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Module - 3 (spectroscopy)

$$\Delta E \propto f \quad \Rightarrow \Delta E = hf = \frac{hc}{\lambda}$$

Q- $\lambda = 3000 \text{ \AA}$, send energy in Kcal mol^{-1} & kJ mol^{-1}

A- $E = \frac{hc}{\lambda} = \cancel{6 \cdot 625}$

$$= \frac{6.625 \times 10^{-34}}{3000 \times 10^{-10}} \times 3 \times 10^8 \times 6.023 \times 10^{23}$$

(high energy)

wavelength \rightarrow comic $< \gamma < \chi < \text{UV} <$ visible

IR $<$ MW $<$ Radio waves
(low energy)

Spectroscopy - study of how matter absorbs &

spectra - emits light & other radiations.

• Different types of spectra :-

- 1- Continuous spectrum \rightarrow
- 2- Emission spectra
- 3- Absorption spectra

4- atomic spectra

5- molecular spectra

• energy changes together -

$$E_{\text{total}} = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$$

order $\rightarrow E_{\text{electronic}} \gg E_{\text{vibrational}} \gg E_{\text{rotational}} \gg E_{\text{translational}}$.

\rightarrow Electronic (U.V-visible) spectroscopy :-

Beer's law :-

$$\frac{-dI}{dn} \propto I \quad \frac{-dI}{dn} = kI$$

or

$$\log_{10} \frac{I_0}{I} - \epsilon \cdot x = A = \frac{k}{2-303} x$$

ϵ = absorptance coefficient, A = absorbance/optical density

$$\tau = \frac{1}{A}$$

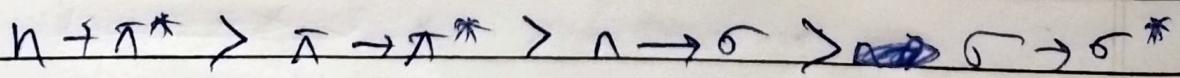
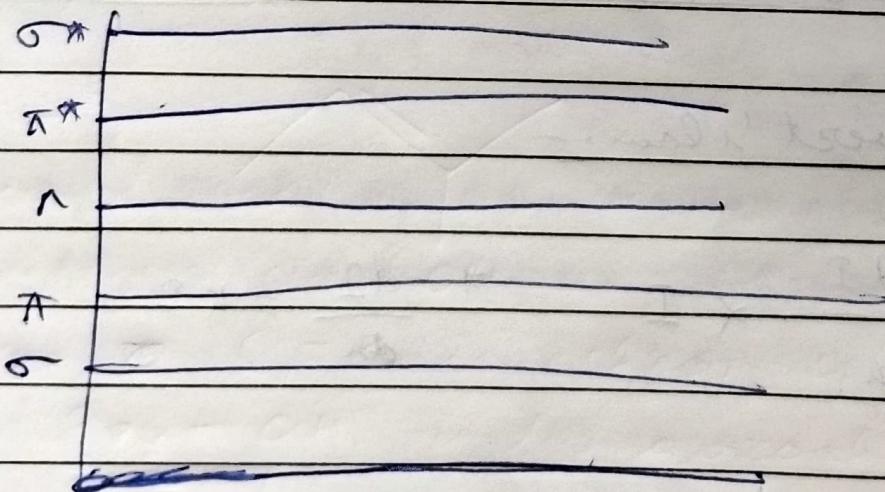
Brewer's law

$$-\frac{dI}{dc} = K I, \quad (c = \text{concentration})$$

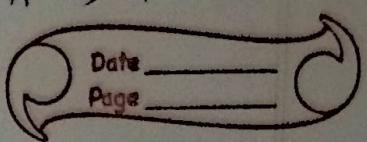
UV spectrometry :-

↳ single beam

↳ double beam



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



Bands Of electronic deconnection:-

 K bands, R bands, B-band, E band.

(i) K bands - $[n \rightarrow \pi^*]$ transition

↳ found in dyes, polyenes, enones.

(ii) R bands - $[n \rightarrow \pi^*]$ transition

(iii) B-bands - $[n \rightarrow \pi^*]$ $(\lambda = 256 \text{ nm})$

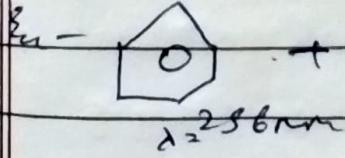
(iv) E bands

Chromophore

functional group
which provide
wavelength of an organic
compound.

~~Auxochrome~~

→ they provide
characteristic absorption
in UV or visible region



$\lambda = 261 \mu\text{m}$

here $-\text{CH}_3$ is a
chromophore

① Chromophore types :-

(i) when $\pi \rightarrow \pi^*$ transition takes place

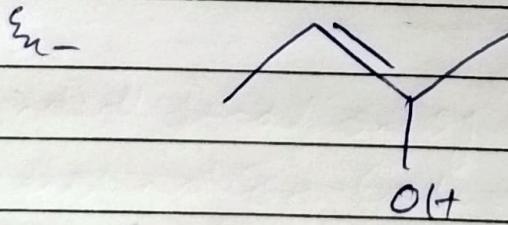
↳ $C=C$ or $C \equiv C$

(ii) when $n \rightarrow \pi^*$

↳ $> C=O, -C \equiv N, -N=N.$

Auxochromes :-

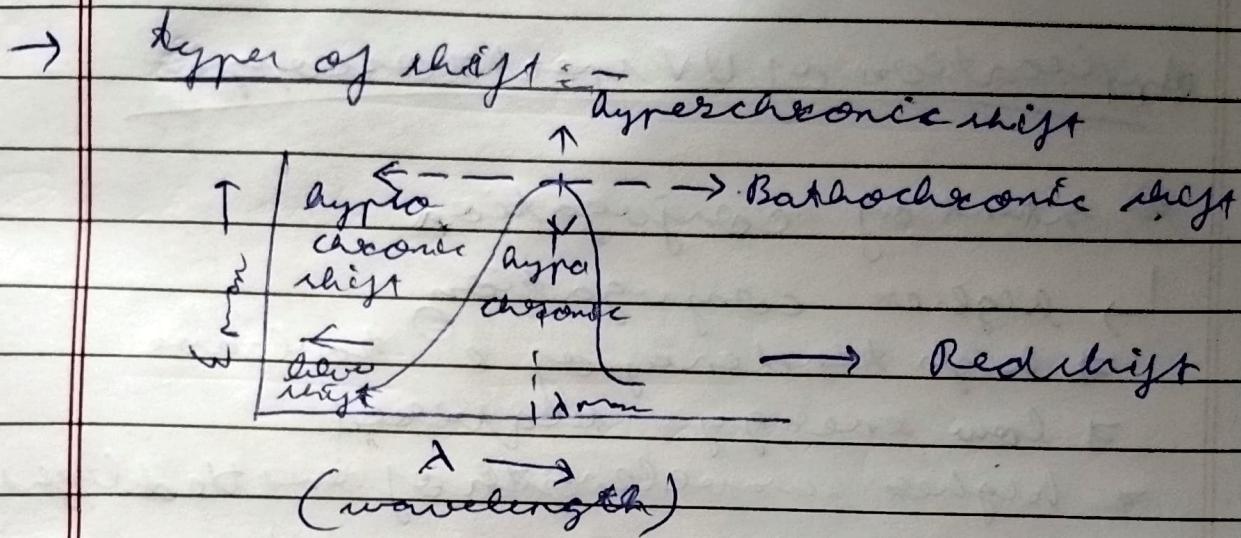
The group that is attached to the chromophore to boost its ~~selectivity~~ wavelength where it does not itself act as a chromophore.



here $\textcircled{2}$ $C=C$ is chromophore,

$\textcircled{2}$ $-OH$ is the auxochrome.

~~by Prayag~~



- based on shift in
 - Δ → hyperchromic shift
 - ¶ bathochromic shift.

Error → hyperchromic shift
hypochromic shift

Red shift ⇒ bathochromic
blue shift ⇒ hypochromic

effect of solvent on shift :-

(i) non polar solvent → very low shift/no shift
↳ ethylene, cyclohexene, aromatic

(ii) polar solvent → high shift
↳ α - β carbonyl compound

→ Application of UV spectrometry -

(i)

• extent of conjugation

↳ higher conjugation

⇒ high tendency of e^- to leave

⇒ low energy required

⇒ higher wavelength of emitted light.

- - $\lambda \propto$ conjugation

(ii)

(iii)

identification of unknown compounds

(iv)

distinction between conjugated & non conjugated compounds.

(v)

detection of impurities -

↳ e.g. - ethanol containing benzene.

(vi)

detection of H-bonding

(vii)

Quantitative analysis

↳ calculations of absorbance

↳ concentration using Beer's law



$$A = Ecl.$$

Q-

Camphor in hexane, 5cm-cell,
 absorbance $A = 2.52$ at 292nm , $\epsilon = 14$.
 what's concentration of camphor?

A-

$$A = \epsilon cl$$

$$\therefore 2.52 = 14 \times c \times 5\text{cm}$$

$$\therefore c = \frac{2.52}{14 \times 5} =$$

 \rightarrow FTIR :-

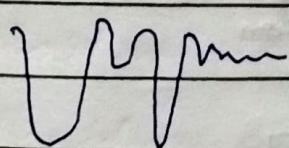
(Foster changes infrared spectroscopy)

- Electromagnetic radiation -

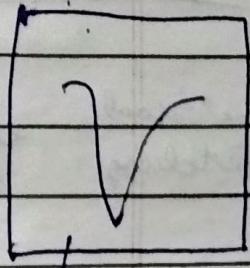
4000 to 400 cm^{-1} (vibrational

$$f = \frac{1}{\lambda} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \begin{array}{l} \text{Shank's} \\ \text{law} \end{array} \quad \begin{array}{l} \text{frequency} \\ \text{Deconvergence vector} \end{array}$$

T%



$$f_1 = \frac{m_1 \nu_e}{m_1 + m_2}$$

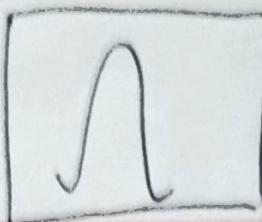


(Deconvolution percentage)

(cm⁻¹) f (frequency)

FTIR

Absorbance \rightarrow
spectra



UV-visible

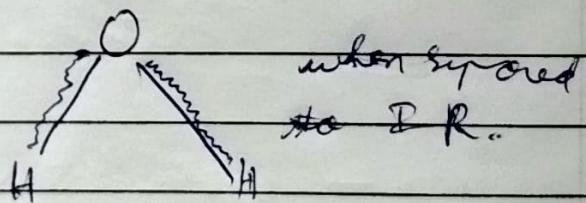
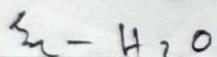
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Important observation :-

Q1 - why vibration?

A1 - In case of UV-visible, the range of wavelength is $400-800\text{ nm}$.

The vibration of a bond is detected ^{chemical} when it is exposed to infrared ~~red~~ light.



• Types of IR vibration?

stretching vibration

symmetrical stretching

asymmetrical stretching

Bending vibration

Rocking wagging torsion bending

vibration

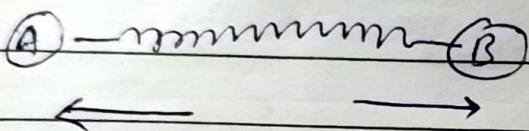
inward outward
Rocking Rockward

wagine a spring - either we can stretch or bend it.

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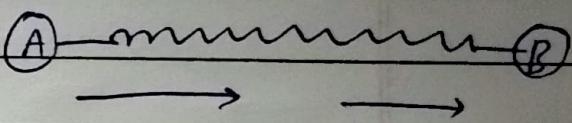
1- Matching vibrations :-

symmetrical



Opposite stretching

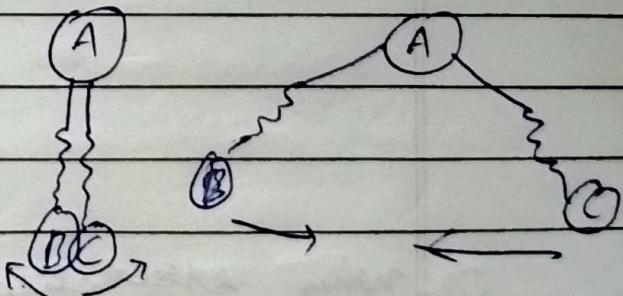
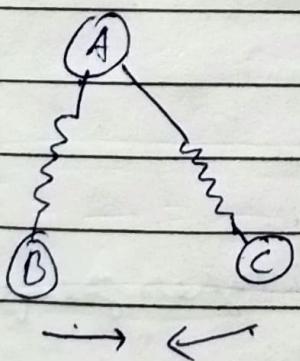
unsymmetrical



same dir^n stretching

2- Bending vibration

(i) recoupling



movement of bond length in dir^n towards each other dir^n.

(ii) Rocking vibration

(iii) wagging

(iv) torsional

Q2- why edge-tapping gives higher frequency than bending vibration

$$\text{Ans- } E = h f \Rightarrow E \propto f$$

A we know the range of vibration is from

$4000 - 900 \text{ cm}^{-1}$. But it is observed that from $4000 - 1500 \text{ cm}^{-1}$ → show stretching vibration & from $1500 - 400 \text{ cm}^{-1}$ it shows bending vibration.
Hence ~~it~~ stretching vibration

- All compounds show a unique vibration pattern, hence ~~these~~ ^{the} ~~are called~~ vibrations are called a fingerprint of any compound.
- However, enantiomers are exceptions.

Q- How vibration occurs.

Hooke's law :-

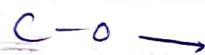
$$f = \frac{1}{2\pi} \times \sqrt{\frac{k}{\mu}}$$

wave no. (F) & force constant $\propto \frac{1}{\text{reduced mass}}$

$$\text{reduced mass} (\mu) = \frac{m_1 \times m_2}{m_1 + m_2} \quad \left| \begin{array}{l} m_1 = \text{mass of atom 1} \\ m_2 = \text{mass of atom 2} \end{array} \right.$$

Q - C-O bond vs C-H bond for

Ans - $C - \overset{H}{\bullet} \rightarrow I_e = \frac{m_1 m_2}{M_1 + M_2} = \frac{12}{13}$



Degrees of freedom

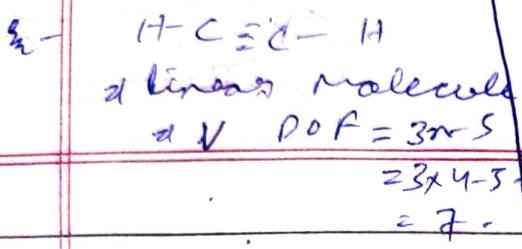
1) Total degrees of freedom = $3n$
translational degrees of freedom = 3
rotational DOF = 2

~~Translational~~

rotational DOF = $3n - 3 - 2 = 3n - 5$.

$$\therefore DOF = T + V + R$$

$$3n =$$



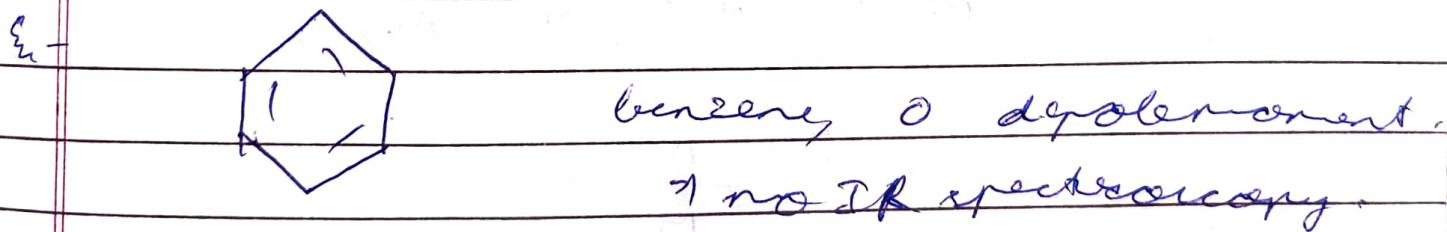
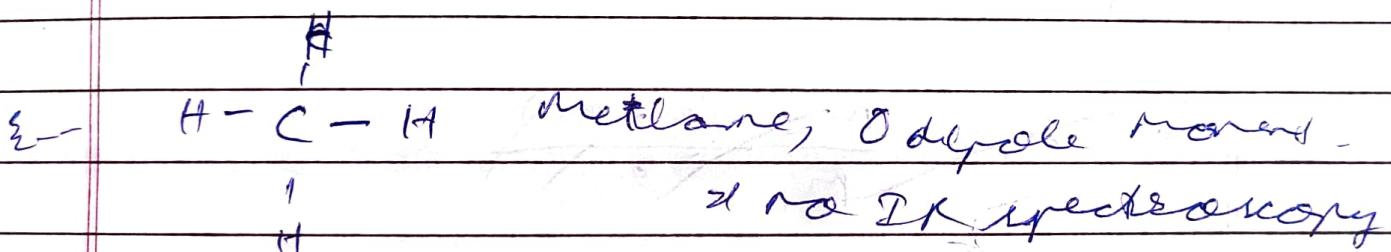
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electrostatic desorctional \rightarrow vibrational \rightarrow rotational

~~translational \rightarrow rotational \rightarrow vibrational \rightarrow~~

UV visible \rightarrow IR \rightarrow microwave

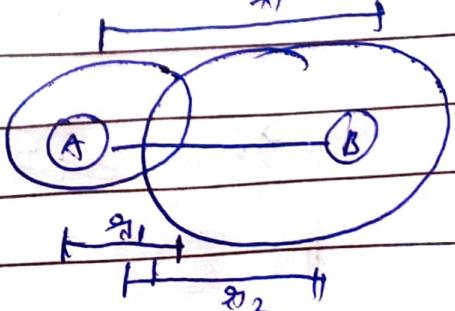
- IR spectroscopy depends on dipole moment of molecule. When molecule contains O dipole moment, hence ~~is~~ IR inactive.



→ Rotational spectroscopy:
 when MW fall on a bond, rotation takes place.

Microwave region \rightarrow 1 cm to 100 cm

$$\pi \neq \pi_1 + \pi_2 \quad (\text{bcz of overlapping})$$



We know, Moment of inertia,

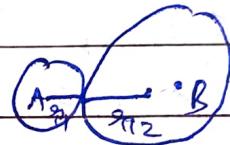
$$I = \sum m r^2 \Rightarrow I = m_1 r_1^2 + m_2 r_2^2 \quad (\text{kg m}^2)$$

$$\therefore I = m_1 r_1^2 + m_2 r_2^2$$

~~$$r = r_1 + r_2$$~~

~~$$r_2 = r - r_1$$~~

~~$$m_1 r_1 = m_2 (r - r_1)$$~~



~~$$r_1 = \frac{m_2 (r - r_1)}{m_1}$$~~

$$m_1 r_1 + m_2 r_1 = m_2 r$$

$$r_1 = \frac{m_2 r}{m_1 + m_2}$$

$$r_2 = \frac{m_1 r}{m_1 + m_2}$$

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

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

Rotational spectroscopy of rigid rotors:-

- Rigid rotor -

$$L = \sqrt{J(J+1)} \frac{\hbar}{2\pi} \quad (J=0, 1, 2, 3, \dots)$$

~~magnetic quantum no.~~

~~$E_{energy} = \frac{I\omega^2}{2} = J(J+1) \frac{\hbar^2}{2\pi}$~~

$$E_J = \frac{1}{2} I \omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$$

$$\gamma E_J = J(J+1) \frac{\hbar^2}{8\pi^2 I} \quad \gamma = \frac{J(J+1)}{\hbar^2}$$

~~$B = \frac{\hbar}{8\pi^2 I}$~~

$$\gamma \lambda = \frac{E}{hc} = \gamma f = J(J+1) \frac{\hbar}{8\pi^2 I}$$

$$\text{here } B = \frac{\hbar}{8\pi^2 I}$$

$$f = J(J+1) - B$$

(J = magnetic rotation quantum no.)

when $J=0$, $\bar{f}=0$

when $J=1$, $\bar{f}=2B$

$J=2$, $\bar{f}=6B$

$J=3$, $\bar{f}=12B$

$J=4$, $\bar{f}=20B$.

$J=5$, $\bar{f}=30B$

These are an overlap of MW & IR range
hence sometimes vibrational & rotational
occurs simultaneously

$$J_0 \rightarrow J_1 = 2B$$

$$J_1 \rightarrow J_2 = 4B$$

$$J_2 \rightarrow J_3 = 6B$$

$$J_3 \rightarrow J_4 = 8B$$

$$J_4 \rightarrow J_5 = 10B$$

Q - for $J_0 \rightarrow J_2$, $\bar{f} = 3.8424 \text{ cm}^{-1}$, for CO.

Find - moment of inertia & bond distance

Ans -



$$\text{for } J_0 \rightarrow J_2 \Rightarrow \bar{f} = 6B$$

$$\Rightarrow 6B = 3.8424 \text{ (given)}$$

$$\Rightarrow B = 0.6404$$

$$f = \frac{1}{2\pi} \sqrt{\frac{K}{e_1}}$$

$$e_1 = \frac{m_1 m_2}{m_1 + m_2} \quad \Rightarrow \text{mass } m_1(c) = \frac{12}{N_{12c}}$$

$$m_2(0) = \frac{88}{N_{120}}$$

$$e_1 = \cancel{12} \cdot \frac{12}{N_{12c}} \times \frac{8}{N_{120}}$$