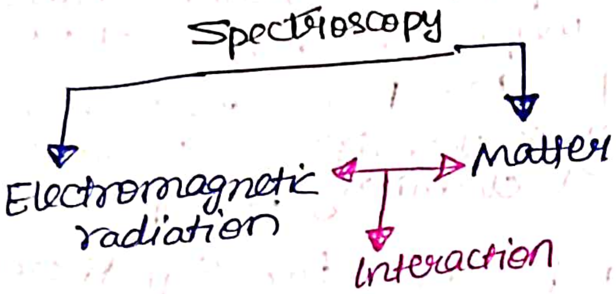
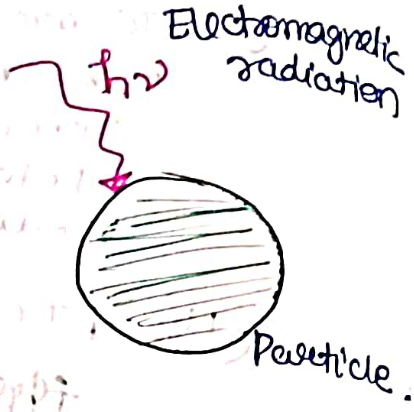
Module - 4





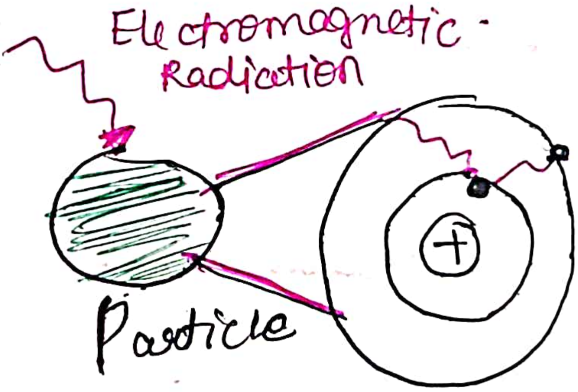
Definition :- The branch of science dealing with the study of interaction of Electromagnetic radiation with particle is known as spectroscopy.

1. Spectroscopy ✓
2. Electromagnetic Radiation
3. Electromagnetic spectrum
4. Types of Interaction
5. Advantages of spectroscopy

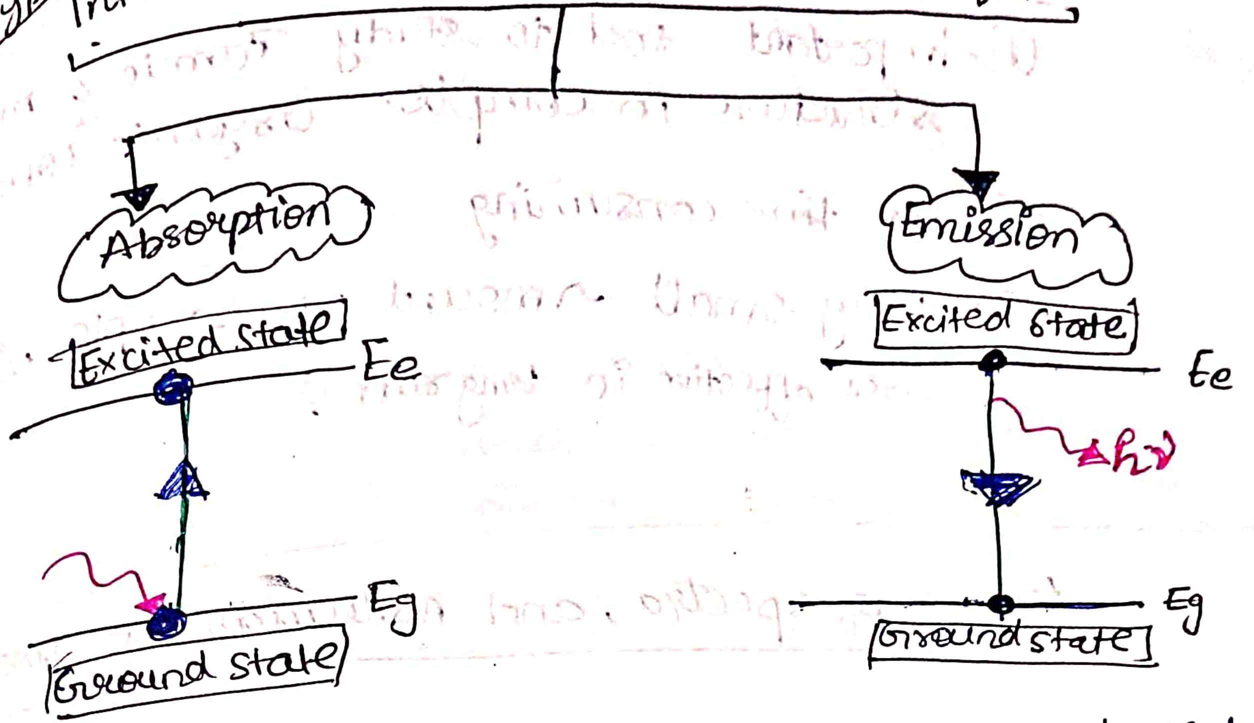
Electromagnetic Radiation

Electromagnetic radiation is a form of radiant energy has both particle as well as wave nature.

→ Electric field
→ magnetic field

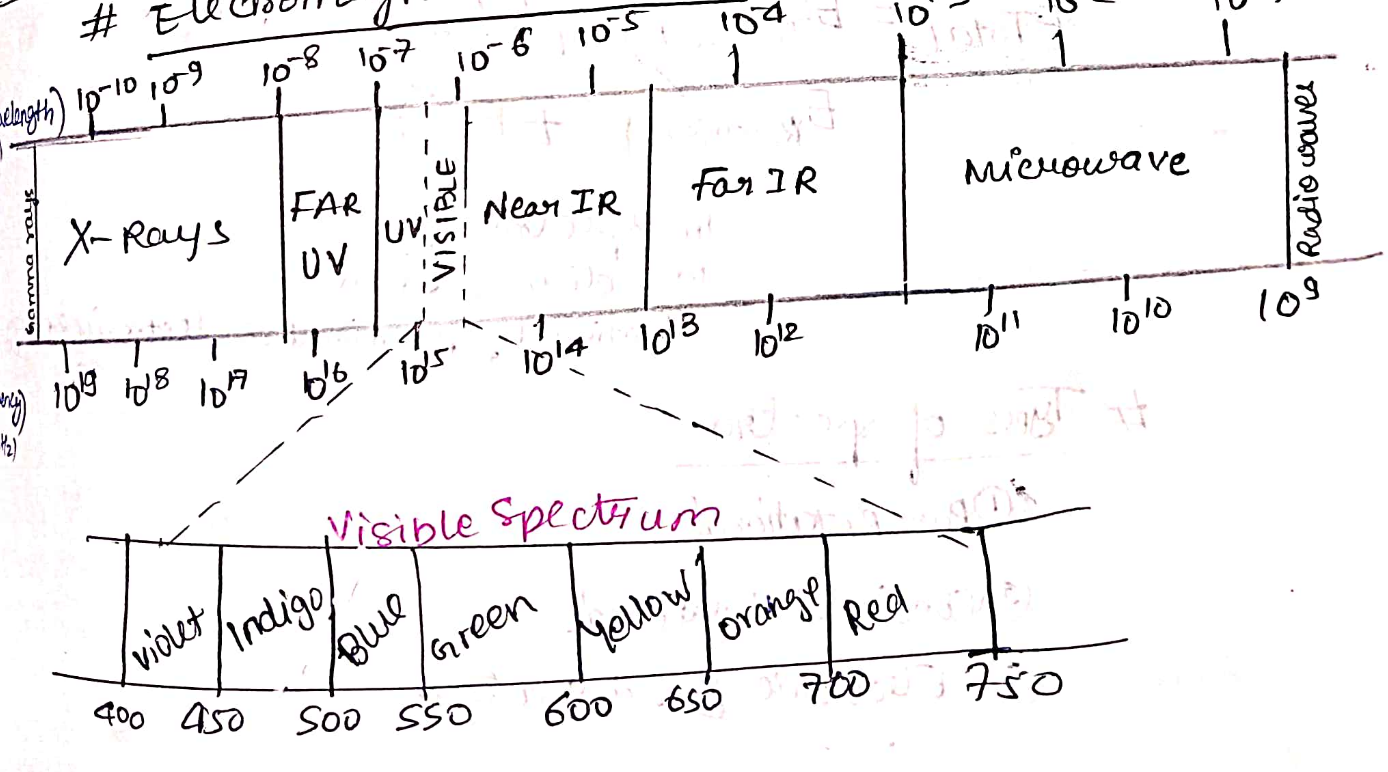


Types Interaction of Electromagnetic wave & Matter



- Energy in the form of light, heat or chemical agents is given to an element
- $\bar{e}$s of atoms accept the energy & go to higher energy levels. (Absorption) However these $\bar{e}$s have to emit energy to return to ground state since excited state is unstable
- when an $\bar{e}$ comes down from an excited state to ground state it emits a photon of energy (Emission)

Electromagnetic spectrum



Advantages of spectroscopy.

① Important tool to study Atomic & molecular structure in complex organic compounds

② Less time consuming

③ very small amount of sample is required

④ cost effective in long run.

Types of spectra, and molecular spectroscopy

#spectra :-

The energy change or frequency of electromagnetic radiation emitted or absorbed can be recorded (spectr with the help of instrument which is known as spectrophotometer

Types of Energy change

$$E_{Total} = E_{Translational} + \overset{\checkmark}{E_{Vibrational}} + \overset{\checkmark}{E_{Rotational}} + \overset{\checkmark}{E_{electronic}}$$

In spectroscopy we discuss about vibrational, Rotational & electronic energy.

Types of spectra

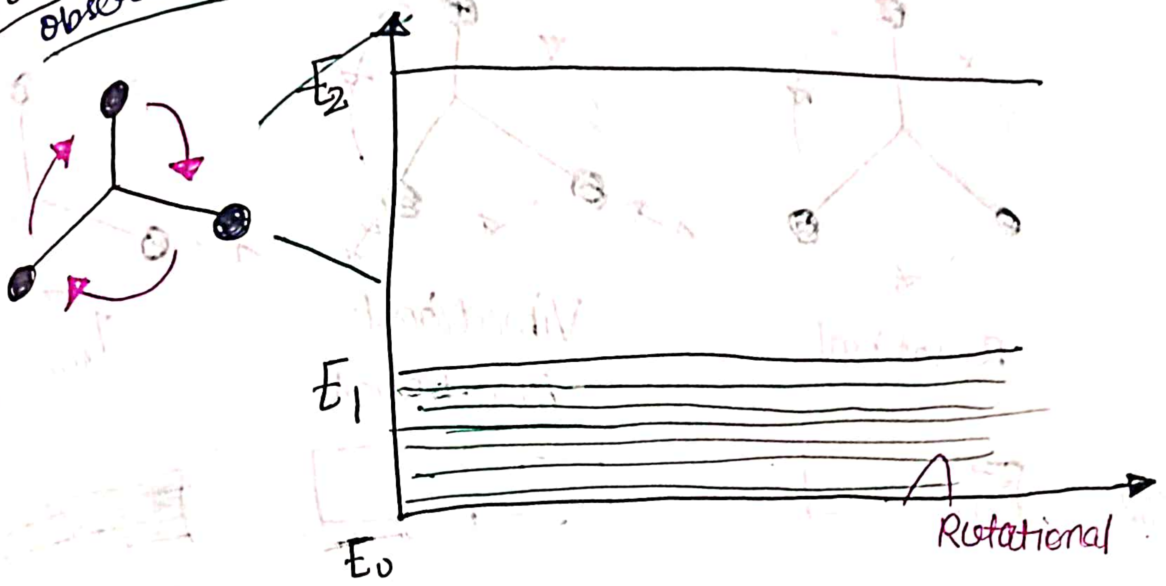
① Pure Rotational

② Vibrational Rotational

③ Electronic Band spectra

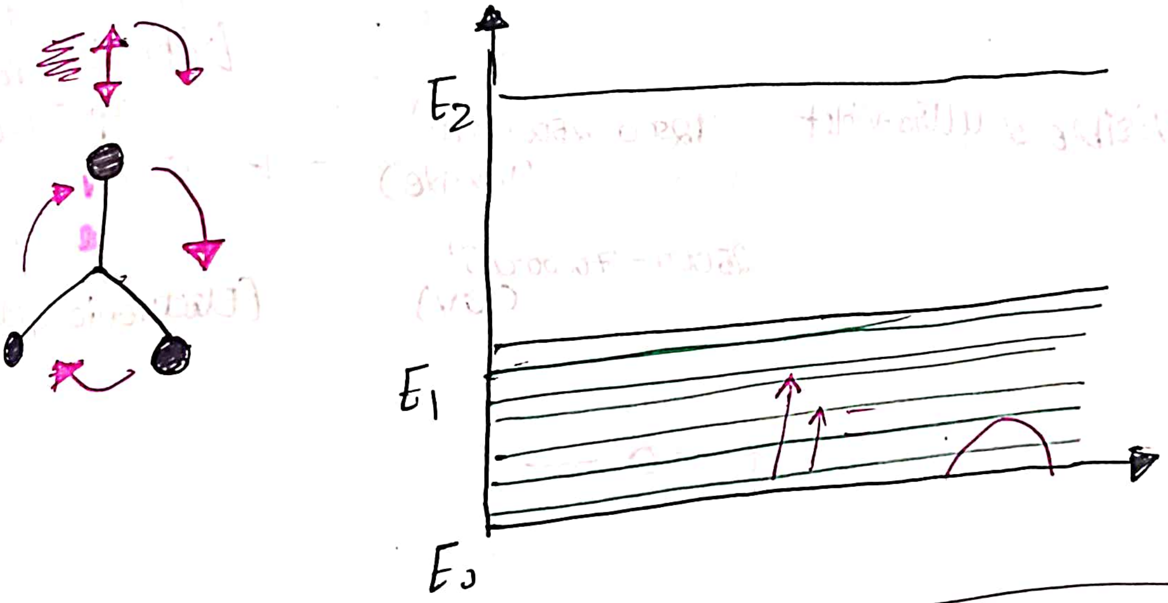
① Rotational

observe in - Far Infrared or in Microwave region.



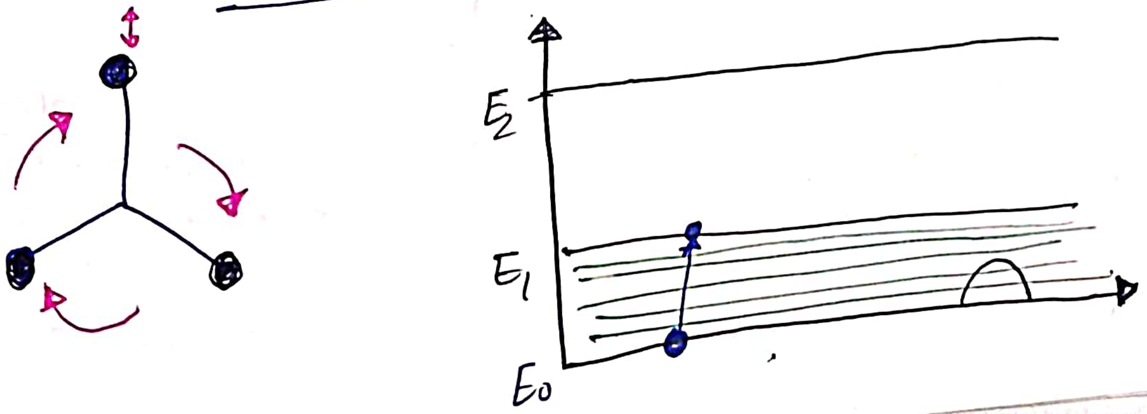
② Vibrational & Rotational Spectra

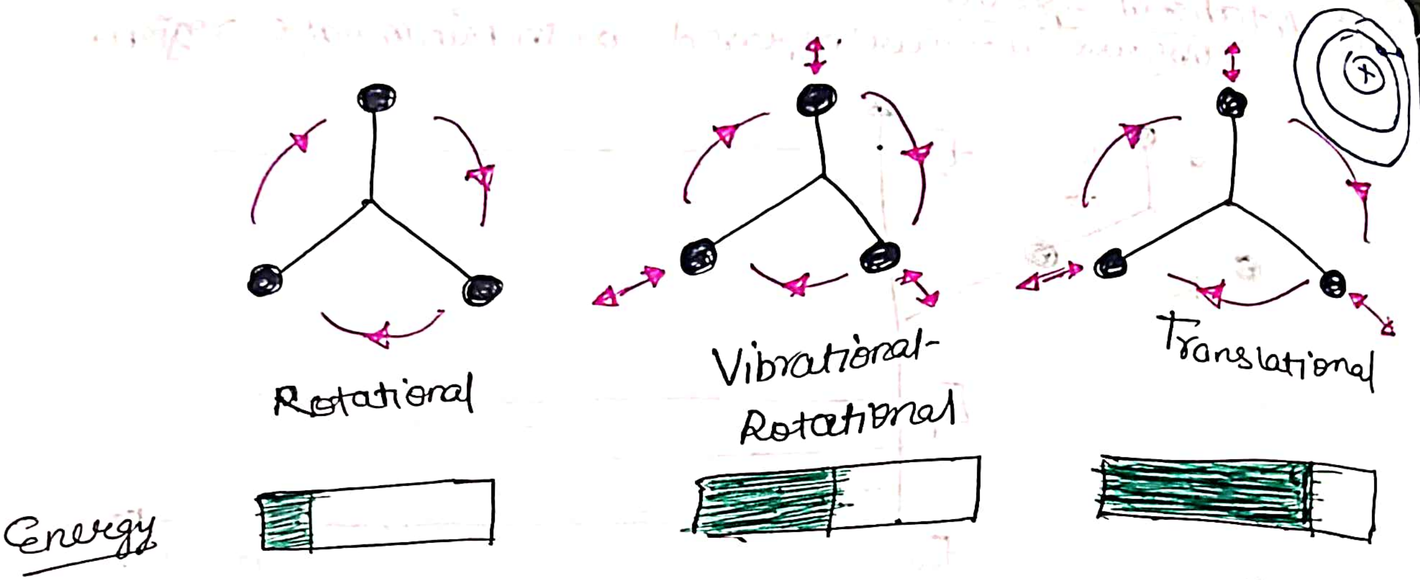
observed in - Near Infrared Region



③ Transitional Spectra: (Electronic Band spectra)

observed in - Visible & ultraviolet region

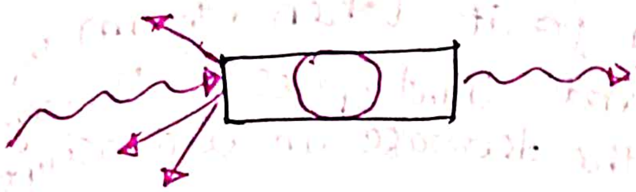


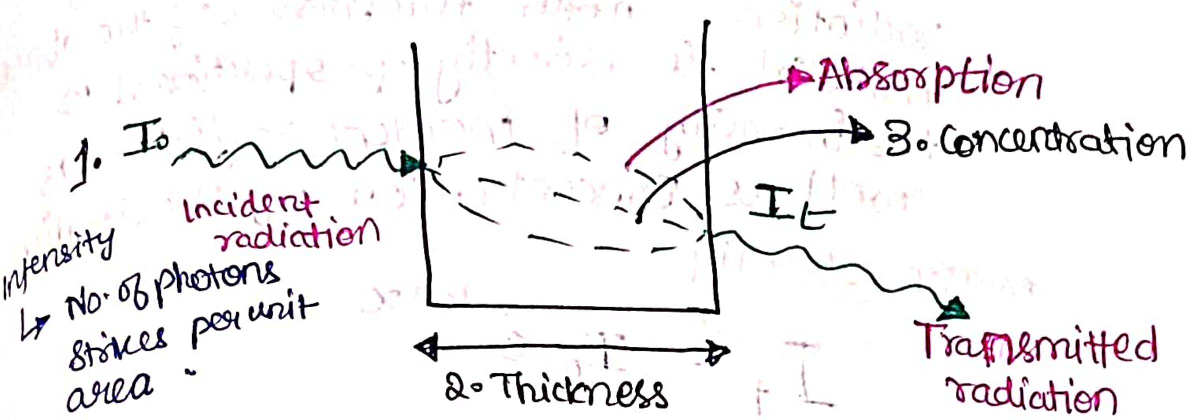


Spectral Region	Wavelength Involve	Spectroscopy
Microwave	$1 - 100\ cm^{-1}$ →	Microwave spectro [Rotational Spectroscop
Infrared	$500 - 400\ cm^{-1}$ →	Infrared spectroscopy [Vibrational-Rotational Spectroscopy]
Visible & ultra-Violet	$12500 - 25000\ cm^{-1}$ (Visible) → $25000 - 70000\ cm^{-1}$ (UV)	ultra-Violet-Visib spectroscopy. [Electronic spectroscop

— o —

Law of … Beer's Law ”





Lambert's Law :

It states that when a beam of monochromatic light passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the incident radiation.

$$\boxed{I_t = I_0 . e^{-Kx}}$$

I_t = Intensity of Transmitted light

I_0 = Intensity of incident light

x = thickness or length of the cell.

K = absorption coefficient

e = exponential

Beer's law

It states that when a beam of monochromatic light passes through a homogeneous solution, the decrease of intensity of radiation is directly proportional to the concentration of the solution.

Beer - Lambert's law :-

It is combined Form of Beer's law & Lambert's law.

According to it when a beam of monochromatic light passed through a solution, the decrease in intensity of radiation with thickness of the absorbing material is directly proportional to the intensity of incident radiation as well as concentration of the solution.

Mathematically

$$I_t = I_0 e^{-KCx}$$

$$\boxed{x = l}$$

By rearranging

$$\boxed{\ln \frac{I_0}{I_t} = KCl}$$

$$\ln \frac{I_t}{I_0} = -KCl$$

$$\frac{I_t}{I_0} = T \text{ (Transmittance)}$$

$$-\log T = \left(\frac{K}{2.303}\right) Cl$$

$$a = \frac{K}{2.303} \rightarrow \text{Absorptivity}$$

$-\log T = acl$

$-\log T = A$ (Absorbance)

$\boxed{A = acl}$ Absorbance

$$\boxed{\log_{10} \frac{I_o}{I_t} = A = acl}$$

$$\boxed{A = \varepsilon C_m l}$$

ε = molar Absorptivity

I_o : intensity of incident light
I : intensity of transmitted light
ε : molar extinction coefficient
l : path length of cell
C_m : concn of sample.

Q. A compound having concentration 10^{-3} g/L resulted absorbance value 0.20 at λ_{max} = 510nm using 1 cm cell. Calculate its absorptivity and molar absorptivity values. molecular weight of compound is 400.

Concn (C) = 10^{-3} g/L

$A = 0.20$

$l = 1.0$ cm

$A = acl$

$0.2 = a \times 10^{-3} \times 1$

$$\boxed{a = \frac{0.2}{10^{-3}} = 200 \text{ l/g cm}}$$

Molar absorptivity

$A = \varepsilon C_m l$

$0.2 = \varepsilon \times \frac{10^{-3} \times 1}{400}$

$\varepsilon = \frac{0.20}{2.5 \times 10^{-5}} \Rightarrow \boxed{\varepsilon = 0.8 \times 10^{5} \text{ l/mol cm}}$

Q. At definite wave length, an absorber when placed in a cell of 1 cm path length absorbs 20% of incident light. If the Absorptivity of the absorber at this wave length is 2.0. Find out, its concentration

$$A = a c l$$

$l = 1\ \text{cm}$ $\quad = 20\%$ absorbed

$a = 2.0$

$I_0 = 100\%$

$I_t = 80\%$

$$A = \log \frac{I_0}{I_t} = \log \frac{10}{8}$$

$$A = 0.0969$$

$$A = a c l$$

$$0.0969 = 2.0 \times c \times 1$$

$$c = \frac{0.0969}{2 \times 10^{-2}}$$

$$\boxed{C = 0.04845\ \text{gm/L}}$$

Ans

Limitations of Lambert Beer's Law

The linearity of the Beer-Lambert law is limited by chemical & instrumental factors. Causes of non-linearity include:

① Deviations in absorptivity coeffecients at high conc^n ($>0.01M$) due to electrostatic interactions between molecules in close proximity.

② Scattering of light due to particulates in the sample.

③ Fluorescence or phosphorescence of the sample

④ changes in refractive index at high analyte concentration.

⑤ shift in chemical equilibria as a function of concentration.

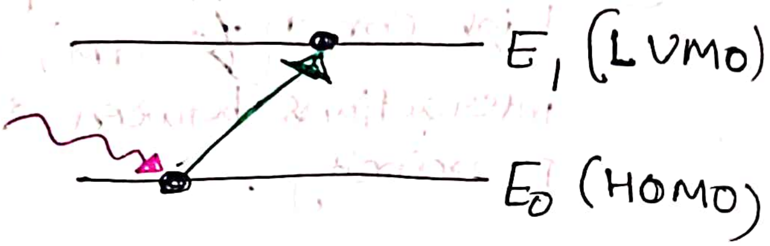
=o=

UV-Visible Spectroscopy

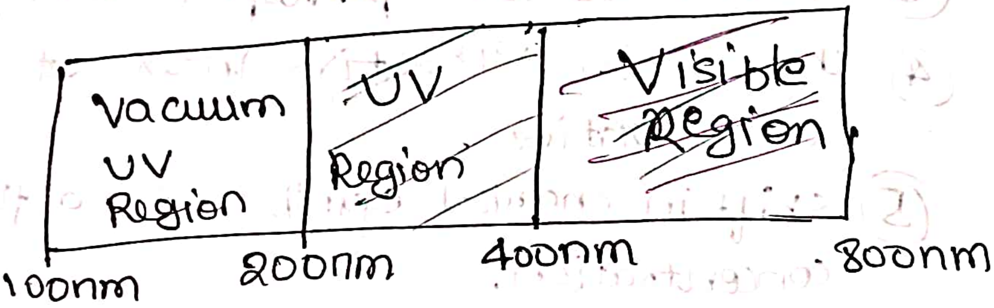
Electronic spectroscopy

Transition

HOMO → LUMO



Range : 190nm - 800nm



since absorption of UV-VIS radiation by a molecule leads to transition among electronic energy levels of the molecule it is also often called as electronic spectroscopy.

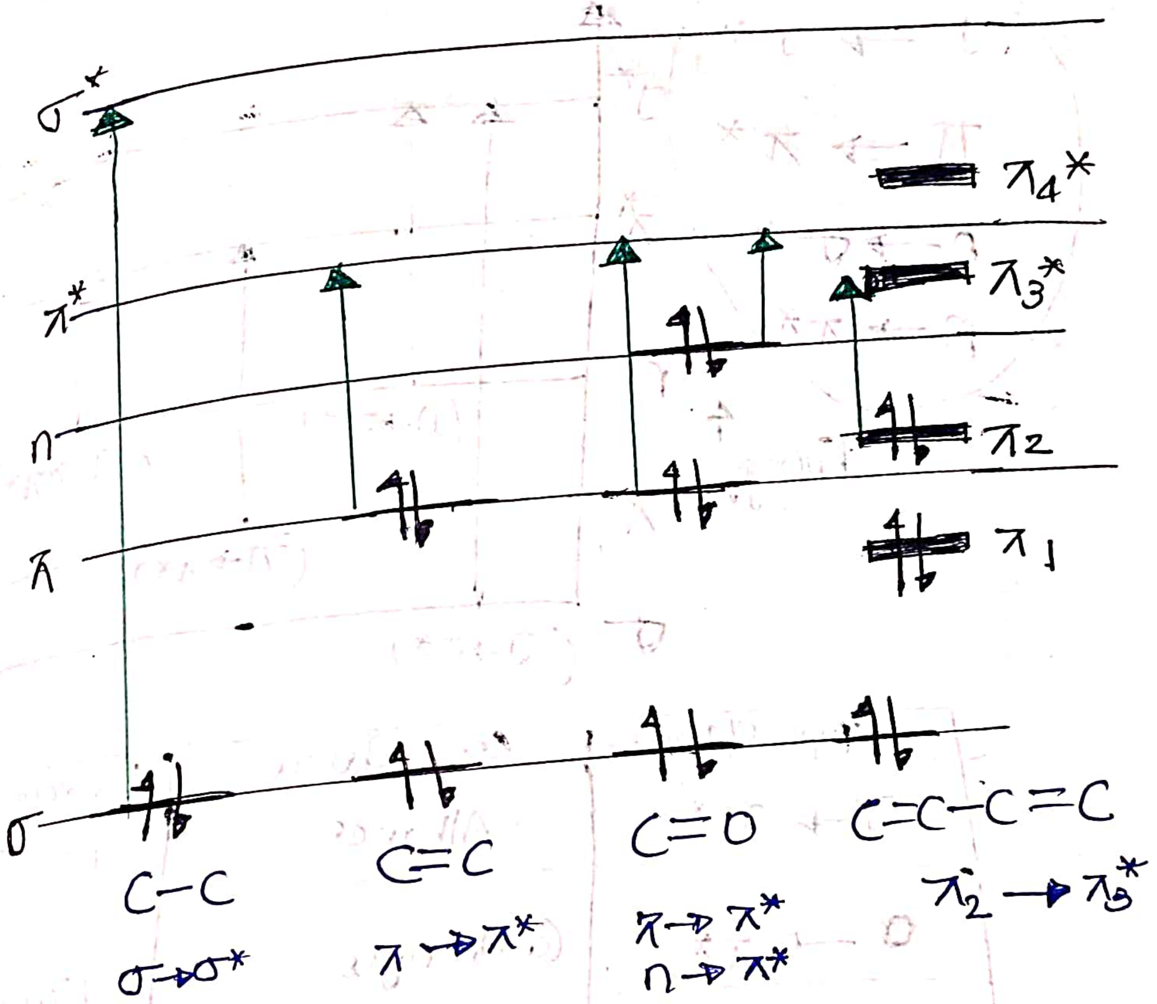
The info provided by this spectroscopy combined with info provided by NMR&IR spectral data leads to valuable structural proposals

Electronic Transitions :-

Ground State (E_0) ——→ Excited State
HOMO ——→ LUMO

The transition of an ē from one energy level to another, is thus accompanied by a simultaneous change in vibrational & rotational states & causes transitions between various vibrational & rotational levels of lower & higher energy levels. Therefore many radiations of closely placed frequencies are absorbed & a broad absorption band is obtained.

Electronic Transition



$n \to \pi^* < n \to \sigma^* < \pi \to \pi^* < \sigma \to \pi^* < \sigma \to \sigma^*$

Types of electrones

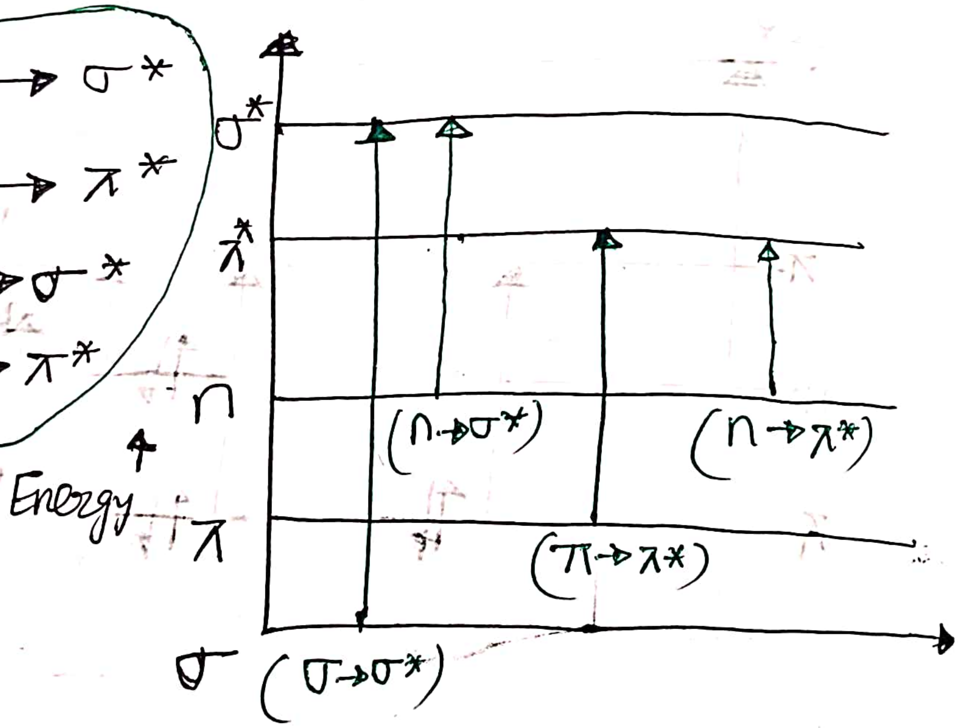
(1) σ electrones → Saturated CH_4 / Unsaturated C_2H_4

(2) π-electrones → Unsaturated

(3) n-electrones → O, N, Cl, F

Types of Transitions

σ → σ*
π → π*
n → σ*
n → π*



Types of Transition	Compounds	Wavelength
σ → σ*	Alkanes	150 nm
σ → π*	Carbonyls	170 nm
π → π*	Unsaturated compounds	180 nm
n → σ*	O, N, S, halogens	190 nm
n → π*	Carbonyls	300 nm

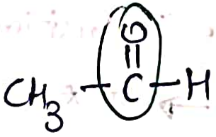
1. σ → σ* Transition → C_nH_{2n+2} , C_nH_{2n+1}
Alkanes Alkyl

2. n → σ* Transition → un/saturated Non-bonding ē
(N, O, S, Cl, F)

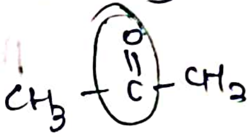
$C_2H_5NO_2$, C_2H_5Cl , C_2H_5OH .

3. π → π* Transition → Unsaturated compds
C_nH_{2n} , C_nH_{2n-2} .
eg. C_2H_4 , C_2H_2

4. n → π* Transition → unsaturated non-bonding ē
eg. CH_3CHO , CH_3COCH_3



$CH_3-\overset{O}{\overset{\|}{C}}-H$



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

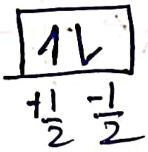
Energy Order

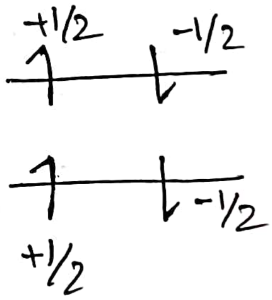
$$\underbrace{\sigma \rightarrow \sigma^* > n \rightarrow \sigma^*}_{200-400\,nm} > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

✓✓

Selection Rules Of UV-spectroscopy

(1) ΔS = 0





(2) n → σ* → Forbidden

(3) Forbidden Transition arises due to symmetry of transition state.

UV active/UV inactive compounds

✓ ✗ ✓ ✓

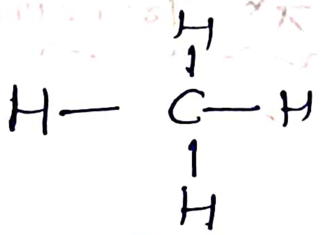
$$\underbrace{\sigma - \sigma^* > n - \sigma^*}_{200nm-400nm} > \pi \rightarrow \pi^* > n - \pi^*$$

Saturated → UV Inactive

Unsaturated → UV Active

(1) CH_4 (C_nH_{2n+2})

Transition ($\sigma \rightarrow \sigma^*$)



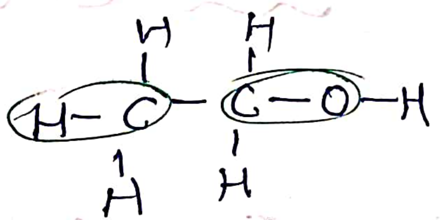
$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$

(2) C_2H_5OH (C_nH_{2n+1})

Possible Transition

$$\left(\begin{array}{l} \sigma \rightarrow \sigma^* \\ n \rightarrow \sigma^* \end{array}\right)$$

→ [UV inactive]

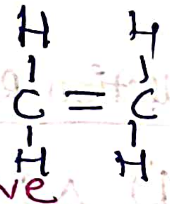


$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H$$

(3) C_2H_4 (C_nH_{2n})

Possible Transition -

$$\left[\begin{array}{l} \sigma \rightarrow \sigma^* \\ \pi \rightarrow \pi^* \end{array}\right] \rightarrow$$ UV Active.



$$\overset{\displaystyle H}{\underset{\displaystyle H}{C}}=\overset{\displaystyle H}{\underset{\displaystyle H}{C}}$$

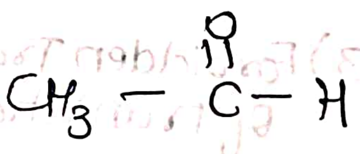
(4) CH_3CHO

$\sigma \rightarrow \sigma^*$ — Not ⓧ

$\pi \rightarrow \pi^*$ — ✓

$n \rightarrow \sigma^*$ — ⓧ

$n \rightarrow \pi^*$ ✓



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

UV active → CH_3COOH, CH_3NO_2

Chromophores & Auxochromes :-

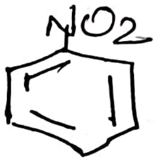
(I) Chromophores

Chromo	Phores
Colour	bearing group

Chromophores are unsaturated group (covalently bonded), responsible for electronic absorption

eg. $>C=C<$, $>C=O$, $-NO_2$

Benzene (Colourless)



Nitro-benzene (yellow)

① $\pi \rightarrow \pi^*$

② $\pi \rightarrow \pi^*$
$n \rightarrow \pi^*$

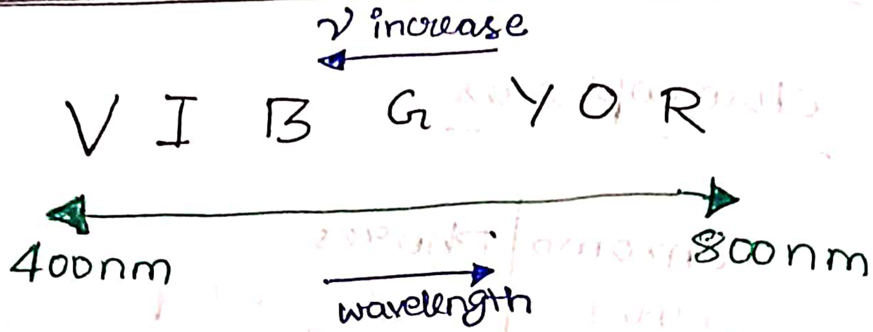
(II) Auxochromes

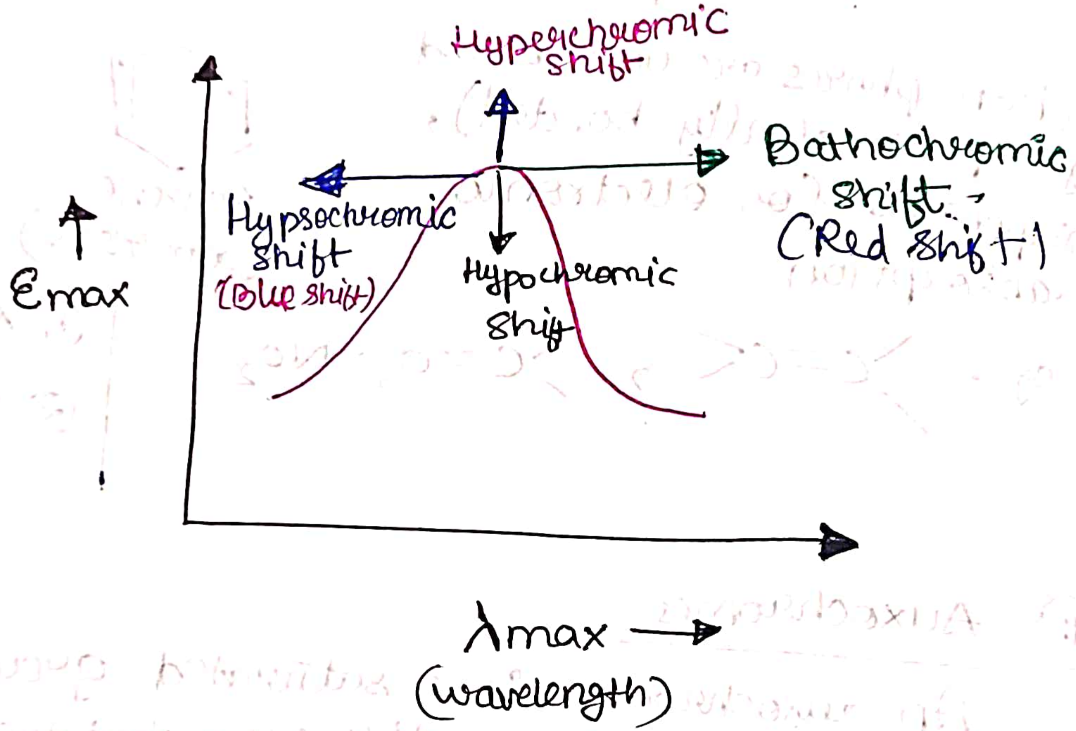
An auxochromes is a saturated group, which are not chromophore themselves but their presence can cause the increase in colour intensity of compounds.

Absorption shift → Longer wavelength.

eg. Amino gp, OR, NR_2, NHR, $-SH$ etc

Absorption and Intensity shifts :-





(i) Bathochromic shift (Red Shift)

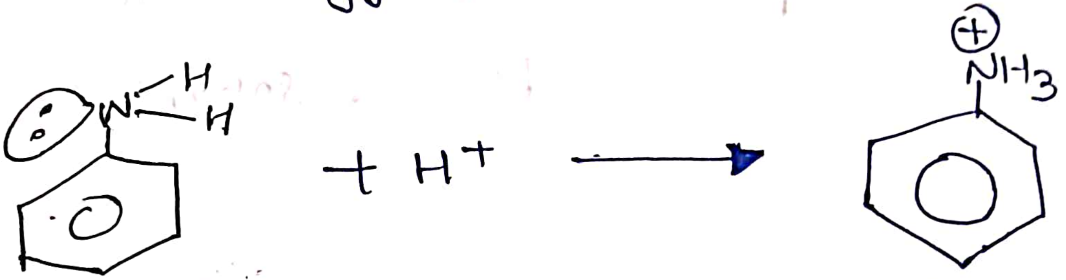
A shift of an absorption maximum towards longer wavelength or lower energy.

$CH_2=CH_2$
Ethylene
λ_{max} 175 nm

$CH_2=CH-CH=CH_2$
1,3 butadiene
$\lambda_{max} = 217 nm$

) Hypsochromic Shift (Blue shift)

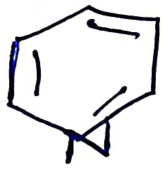
A shift of an absorption maximum towards shorter wavelength or higher energy.



$\lambda = 280$ nm

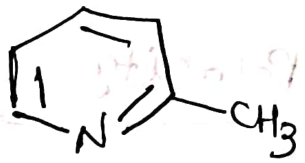
$\lambda = 203$ nm

(iii) Hyperchromic Shift : (Increase in absorption intensity)



Pyridine

2750

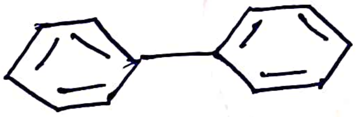


2-methyl Pyridine

3560

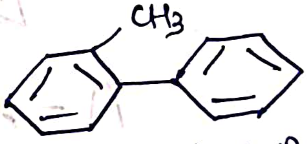
Emax

(IV) Hypochromic shift : [Decrease in absorption intensity]



Biphenyl

Emax 19000



2-methyl Biphenyl

10,250

Solvent effects

Sample - Non-polar - solvent
Polar - Solvent

Non-polar + solvent → (Polarity) → little shift

Polar + solvent → (Polarity) → Major shift

Effect of Polarity

V I B G Y O R

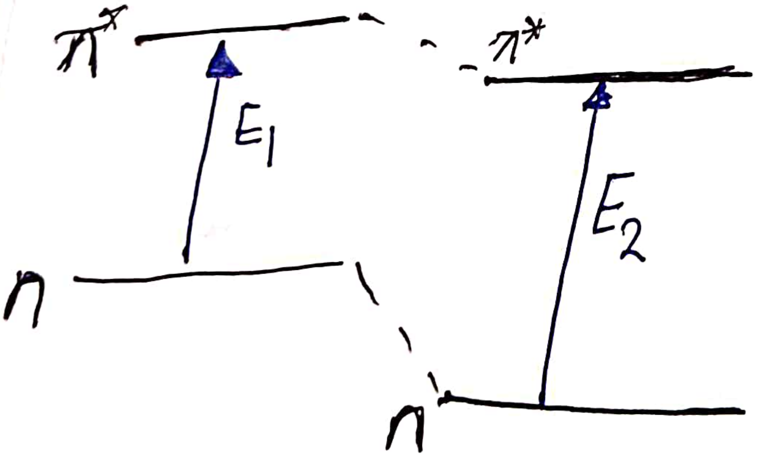
400nm [Blue shift] $\xrightarrow{\lambda_{max}}$ 800nm [Red shift]

$n \rightarrow \pi^*$ [Blue shift]

Polar solvents stabilize n-orbitals.

$\pi \rightarrow \pi^*$ [Red shift]

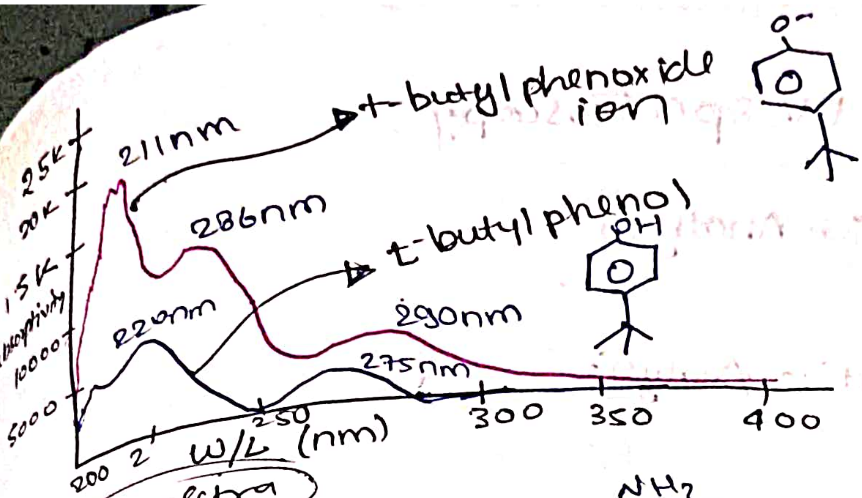
due to dipole-dipole interaction



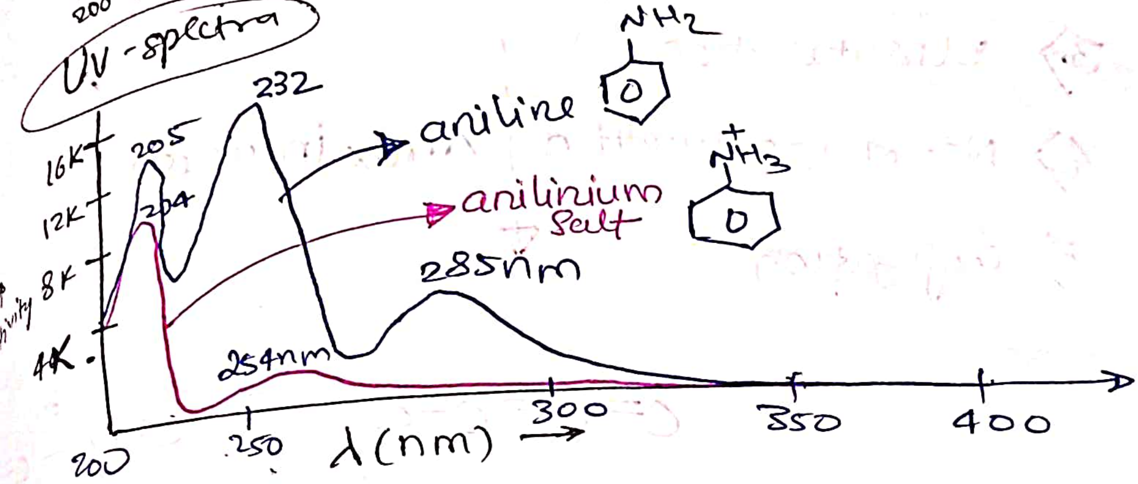
$E_2 > E_1$
(Blue shift)

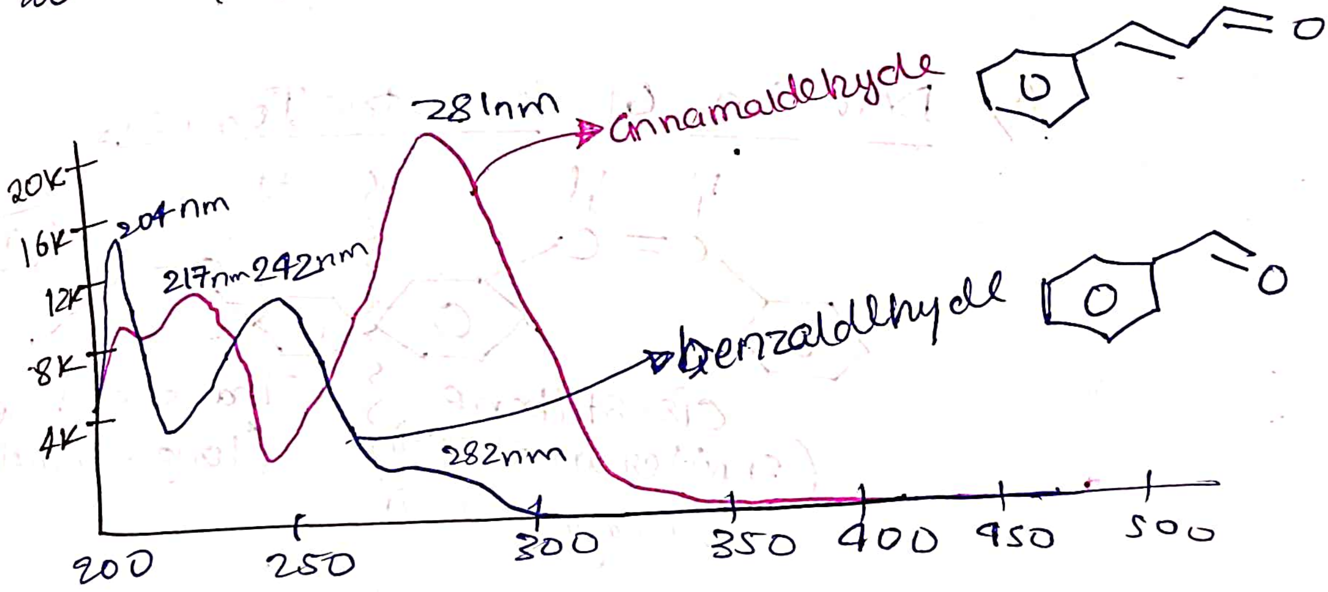
$E_2 < E_1$
(Red shift)

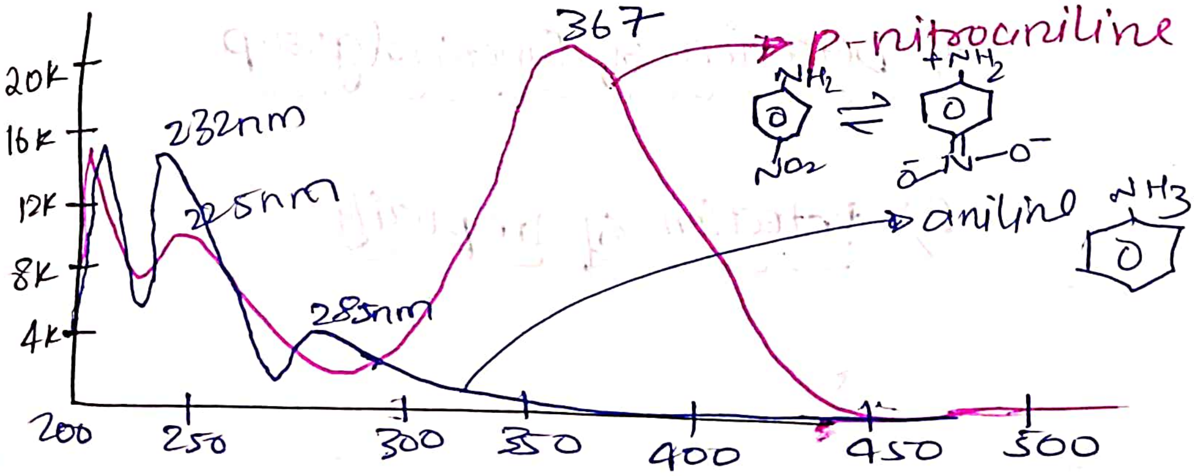
UV-spectra



UV-spectra







#Application of UV spectroscopy.

1.) Qualitative Analysis -

2.) Quantitative Analysis

3.) Unsaturation

4) No. of unsaturation

5) conjugation

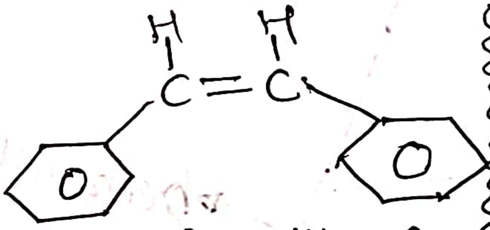
λmax increase

$C=C=C-C$

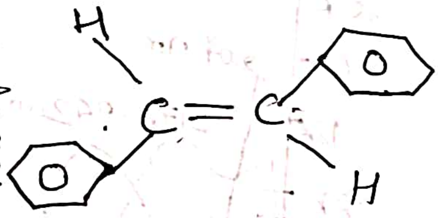
conjugation

$C=C-C=C$

6) Detection Of Geometric Isomers



Cis-stilbene
(shorter wavelength)
(Sterically hindered)



Trans-stilbene
(Longer wavelength)

7) Detection of functional group

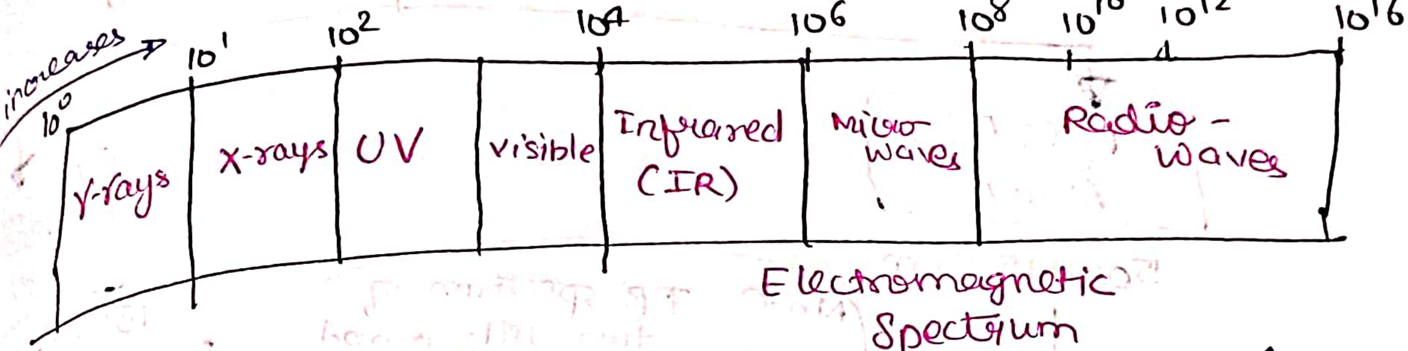
8) Detection of Impurity

spectroscopy

Introduction & Principle

UV → Saturation & unsaturation
Conjugation.

IR → Functional group in solid, liquid or gas forms

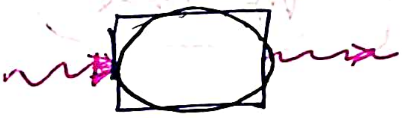


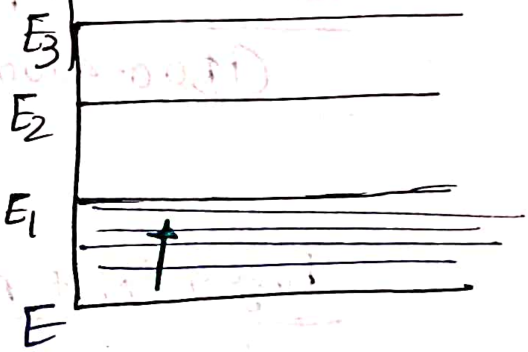
Electromagnetic Spectrum

IR Region - 2.5 μ - 15 μ
400 - 4000 cm^{-1}

1 μ = 10^{-4} cm^{-1}

IR spectrum
Absorbance or Transmittance
vs
frequency





Rotational
Vibrational - Rotational → IR spectrum
Electronic
↳ Vibrational Rotational Spectroscopy

Principle

IR → Vibrational & Rotational energy changes.

Energy changes depends on

(1) Mass of the atoms present in a molecule

(2) Arrangement of atoms within a molecule

(3) The strength of bonds

A common laboratory instrument that uses this technique is a Fourier transform Infrared (FTIR) spectrometer.

Q. why IR spectro is also known as Finger Print of the molecule.

Finger Point Region

→ Vibrational & Rotational energy.

IR Region — 2.5 - 25 μ

400 - 4000 cm⁻¹

Finger Point Region

500 - 1500 cm⁻¹

→ Bending Vibrations

Functional Group Region

1500 - 4000 cm⁻¹

→ Stretching Vibrations

Note IR spectrum of two diff. compd can never be same

Functional Group Region

(1500-4000 cm⁻¹)

→
- —
- =
- ≡
- OH
- CHO
- COOH
- COOR

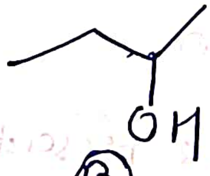
Finger Point Region (500 - 1500 cm⁻¹)

↳ Every compound shows a characteristic absorption.

p-alcohol

Ⓐ

→ OH



S-alcohol (Finger Point)

Ⓑ

→ OH

[Function group Region]

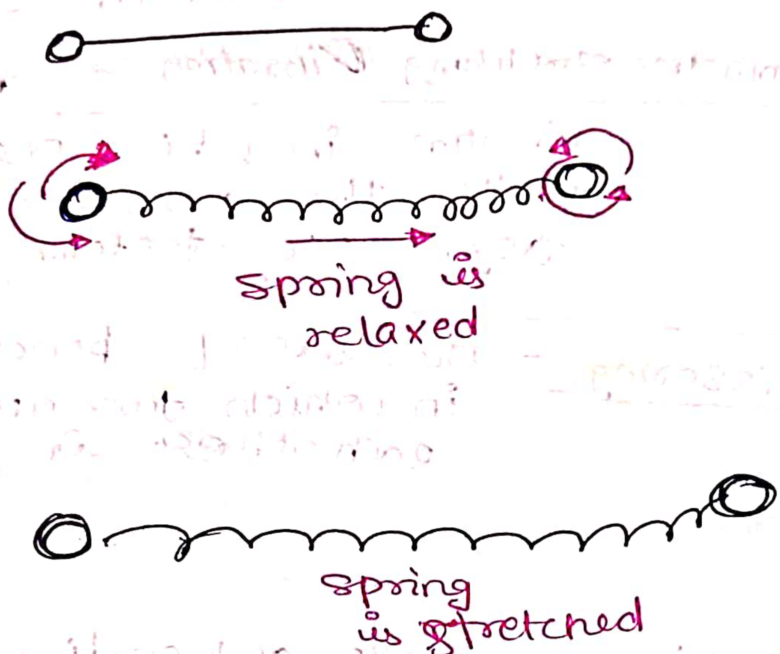
↓

Same absorpt

↓ characteristic absorption

(Vibration - Rotational)

lecular Vibrations



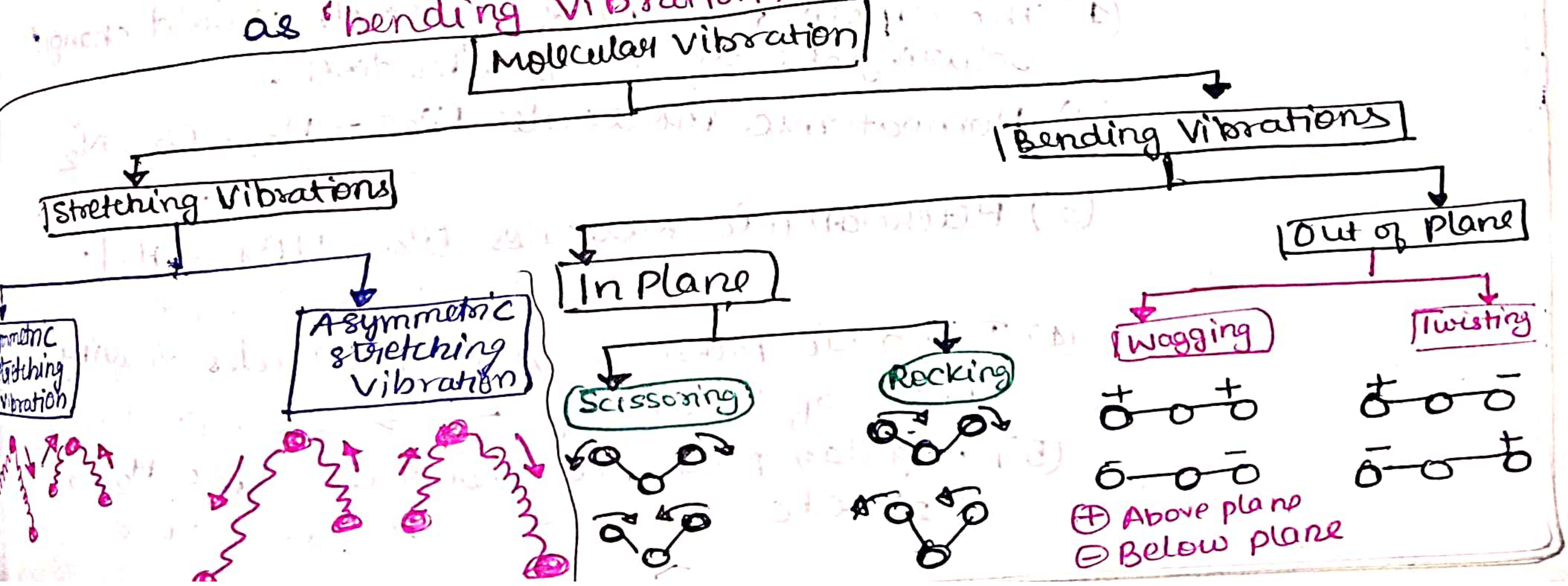
Types of Vibrations :-
1. Stretching Vibration
2. Bending Vibration

1. Stretching Vibration

"Vibration in which distance b/w two atoms increases or decreases. but the atoms remain in the same bond axis are known as "stretching vibrations".

2. Bending Vibration

"Vibration in which positions of atom changes relative to the original bond axis are known as 'bending vibration'.



Stretchin

(I) <u>Symmetric stretching vibration</u> - The mode of stretching vibration in which both the atoms move in & out simultaneously is known as symmetric stretching Vi

(II) <u>Asymmetric stretching Vibration</u> - The mode of stretching vibration in which one atom moves in while other moves out is known as asymmetric stretching vibrations

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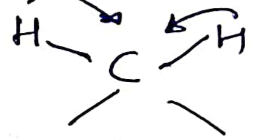
Bending

(I) <u>Scissoring</u> - The mode of bending vibrations in which two atoms approach each other is scissoring.



(2) <u>Rocking</u> The mode of bending vibration in which both atoms move to the same side & then to the other side

(3) <u>wagging</u> - The mode of bending vibration in which two atoms move up & below the plane with respect to central atom.

(4) <u>Twisting</u> - The mode of bending vibration in which one of the atom moves up the plane while the other moves down the plane with respect to central atom

---

Selection Rule :-

(1) The dipole moment of molecule should change during the course of vibration.

(2) Homoatomic molecules like - H_2, O_2, N_2
└→ IR Inactive

(3) Heteroatomic molecules like - HBr, HCl.
└→ IR active

(4) Triatomic Molecules / other molecules having centre of symmetry → IR inactive.
eg. CO_2

(5) Angular Triatomic molecules like H_2O, SO_2, H_2S etc → IR active

Difference b/w IR & Raman spectroscopy

IR spectroscopy	Raman spectroscopy
① It is due to the absorption of a radiation by a vibrating molecule	① It is due to the scattering of a radion by a vibrating molecule
② The basic concept of IR spectra is the presence of permanent dipole moment in a molecule.	② The polarizability of the molecule changes
③ Homonucleus diatomic molecules are IR-inactive	③ Homonucleus diatomic molecules are Raman active
④ Condition for a substance i.e. purity & impurity is not rigid	④ Substance must be pure & colourless
⑤ water cannot be used as solvent because it is opaque to IR spectrum	⑤ water can be used as solvent
⑥ Method is accurate & sensitive	⑥ less accurate & less sensative
⑦ generally dilute sol^{n}s are used	⑦ As Raman lines are weak in intensity. so concentrated solutions are used to increase intensity.

Total no of vibrational modes

Non linear → $(3n-6)$. n: no of atoms

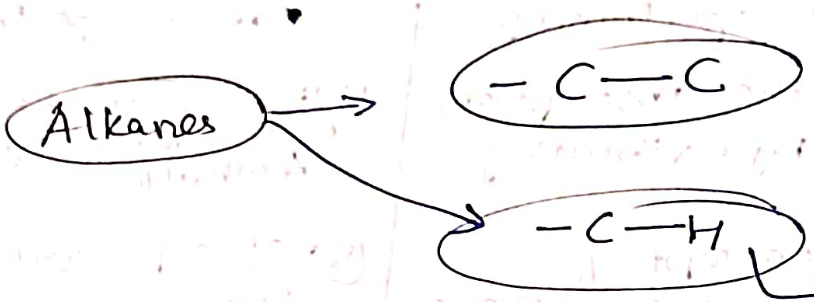
Linear → $(3n-5)$

H_2O (Non Linear)
↙ ↘
2 str 1 bendy

$V_m = ④$

CO_2
↙ ↘
2 str 2 bendin

Stretching frequency of Alkane

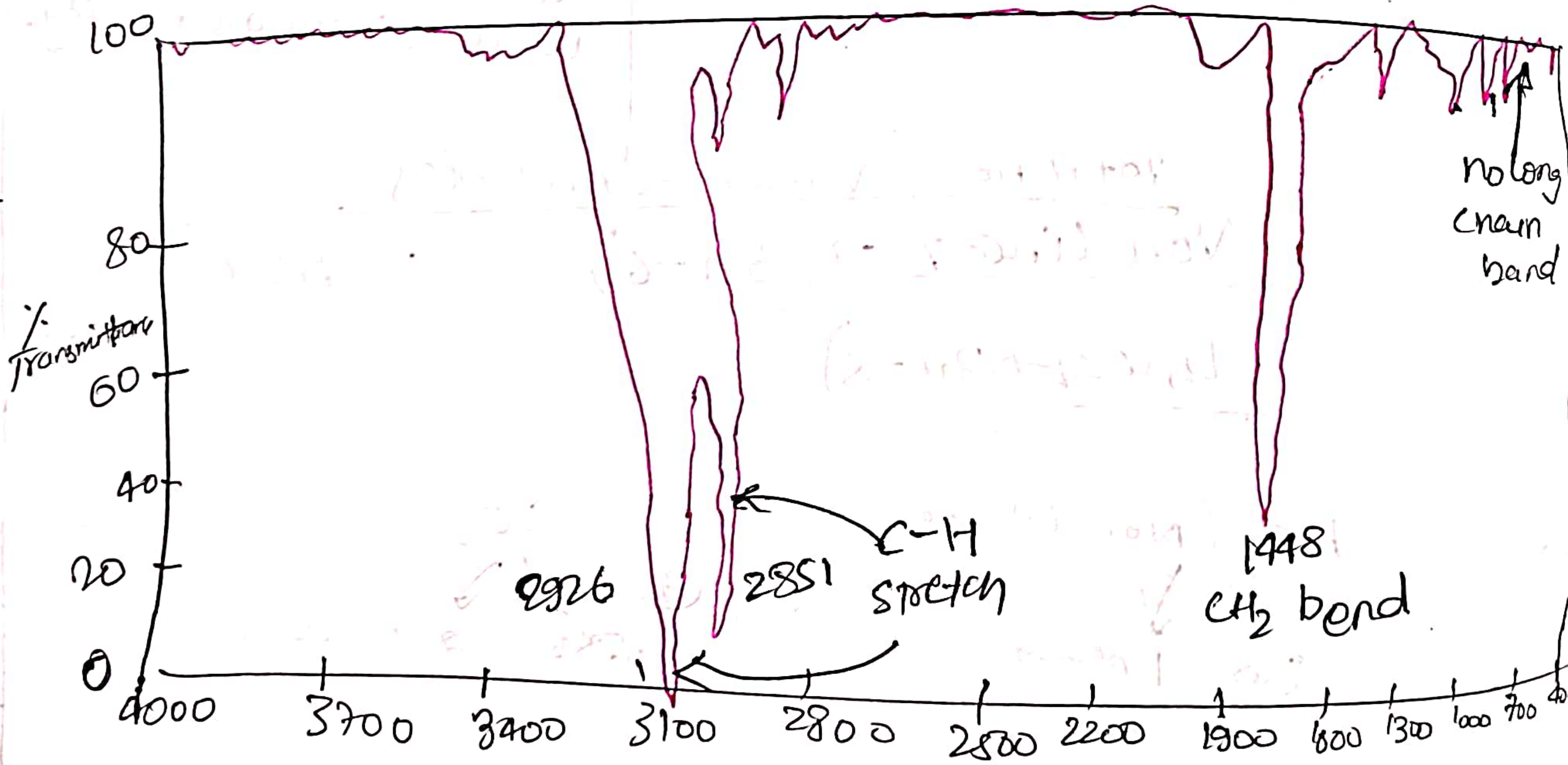


occur in region b/w 3300 cm^{-1} (alkynes) & 2700 cm^{-1} (aldehydes)

Hydrocarbon containing a methyl gp usually shows two distinct bands. one at 2960 cm^{-1} due to asymmetric stretching & due to symmetric stretching other at 2870 cm^{-1}

→ C–H bending vibrations of methyl gps in HC normally occurs at 1450 & 1375 cm^{-1}

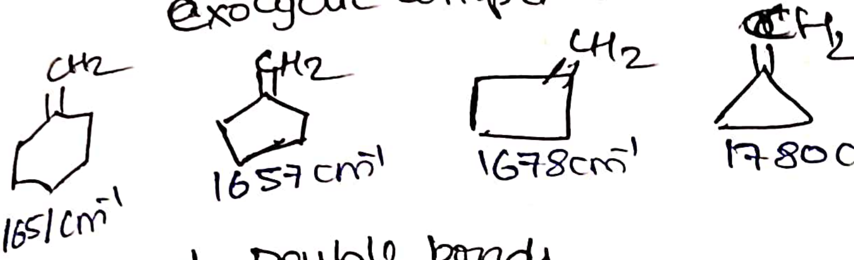
→ The C–C bond vibrations appear as weak bands in 1200–800 cm^{-1} regions



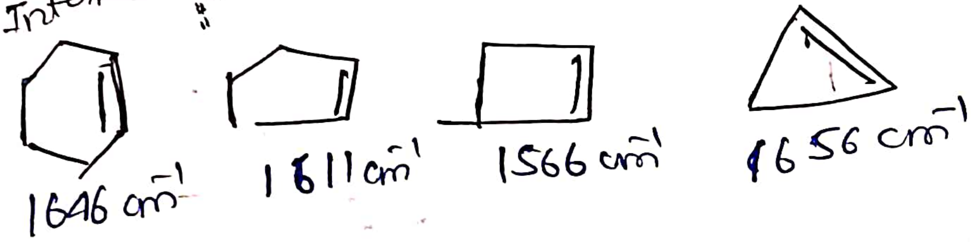
Alkenes

$C=C$ has higher force constant than $C-C$.
& . In non conjugated olefin, $C=C$ stretching vibration appear at high freq. (1680 - 1620 cm^{-1}) than that of $C-C$ stretching vibrations (1200-800 cm^{-1})

exocyclic compd.

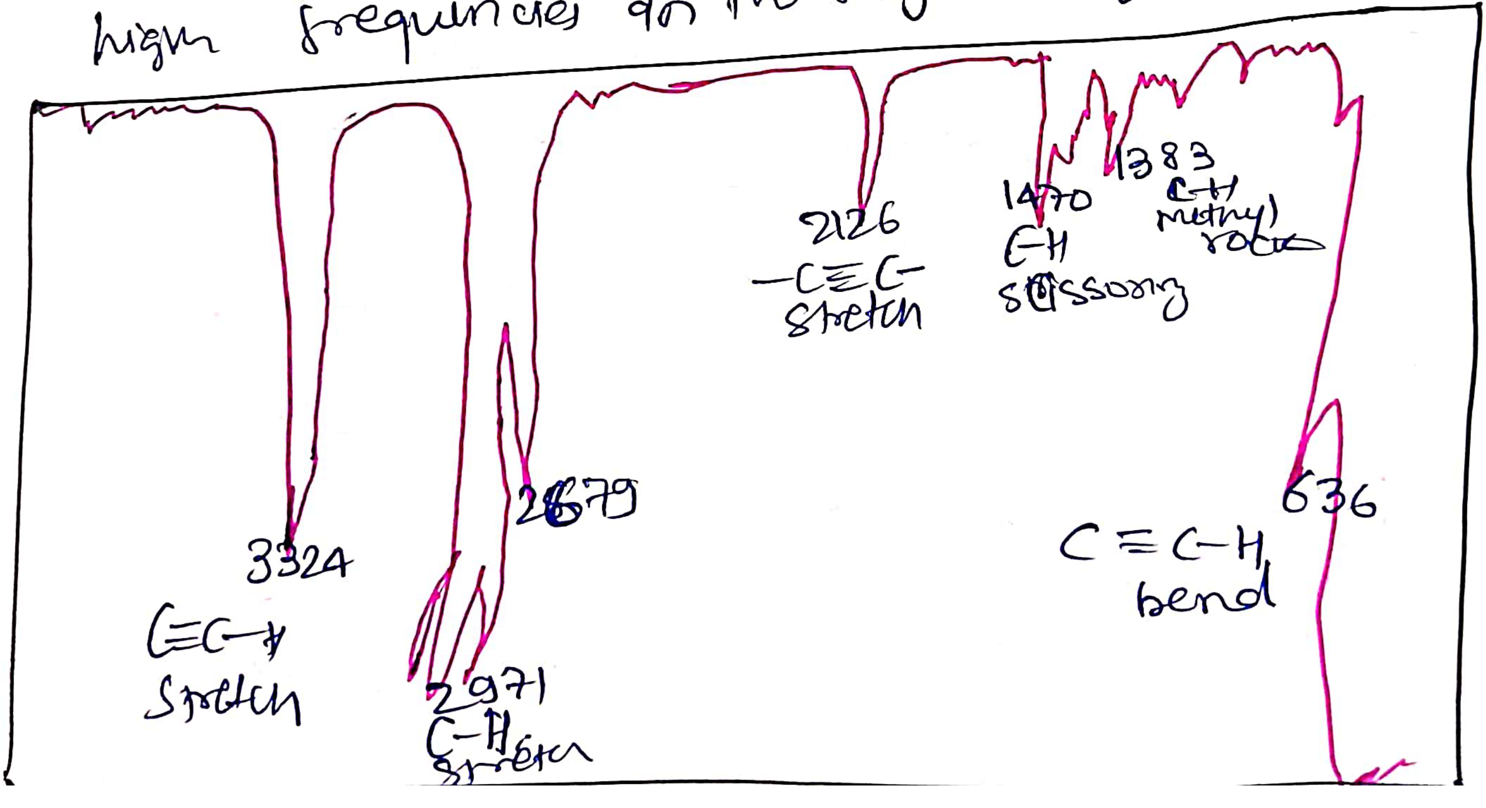


Internal Double bonds



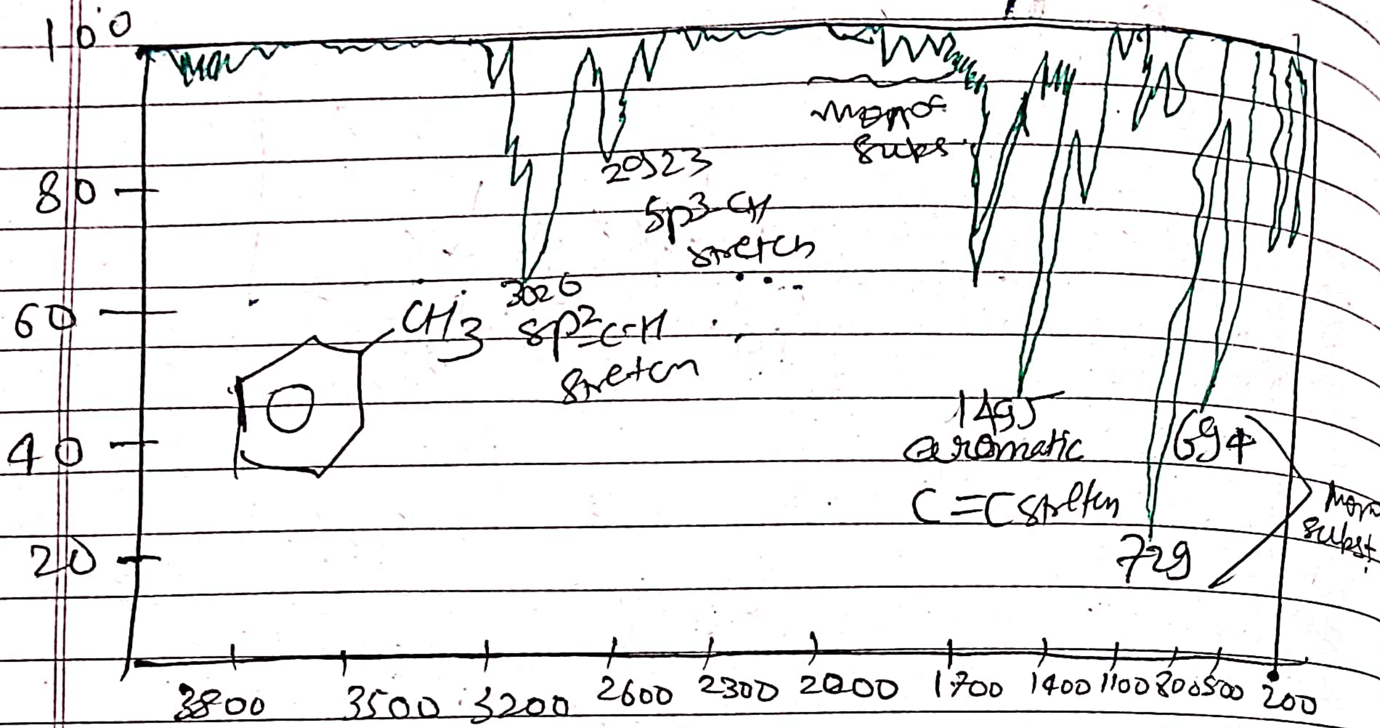
Alkynes
$R-C\equiv CH$ or $R-C\equiv CR$

$C-C$ stretching Vibrations occur b/w 1300-800 cm^{-1}
& $C=C$ stretching vibration occurs in region 1700-1500 region
& $C\equiv C$ vibrations observed at significantly high frequencies in the region of 2300 to 2050 c

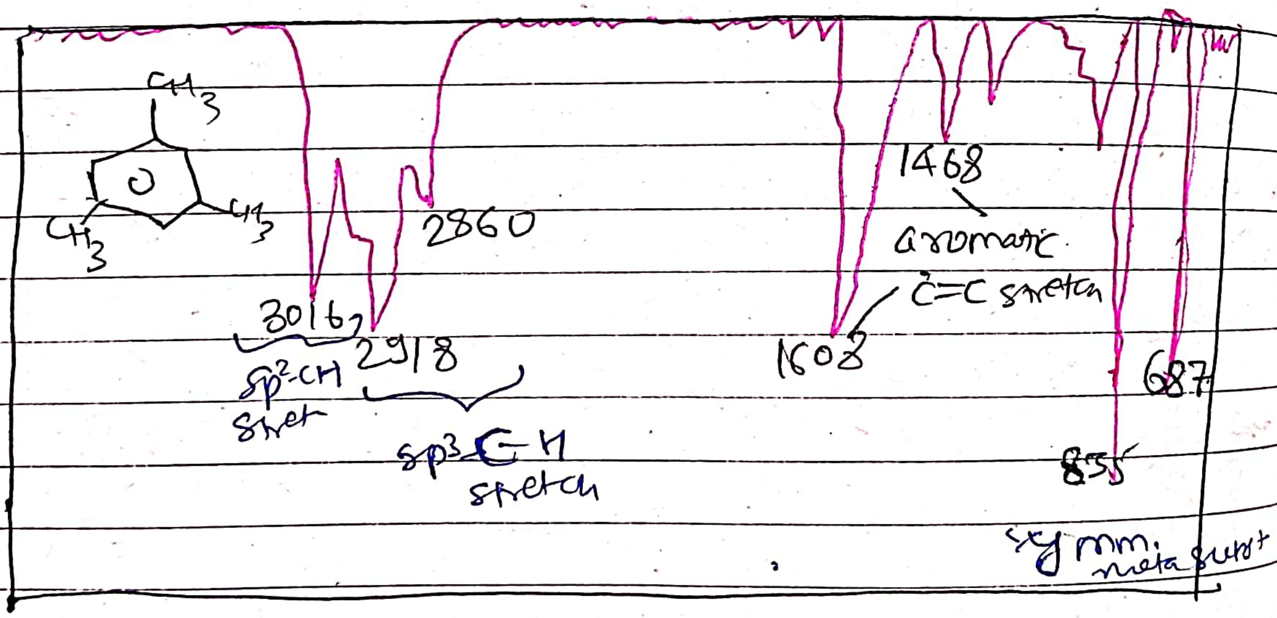


IR spectroscopy

Aromatic Hydrocarbons

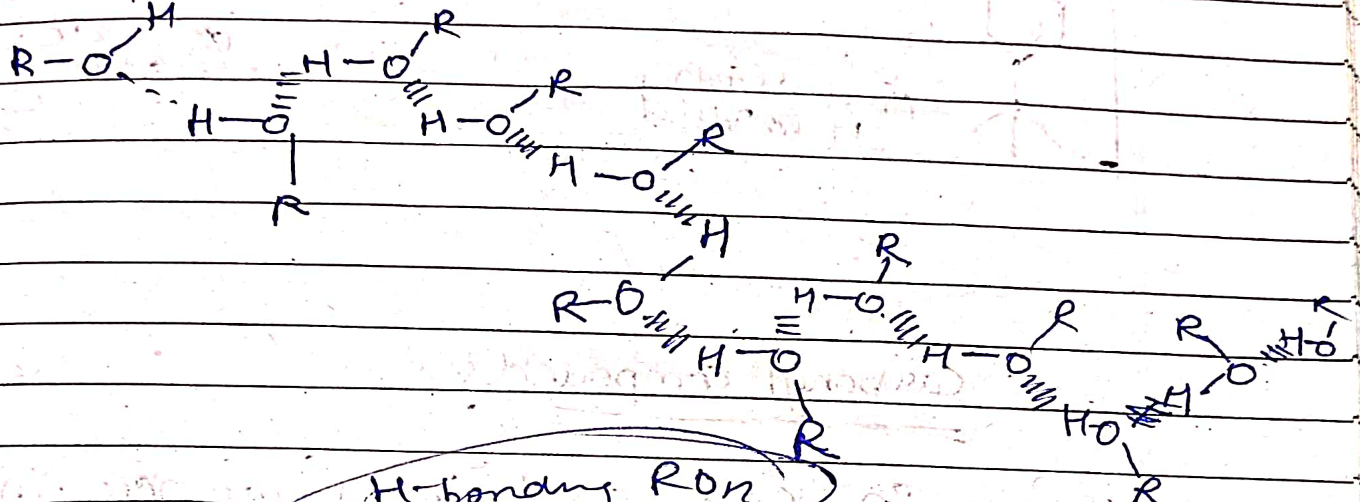


Aromatic Hydrocarbon

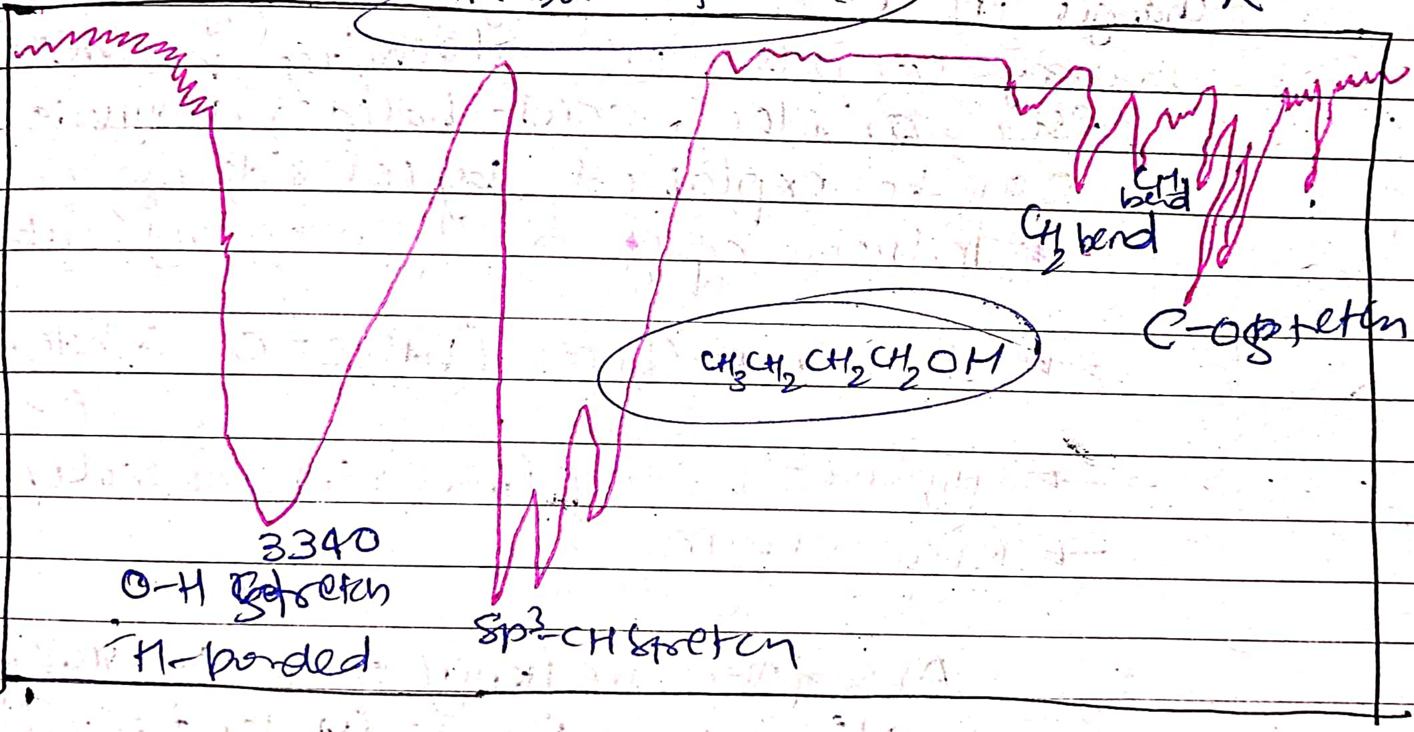


Alcohols & Phenol

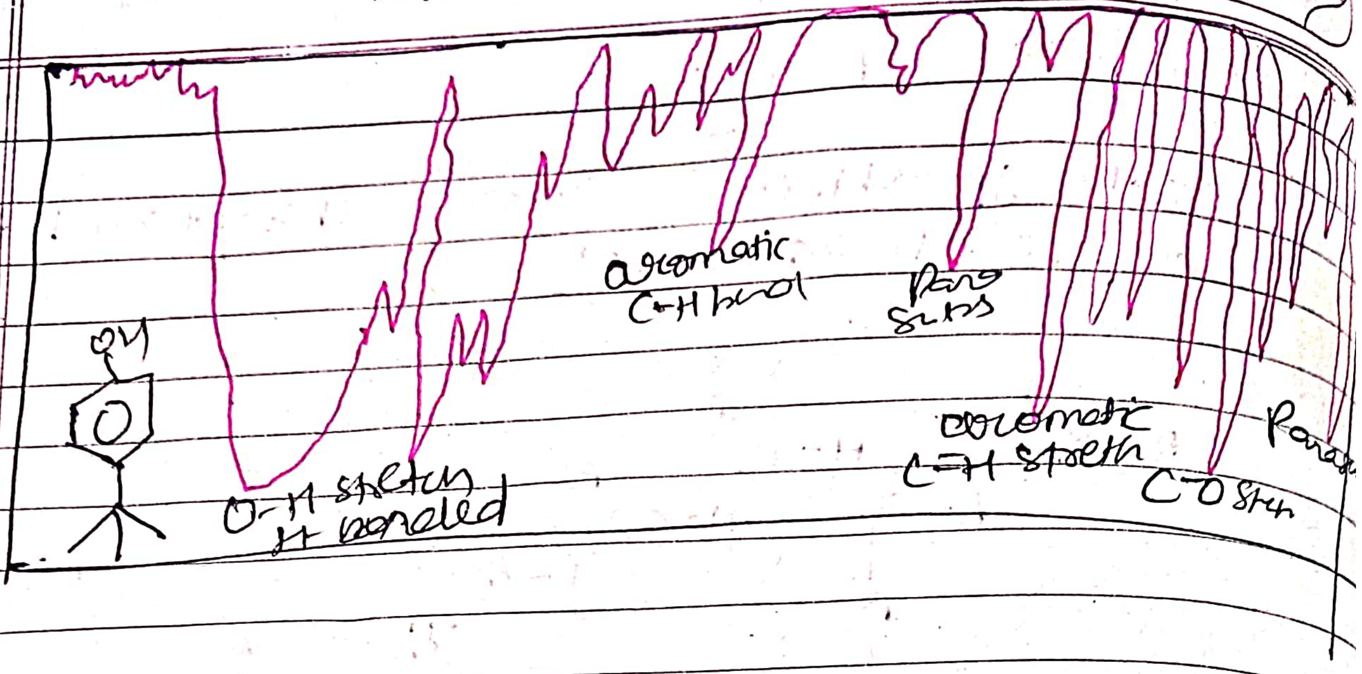
-OH gp exhibits a strong absorption band at 3700 to 3400 cm^{-1}



H-bonding ROH



Alcohols & phenol



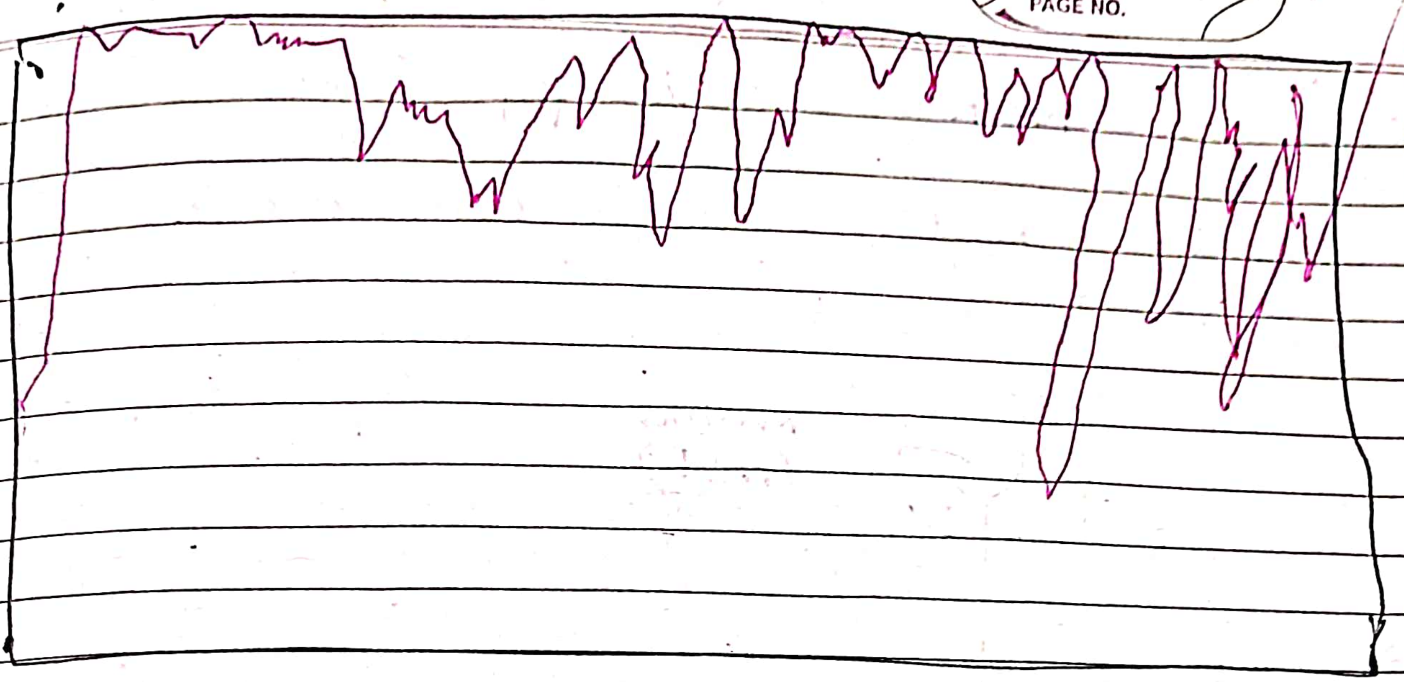
• Carbonyl compounds

changes in C=O stretching frequency in various Carbonyl compds viz aldehydes, ketones, acid esters, amides, acid-halides anhydrides etc. can be explained by considering,

- → Inductive effect of neighbouring Substituent
- → Resonance Effects (both C=C & heteroatom lone pair)
- → Hydrogen bonding (inter & intramolecular)
- → Ring strain

Absorption frequency of a saturated aliphatic ketone at 17 ± 5 cm^{-1} as a normal value.

* conjugation effect

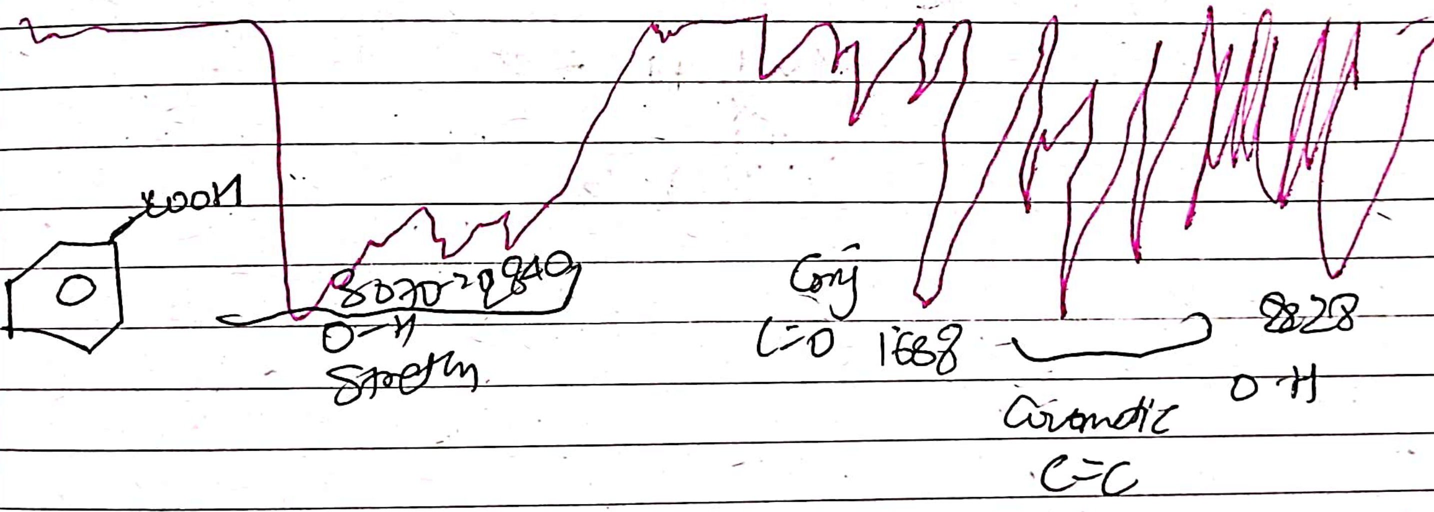


Carboxylic acids

O-H stretch appears a very broad band b/w 3400-2500 cm^{-1}.

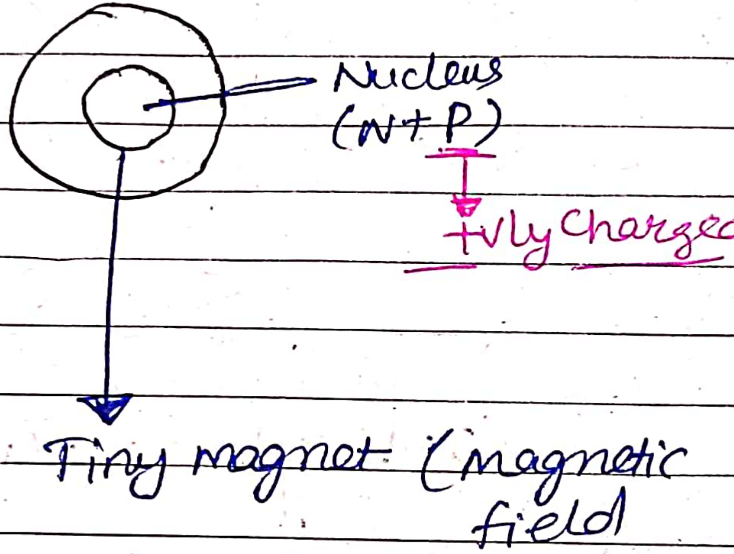
weak C=O bonds stretch 1720 :

Strong C=O stretching along ~300 cm^{-1}



NMR Spectroscopy

(Nucleus magnetic Resonance Spectroscopy)



Magnetic Quantum No.

$(2 \times S + 1)$

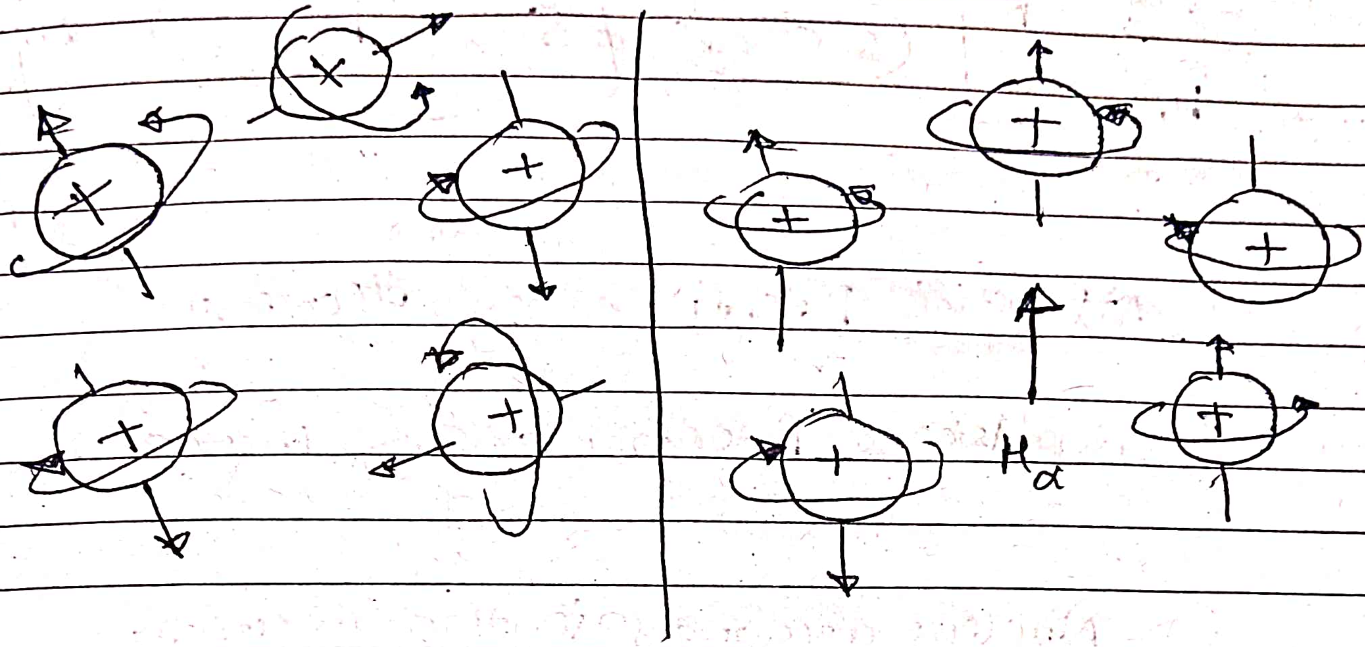
S = Spin Quantum no.

$S = \frac{1}{2}$

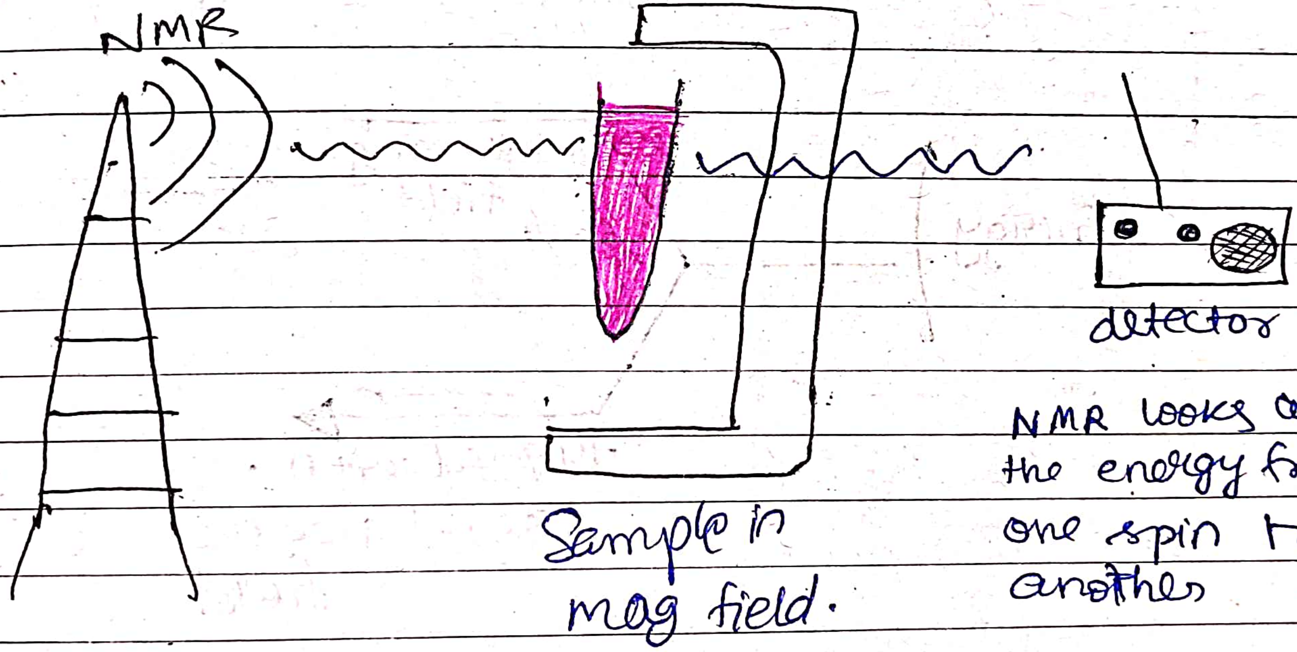
$\cancel{2} \times \frac{1}{\cancel{2}} + 1 = 2$

$= +\frac{1}{2}, -\frac{1}{2}$

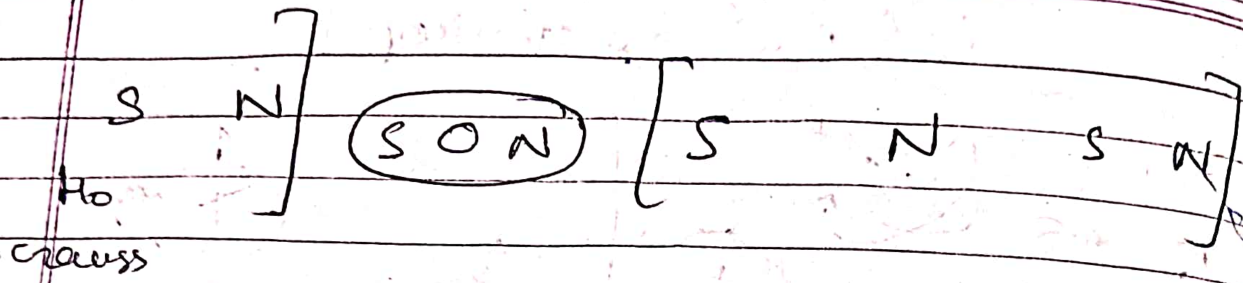
NMR Spectroscopy

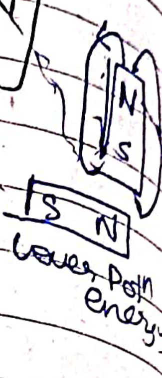


NMR uses radiowaves, measured in MHz



NMR looks at the energy from one spin to another



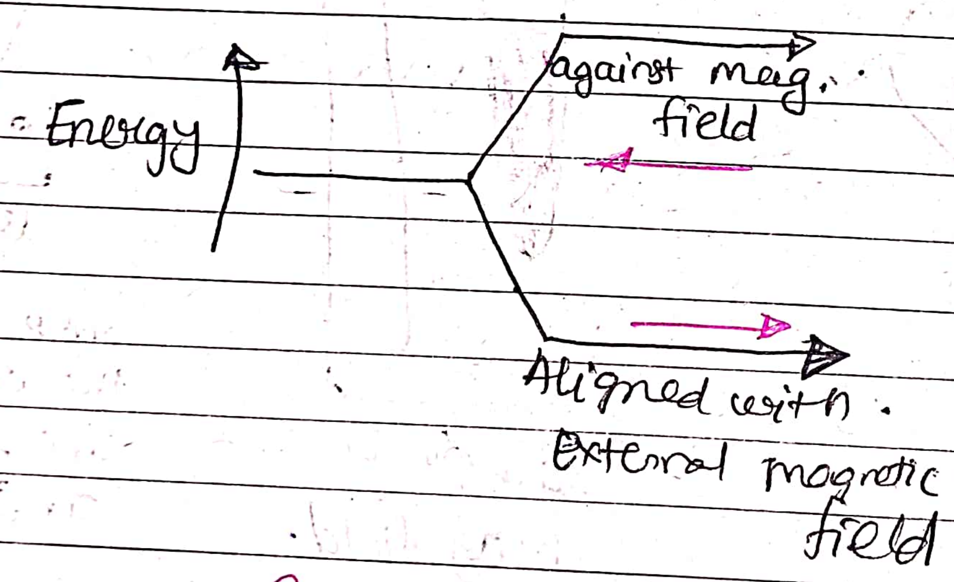


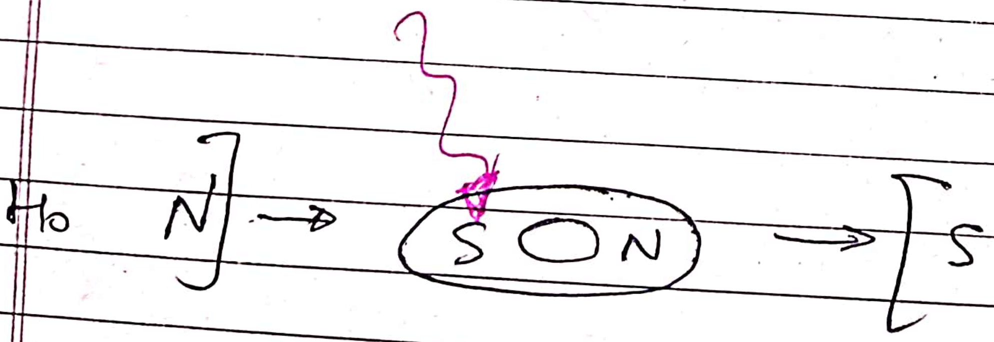
Attraction Potential energy decreases

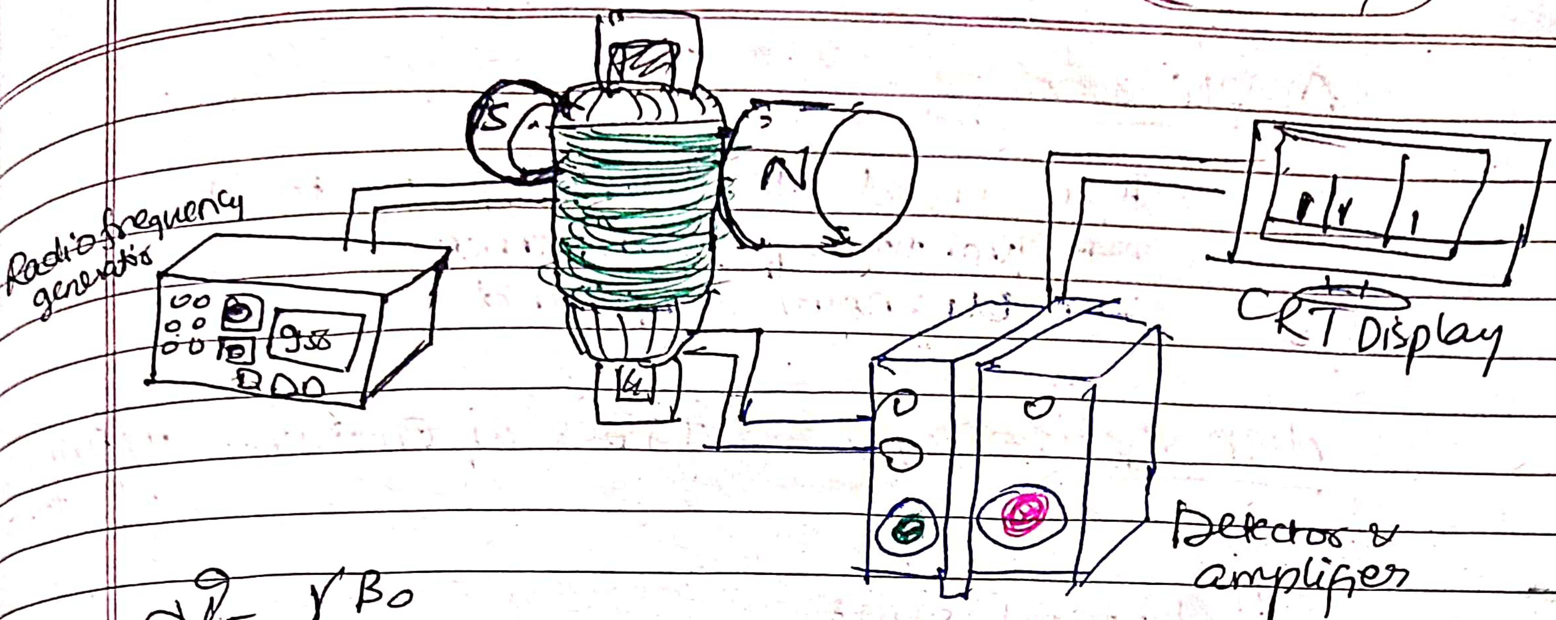
Repulsion - Potential energy increases

Nucleus arranges in two direction.

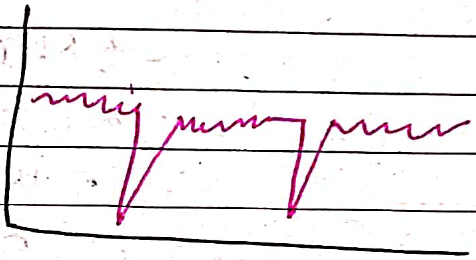
i) low energy   ii) High energy







$$\nu = \frac{\gamma B_0}{2\pi}$$



NMR Active or Inactive Nuclei

Mass No.	Atomic No.	spin quantum No.
Odd	odd or even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$
Even	Even	0
Even	odd	1, 2, 3

→ Nuclei like $_6C^{12}$, $_8O^{16}$, $_{16}S^{32}$ with $I=0$ are spin inactive

→ Nuclei $_1H^1$, $_6C^{13}$, $_9F^{19}$ are spin inactive exhibit NMR spectroscopy.

Application

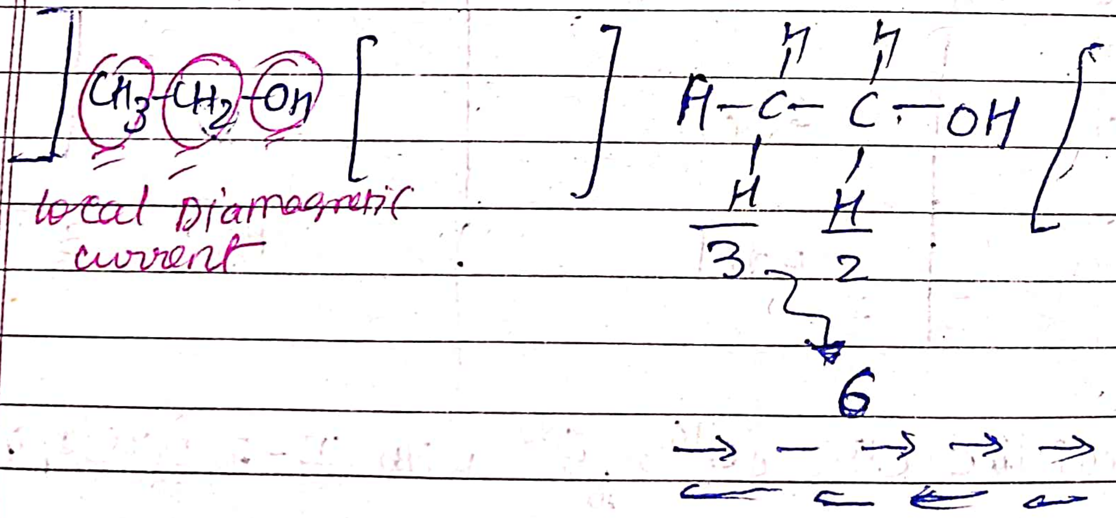
It is used to identify or to study
→ quantity of substance
→ unknown compound

NMR spectroscopy → Types of Environment/Forms of atom

Chemical shift

- Shielding
- Deshielding
- Use of TMS as reference
- δ-scale
- τ-scale

Position of signals – (Chemical shift)



Position of signals (Chemical shift)

↳ The no. of signals in an NMR spectrum tell the no. of sets of equivalent protons in a molecule.

Shielding - If the induced field opposes the applied field, then proton is said to be shielded. And this effect is known as shielding effect. Shielding shifts the absorption upfield to get an effective field strength necessary for absorption

Deshielding - If the induced field reinforces the applied field, the protons feels a higher field strength & thus such a proton is said to be deshielded And this effect is known as Deshielding effect.

Deshielding shifts are absorption downfield to get an effective field strength necessary for absorption.

Such shifts (compared with a reference) in the positions of NMR absorptions which arise due to shielding & deshielding of protons by electron are called chemical shift.

The difference in the absorption position of proton w.r.t TMS signal is called chemical shift (δ-value)

Equivalent Protons : Protons with same chemical shift are called equivalent protons

$$\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{a}{CH_3}$$

No. of signals

(1) $\overset{a}{CH_3}-\overset{a}{CH_3}$ = 1 (a)

$\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{c}{OH}$ = 3 (a, b, c)

$\underset{a}{CH_3}-\underset{b}{CH_2}\,\underset{c}{CH_2}-Br$

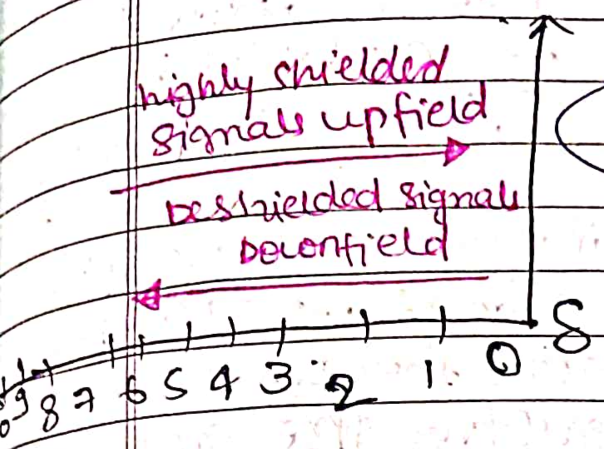
$$\delta_x = \frac{\nu_x - \nu_{TMS}}{\nu_0}$$

Chemical shift

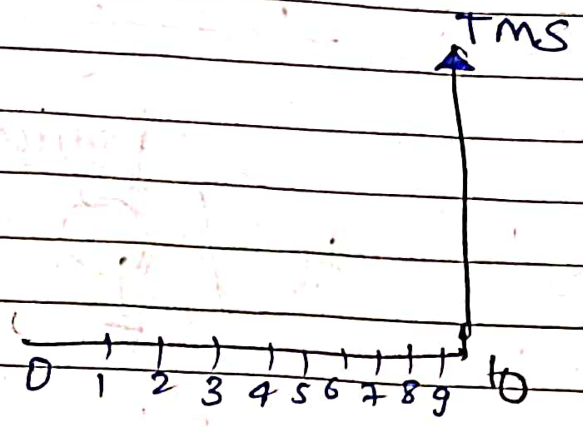
$$\delta\text{value} = \frac{\nu_{sample} - \nu_{reference}}{\text{operating frequency in megacycles (per sec)}}$$

δ-scale

τ scale

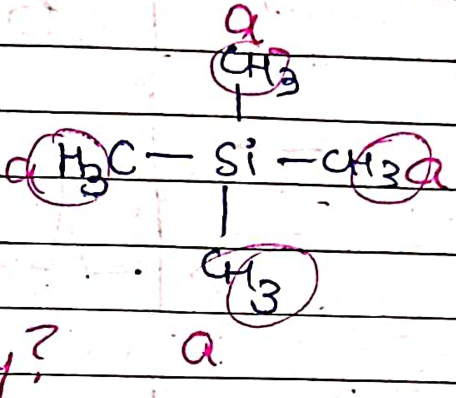


$\tau = 10 - \delta$



TMS as a reference

Tetra methyl silane



$$\begin{array}{c} CH_3 \\ | \\ H_3C - Si - CH_3 \\ | \\ CH_3 \end{array}$$

Why TMS is chosen as a reference in NMR spectroscopy?

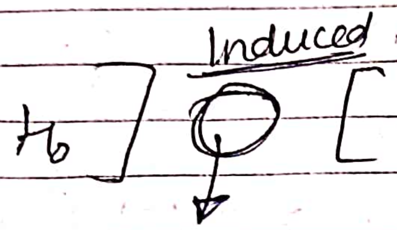
- It is chemically inert and miscible with a large range of solvents.
- Its twelve protons are all magnetically equivalent to give only one (sharp) signal.
- It is highly volatile and can be easily removed to get back the sample
- It does not take part in intermolecular association with the sample.

Factors affecting chemical shift

Inductive effect
Hydrogen bonding
Anisotropic effects

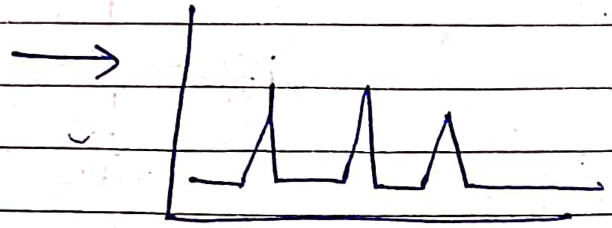
Environment effect
① Chemical shift
⑪ spin-spin coupling

Spin-spin coupling : Splitting of signals into multiplets is explained by spin-spin coupling



The interaction b/w the spins of two or more neighbour protons through the bonds resulting the splitting of the spectral line is known as spin-spin coupling

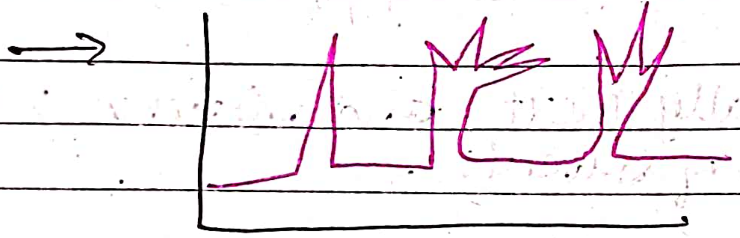
] CH_3CH_2OH [



(n+1).

n = No. of neighbour H-atom

$\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{c}{OH}$



No. of signals = 3(a,b,c)

splitting for signal a = n+1
= 2+1
= 3
(triplet)

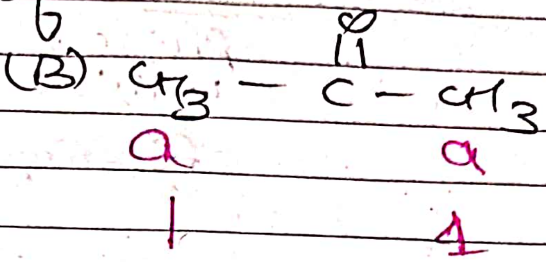
splitting for signal b = n+1 =
= 3+1
= 4

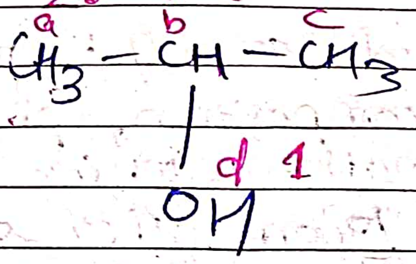
Splitting for signal c = n+1
= 0+1
= 1(singlet)

Predict NMR spectrum of

(A) $\overset{a}{CH_3}\overset{b}{CH_2}\overset{c}{CH_2}\overset{d}{OH}$

3 : 6 : 3 : 1

(B)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

2 : 7 : 2

$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$