

Date _____
Page _____

(3) Module 4 - Instrumental methods of Analysis

6/3/17

Monday

Spectroscopy

Electromagnetic radiations -

e.g. - γ rays, X-rays, radio waves, IR, UV, μ , visible

X-rays UV visible IR μ wave

$\lambda \uparrow$ \downarrow energy

energy \downarrow

Spectroscopy is a branch of science which deals with study of interacⁿ of emradiation with matter. These radiations have energy & are transmitted through space at very high velocity.

Types of energy changes these radiations cause -

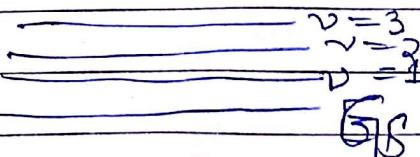
1) Electronic energy change -
excitatⁿ from GS to Exc S

- energy (high required)
- so UV (is suitable for such change, visible)

2) Vibrational - E_S

(energy absorbed for vibraⁿ of atoms)

IR \rightarrow gives VEC



GS

each vibrⁿ level
divided in rotational energy levels
 \rightarrow high

Date / /
Page

3) Rotational energy change - ES

$$\begin{array}{l} J=5 \\ \hline J=4 \\ \hline J=3 \\ \hline J=2 \\ \hline J=1 \\ \hline \text{GS} = 1 \end{array}$$

higher energy

(any)

4) Translational energy change radiation

rotatn or vibrⁿ with change in COG

$$\therefore \text{Total } E_{\text{C}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}$$

negligible

Born Oppenheimer
approximation

Spectroscopy

Absorption

some

absorbed rest

transmitted

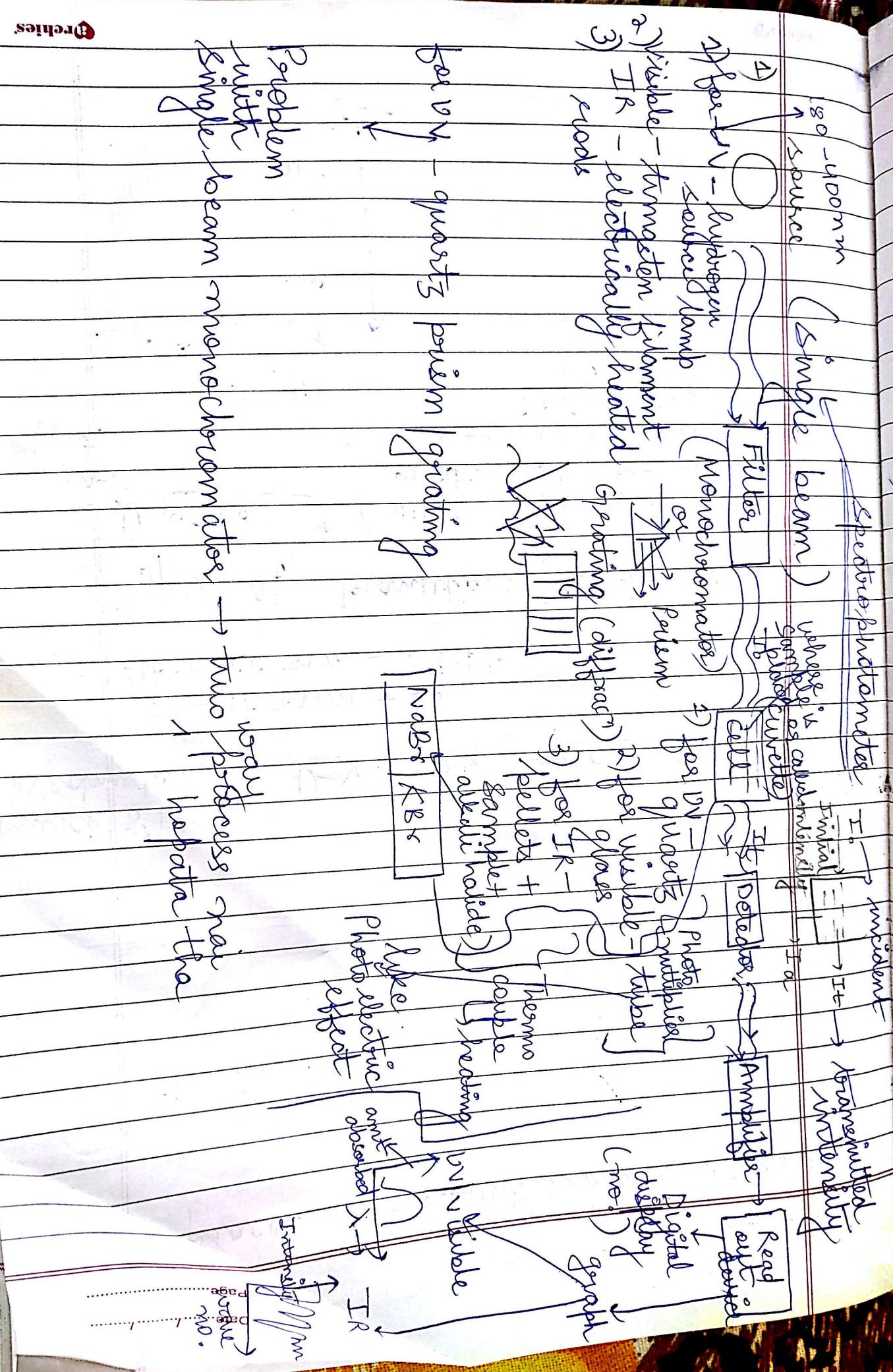
Emission

$e^- \text{ GS} \rightarrow \text{ES}$ (as not stable)

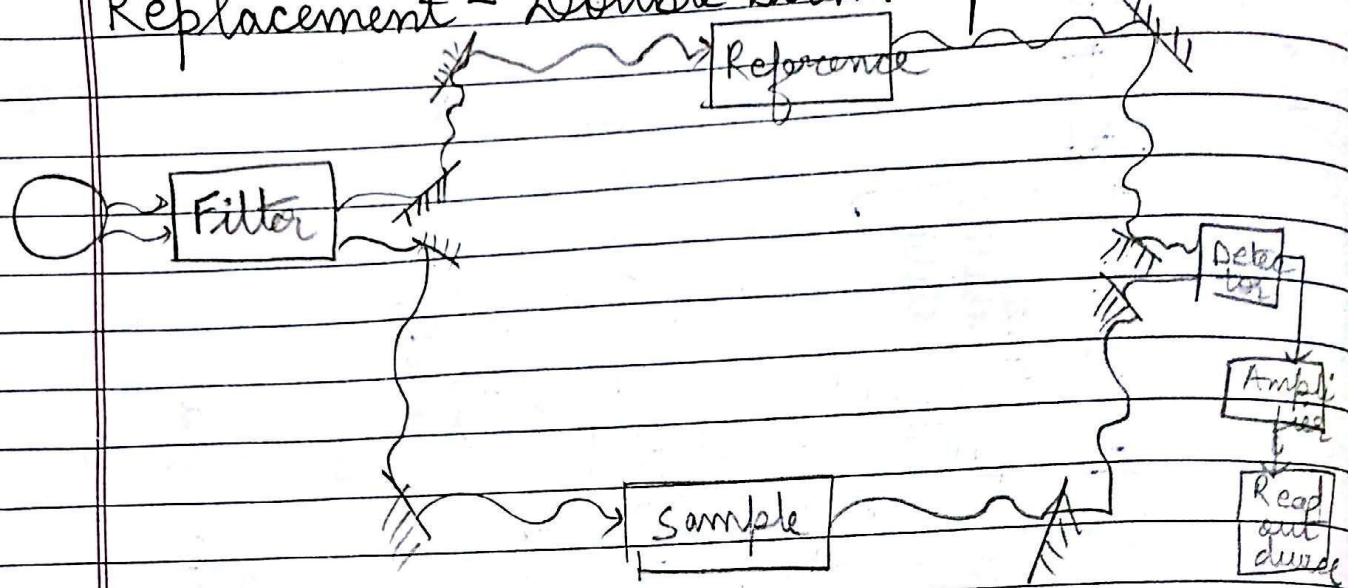
e^- comes back to GS
& emits radi?

Instrument for Spectroscopy - SPECTROPHOTOMETER

Spectrophotometer



Replacement - Double beam spectrometer.



March 8'17

Wednesday

U-V visible spectrometer -

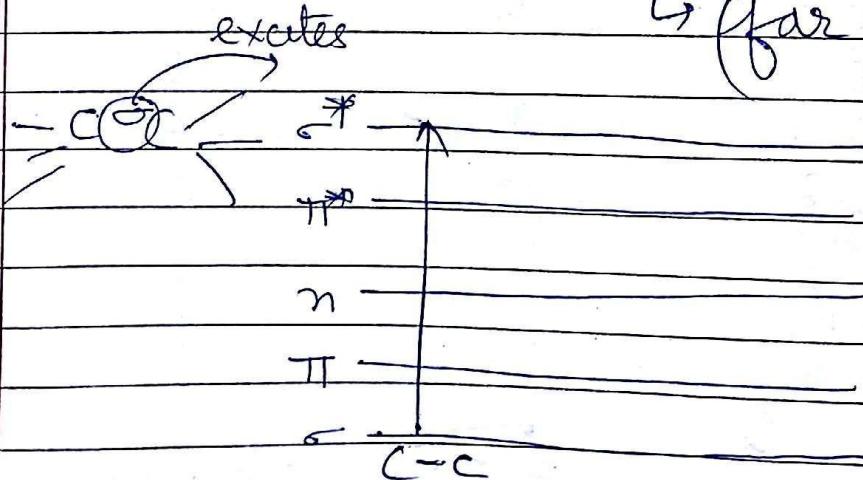
180-400nm - UV

400-700 nm - Visible

Types of transitions (due to UV/visible radiation)

1) σ -to- σ^* (very high energy reqd)
takes place in strongest bonds

$\lambda \rightarrow 180-200\text{nm}$
 \hookrightarrow (far U.V.)

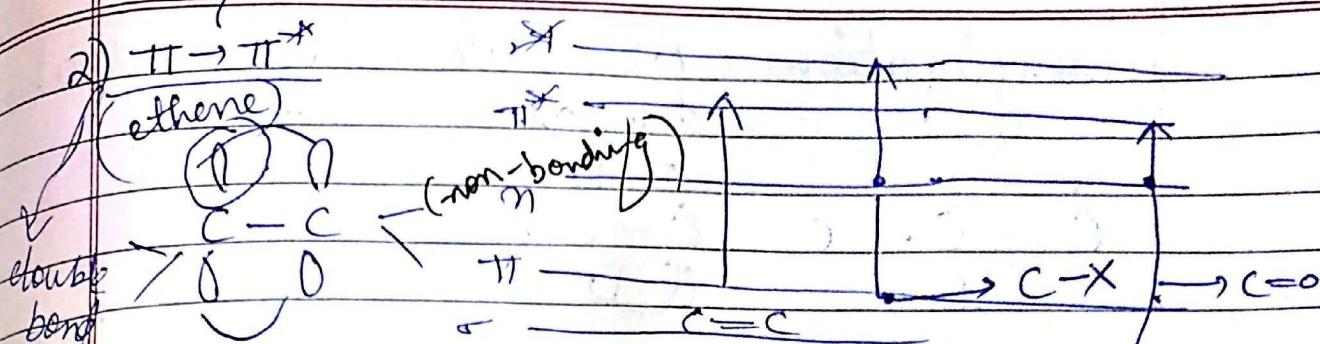


σ to σ^* \rightarrow sabse nota hai

any molecule which has π bond

Date..... /

Page.....



3) any halogen -
($C-X$)

$n \rightarrow \sigma^*$

4) $C=O \rightarrow n \rightarrow \pi^*$

$\text{CH}_4 \rightarrow \sigma \rightarrow \sigma^*$

$\text{CH}_3\text{Cl} \rightarrow n \rightarrow \sigma^*$

$\sigma \rightarrow \sigma^*$

$\text{CH}_3\text{NH}_4^+ \rightarrow \sigma \rightarrow \sigma^*$

$n \rightarrow \sigma^*$

$\text{CH}_3\text{CN} \rightarrow \sigma \rightarrow \sigma^*$

$\text{C}\equiv\text{N} \rightarrow \pi \rightarrow \pi^*$

$\begin{matrix} \text{II, lone} \\ \text{bond, pair} \\ \text{on N} \end{matrix} \rightarrow n \rightarrow \sigma^*$



$\text{CH}_3\text{COOH} \rightarrow n \rightarrow \pi^*$

$n \rightarrow \sigma^*$

$\sigma \rightarrow \sigma^*$

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

$\pi \rightarrow \pi^*$

$\rightarrow \text{CH}_3\text{CH}=\text{CH}_2 \rightarrow \sigma \rightarrow \sigma^*$

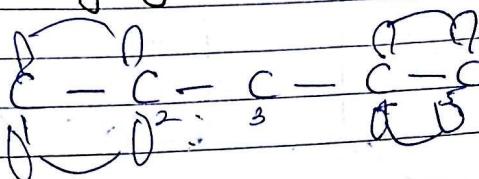
$\pi \rightarrow \pi^*$

$\pi \rightarrow$ bonds sideways overlapping

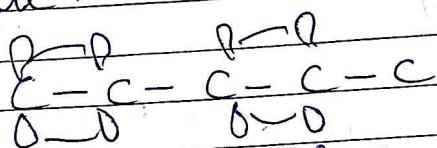
Date...../...../.....

Page.....

Conjugation - Alternate single & double bonds



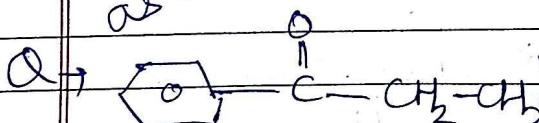
Conjugated molecule →



Whenever there's "congig", energy required is less, \rightarrow high \rightarrow but

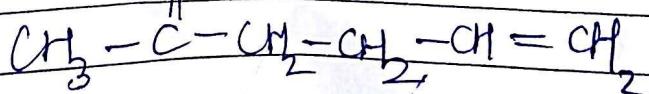
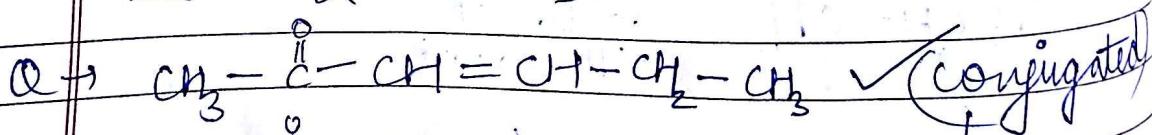
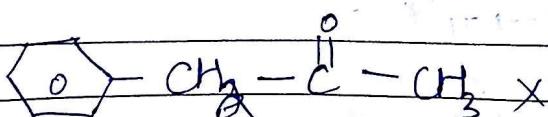
but when e^- is stuck with $c \rightarrow$ high energy is reqd, less wavelength each over region.

why molecules in colour
are not white in colour
as they go to visible light
bcz of energy as energy



→ conjugation-hai

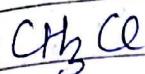
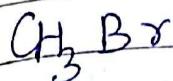
higher λ ,
lower energy



~~highest
low energy~~

bigger size

α - $\text{CH}_3 \text{I} \rightarrow$ high λ , low energy to excite e^-



* as electro-vity \uparrow see, the energy to excite the e^- is more & wavelength is less.

Chromophore - Any isolated covalently bonded grp that shows absorption in UV or visible region irrespective of whether color is produced or not.

2 types

only πe^-
 $\text{C}=\text{C}, \text{C}\equiv\text{C}$

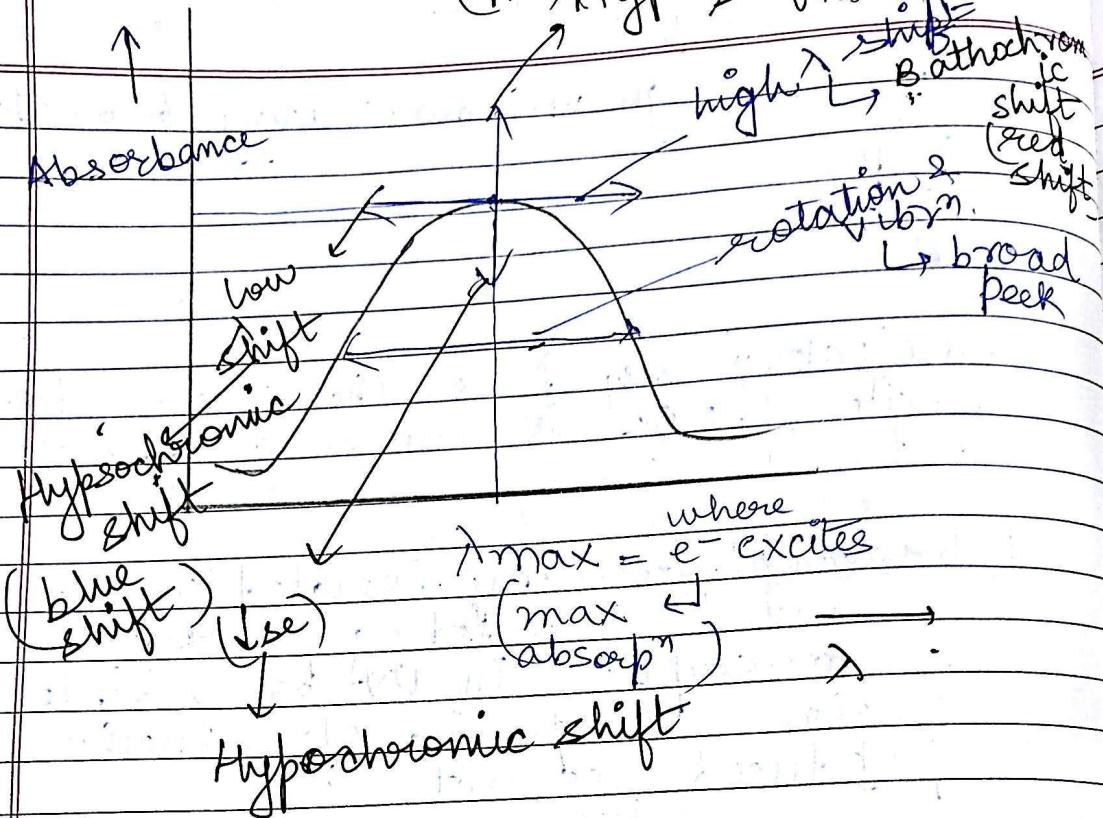
both π & non-bonding
 e^-
 $\text{C}=\text{O}, \text{C}=\text{N}$

Auxochrome - It is a color enhancing group which when attached to a chromophore shifts the absorption to a higher λ .

for eg $\rightarrow -\text{OH}, -\text{NH}_2, -\text{SH}$

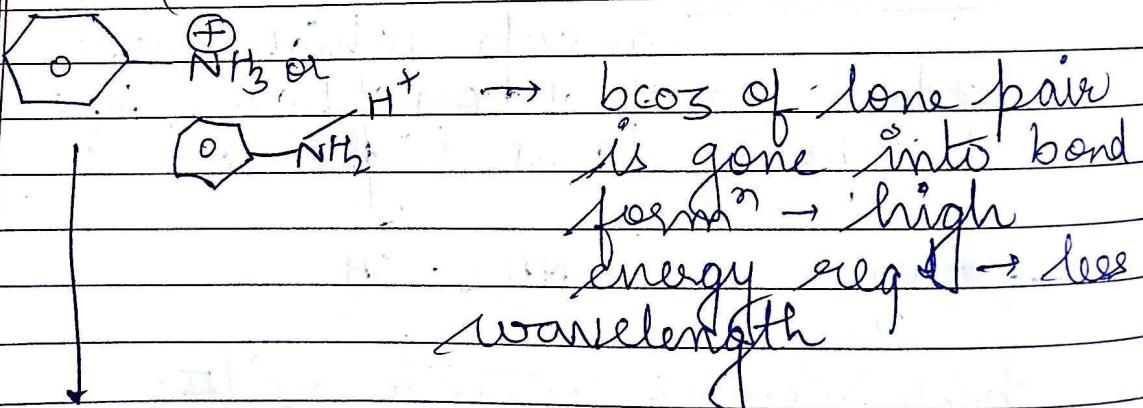
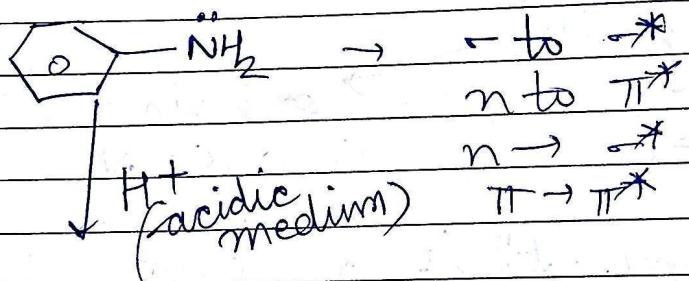
Absorption & Intensity shifts -

(↑se) Hyperchromic shift Date.....
Page.....



$$\lambda_{\text{max}} = \text{where } e^- \text{ excites}$$

$$(\text{max} \leftarrow \text{absorp}^*)$$



⇒ Aniline in acidic medium forms anilinium ion. The lone pair of N goes into bond form \rightarrow more energy will be reqd to excite the e⁻

less λ .
↑
and blue / hypsochromic shift is absorbed.

Absorption laws -

i) Lambert's law - When a beam of monochromatic radiation is allowed to pass through a transparent medium the rate of loss of intensity of the radiation with thickness of medium is directly proportional to intensity of the incident radiation.

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

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

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

integrate

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

I_0

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

I_0

$$\log_{10} \frac{I_t}{I_0} = \frac{-K}{2.303} x$$

$$\log \frac{I_0}{I_t} = \frac{K}{2.303} x$$

specific
absorption
coefficient.

Absorption coefficient is the reciprocal of the thickness required to reduce intensity of light to $\frac{1}{10}$ th of its original intensity.

- 2) Beer's law (Beer-Lambert law): When a beam of monochromatic radiation is allowed to pass through a transparent medium, the rate of decrease of intensity of the radiation with the thickness of the medium is directly proportional to intensity of incident radiation as well as concentration of soln.

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

$$\log \frac{I_{t0}}{I_{t0}} = -K C x$$

$$\Rightarrow \log \frac{I_0}{I_t} = \epsilon C x$$

$$A = \epsilon C x$$

where $\epsilon \rightarrow$ molar absorption coeff /
 $(\text{dm}^3/\text{mol/cm})$ molar absorptivity /
molar extinction coeff

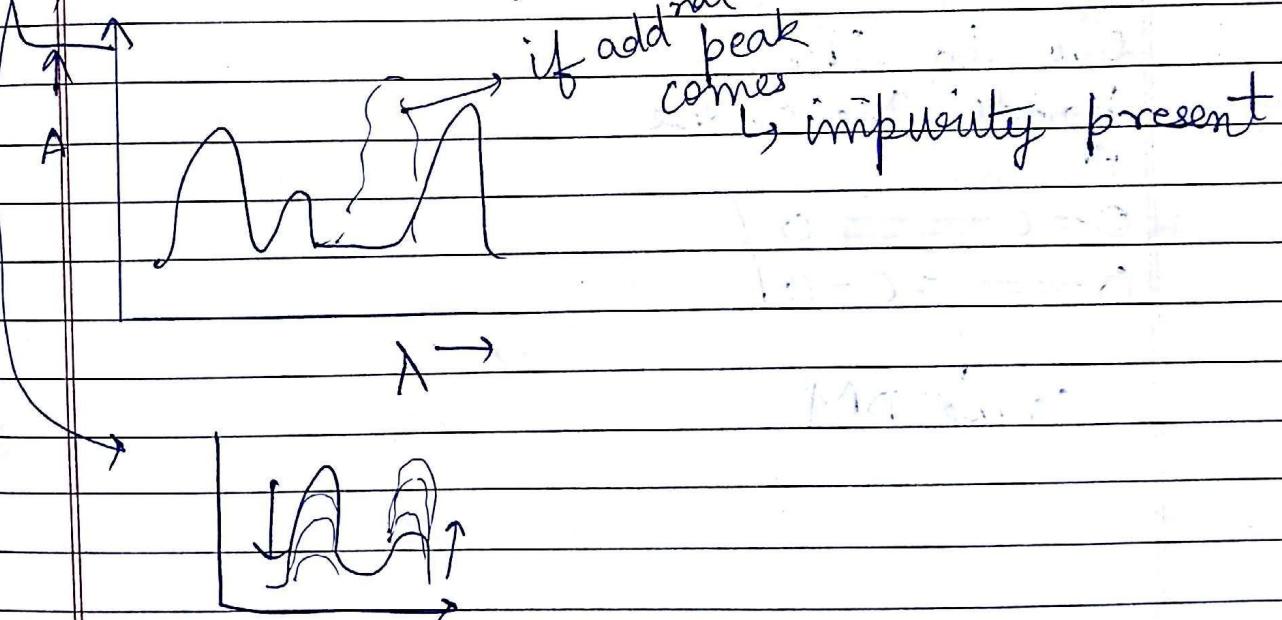
$$\log \frac{I_0}{I_t} = A = \text{Absorbance}$$

$$\frac{I_t}{I_0} = \text{Transmittance.}$$

ϵ → specific absorbⁿ coeff for a concen-
eration of 1 mol / dm³. path length
of 1 cm
It is independent of concentrⁿ & concn.
at a given wavelength for a particular
substance.

Applications -

- 1) for detecting aromatic compounds & conjugated dienes (low energy, high λ)
- 2) for detection of impurities
- 3) control of purification
- 4) Determination of unknown concentrⁿ
- 5) determination of molecular wgt.
- 6) determination of Kinetics of a given rx



in terms of

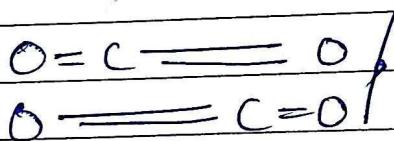
March 14'17 Infrared Spectroscopy (wave no.)
Tuesday ↗ can't cause electrostatic energy
but causes vibrational energy ↘

Wave no range → 500 to 4000 cm⁻¹
Molecules

IR ACTIVE
→ permanent
dipole moment (DM)
or show is in
DM on vibration

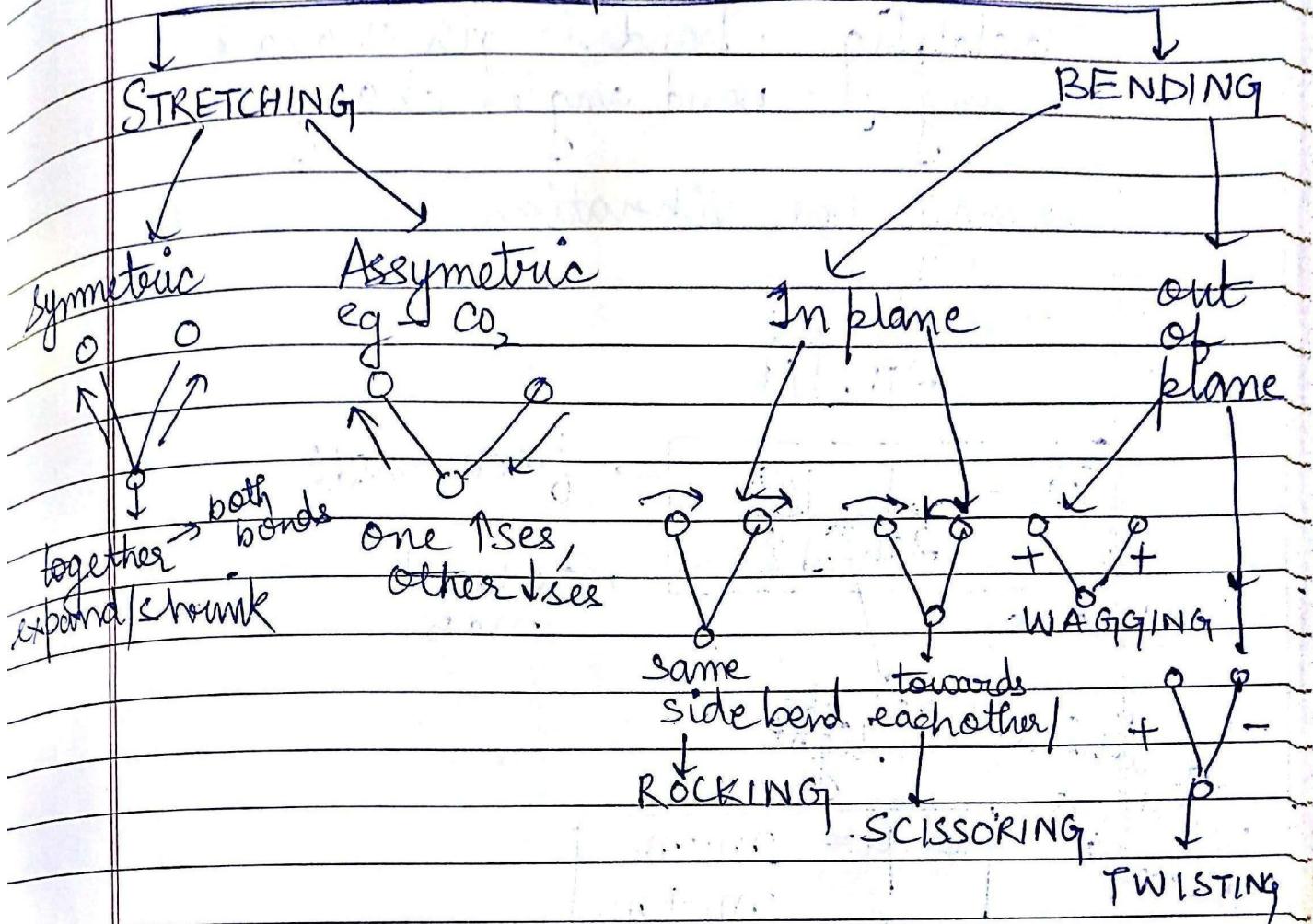
eg - NH₃, H₂O
CO₂ → O=C=O
Due to vibrⁿ
bonds ↑ se or ↓ se

IR inactive
→ No perm. D·M
→ shows no Δ in DM
vibrⁿ
eg - O₂, N₂, H₂
(any diatomic
molecule)

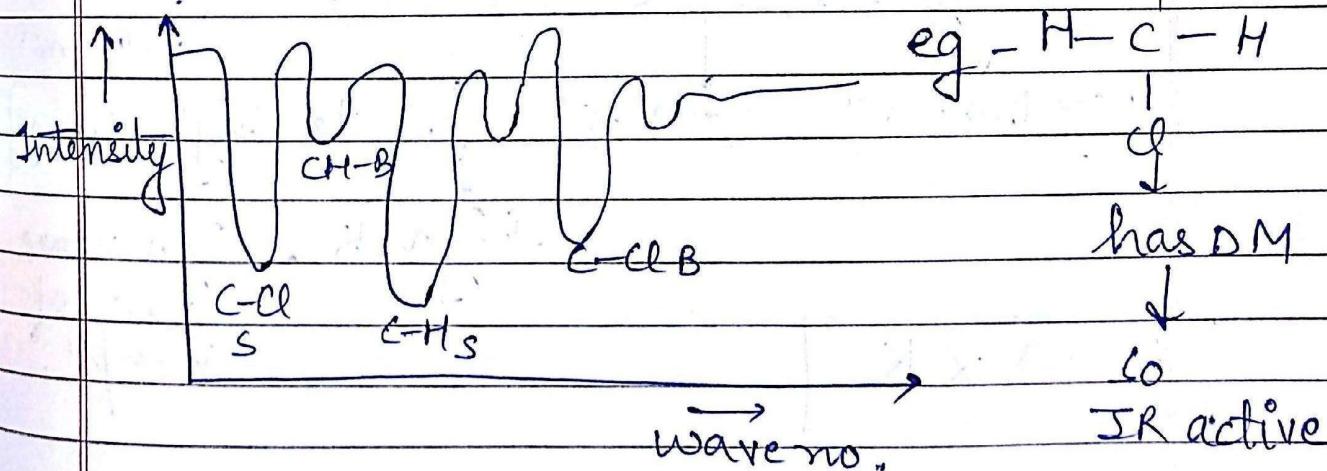


cause DM

Types of Vibration -



→ on each energy, different peaks are observed →



- * Stretching requires more energy than bending
- Stretching \rightarrow bond length changes
- Bending \rightarrow bond angle changes

Energy for Vibration -

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

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

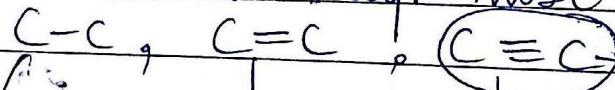
waves. at which we'll get absorpt.

Vel of light

\rightarrow force constl
reduced mass

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

- * eg - which will req. most energy?



$\nu = 1200 \text{ cm}^{-1}$

1600 cm^{-1}

2100 cm^{-1}

3 bonds, high energy

high k, high wave no of absorpt.

$\star \nu \propto k$

eg - which will have more μ ?

$$\text{C-C} / \text{O-H}$$

$$12-12 = \frac{12 \times 12}{24} \rightarrow \frac{8 \times 1}{9}$$

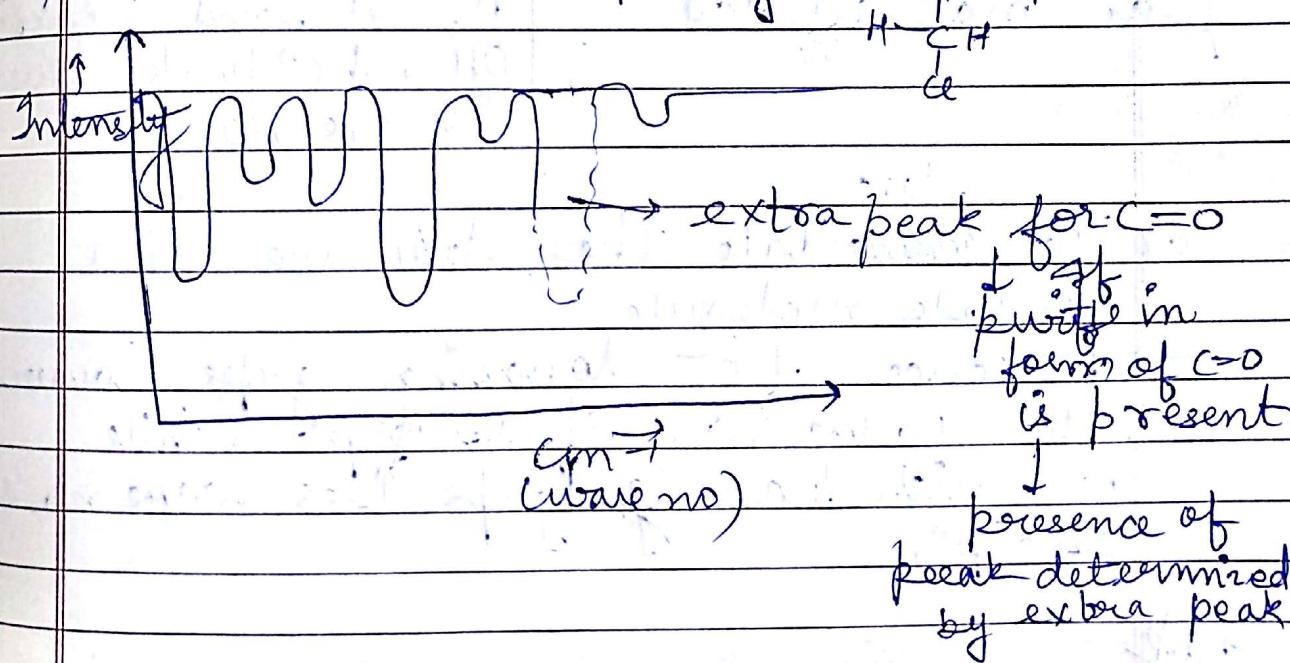
$$\boxed{\bar{\nu} \propto \frac{1}{\mu}}$$

Applications -

- for determination of force constt from the given vibrational freq or wave no. of absorption by -

$$\boxed{\bar{\nu} = \frac{1}{2\pi c} \sqrt{k \mu}}$$

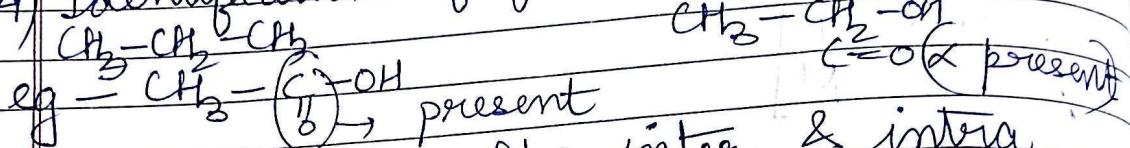
- Determination of purity of compound \rightarrow



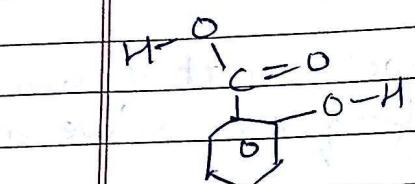
- Identification of unknown compounds - Every molecule has a unique IR spectra from $900 - 1500 \text{ cm}^{-1}$ which is called.

fingerprint region thus this technique acts as fingerprint technique for identification of Compounds.

4) Identification of functional group

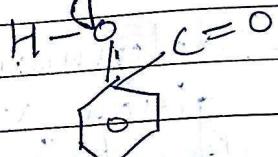


Expt 5) Distinguishing b/w inter & intra molecular H-bonding -



o-hydroxy benzoic acid
(Intra H-bonding)

↑ in conc → OH-vibrⁿ
peak not affected



(p-hydroxy benzoic acid) Inter molecular

H-bonding
as conc ↑, H bonding ↑, OH bond weakens
OH vibrⁿ peak lowers
wave no.

eluc

6) To elucidate the structure of a whole molecule

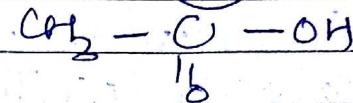
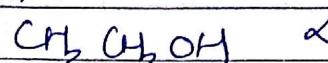
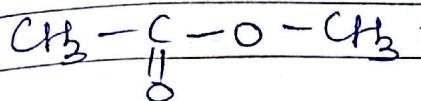
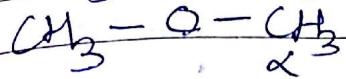
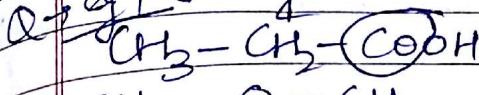
Presence of e⁻ donating groups lowers the wave no. of absorpⁿ while e⁻ with drawing groups increases wave no. of absorpⁿ.

Expt 6) To distinguish b/w 2 molecules using IR-spectroscopy -

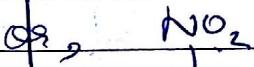
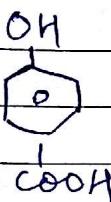
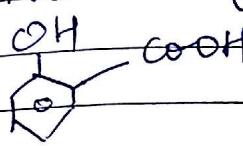
1) Presence/Absence of a bond

2) Inter/Intra molecular H-bonding

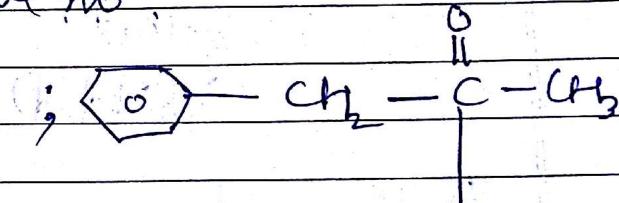
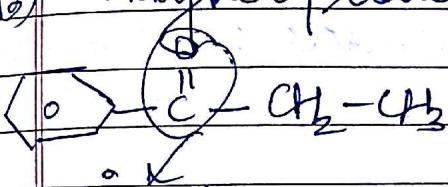
3) Higher wave no. / lower wave no
~~eg 1~~



~~eg 2~~ Now if all bonds are same -



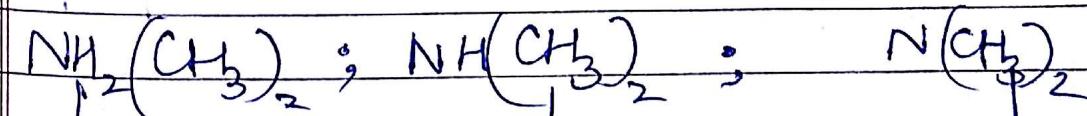
~~eg 3~~ Higher / lower wave no.



conjugⁿ → due to
 which partial
 bond char
 lower $\bar{\nu}$,
 lower energy

higher
 energy to
 break bond
 higher $\bar{\nu}$

Exceptions -



2 NH peaks

1 NH peak

no NH peak.

A.T right hand thumb rule
Anticlockwise → upward
clockwise → downward

Date...../...../.....
Page.....

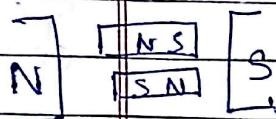
15/3/17 (NMR)

Wednesday Nuclear Magnetic Resonance Spectroscopy

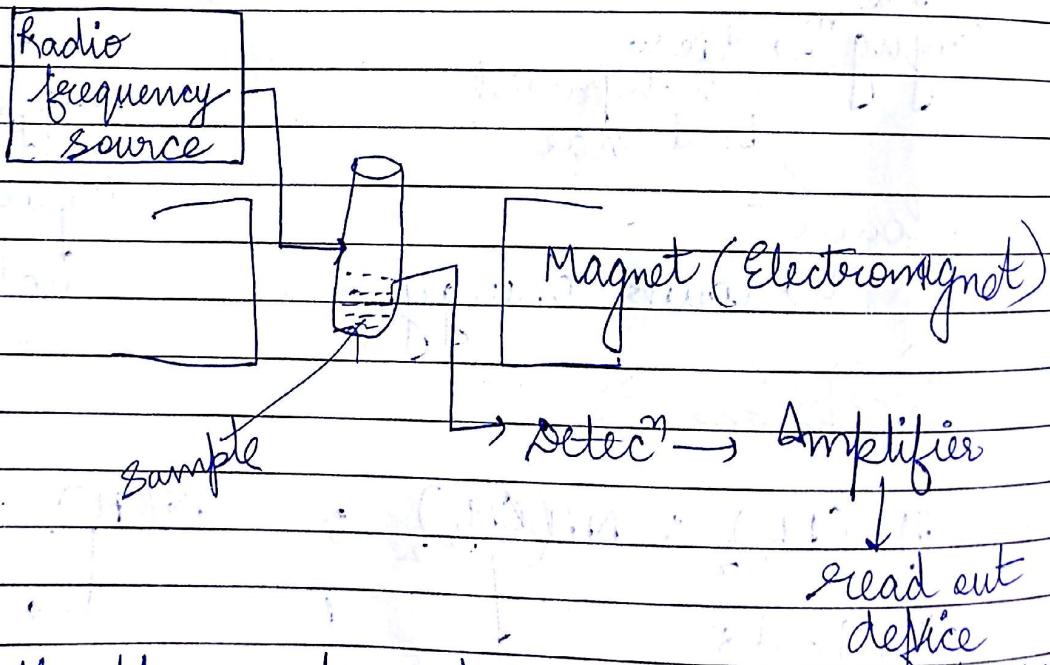
Radio frequency radiations → magnetic energy level

spin quantum no. $I > 1 \rightarrow$ shows NMR
(Hydrogen / proton $I = \frac{1}{2}$)

$$\text{no. of orient}^n = 2I + 1 \\ = 2 \times \frac{1}{2} + 1$$



opposed aligned
(nucleus → shielded) (nucleus → disshielded)



All the protons of a molecule don't spin with same freq but is dependent on the chemical environment of a proton

At a given B - the diff. sets of chemically equal protons required slightly diff. freq for absorpt". The shift in freq. based on chemical envt is called a CHEMICAL SHIFT.

TMS → taken as reference - Tetramethyl silane std

CH_3 silicones

$\text{CH}_3-\text{Si}-\text{CH}_3$ gives highest peak

CH_3 TMS

upfield shielding

downfield shielding

Scales -
delta, δ or τ (Tau, τ)

Presence of e- donating groups → proton-

causes shielding of proton

→ shift towards ref. std

Presence of e- withdrawing group → deshielding of proton

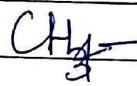
away Δ from ref. std

- No of peaks & no. of chemically eqvt protons
- Int of peak & no. of protons in a particular envt.

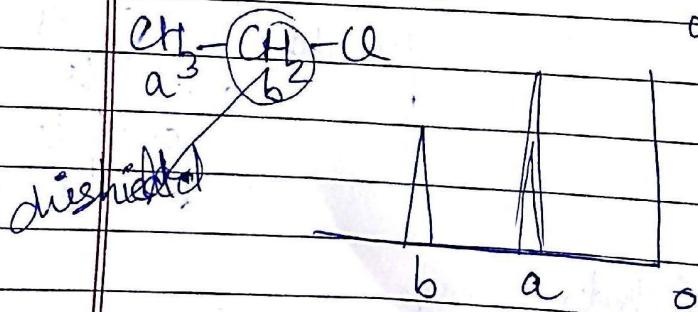
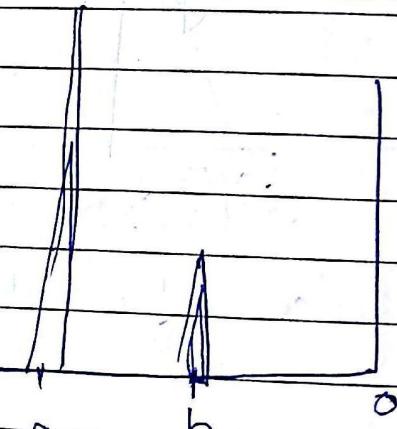
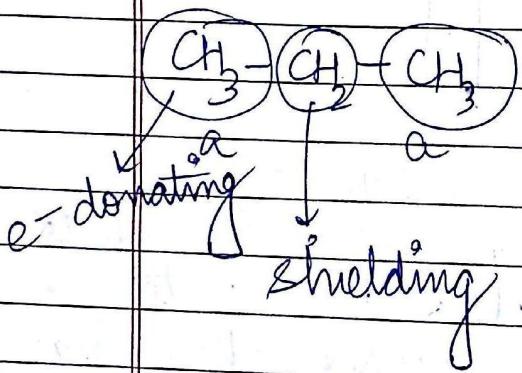
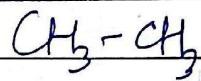
* TMS is used as a ref. std bcoz -

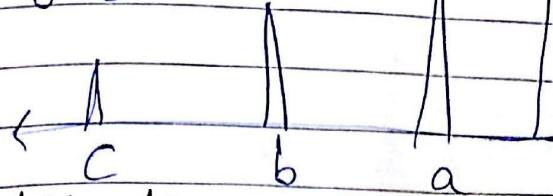
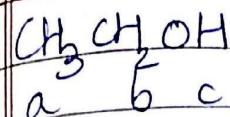
- i) It has 12 eqvt protons
- ii) It has low boiling pt & can be easily removed from sample
- iii) It is chemically inert
- iv) Soluble in organic solvents
- v) can be used as internal std.

eg -



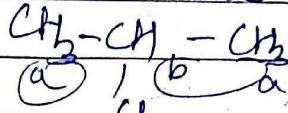
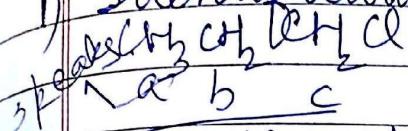
eqvt to
protons





Applications -

1) Identification of structural isomers-



→ 2 peaks

2) Detection of H bonding

Intermolecular H bonding shifts absorbⁿ downfield & is concⁿ dependent while intramolecular is concⁿ independent

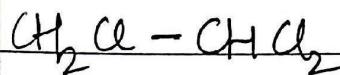
3) Detection of aromaticity -

i) Difference b/w cis & trans isomers

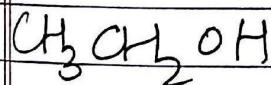
ii) Deteⁿ of electro-ve atoms

iii) Distinguishing b/w Keto-enol tautomerism.

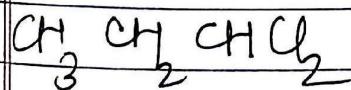
No. of peaks



2



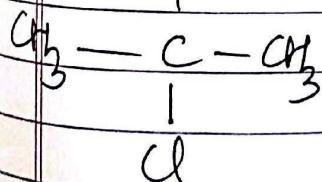
3

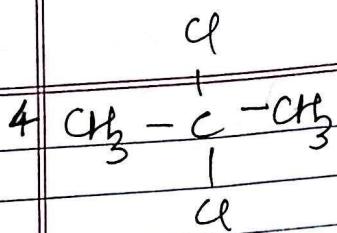


3

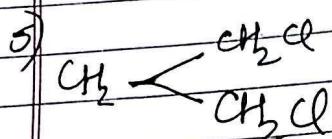
Cl

1

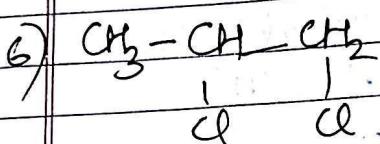




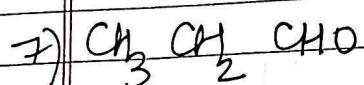
2 1



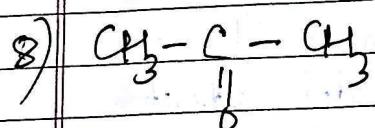
2



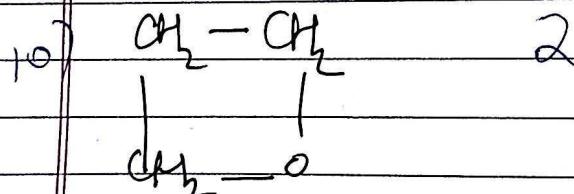
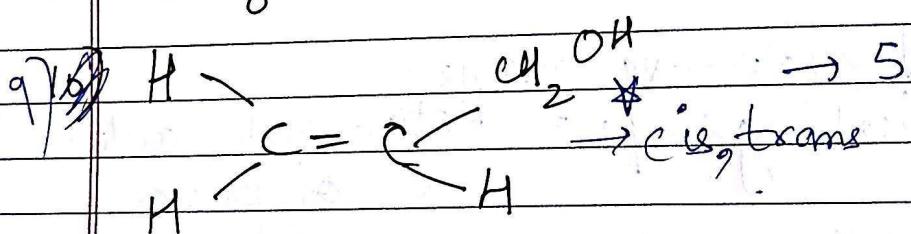
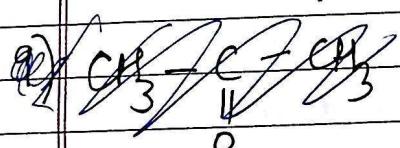
3



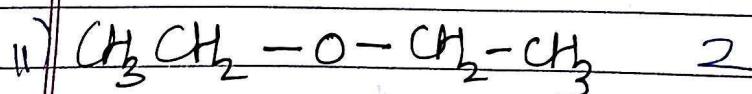
3



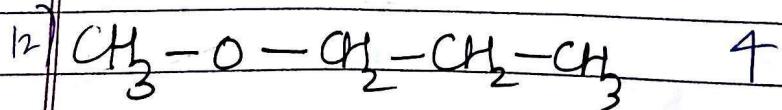
1



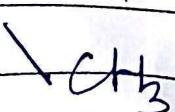
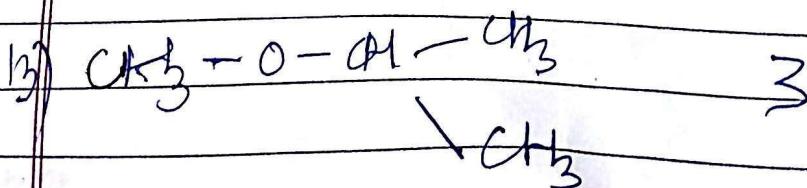
2



2



4



3

