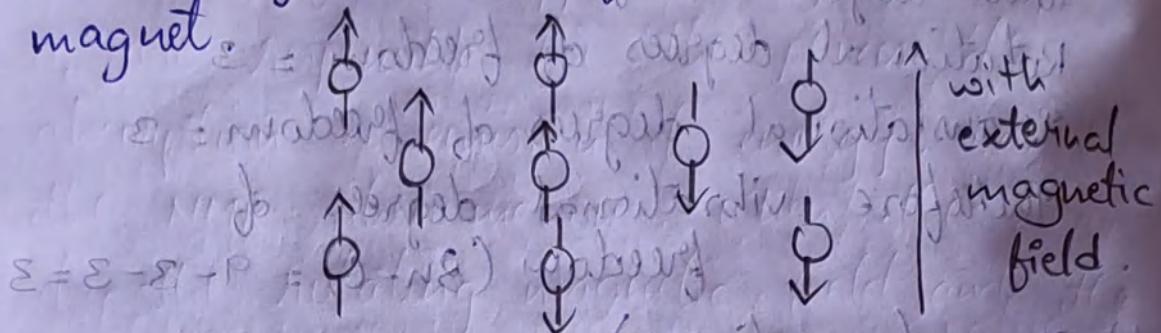
⑥ Explain the principle involved in NMR spectroscopy.

The theory behind NMR comes from the spin of a nucleus and it generates a magnetic field. Without an external applied magnetic field, the nuclear spins are random in directions.



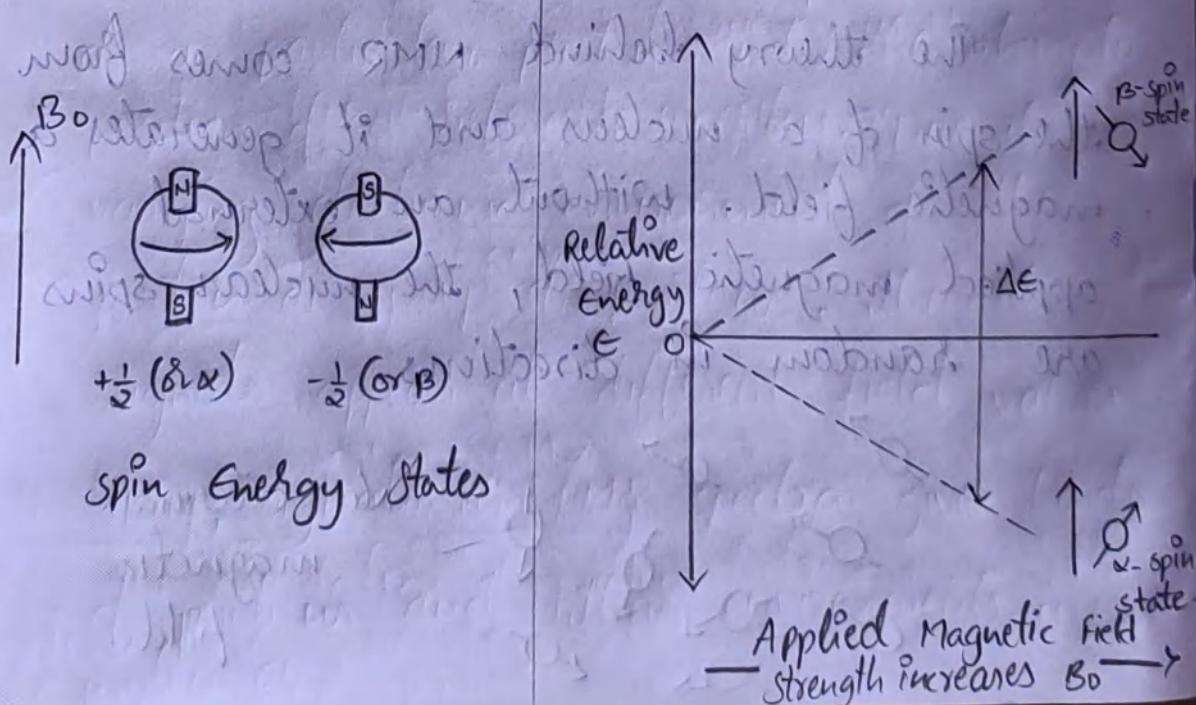
No external magnetic field.

But when an external magnetic field (B_0), is present the nuclei align themselves either with or against the field of the external magnet.



If an external magnetic field is applied, an energy transfer (ΔE) is possible between ground state to excited state when the spin returns to its ground state level, the absorbed radio frequency energy is emitted at the same frequency level.

The emitted radio frequency signal that give the NMR spectrum of the concerned nucleus.



The emitted radio frequency is directly proportional to the strength of the ~~heat~~ applied field.

$$v = \frac{1}{2\pi} \gamma B_0$$

B_0 = External magnetic field experienced by proton

γ = Magnetic magnetogyric ratio

is also the ratio between the nuclear magnetic moment and angular momentum.

(Or)

The energy difference ΔE has been shown to be a function of the applied magnetic field H_0 . The following fundamental NMR equation correlated the electromagnetic frequency v for the transition in a given field H_0 .

$$\Delta E = h\nu = \frac{\gamma h B_0}{2\pi} \quad (\text{Or}) \quad v = \frac{\gamma H_0}{2\pi}$$

$$\therefore v \propto H_0$$

where, h = plank constant

$H_0 = B_0$ = applied magnetic field.

and v = frequency of emr.

The nuclei aligned in such a way that their magnetic axes make an angle with the axis of the applied magnetic field H_0 are responsible for the process of absorption or emission of energy, i.e. for the NMR phenomenon. When the frequency of the rotating magnetic field and the precessional frequency of the nucleus become equal, they are said to be in resonance, and absorption or emission of energy by the nucleus can occur.

⑦ what is meant by term chemical shift and define the terms, shielding and deshielding.

The chemical shift is expressed as the difference between the absorption position of a particular proton and the absorption position of a reference proton. Due to varying electronic environment of the proton or group of protons, their absorption signals appear at different field values.

Thus, signals in PMR spectra give kinds of protons and their environments in molecules.

we can express the chemical shifts in terms of Hz by setting the TMS peak at 0Hz at the right-hand edge. The chemical shifts are commonly expressed in s unit which is a proportionality and thus dimensionless. It is independent of the field strength. Chemical shift values in Hz, i.e. ν are converted into s units as follows:

$$s(\text{or ppm}) = \frac{\text{chemical shift in Hz}}{\text{Oscillator frequency in Hz}} \times 10^6.$$

Oscillator frequency is characteristic of the instrument, e.g. a 60 MHz instrument has an oscillator frequency 60×10^6 Hz. The factor 10^6 is included in the above equation simply for convenience, i.e. to avoid fractional values. Since s , which is dimensionless, is expressed in parts per million, expression ppm is often used. Thus, a peak at 60 Hz ($\nu = 60$) from TMS at an applied frequency 60 MHz would be at $s 1.00$ or 1.00 ppm.

$$s(\text{or ppm}) = \frac{60}{60 \times 10^6} \times 10^6 = 1.00.$$

The same peak at an applied frequency of 100 MHz would be at 100 Hz (ν) but

would still be at 81.00 or 1.00 ppm.

$$\text{So } \delta(\text{ppm}) = \frac{100}{100 \times 10^6} \times 10^6 = 1.00$$

The δ unit has been criticized because δ values increase in the downfield direction; the reply is that these are really negative numbers. In the other commonly used unit, a value of 10.00 is assigned to TMS peak. This unit expresses chemical shift in τ values as

$$\tau = 10.00 - \delta$$

Example 1: Protons of a compound exhibit a NMR signal at δ 2.5. What will be the value of chemical shift of these protons in Hz if the spectrum is recorded on a 60 MHz spectrometer?

Solution:

$$\text{Chemical shift in Hz} = \frac{\delta \times 10^6}{\text{Oscillator frequency in Hz}}$$

Let, chemical shift in Hz = ω

$$2.5 = \frac{\omega}{60 \times 10^6}$$

$$\omega = 60 \times 2.5$$

Shielding and Deshielding:

The circulation of proton's electron around the proton itself generates field in such way that it opposes the applied field.

Shielding of protons :-

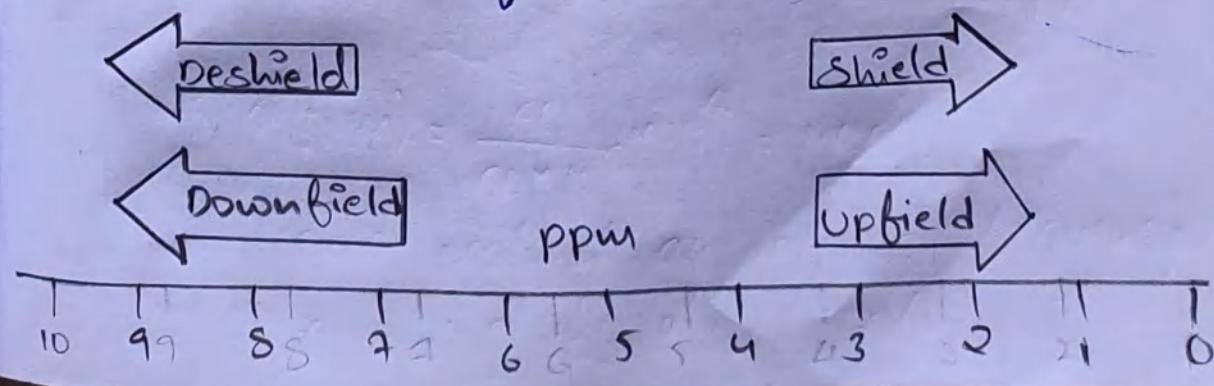
High electron density around a nucleus shields the nucleus from the external magnetic field and the signals are upfield in the NMR spectrum.

The field felt by the protons is thus diminished and the proton is said to be shielded and the absorption said to be upfield.

Deshielding of protons :-

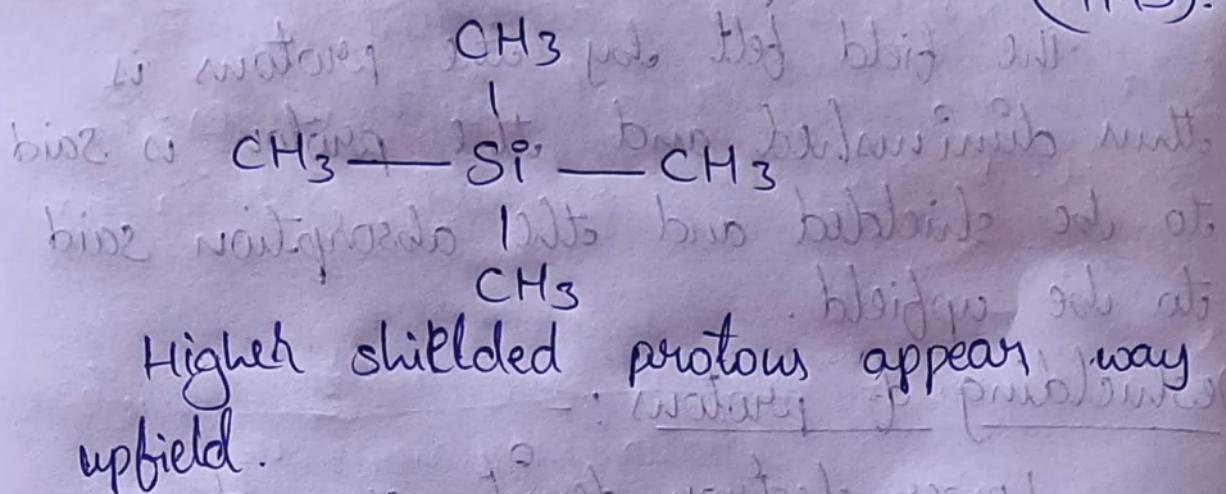
Lower electron density around a nucleus deshields the nucleus from the external magnetic field and the signals are downfield in the NMR spectrum.

If the induced magnetic field reinforced the applied magnetic field, then the field felt by the proton is augmented and the proton is said to be deshielded and the absorption is known as downfield.

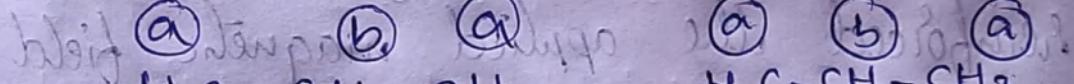
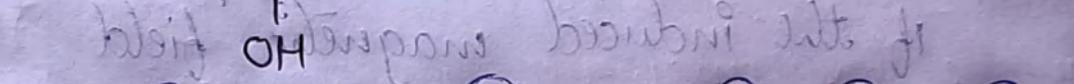
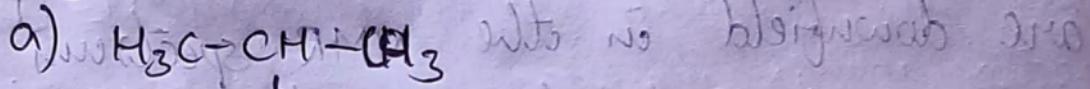


Rather than measure the exact resonance position of a peak, we measure how far downfield it is shifted from TMS.

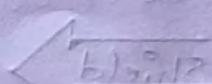
Reference compound tetramethylsilane (TMS):

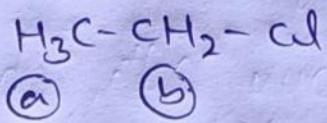
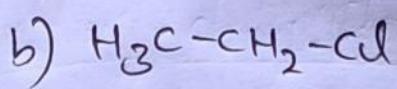


⑧ predict and calculate the NMR signals of following compounds

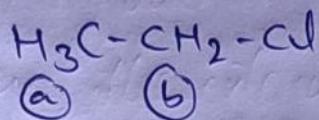


$\xrightarrow{\text{H-NMR}} \textcircled{3} \xrightarrow{\text{GCNMR}} \textcircled{2}$



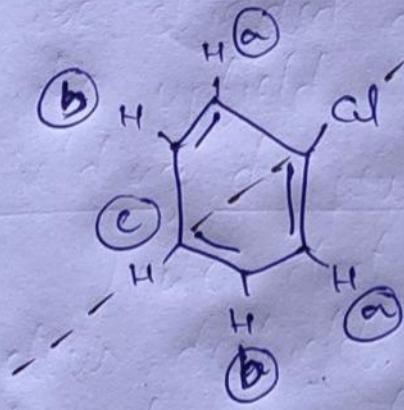
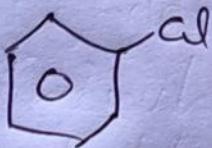


H-NMR \rightarrow ②

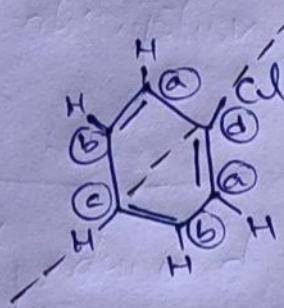


C-NMR \rightarrow ②

c)



H-NMR signals \rightarrow ③



C-NMR signals
 \rightarrow ④