Instrumental Techniques

Spectroscopy: It is a branch of science concerned with the investigation and measurement of spectra produced when matter interacts with electromagnetic radiation (emr).

Spectrum: An array of waves arranged according to either increasing or decreasing wavelength (λ) or frequency (ν).

Spectroscopy deals with the transition of electron / molecule that undergoes between its energy levels upon absorption of suitable electromagnetic radiation determined by quantum mechanical selection rules.

Electromagnetic Spectrum:-
The arrangement of all types of emr in order of their increasing wavelengths or decreasing frequency is known

as electromagnetic Spectrum.

	γ-rays	X-rays	UV	Vis	IR	MW	RW
λ(m)	0.0001 nm	0.01 nm	10 nm	400-750 nm	0.01 cm	1 m	1 m - Km
	Ionising				non-ionising		
λ(m)	10^{-12}	10^{-10}	10^{-8}	10^{-6}	10^{-5}	10^{-2}	10^{3}

Electromagnetic Radiation:

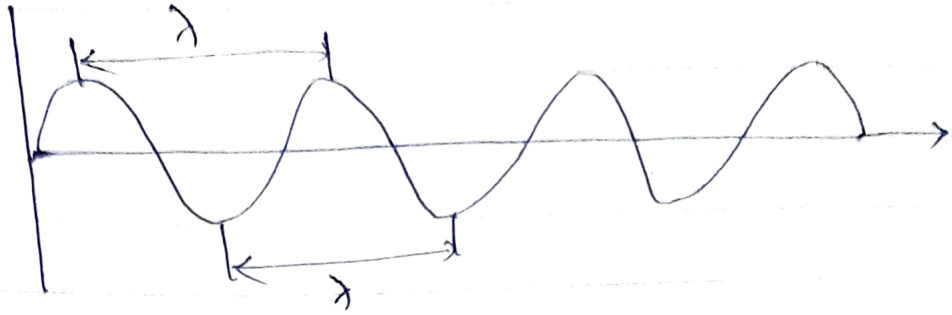
* EMR is obtained by oscillation of electric charge and magnetic field residing on the atom.

* All EMR are characterised by their wavelength (λ), or frequency (ν) or wavenumber ($\bar{\nu}$).

* The energy carried by an EMR (E) $= nh\nu = n\frac{hc}{\lambda} = nhc\bar{\nu}$

$(n = 1, 2, 3, ----)$

* Regarded as sinusoidal wave.



1) Wavelength (λ):

The distance between two crest or troughs in a particular wave.

unit: Å, nm, pm, μm, etc.

2) Wave number (cm^{-1}):

It is the reciprocal of λ

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

unit: cm^{-1}

It is the total number of wave which can pass through a space of 1 cm.

3) Frequency (ν):

It is the number of waves which can pass through a point in 1 s.

Unit: Hz, s^{-1}, etc.

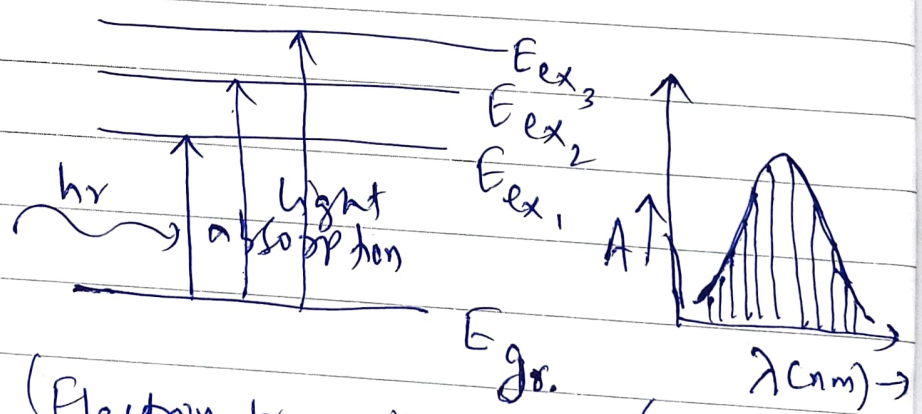
$$\boxed{\nu \propto \frac{1}{\lambda}} \Rightarrow \nu = \frac{c}{\lambda}$$

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

Absorption Spectrum:

Formation:

Consider two energy levels E_{ground} and $E_{excited}$. If a light of suitable λ falls on a molecule or atom in the ground state and its energy $h\nu$ is exactly equal to the energy difference ΔE ($E_{ex} - E_g$) between the energy levels, the atom/molecule/electron undergoes a transition from the lower energy level to the higher energy levels with the absorption of light of energy $h\nu$. The absorption of energy results in an absorption spectrum.



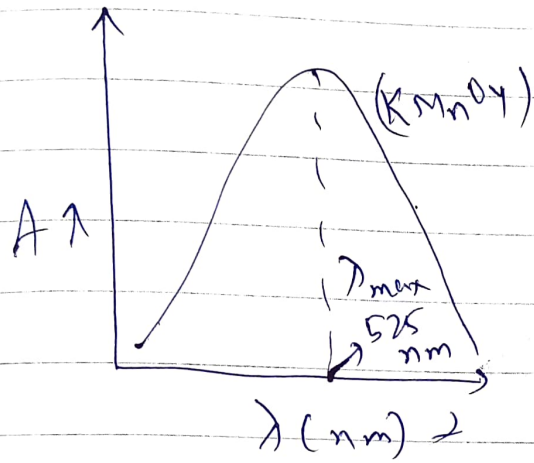
(Electron transition) (Spectrum)

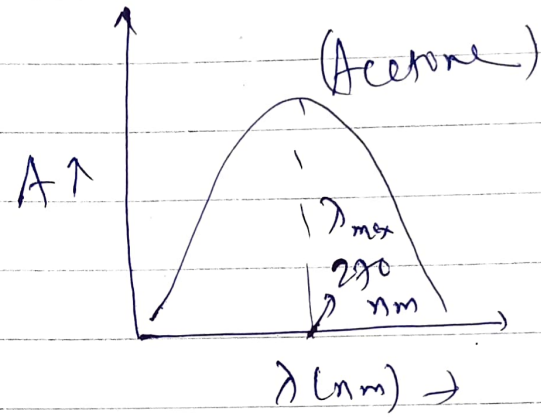
The wavelength (λ) of absorbed radiation is measured by a spectrophotometer.

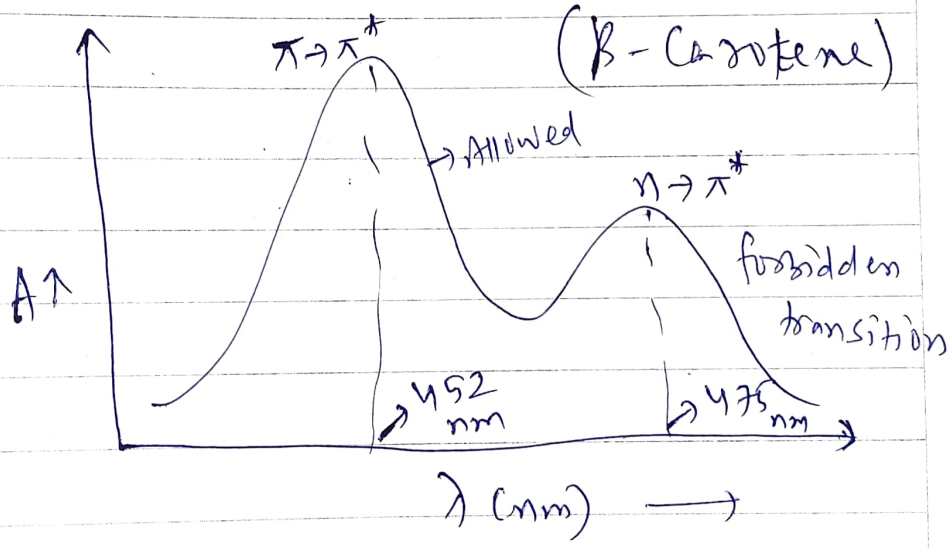
Def^n

Absorption spectrum is a graph of Absorbance (A) Vs wavelength (λ). It may contain one band or more than one bands.

It is a record of the amount of light absorbed (A) by the sample as a function of λ.







Molecular Spectroscopy :-

It deals with the study of interaction between molecules and light.

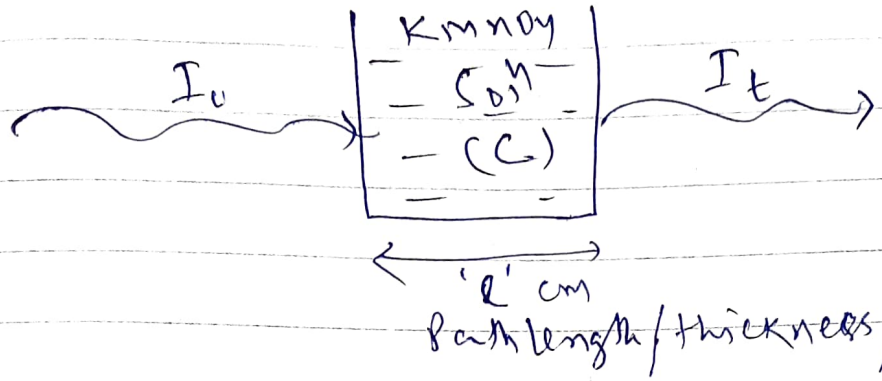
Types:

1. UV-visible or electronic spectroscopy
2. Infrared or Vibrational spectroscopy
3. Microwave or rotational spectroscopy

Light absorption law :
(Beer-Lambert's law)

It states that "when a monochromatic light is passed through a dilute solution the rate of decrease of intensity of light with thickness of the medium is proportional to the intensity (I_0) as well as concentration of the solution.

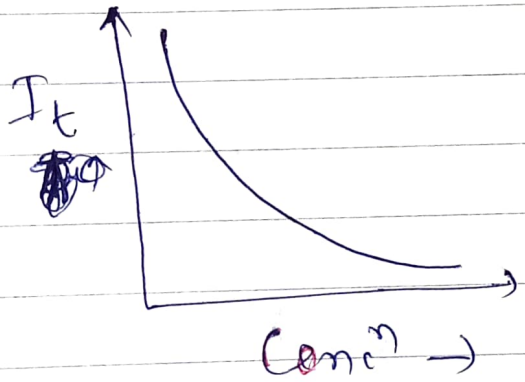
Silicon
.... beyond teaching



Mathematically, $-\frac{dI}{dl} \propto I \cdot C$

or,

The intensity of light decreases exponentially as it passes through an absorbing medium.



$$\boxed{I_t = I_0 \cdot 10^{-\epsilon \cdot C \cdot l}}$$

$$I_0 = I_t \cdot 10^{\epsilon \cdot C \cdot l}$$

where,

$I_0 \rightarrow$ Intensity of light before passing through the solution

$I_t \rightarrow$ Intensity after passing through the solution.

$c \rightarrow$ Conc^n of soln (M) mol/L mol/dm^3

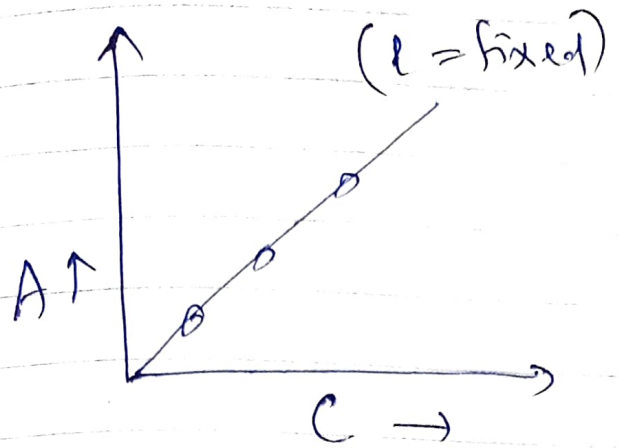
$l \rightarrow$ Path length (in cm)

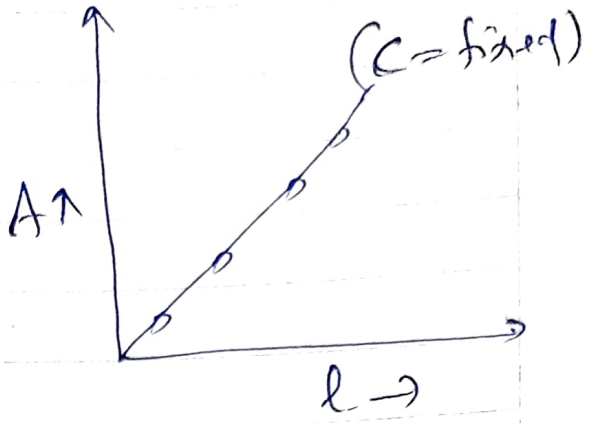
$\epsilon \rightarrow$ Molar extinction coefficient or Molar Absorptivity

or,

At a given wavelength Absorbance (A) is directly proportional to Conc^n as well as path length.

$$\boxed{A = \epsilon \cdot c \cdot l}$$





Absorbance (A):

It is the logarithmic ratio of I_0 and I_t.

$$A = \log\left(\frac{I_0}{I_t}\right)$$

It is otherwise known as Optical density".

It has no unit.

It is a measure of the capacity of a substance to absorb light of specified wavelength.

Transmittance (T):-

It is the ratio of I_t to I_0.

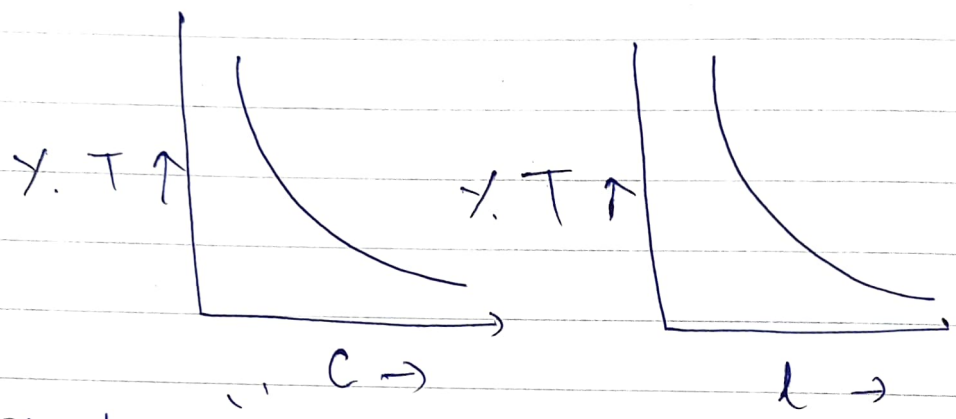
$$T = \frac{I_t}{I_0}$$

✓ It has no unit.

$$A = \log\left(\frac{I_0}{I_t}\right) = -\log\left(\frac{I_t}{I_0}\right)$$

$$\boxed{A = -\log T}$$

$$\Rightarrow \quad T = 10^{-A} = 10^{-\epsilon \cdot c \cdot l}$$



Percentage T

% T = T × 100

$$\boxed{\% T = \frac{I_t}{I_0} \times 100}$$

Molar Absorptivity (ϵ) :-

It is a measure of intensity of light absorption.

i.e It is a measure of

absorption efficiency of a species at a given λ.

$$\# \quad \boxed{\epsilon = \frac{A}{c \cdot l}}$$

unit :- $\longrightarrow M^{-1} \cdot cm^{-1}$

$$= (Mol/lt)^{-1} \cdot cm^{-1} = lt\, mol^{-1}\, cm^{-1}$$

✓ It gives information about the strength of electronic transition.

✓ Measures how strongly a chemical species absorb light at a given λ.

Applications of Beer-Lambert's law :-

(1) Finding the conc of absorbing species

(2) Finding the molecular mass of absorbing species.

(3) To study kinetics of a reaction.

Deviation from Beer-Lambert's law :

It deviates when :

(1) Absorbing solution is fluorescent in nature

(2) Absorbing molecules are in equilibrium state.

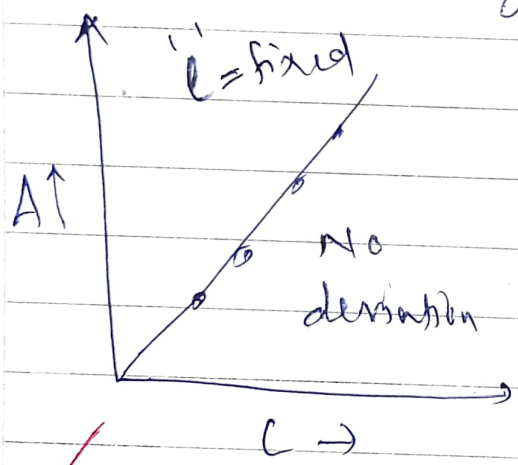
(3) Some interactions occurs between solute & solvent molecules

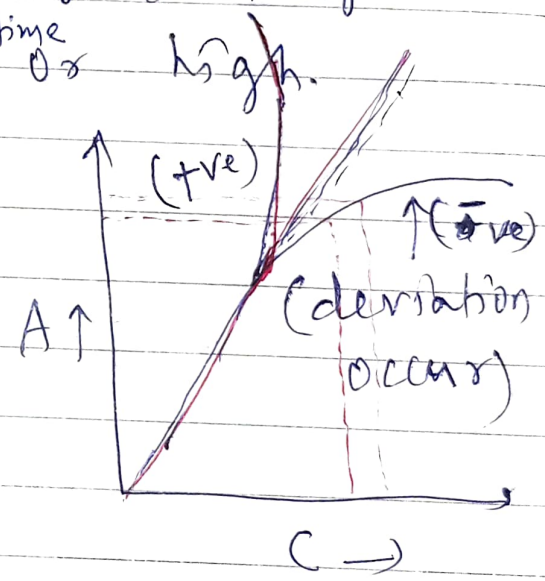
(4) Solution is turbid in nature

(5) Light is not monochromatic

(6) Solution's conc^n is high ($> 10^{-3}$ M)

(7) Solution's temp. keep changing with time or high.





(*) Prove that $A = 2 - \log(\%T)$

Ans: We know that $\%T = 100 \times T$

$\log(\%T) = \log(100 \times T)$

$= \log 100 + \log T$

$= 2 + \log T$

N-B: $A = -\log T$

$\Rightarrow -\log T = 2 - \log(\%T)$

$\Rightarrow A = 2 - \log(\%T)$ (Proved)

Silicon
... beyond teaching

Numerical

(1) A light of wavelength 345 nm is passed through a solution of conc^n 2.5×10^{-4} M. The width of the sol^n is 1 cm and absorbance is 1.17. Find molar absorptivity. (ϵ).

Sol^n:-

$$A = \epsilon \cdot C \cdot l$$

$$\epsilon = \frac{A}{C \cdot l} = \frac{1.17}{2.5 \times 10^{-4} \times 1}$$

$$= 0.468 \times 10^{4}\ M^{-1} cm^{-1}$$

(2) When UV-light is passed through a solution, the intensity of light has reduced to 50%. Find A and T.

Sol^n:- here, $I_t = \frac{I_0}{2}$

$$A = \log\left(\frac{I_0}{I_t}\right) = \log\left(\frac{I_0}{I_0/2}\right) = \log 2$$

$$= 0.3010$$

$$T = 10^{-A} = 10^{-0.3010} = 0.50$$

$$\left(T = \frac{I_t}{I_0} = \frac{50}{100} = 0.5\right)$$

(3) A light of wavelength 400 nm is passed through a sol^n (0.1×10^{-2} Mol/dm^3). The 'ϵ' is $0.5 \times 10^{3}\ M^{-1} cm^{-1}$. Find A & %T.

Silicon ... beyond learning

Soln:-

i) $A = \epsilon \cdot C \cdot l$

$= 0.5 \times 10^{3} \times 0.1 \times 10^{-2} \times 1$

$= 0.5$

ii) $T = 10^{-A} = 10^{-0.5} = 0.3162$

now, $\% T = 0.3162 \times 100$

$= 31.62$

(4) The percentage transmittance of an aqueous soln of a substance at $25^{\circ}C$ is 19.2 % for 5×10^{-4} M soln in a 10 mm quartz cell.

Find (i) ϵ, A & T

(ii) % T of 1.75×10^{-5} M soln in 10 cm cell.

Soln:- i) $\% T = 100 \times T$

$\Rightarrow T = \frac{\% T}{100} = \frac{19.2}{100} = 0.192$

now, $A = -\log T = -\log(0.192)$

$= 0.716$

$\epsilon = \frac{A}{C \cdot l} = \frac{0.716}{5 \times 10^{-4} \times 1}$

$= 1.43 \times 10^{3}\ M^{-1} \cdot cm^{-1}$

$\boxed{10\ mm = 1\ cm}$

ii) $A = \epsilon \cdot c \cdot l$

$= 1.43 \times 10^{3} \times 1.75 \times 10^{-5} \times 10$

$= 0.25$

$T = 10^{-A} = 10^{-0.25} = 0.5623$

now, $\% T = T \times 100 = 56.23$

(5) Radiation of wavelength 280 nm is passed through 1.00 mm cell containing protein soln of conc^n 0.5 mmol/lt. The light intensity has reduced to 54 % of its initial value.

i) find A and ϵ

ii) What would be the 'T' through a cell of thickness 2.00 mm.?

Soln:- i) given, $\% T = 54$

$= T \times 100$

$\Rightarrow T = \frac{54}{100} = 0.54$

$A = -\log T = -\log(0.54) = 0.27$

now, $\epsilon = \frac{A}{c \cdot l} = \frac{0.27}{0.5 \times 10^{-3} \times 10^{-1} cm}$

$= 5.4 \times 10^{3} M^{-1} cm^{-1}$

ii) $T = 10^{-A} = 10^{-\epsilon \cdot c \cdot l}$

$$= 10^{-(5.4 \times 10^{3} \times 0.5 \times 10^{-3} \times 2 \times 10^{-1})}$$

$$= 10^{-0.54} = 0.29$$

(6) A solⁿ of thickness 3 mm transmits 30% incident light. Find concⁿ of the solⁿ. $\epsilon = 4000\ dm^3\ mol^{-1}\ cm^{-1}$

Solⁿ:- $T = \frac{30}{100} = 0.3$

$$A = -\log T = -\log(0.3) = 0.5228$$

Now, $C = \frac{A}{\epsilon \cdot l} = \left(\frac{0.5228}{4000 \times 3 \times 10^{-1}\ cm}\right)$

$$= 4.356 \times 10^{-4}\ M$$

(7) The concⁿ of yeast in an aqueous solution is 10 mM. The absorbance is found to be 0.209 when it is placed in a 1.00 cm cuvette and 258 nm radiations are passed through it.

(a) Find ϵ.

(b) Find A if solⁿ is 5×10^{-2} M.

(c) Find A if path length has increased to 5.00 cm.

Soln:-

(a) $\epsilon = \frac{A}{C \cdot l} = \frac{0.209}{10 \times 10^{-3} M \times 1 cm}$

$= 0.209 \times 10^{2} M^{-1} cm^{-1}$

(b) $A = \epsilon \cdot C \cdot l$ (l = fixed)

$= 0.209 \times 10^{2} \times 5 \times 10^{-2} \times 1$

$= 1.045$

(c) $A = \epsilon \cdot C \cdot l$ (C = fixed)

$= 0.209 \times 10^{2} \times 10 \times 10^{-3} M \times 5$

$= 1.045$

(8) A substance 'x' has an extinction coefficient $3739 M^{-1} cm^{-1}$ at 423 nm. What is the conc^n of 'x' when you measure an optical density of 0.445 in a cell of pathlength 10 mm?

10 mm = 1 cm

Soln:-

$C = \frac{A}{\epsilon \cdot l} = \frac{0.445}{3739 \times 1}$

$= 1.19 \times 10^{-4} M$ (Ans.)

Energy levels in a Molecule:

(A) Electronic Energy levels:-

At RT, the molecules are in the lowest energy level E_0. When a molecule absorb UV-Visible light ($\lambda = 200 - 800$ nm), electrons are promoted to the higher electronic energy levels such as $E_1, E_2, E_3 \cdots E_n$, etc. are called as electronic transition.

⇒ Absorption of UV-Vis light by a molecule results in electronic transition.

⇒ The difference in electronic energy levels ($\Delta E_{el.}$) = $100 - 10^4$ kJ/mole.

(B) Vibrational Energy levels:-

They lies in between electronic energy levels.

⇒ Absorption of IR light ($\lambda > 800$ nm) but < 1 mm results in vibration of molecule.

The spacing between two adjacent vibrational levels ($\Delta E_{vib.}$) = 1 - 100 KJ/mole.

When IR light is absorbed by a molecule, molecules are excited from one vibrational level to another.

(c) Rotational Energy Levels
($\lambda = 10^{-3}$ mm - 10^{-1} mm)

When microwave light is absorbed by a molecule transition occurs between rotational levels.

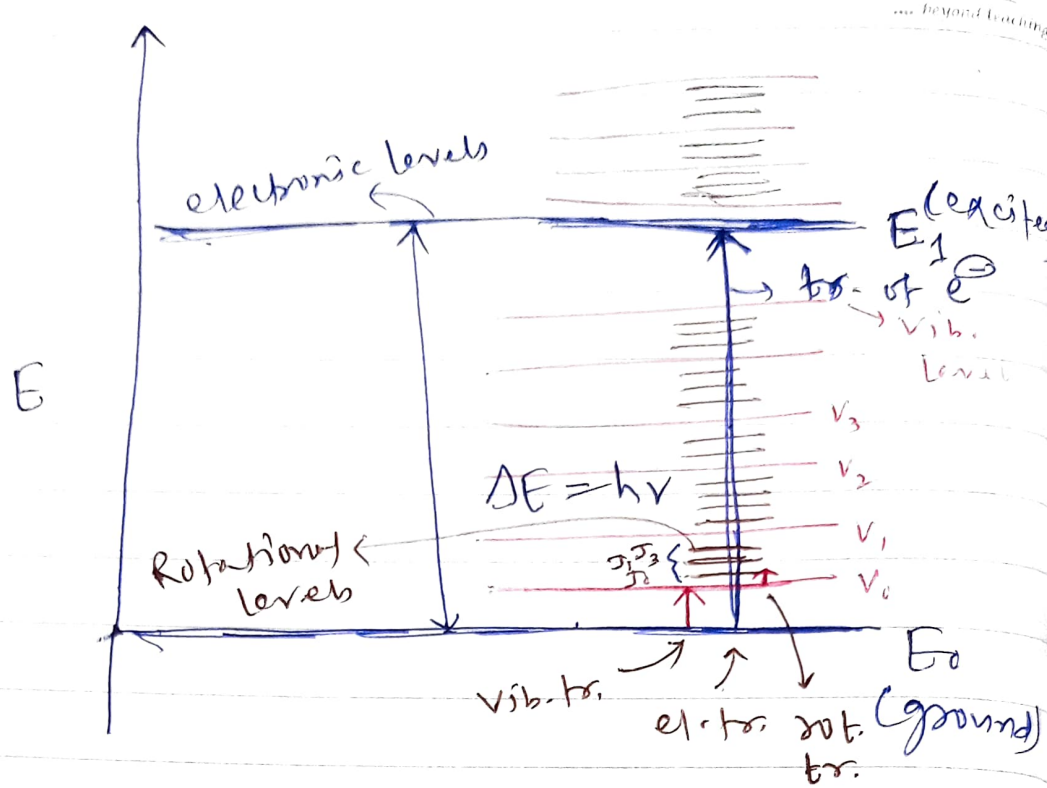
The spacing between two adjacent rotational levels ($\Delta E_{rot.}$) = 0.01 - 10 KJ/mole.

Conclusion:-

$$\boxed{\Delta E_{el.} >>> \Delta E_{vib} >> \Delta E_{rot.}}$$

So, vibrational levels are lies between electronic levels and rotational levels are lies between vibrational levels.

* Transition between energy levels occur by absorption of light or photons.



(Molecular Energy levels)

N.B. Rot. tr. << Vib tr. << El. tr.

(1 - 20 cm^{-1}) (MW region)

(2000 - 4000 cm^{-1}) (IR-region)

(10,000 - 50,000 cm^{-1}) (UV-vis region)

⇒ The various types of energy transitions occur in different regions of the EM-spectrum and do not overlap.

⇒ Electronic, vibrational and rotational energy levels are superimposed.

Silicon
... beyond teaching

Electronic / UV - Visible Spectroscopy

UV-Visible spectroscopy deals with the study of interaction between UV-vis light (λ = 200 - 800 nm) and molecule.

It is a type of molecular absorption spectroscopy in which light of UV-vis region is absorbed by molecule to results in the transition / excitation of electrons from the ground state (E_0) to the higher energy states (E_1, E_2, E_3 ----)

The amount of energy that is absorbed by a molecule is equal to the energy difference between E_{ground} and $E_{excited}$.

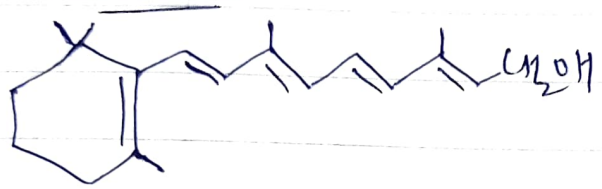
i.e $E = h\nu = (E_{exc.} - E_{gr.}) = \Delta E$

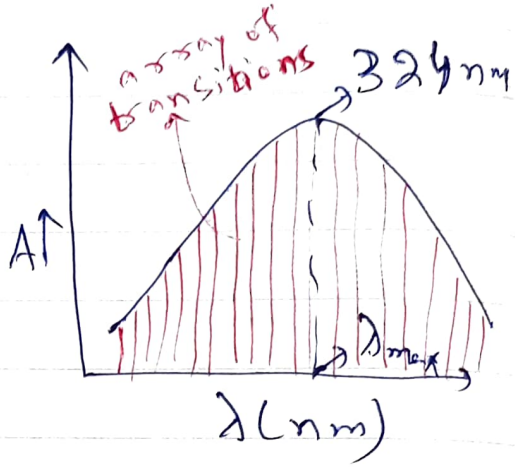
N.B Most favoured electronic transition is from the highest occupied Molecular Orbital (HOMO) to Lowest Unoccupied Molecular Orbital (LUMO).

Broad Nature of Absorption Band

An absorption spectrum is not consists of sharp peaks but consists of broad bands.

Vitamin-A





Absorption bands are broad because the excitations of electrons are also accompanied by the vibrational & rotational transitions.

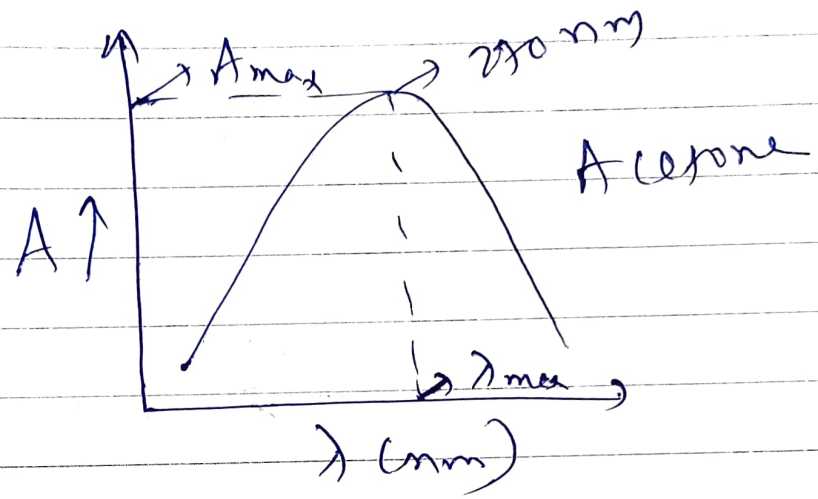
This array of transitions arranged in increasing order of λ results in band.

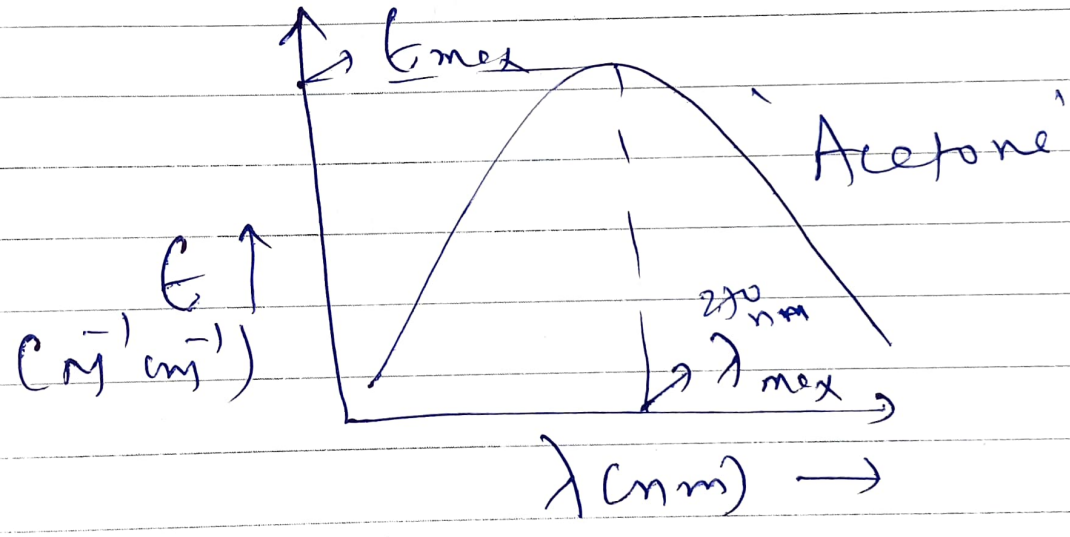
Silicon
... beyond teaching

Significant features of an absorption Band:

(A) λ_{max} (Wavelength corresponds to maximum Absorbance (A_{max})

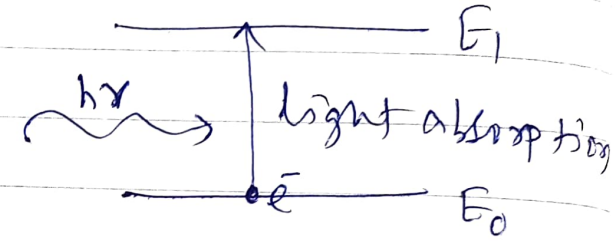
(B) ϵ_{max} or A_{max}





Principle of Electronic Spectroscopy

When a light of appropriate wavelength falls on a sample, electron transition occurs from the ground state (HOMO) to the excited state (LUMO) provided that $E_{incident\ light} = h\nu = E_{exc.st.} - E_{gr.st.}$



Selection Rules:

The restrictions imposed on the various electronic transitions is called "Selection Rules".

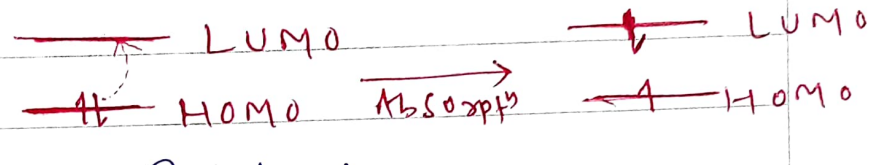
(A) The Spin Rule:-

It says that spin inversion during electronic transition is not allowed.

It means that Singlet to Singlet transition is allowed whereas Singlet to triplet transition is not allowed.

Singlet means Spin multiplicity = 1
Triplet " " " = 3

"Spin Retention"



(B) Symmetry Rule :-

It says that transition of $e^{\ominus}$ between orbitals of same symmetry is not allowed.

i.e $g \rightarrow u$ & $u \rightarrow g$ is allowed

$g \rightarrow g$ & $u \rightarrow u$ is not allowed.

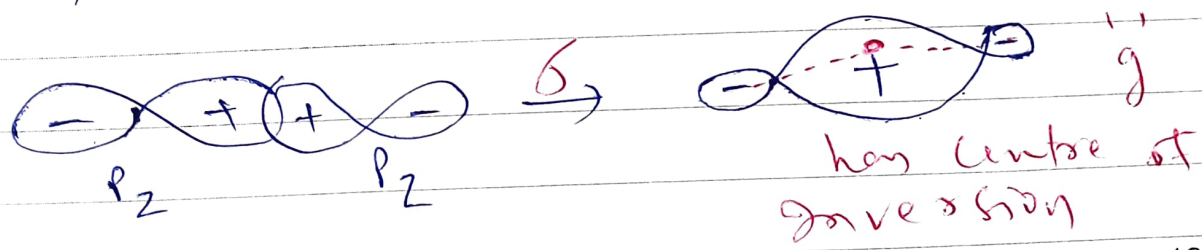
N.B:

$g \rightarrow$ gerade
$u \rightarrow$ ungerade

Gerade (g) and Ungerade (u) :-

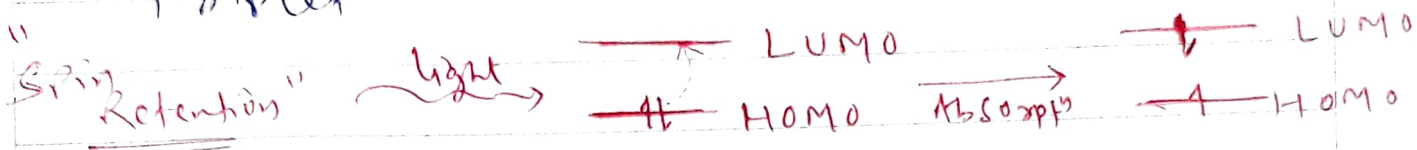
Gerade ~~[illegible]~~ has centre of inversion.

(1) σ^b



It means that Singlet to Singlet transition is allowed whereas Singlet to triplet transition is not allowed.

Singlet means Spin multiplicity = 1
Triplet " " " = 3



(B) Symmetry Rule :-

It says that transition of e^- between orbitals of same symmetry is not allowed.

i.e. $g \rightarrow u$ & $u \rightarrow g$ is allowed

$g \rightarrow g$ & $u \rightarrow u$ is not allowed.

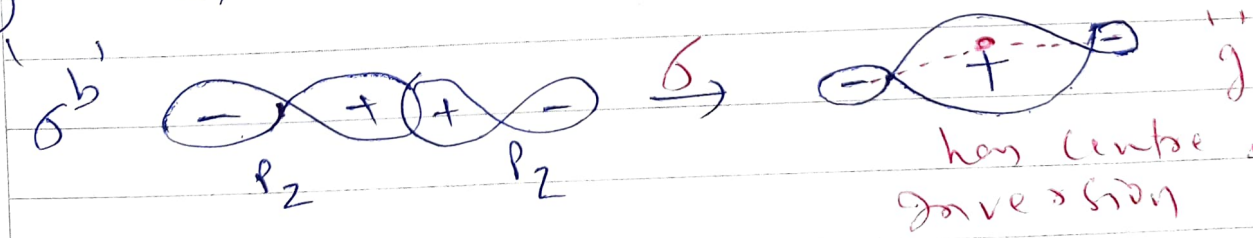
N.B:

g → gerade	
u → ungerade	

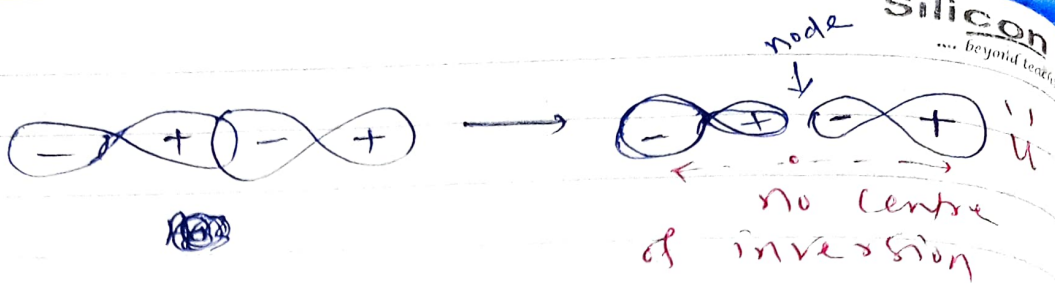
Gerade (g) and Ungerade (u) :-

Gerade ~~[illegible]~~ has centre of inversion.

(1)



σ^*



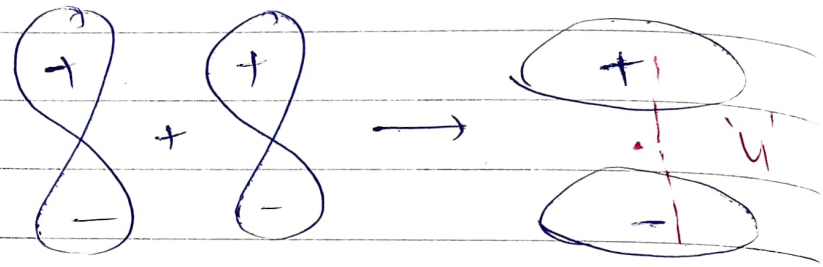
$\sigma \rightarrow \sigma^*$ transition

means $g \rightarrow u$ (Allowed)

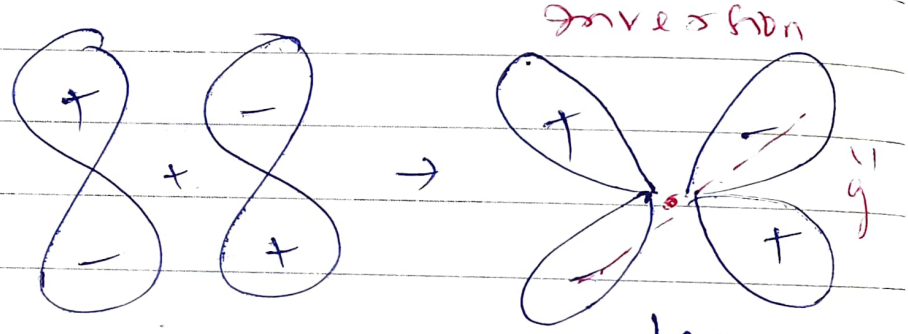
(2) $\pi \rightarrow \pi^*$

$u \rightarrow g$ (Allowed)

π



π^*



(3) $\sigma \rightarrow \pi^*$

$g \rightarrow g$ (not allowed)

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

$u \rightarrow u$ (not allowed)

Allowed and Forbidden electronic Transitions :-

(A) Allowed Transitions :

→ has high ϵ_{max} - value (more than 10^4)

→ Obeys Symmetry Rule

$$\underset{u}{\pi} \rightarrow \underset{g}{\pi^*}, \quad \underset{g}{\sigma} \rightarrow \underset{u}{\sigma^*}$$

(B) Forbidden Transitions :-

→ has low ϵ_{max} - value (below 10^4 M^{-1} cm^{-1})

→ do not obeys Symmetry Rule

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

Example :-

In Benzophenone, $C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$

i) Transition at $\lambda = 252$ nm is allowed ($\pi \rightarrow \pi^*$), $\epsilon_{max} = 20,000$ M^{-1} cm^{-1}

ii) at $\lambda = 325$ nm, Forbidden to occur. $n \rightarrow \pi^*$, $\epsilon_{max} = 180$ M^{-1} cm^{-1}

Q: Between $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transition which transition has lower intensity and why?

Ans:- $n \rightarrow \pi^*$

✓ $\epsilon_{max} < 200\ m^{-1} cm^{-1}$

✓ not obey symmetry Rule.
(A forbidden Transition)

Types of Electronic Transitions

According to the MOT, when a molecule absorbs UV-visible light then transition of electron occurs from the ground state levels (σ, π, n - orbitals) to the excited levels (π^*, σ^* - orbitals).

So, the allowed electronic transitions are:

i) $\sigma \rightarrow \sigma^*$

ii) $n \rightarrow \sigma^*$

iii) $\pi \rightarrow \pi^*$

iv) $n \rightarrow \pi^*$

(i) $\sigma \rightarrow \sigma^*$ transitions:-

✓ Such transition require a large amount of Energy ($\lambda < 150$ nm).

✓ All molecules exhibit $\sigma \rightarrow \sigma^*$ tr.

✓ Examples:- All HC's, O_2, N_2, Cl_2, H_2, NH_3, CH_3OH, CH_3COCH_3, etc.

(ii) $n \rightarrow \sigma^*$ transitions:-

✓ requires less energy than $\sigma \rightarrow \sigma^*$ tr. ($\lambda < 200$ nm). (150 - 200 nm)

✓ Saturated compounds containing heteroatom (O, S, N) or having unshared pair of electrons are undergo $n \rightarrow \sigma^*$ transition.

Examples:- Cl_2, O_2, N_2, $CH_3\ddot{O}H$, $CH_3\ddot{S}H$, $H_3C(H_3C)C=\ddot{O}$ ethers, Aldehydes, Amines, $R-\ddot{Cl}:$ etc.

$:\ddot{O}=\ddot{O}:$, $\ddot{N}\equiv\ddot{N}$, $:\ddot{Cl}-\ddot{Cl}:$

iii) $\pi \rightarrow \pi^*$ transitions :-

- It requires lower energy than $n \rightarrow \sigma^*$ transition.
  (λ = 200 - 500 nm)

- Exhibited by compound containing π-bond (double & Triple bonds).

Examples :- Alkenes, Alkynes, Aromatics, O_2, N_2, Acetone, Aldehydes, Amides, Azo compounds, Carboxylic Acids, etc.

iv) $n \rightarrow \pi^*$ transitions :-

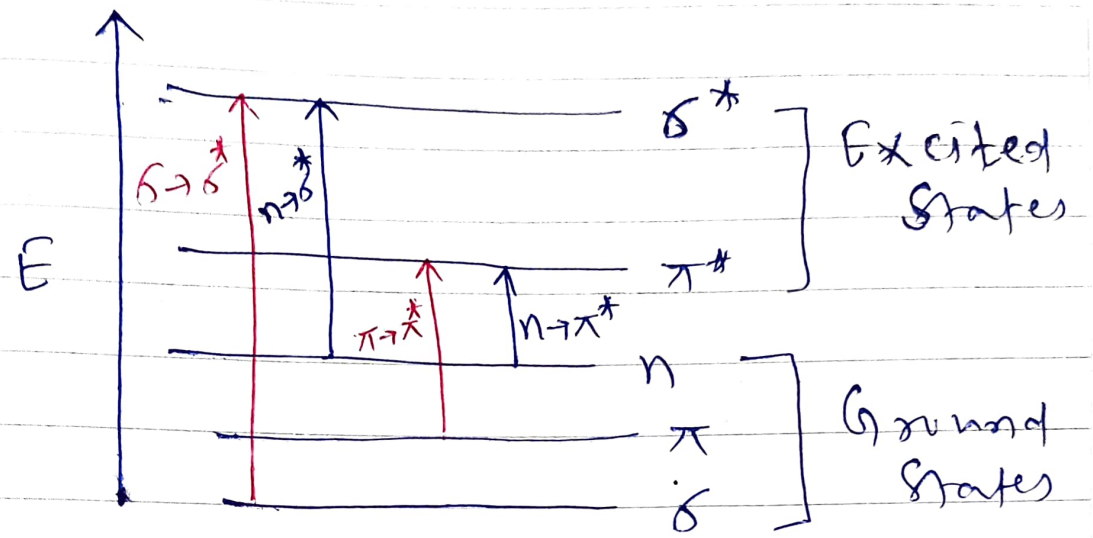
- requires Least amount of energy out of all the transitions.
  λ = (200 - 700 nm)

- Compounds having unsaturation with heteroatoms or lone pairs exhibit this transition.

Examples :- Aldehydes, Ketones, Amides,

O_2, N_2, Azo compounds ($-N=N-$), etc..

Energy level Diagram:-



$\Delta E_{\sigma\to\sigma^*} > \Delta E_{n\to\sigma^*} > \Delta E_{\pi\to\pi^*} > \Delta E_{n\to\pi^*}$

λ: <150nm (150-200nm) (200-400nm) (400-700 nm)

Electronic Transitions in Some Selected Molecules / Compounds:-

i) H_2: $H-\sigma-H$ Only $\sigma\to\sigma^*$

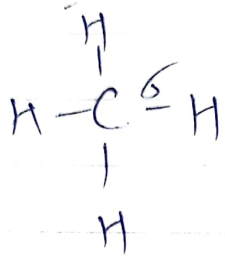
ii) $:\ddot{Cl}-\ddot{Cl}:$ $\sigma\to\sigma^*$, $n\to\sigma^*$

iii) $\ddot{O}=\ddot{O}:$ $\sigma\to\sigma^*$, $\pi\to\pi^*$, $n\to\sigma^*$, $n\to\pi^*$

iv) N_2 $\ddot{N} \equiv \ddot{N}$ $\sigma \to \sigma^*$, $\pi \to \pi^*$, $n \to \sigma^*$, $n \to \pi^*$

v) Alkanes:-

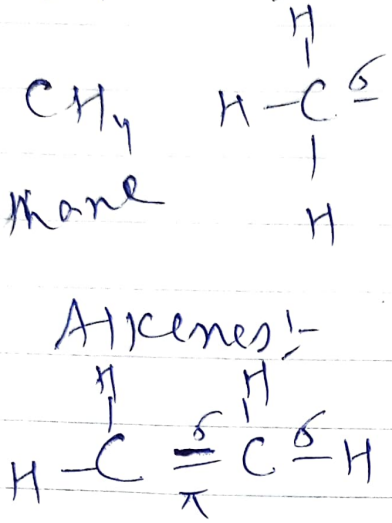
CH_4



Methane

Only $\sigma \to \sigma^*$

vi) Alkenes:- C_2H_4 (ethene)



$\sigma \to \sigma^*$, $\pi \to \pi^*$

vii) Alkynes:- C_2H_2 (ethyne)

$H - C \equiv C - H$ $\sigma \to \sigma^*$, $\pi \to \pi^*$

viii) Aldehydes:- $R - \overset{\overset{\ddot{O}:}{||}}{C} - H$

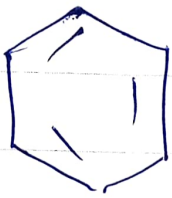
$\sigma \to \sigma^*$, $\pi \to \pi^*$, $n \to \pi^*$, $n \to \sigma^*$

ix) Ketones:- $R - \overset{\overset{O}{||}}{C} - R$

(All the 4- transitions)

x) Aromatics:-

$\sigma \to \sigma^*$, $\pi \to \pi^*$



Benzene C_6H_6

xi) Amides:- $R-\overset{:O:}{\overset{\|}{C}}-NH_2$

(All the π- transitions)

x ii) Alcohols:-

$CH_3\ddot{\underset{..}{O}}H$ $\sigma \rightarrow \sigma^*$

$n \rightarrow \sigma^*$

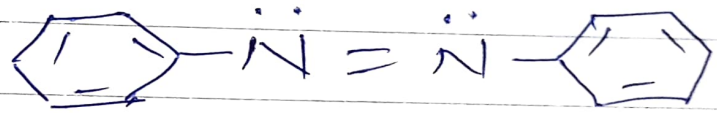
Phenols

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

$n \rightarrow \sigma^*$

(✓ no $n \rightarrow \pi^*$ transition)

x iii) Azo Compounds:-



(All the π- transitions)

x iv) Amines:- $CH_3-\ddot{N}H_2$

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

x v) Acyl $R-\overset{:O:}{\overset{\|}{C}}-Cl$

All the π- transitions

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

$n \rightarrow \pi^*$

Silicon
.... beyond teaching

Chromophore:-

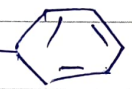
A portion of a molecule responsible for colour or responsible for light absorption in the UV-visible region (200-800 nm).

For a chromophore, the energy difference between two separate MOs falls within the UV-vis range.

✓ Chromophore usually undergoes $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$ transitions

✓ Are unsaturated group / F.G.

Examples:-

		Excitation
Phenyl group		$\pi \rightarrow \pi^*$
Nitro group	$-NO_2$	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$
Nitriles	$-C \equiv N$	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$
Azo	$-N = N-$	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$
Carbonyl	$-C = O$	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$
Alkyne	$-C \equiv C-$	$\pi \rightarrow \pi^*$
Conjugated diene	$-C = C - C = C-$	$\pi \rightarrow \pi^*$
Thio Carbonyl	$-C = S$	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$
Acids	$-COOH$	$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$

Q. Find the chromophoric group in the following molecules.

chromophore

i) $CH_3-C(=O)-CH_3$ — $>C=O$

ii) —

iii) CH_3-NO_2 — $-NO_2$

iv) $C_6H_5-N=N-C_6H_5$ — $-N=N-$

v) $CH_2=CH-CH=CH_2$ — $-C=C-C=C-$

vi) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ — $-\overset{O}{\overset{\|}{C}}-NH_2$

vii) $CH_3-CH_2-CH_2-CH_2-C\equiv CH$ — $-C\equiv C-$
1-Hexyne

viii) CH_3CN — $-C\equiv N$

ix) β-Carotene & lycopene — $-C=C-C=C-$
Conjugated diene

Silicon
.... beyond teaching

Auxochrome :-

A functional group with one or more lone pair of electrons. When attached to a chromophore, ~~called~~ shifts the absorption band towards longer wavelength (i.e, towards red end of visible spectrum).

That means auxochrome results in red-shifting of band.

✓ Auxochrome groups are called colour enhancing group.

✓ It also increases the intensity of absorption.

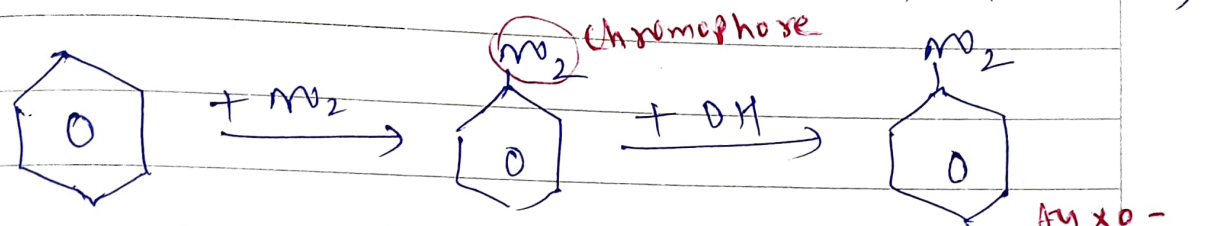
Examples :- $-\ddot{\underset{..}{O}}H$, $-\ddot{\underset{..}{X}}:$, $-\ddot{\underset{..}{O}}R$, $-\ddot{N}H_2$, $-\ddot{\underset{..}{S}}H$

✓ An auxochrome itself can't cause the development of colour.

✓ It is a modifier of a chromophore.

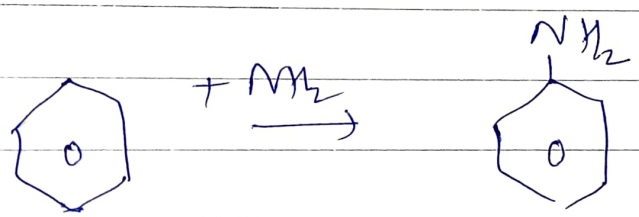
i) Benzene is a colourless compound. But nitrobenzene is a yellow-coloured compound. (Nitro group is a chromophore).

When a hydroxyl group (–OH) gets attached to the para position of nitrobenzene, it appears in a dark yellow colour. (–OH is an auxochrome)



Benzene	Light yellow	Dark yellow
Col. less		
λ_{max} = 255 nm	265 nm	400 nm

ii)



(Red-shift occurs)

λ_{max} = 255 nm. 280 nm

Q:- Benzene is colourless while Nitrophenol is dark yellow in colour. Give Reason.

Ans:- Nitrophenol has an Auxochrome (–OH group).

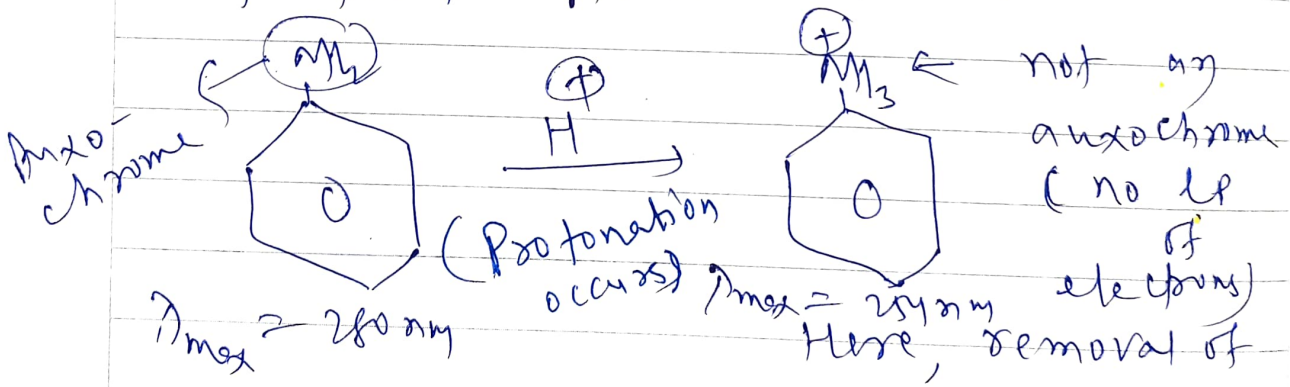
Q.2 Benzene absorbs at 255 nm whereas aniline absorbs at 280 nm. Give reason.

Ans:-

, It has an auxochrome group. ($-NH_2$)

Q.3 λ_{max} of aniline shifts from 280 nm in neutral medium to 254 nm in acidic medium. Give Reason.

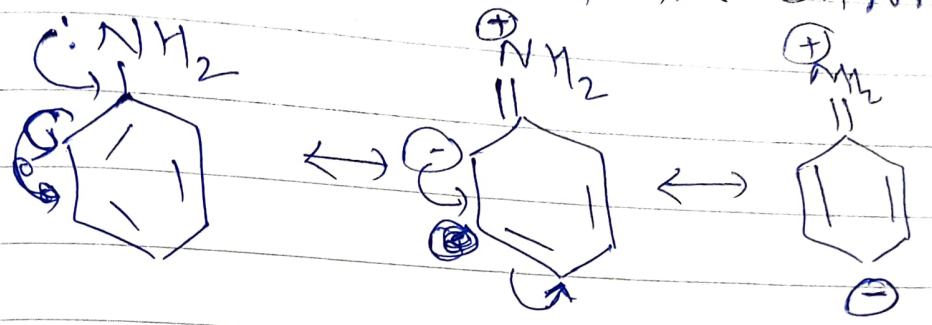
Ans:- In acidic medium, aniline reacts with H^+-ion to form Anilinium ion.



Here, removal of an auxochrome results in blue-shift of the absorption band.

Cause of Red-Shift in Presence of an Auxochrome:

Auxochrome contains lone pair of electrons. The lone pair of $\bar{e}$s undergoes delocalization with the π-electron system of the chromophore.



Delocalisation of $\bar{e}$ happens via resonance as shown above. Delocalisation causes a decrease in the energy of the system and hence an increase in the wavelength.

$$E = \frac{hc}{\lambda}, \quad \text{as } E \downarrow, \ \lambda \uparrow$$

* Increase in wavelength means red-shift.

Shifting of Absorption Band:

Four types of shifting are seen for the Absorption band.

(A) Bathochromic Shift / Red-shift

(B) Hypsochromic Shift / Blue Shift

(C) Hyperchromic Shift

(D) Hypochromic shift

* **Bathochromic Shift:-** "$\lambda_{max} \uparrow$"

It is the shifting of λ_{max} of the band to the longer wavelength (i.e to the red side of the visible spectrum).

Silicon
.... beyond teaching

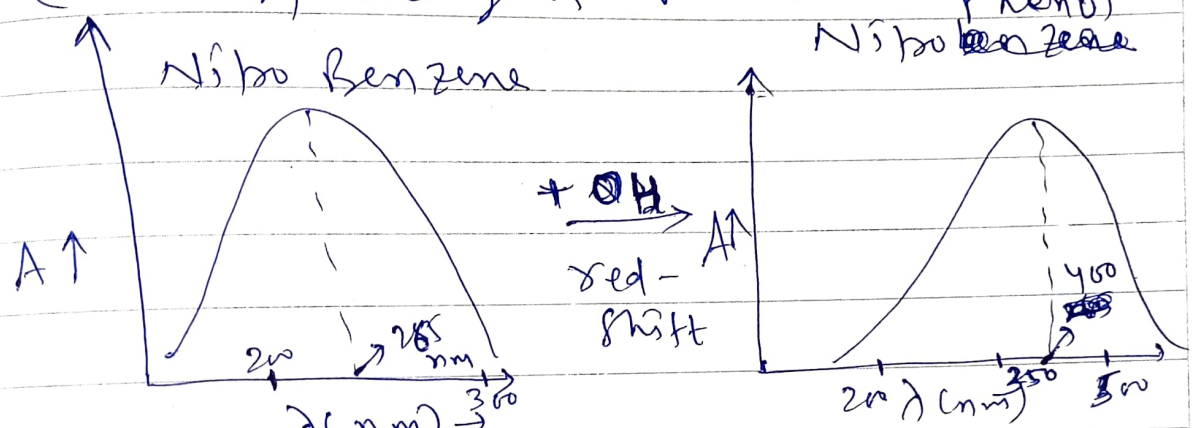
Causes:-

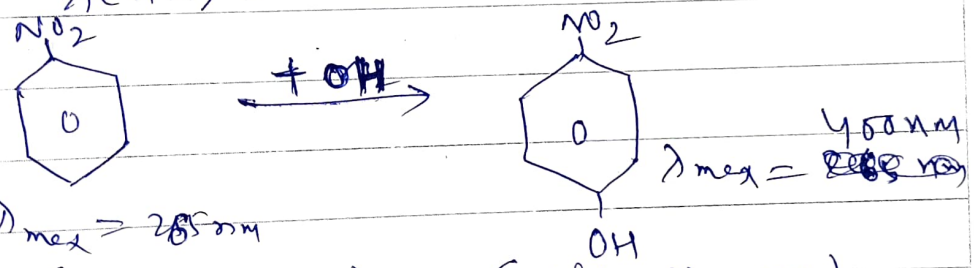
(i) Due to the presence of an auxochrome.

(ii) By (Decreases) change of polarity of the solvent

(iii) Introduction of conjugated double bond in the molecule

(iv) By change of pH of the medium





(Nitrobenzene) (Nitrophenol)

Red-shifting of $n \rightarrow \pi^*$ band occurs due to decrease in the polarity of the solvent

1-3-Butadiene absorbs at 175 nm whereas 1,3,5-Hexatriene at 256 nm. (Due to extension of conjugation)

Hypsochromic Shift: "$\lambda_{max}\downarrow$"

It is the shifting of λ_{max} of the band to shorter wavelength (i.e to blue side of the visible spectrum).

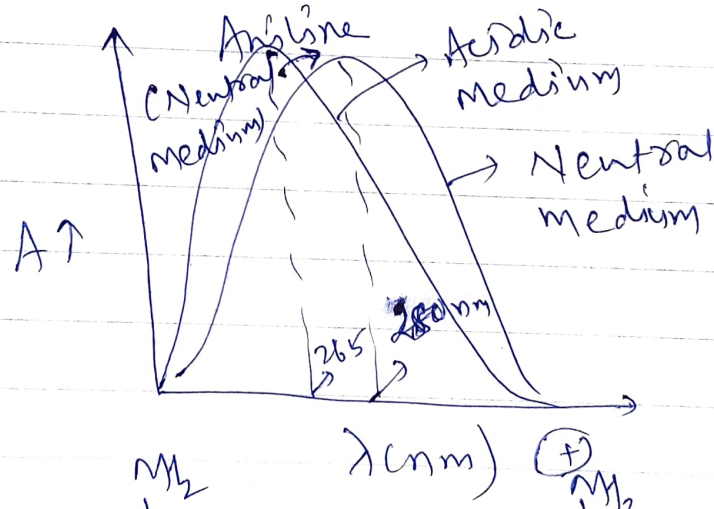
Causes:-

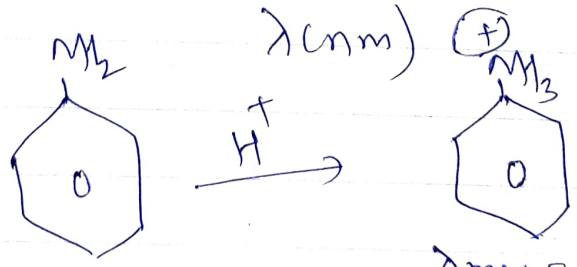
i) Removal of conjugated double bond

ii) Removal of Auxochrome

iii) By (increase) change of polarity of the solvent

iv) By change of pH of the medium





$\lambda_{max} = 280$ nm $\qquad$ $\lambda_{max} = 265$ nm

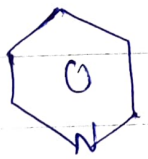
Hyperchromic Shift :- "$\epsilon_{max}\uparrow$" or $A_{max}\uparrow$

An increase in the intensity (i.e height of band) of absorption band is called hyperchromic shift.

Causes :

i) Introduction of an auxochrome

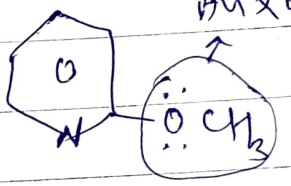
ii) Extension of conjugation system



Pyridine

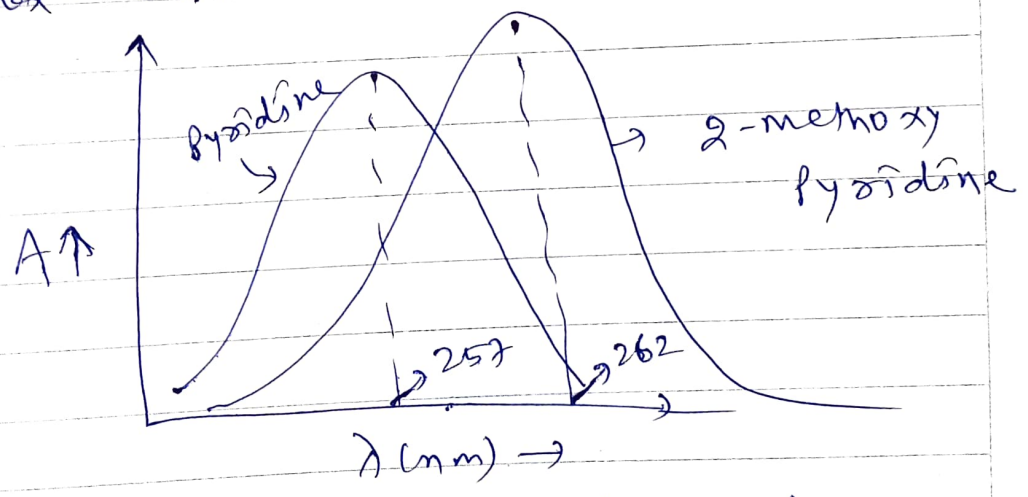
$\epsilon_{max} = 2750\ M^{-1} cm^{-1}$

$\lambda_{max} = 257\ nm$



$\epsilon_{max} = 3560\ M^{-1} cm^{-1}$

$\lambda_{max} = 262\ nm$

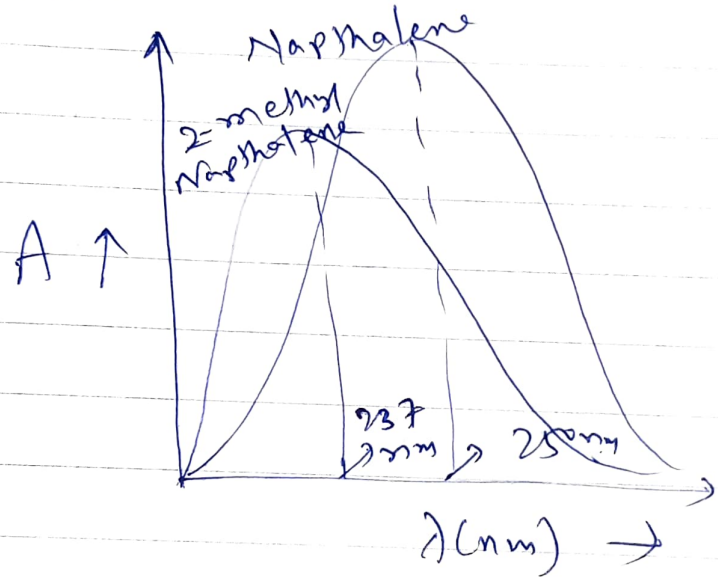


Height of the band has increased due to introduction of an auxochrome ($-\ddot{O}CH_3$).

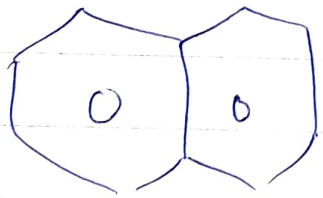
Hypochromic Shift: (ϵ_{max} or A_{max})

A decrease in the height of the band or intensity of band is called hypochromic shift.

Due to hypochromic shift, ϵ_{max} or A_{max} decreases due to the removal of an auxochrome or any distortion in the geometry of the molecule.



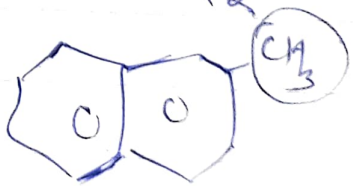
distorts the geometry



$\epsilon_{max} = 19,000\ M^{-1} cm^{-1}$

$\lambda_{max} = 250\ nm$

(Naphthalene)



2-methyl Naphthalene

$\epsilon_{max} = 10,250\ M^{-1} cm^{-1}$

$\lambda_{max} = 237\ nm$

Factors affecting A_{max} or λ_{max} or both :-

The various factors are as follows:

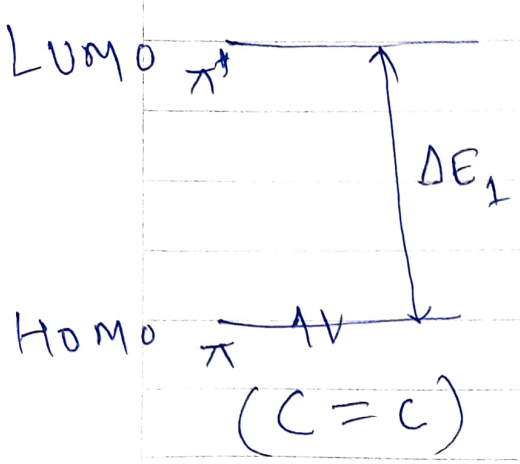
(i) Presence of Substituents
(A) Conjugation
(B) Auxochrome

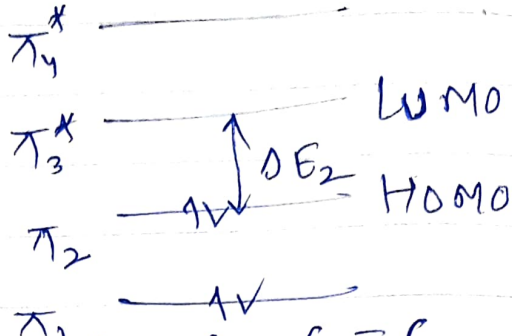
(ii) Nature of Solvent

(iii) Steric hindrance & coplanarity

Effect of Substituents

(A) Conjugation: Conjugation of double bonds reduces the energy gap between HOMO(π) and LUMO(π^*) to result in red-shift of λ_{max}-value for the $\pi \rightarrow \pi^*$ electronic transition.





$\Rightarrow \Delta E_2 < \Delta E_1$

$\Rightarrow \boxed{\lambda_2 > \lambda_1}$

Q.1 Ethene absorbs at 170 nm whereas butadiene absorbs at 217 nm. Give reason.

Ans:- Due to presence of conjugated double bond in butadiene. ($CH_2=CH-CH=CH_2$)

Q.2 β-Carotene & lycopene absorbs light in the visible range. Give reason.

Ans:- Due to extensive conjugation of double bond.

Both Contains 11 - conjugated double bond.

Each additional double bond in the conjugated electron system shifts the λ_{max} about 30-45 nm. towards higher wavelength side.

Also, ϵ_{max} roughly doubles with each new conjugated double bond.

Greater is the number of conjugated double bonds, greater is the redshift and hyperchromic shift.

(B) Auxochromes:-

Attachment of auxochromes (-$\ddot{O}H$, -$\ddot{O}R$, -$\ddot{S}H$ -$\ddot{N}H_2$ -NHR -X) results in a bathochromic shift of $\pi \rightarrow \pi^*$ electronic transition due to conjugative effect between n-orbital and π-bond system.

Silicon
.... beyond teaching

Solvent effect:-

An increase in the polarity of solvent generally shifts $n \rightarrow \pi^*$ to shorter λ and $\pi \rightarrow \pi^*$ to longer λ.

Steric Hindrance & Coplanarity

Trans-isomer is found to absorb at longer λ with higher ϵ_{max} as compared to cis-isomer.

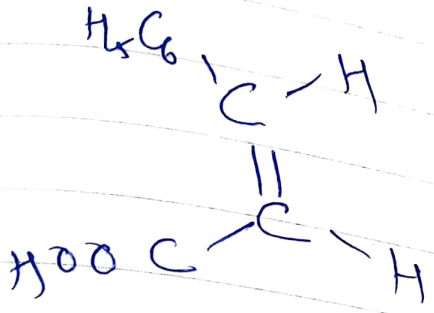
In trans-isomer, there is no steric-hindrance. So, more effective π-orbital overlapping is possible and coplanarity is achieved for π-electron system. Hence, conjugation is achieved and λ_{max} shifts to longer value.

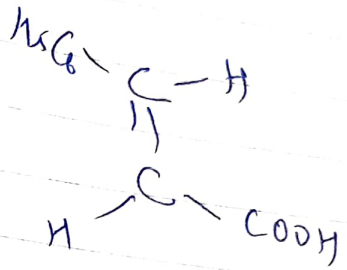
In cis-isomer the steric crowding disturbs the geometry. So, it disturbs the coplanarity of π-e^- system. This results in shifting of λ_{max} value

to ~~[illegible]~~ Small Value.

Examples:-

i)





Cis - Cinnamic Acid

$\lambda_{max} = 268$ nm

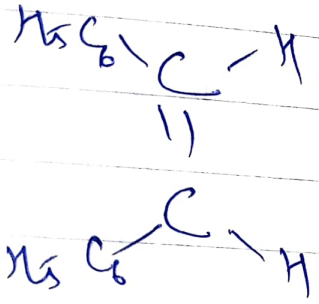
$\epsilon_{max} = 10,700\ M^{-1} cm^{-1}$

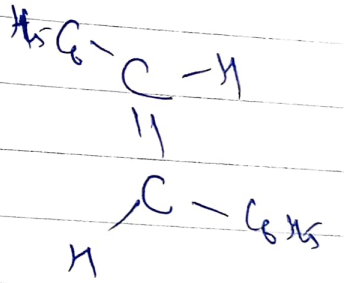
Trans - form

$\lambda_{max} = 272$ nm

$\epsilon_{max} = 15,900\ M^{-1} cm^{-1}$

ii)





Cis - Stilbene

$\lambda_{max} = 283$ nm

$\epsilon_{max} = 12,300\ M^{-1} cm^{-1}$

Trans - form

295 nm

$25,000\ M^{-1} cm^{-1}$

Applications of UV-vis Spectroscopy:

Some of the applications are:

1. Detection of Substituents and Functional groups in a Compound.
2. Detection of extent of Conjugation
3. Distinction between Conjugated and non-Conjugated System
4. Detection of impurity
5. Determination of Conc^n of a Solution (Beer-lambert's law)
6. To Study the rate of a reaction
7. To elucidate / Explain the Structure of Vitamin-A
8. To detect the presence of H-bonding in compound

(9) Distinguish between cis and trans isomers

(10) To monitor the denaturation of of double-stranded DNA

(11) To detect environmental contamination

(12) To detect synthesis of nanoparticles in a sample

(13) Detection of charge-transfer complexes

(14) Examination of polynuclear hydrocarbons (e.g naphthalenes)

(15) To study the nature of solvent (polar or non-polar)

To study band shifting by changing the polarity of the solvent.

IR - Spectroscopy

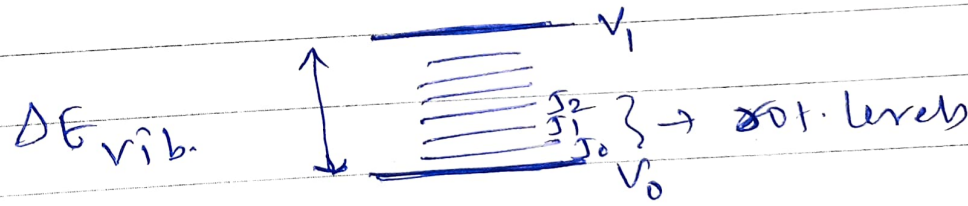
- IR - Spectroscopy deals with the study of interaction of IR-light (λ = 800 nm - 2,000 nm) with the molecule. (0.8 - 200 μm)

- The absorption of IR-radiation causes an excitation of vibrating molecule from a lower to higher vibrational energy levels.

- Absorption of IR-light causes vibration in a molecule.

- $\Delta E_{vibration}$ = 1 - 100 kJ/mole.

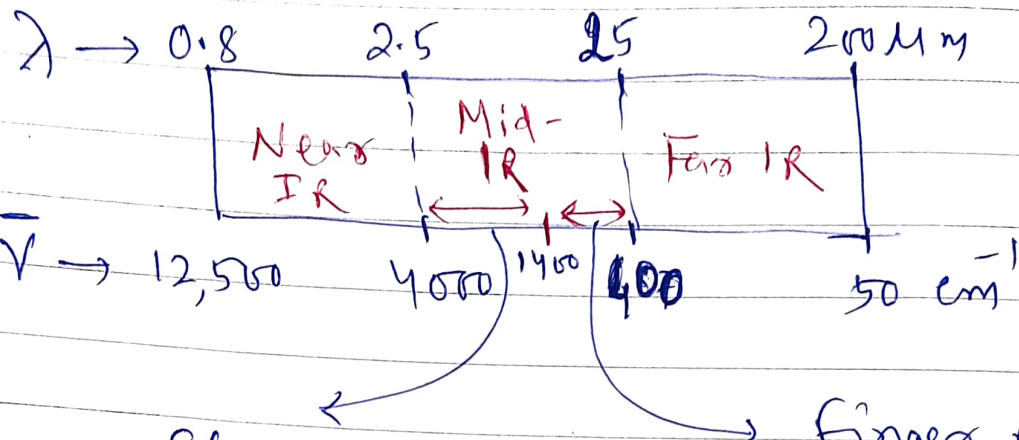
- Each vibrational level is associated with a number of closely spaced rotational energy levels.



- Vibrational band is also broad but less broader than

electronic absorption band.

✓ The whole IR spectrum is divided into 3-sub regions.



✓ $\bar{\nu}$ = Wave number = $\frac{1}{\lambda} = \frac{\nu}{c}$

#

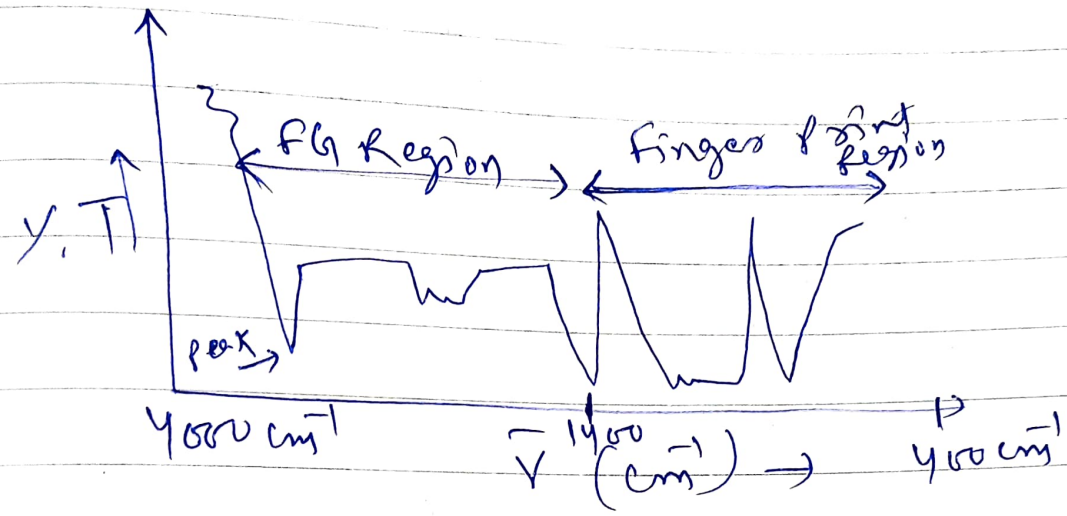
✓ Mid IR-region is used for study

✓ For excitation to occur, there must be an exact match between the frequency of the applied radiation and the frequency of the vibration.

✓ IR-spectroscopy is an absorption spectroscopy. Used for both qualitative & quantitative analysis.

IR - Spectrum:

It is a record of % T as a function of wave no. ($\bar{\nu}$).



Peak Intensity:-

#1 Peak intensity depends on the change in the dipole moment with the change in Bond distance

i.e $\left(\frac{dM}{dx}\right)$

✓ larger is the change, larger is the intensity

#2 Also peak intensity depends on the Conc^n of the solution.

$$A = \epsilon . c . l.$$

as $c \uparrow$, $A \uparrow \Rightarrow$ intensity $\uparrow$

Principle of IR- Spectroscopy

Vibrational transition occurs only when there is an exact match between the frequency of the applied IR-radiation and the frequency of the vibrating molecule.

Condition for absorption of IR-light :-

IR-light is absorbed only when a molecule of the substance under examination undergoes a net change of dipole moment.

So, dipole moment of the molecule must change periodically during a vibration for transition to occur.

N.B! All the bonds in a molecule are not capable of absorbing IR-light but

Only those bonds which are accompanied by a change in dipole moment will absorb IR-light.

✓ Those vibrational transitions which are accompanied by a change in the dipole moment of the molecule are called IR-active transitions and the molecule is called IR-active molecule.

IR-active molecules:-

✓ They are not-centrosymmetric

✓ They are polar molecules e.g H_2O, HCl, NO, CO, CH_3COCH_3

✓ If non-polar, during vibration their dipole moment changes periodically (e.g CO_2)

IR-inactive molecules:-

✓ They are non-polar molecules.
example- CCl_4, Cl_2, H_2, O_2, N_2 etc.

All Homonuclear diatomic molecules are IR-inactive molecules.
For these molecules, net dipole moment is zero.

N.B As N_2, O_2, H_2 molecules are IR-inactive, they do not take part in Global warming.

Various modes of Molecular Vibrations:

When IR-light is absorbed by a molecule, there will be increase in the vibrational energy of the molecule. It results in two kinds of fundamental vibrations

(A) Stretching Vibration

(B) Bending Vibration

Stretching Vibration:-

In this vibration, the distance between the two atoms increases or decreases but atoms remain in the same bond axis.

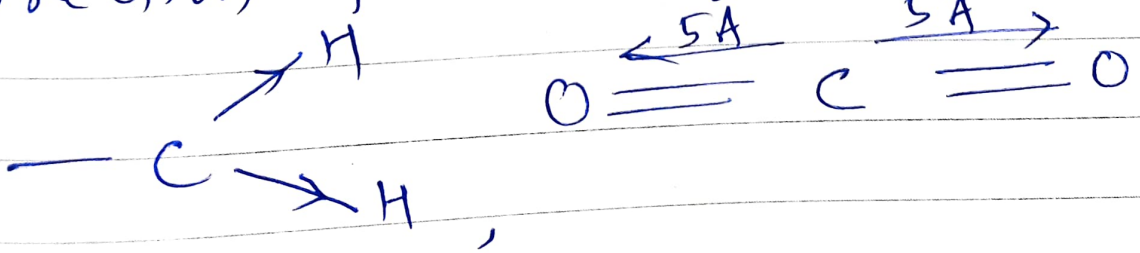
→ Here, there is no change in the bond angle.

Types of Stretching Vibration:-

There are two types:

(i) Symmetric Stretching Vibration:

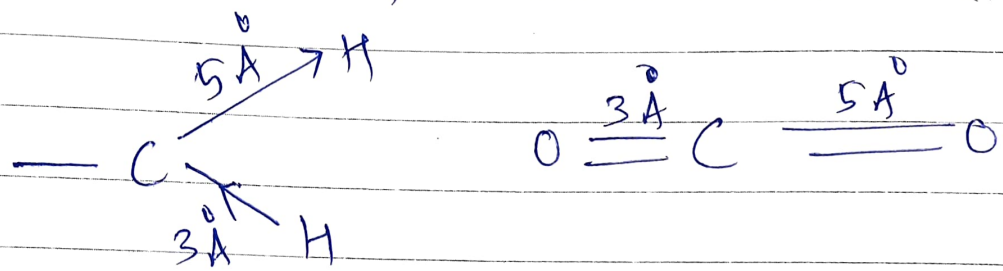
In this type, movement of atoms with respect to a particular atom in a molecule or group is in the same direction to same extent.



For Symmetric vibration, net dipole moment change is zero. So, this mode is IR-inactive.

ii) Asymmetric vibration:-

In this type, one atom approaches the central atom while the other departs from it to different extent.



In this mode, there is a net change in the dipole moment & IR-active.

Q.1 Which of the following molecule is IR-inactive?
CO_2, N_2, HCl, NO, CO, $CHCl_3$

Ans:- N_2-molecule.

Q.2 Asymmetric Vibration occurs at higher Wave number than Symmetric Vibration. Give reason.

Ans:- Asymmetric Vibration needs more energy to occur. More energy means higher wave no.

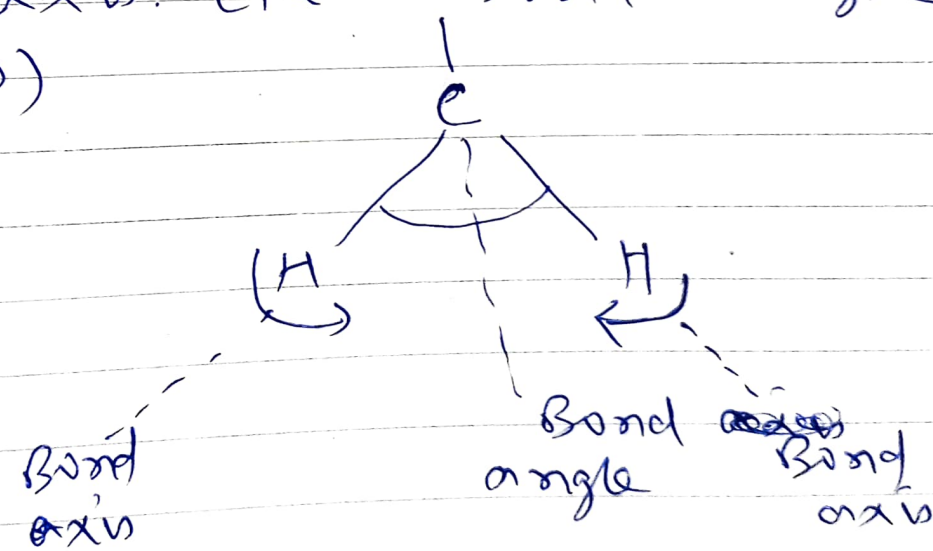
$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

$\bar{\nu} \rightarrow$ Wave no. $\rightarrow$ $(E \propto \bar{\nu})$

Bending Vibrations:-

In this type of vibration, the position of atoms changes w.r.t the original bond axis. (i.e. Bond angle changes)

For, $-CH_2$ Methylene group



Types of bending Vibrations:

✓ Diatomic molecules can't undergo bending vibrations.

ex: NO, HCl, CO, etc.

N.B Hetero nuclear diatomic molecules undergo only stretching vibration.

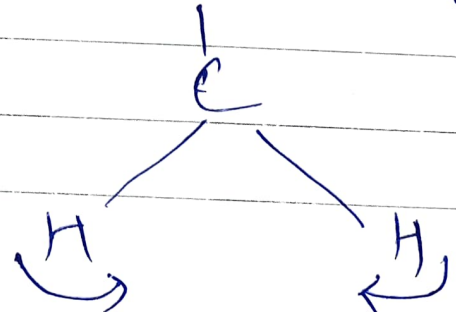
ex- HCl, HF, NO, etc.

A molecule with three or more atoms can experience bending vibration.

ex:- H_2O, $-CH_2$, $CHCl_3$, $-NH_2$, etc.

There are four types of bending vibrations:

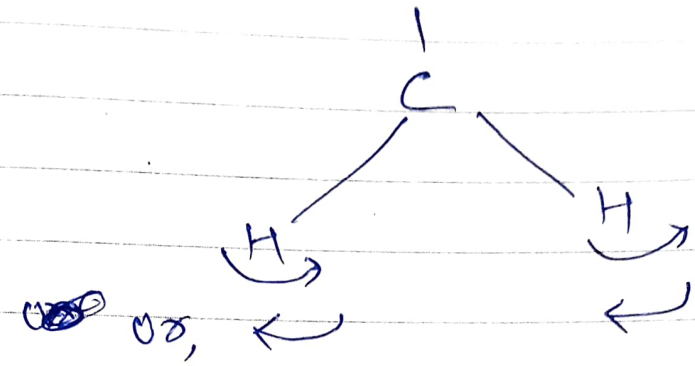
(i) Scissoring:- During this vibration, two atoms approach each other.



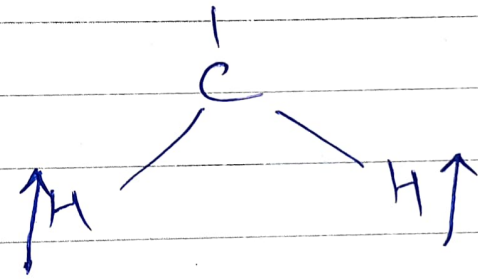
It is an in-plane deformation process.

ii) Rocking:- Here, movement of atoms take place in the same direction.

It is also an in-plane deformation process.



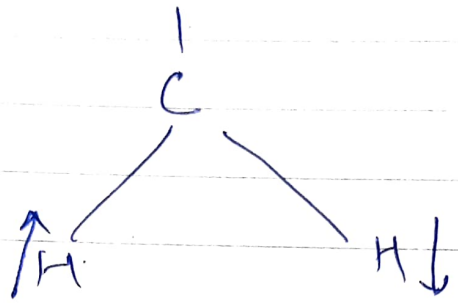
iii) Wagging:- Here, two atoms move up and down the plane w.r.t the central atom.



It is an out-of-plane deformation process.

(v) Twisting:- Here, one of the atoms moves up the plane while other moves down the plane w.r.t the central atom.

It is also an out-of plane deformation process.



N.B In IR-Spectrum, the number of bending vibrations are usually more than the number of stretching vibrations.

Q.3 Stretching vibrations are occur at higher wave no. than the bending vibrations. why?

Ans:- Stretching vibrations occurs by absorption of higher energy than bending vibrations.

i.e $E \uparrow \propto \bar{\nu} \uparrow$

Number of Vibrational Modes:-

Polyatomic molecules may exhibit more than one vibrational absorption bands. The number of these bands is related to the degree of freedom.

For a molecule with 'N' atoms, total number of degree of freedom is '3N'.

Here,

3N degree of freedom (DOF) =

(Total no of Rotational degree of freedom)

+

(Total no of Translational degree of freedom)

+

(Total no of Vibrational degree of freedom)

So, total no of vibrational degree of freedom =

3N − (Total no of Rotational DOF + Total no of Translational DOF)

N.B = Total no of vibrational DOF for linear molecules is different than non-linear molecules.

Type of Molecules	Rot. DOF	Trans. DOF	Vib. DOF	Total DOF
(1) Linear (e.g CO_2)	2	3	3N−5	3N
(2) Non-linear (e.g H_2O)	3	3	3N−6	3N

Q. Find the no. of Rotational translational & Vibrational DOF for the following molecules: CO_2, H_2O, NO, HCl, CS_2, SO_2, $POCl_3$, C_6H_6, CH_4, OCS, NH_3, $CHCl_3$, CH_3Cl

Ans.

Molecules	Rot. DOF	Tram. DOF	Vib. DOF
(1) CO_2 (linear) $N=3$	2	3	$3N-5 = 3\times3-5 = 4$
(2) H_2O non-linear $N=3$	3	3	$3N-6 = 3\times3-6 = 3$
(3) NO linear $N=2$	2	3	$3N-5 = 3\times2-5 = 1$
(4) HCl linear $N=2$	2	3	$3N-5 = 1$
(5) CS_2 linear $N=3$	2	3	$3N-5 = 4$
(6) SO_2 non-linear $N=3$	3	3	$3N-6 = 3$
(7) $POCl_3$ non-linear $(N=5)$	3	3	$3N-6 = (3\times5)-6 = 9$

	Molecule	Rot. DOF	Trans. DOF	Vib. DOF
(8)	C_6H_6 Non-linear ($N=12$)	3	3	$3N-6 = 3\times12-6 = 30$
(9)	CH_4 Non-linear $N=5$	3	3	$3N-6 = (3\times5)-6 = 9$
(10)	OCS linear $N=3$	2	3	$3N-5 = 4$
(11)	NH_3 Non-linear $N=4$	3	3	$3N-6 = (3\times4)-6 = 6$
(12)	$CHCl_3$ Non-linear $N=5$	3	3	$3N-6 = 9$
(13)	CH_3Cl non-linear $N=5$	3	3	$3N-6 = 9$

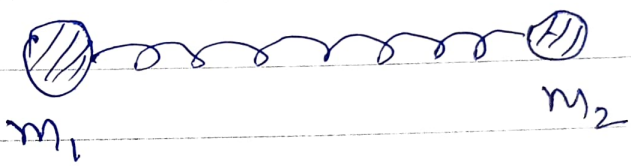
I_3^-, NO_2^+, N_3^- (Azide ion)

(*) Assignment:- Find DOF of C_2H_5OH, CH_3COCH_3 (Ketone), C_4H_4NH (Pyrrole), XeF_4 and CH_3NH_2, PH_3, B_2H_6, C_5H_5N (Py)

Vibrational Frequency (ν):

If the two masses (m_1 & m_2) at each extremes are connected by a spring of force constant K, then vibrational frequency (ν) is given by,

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \quad (s^{-1}) \quad \text{--- (1)}$$



where, $\mu \rightarrow$ Reduced mass

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

unit : Kg or g

K = Force Constant. It is a measure of bond strength

$K_{C\equiv C} > K_{C=C} > K_{C-C}$

unit: N/m or Kg/s^2

dyne/cm or g/s^2

$$\boxed{1N = 1 \, kg.m.s^{-2}}$$

Vibrational frequency depends upon:

(i) Bond strength i.e K and

(ii) mass of atom i.e μ

ν increases when K increases

and

ν decreases when μ increases

Wave number ($\bar{\nu}$):

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

So,

$$\underset{(cm^{-1})}{\bar{\nu}} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \quad \text{— (2)}$$

$\Rightarrow$ $\bar{\nu} \uparrow$ when $K \uparrow$

and

$\bar{\nu} \downarrow$ when $\mu \uparrow$.

So, lighter atoms bonded via a strong bond will vibrate at high freq or wave no.

Numerical :-

Q.1 Find the reduced mass of HCl molecule. given $m_H = 1$ amu and $m_{Cl} = 35.5$ amu

Sol :-

$$\mu_{HCl} = \frac{m_H \times m_{Cl}}{(m_H + m_{Cl})} = \frac{1 \times 35.5}{(1 + 35.5)}$$

$$= \frac{35.5}{36.5} = 0.972 \text{ amu}$$

$$1 \text{ amu} = 1.664 \times 10^{-27} \text{ kg}$$

$$= 1.664 \times 10^{-24} \text{ g}$$

So, 0.972 amu

$$= 0.972 \times 1.664 \times 10^{-24} \text{ g}$$

$$= 1.617 \times 10^{-24} \text{ g}$$

$$= 1.617 \times 10^{-27} \text{ kg}$$

Q.2 Find the vibrational freq & wave number of C–H bond in an alkane.

Given that: $K = 5 \times 10^5 \ g/s^2$

$m_C = 12$ amu & $m_H = 1$ amu

Sol^n:-

$$\mu_{C-H} = \frac{12 \times 1}{12+1} = 0.923 \text{ amu}$$

$$= 0.923 \times 1.664 \times 10^{-24} g$$

$$= 1.535 \times 10^{-24} g$$

Now,

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{5 \times 10^5 \ g/s^2}{1.535 \times 10^{-24} g}}$$

$$= \left(\frac{1}{3.14 \times 2}\right) \times 5.7 \times 10^{14} \ s^{-1}$$

$$\nu = 9.087 \times 10^{13} \ s^{-1}$$

$$\bar{\nu} = \frac{\nu}{c} = \frac{9.087 \times 10^{13} \ s^{-1}}{3 \times 10^{10} \ cm/s}$$

(cm^{-1})

$$= 3.029 \times 10^3 \ cm^{-1}$$

$$\bar{\nu} = 3029 \ cm^{-1}$$

Silicon

Assignment

Q.3

(A) Find the reduced mass of CO - molecule.

given: $m_C = 12$ amu, $m_O = 16$ amu

Ans: 11.38×10^{-27} kg

(B) Find the frequency of oscillation of CO molecule having $K = 1600$ N/m or kg/s^2

Ans: $\nu = 5.9 \times 10^{13}$ s^{-1}

Q.4 Find the force constant of C=C bond in an alkene if the stretching vibration of C=C bond is 5×10^{13} s^{-1}.

(Given, $m_H = 12$ amu)

Sol^n:-

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

$$\Rightarrow \boxed{K = 4\pi^2 \nu^2 \mu}$$

$$\mu_{C=C} = \left(\frac{12 \times 12}{12+12}\right) = 6 \text{ amu}$$

$$= 6 \times 1.664 \times 10^{-24} \text{ g}$$

$$= 9.984 \times 10^{-24} \text{ g}$$

Now,

$$K = 4\pi^2 \nu^2 \mu$$

$$= 4 \times (3.14)^2 \times (5 \times 10^{13}\ s^{-1})^2 \times (9.984 \times 10^{-24}\ g)$$

$$= 984382.46\ g/s^2 \text{ or } dyne/cm$$

Q.5 The wave number of H-Cl bond is $2890\ cm^{-1}$. Find the force constant of HCl molecule.

given: $m_H = 1\ amu$, $m_{Cl} = 35.5\ amu$

Soln:- $\bar{\nu} = 2890\ cm^{-1}$

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

$$\Rightarrow \nu = \bar{\nu} \times c$$

$$= 2890 \times 3 \times 10^{10}\ cm/s$$

$$= 8.67 \times 10^{13}\ s^{-1}$$

$$\mu_{HCl} = \left(\frac{1 \times 35.5}{1 + 35.5}\right) = 0.972\ amu$$

$$= 1.617 \times 10^{-24}\ g$$

Now,

$$K = 4\pi^2 \nu^2 \mu$$

$$= 4 \times (3.14)^2 \times (8.67 \times 10^{13}\ s^{-1})^2 \times 1.617 \times 10^{-24}\ g$$

$$= 479366.3\ g/s^2 \text{ or dyne/cm}$$

Q.6 Assignment

The vibrational frequency of CO molecule is 5.9×10^{13} Hz. Find μ and K.

given: $m_C = 12$ amu, $m_O = 16$ amu

(Ans: $\mu = 11.38 \times 10^{-27}$ kg, $K = 15.62$ kg/s^2)
$= 1562 \times 10^3$ g/s^2

(imp)

ISOTOPE EFFECT

Q.7 The C–H stretching vibration in $CHCl_3$ occurs at 3000 cm^{-1}. Find C–D stretching vibration in cm^{-1} in $CDCl_3$ molecule.

given: $m_H = 1$ amu, $m_D = 2$ amu

Soln:-

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

So,

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}} \quad \text{--- (1)}$$

$$\mu_{C-H} = \left(\frac{12 \times 1}{12+1}\right) = 0.923 \text{ amu}$$

$$\mu_{C-D} = \left(\frac{12 \times 2}{12+2}\right) = 1.714 \text{ amu}$$

from eqn (1)

$$\bar{\nu}_{C-D} = \bar{\nu}_{C-H} \times \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}}$$

$$= 3000 \times \sqrt{\frac{0.923}{1.714}}$$

$$= 3000 \times 0.733$$

$$\bar{\nu}_{C-D} = 2199 \text{ cm}^{-1}$$

$$\approx 2200 \text{ cm}^{-1} \quad \text{(Ans.)}$$

Selection Rule:-

'v' Vibrational quantum number changes by unity.

i.e $\Delta v = \pm 1$

Here '+' for absorption

'−' for emission of light

Vibrational Energy ($E_{vib.}$):

Vibrational Energy is in order of 1—100 kJ/mol.

The vibrational energy of a chemical bond is quantized.

So,

$$E_{vib.} = \left(v + \frac{1}{2}\right) h\nu \quad \text{(Joule)}$$

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

'v' is vibrational quantum number

If $v = 0$, then $\boxed{E_{vib} = \frac{1}{2} h\nu}$

⇒ energy of the lowest vibrational level of an oscillator is not zero but equal to $\frac{1}{2}h\nu$.

This energy is called Zero point Energy (ZPE).

for $v = 1$, $E_{vib} = (1 + \frac{1}{2})h\nu$

$= \frac{3}{2}h\nu$

for $v = 2$, $E_{vib} = \frac{5}{2}h\nu$

$v = 3$, $E_{vib} = \frac{7}{2}h\nu$

So, Spacing between two adjacent levels is,

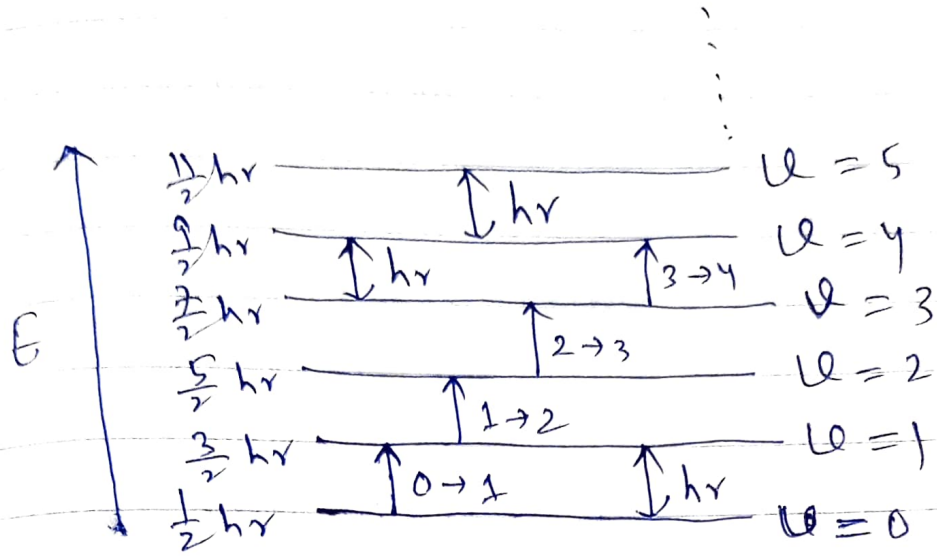
$$\Delta E_{vib} = E_{vib(v=2)} - E_{vib(v=1)}$$
$(v=1 \rightarrow v=2)$

$$= \frac{5}{2}h\nu - \frac{3}{2}h\nu$$

$$= h\nu$$

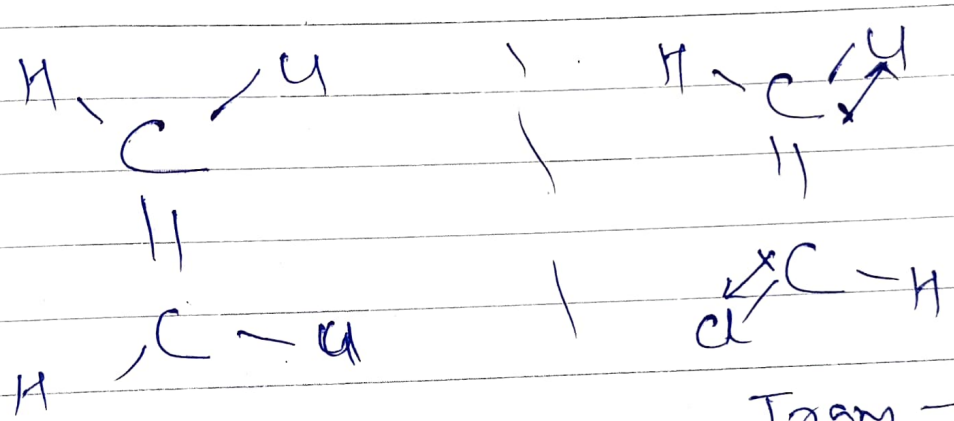
⇒ All vibrational energy levels

are equispaced by a value $h\nu$.



Q = Cis-1,2-dichloroethylene is IR-active while trans form is IR-inactive. Give reason.

Ans:



Cis-form has some net dipole moment IR-active

Trans-form net dipole moment = 0 Hence, IR-inactive

Q. Some of the fundamental vibrations are IR-active while others are not. Explain it.

Soln:- Let take the example of CO_2-molecule.

It is a linear molecule, so no. of fundamental vibrational modes $= 3N-5$ $(N=3)$

$= 9-5 = 4$ modes

i) $O=C=O$ Symm. Stretching (IR-inactive)

(no change in dipole moment)

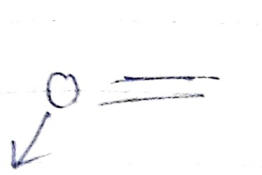
ii) $O=C=O$ Asymm. Stretching (IR-active)

(A change in dipole moment during vibration)

iii) Bending vibration

$\uparrow O=C=O \nearrow$ (IR-active)

$\downarrow$

iv)  (IR-active)

Q what do you mean by fundamental vibration? what is the formulae to calculate it for a linear molecule!

Soln:- The fundamental vibrational transition corresponds to transition of vibrating molecules from $v = 0$ level to $v = 1$ level.

For linear molecule,

No. of fundamental vibration

$= 3N - 5$

where, N = no of atoms in a molecule.

Numerical

Q1 Find vibrational energy spacing and ZPE for the given frequency, $\nu = 9 \times 10^{13}\ s^{-1}$.

Soln:- $\Delta E_{vib} = h\nu = 6.626 \times 10^{-34}\ J\cdot s \times 9 \times 10^{13}\ s^{-1}$

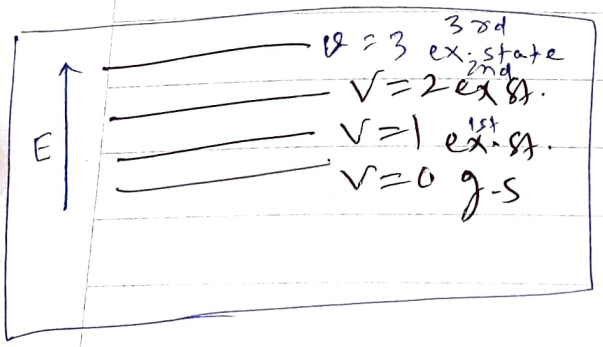
$= 59.63 \times 10^{-21}\ J$

$\Rightarrow PE = \frac{1}{2} h\nu = \frac{1}{2} \times 59.63 \times 10^{-21} J$

$= 29.81 \times 10^{-21} J.$

Q.2 Find the vibrational energy of a molecule for the 2nd excited state that vibrates with a frequency $3.1 \times 10^{13} s^{-1}$.

Soln:- Vibrational energy for the 2nd excited state ($v = 2$),



$E_{vib.} = (v + \frac{1}{2}) h\nu$

$= (2 + \frac{1}{2}) h\nu$

$= \frac{5}{2} h\nu$

$= \frac{5}{2} \times 6.626 \times 10^{-34} Js \times 3.1 \times 10^{13} s^{-1}$

$= 51.351 \times 10^{-21} J$

Q.3 Find the ν, $\bar{\nu}$, ZPE, ΔE_{vib} for CO-molecule.

Given, $K = 1860\ kg/s^2$,

$m_C = 12$ amu, $m_O = 16$ amu)

Soln:

$$\mu_{CO} = \left(\frac{12 \times 16}{12+16}\right) \text{amu}$$

$$= 6.857 \text{ amu}$$

$$= 6.857 \times 1.664 \times 10^{-27}\ kg$$

$$= 11.41 \times 10^{-27}\ kg$$

i) $$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} = \frac{1}{2 \times 3.14}\sqrt{\frac{1860\ kg\ s^{-2}}{11.41 \times 10^{-27}\ kg}}$$

$$= 3.971 \times 10^{14}\ s^{-1}$$

ii) $$\bar{\nu} = \frac{\nu}{c} = \frac{3.971 \times 10^{14}\ s^{-1}}{3 \times 10^{10}\ cm\ s^{-1}}$$

$$= 13236.66\ cm^{-1}$$

iii) $$\Delta E_{vib} = h\nu$$

$$= 6.626 \times 10^{-34}\ J\cdot s \times 3.971 \times 10^{14}\ s^{-1}$$

$$= 26.311 \times 10^{-21}\ J$$

iv) $$ZPE = \frac{1}{2} h\nu = 13.15 \times 10^{-21}\ J$$

Assignment

Calculate the K and ZPE of CO-molecule is the $\bar{\nu} = 2140 cm^{-1}$.

Given, At. mass of C = 19.9×10^{-27} kg

O = 26.6×10^{-27} kg

(Ans: $\mu = 11.38 \times 10^{-27}$ kg

$K = 1849$ kg/s^2,

$ZPE = 2.126 \times 10^{-20}$ J)

Applications of IR-Spectroscopy:

1. Identification of an organic compound with the help of finger print region.

2. To determine the presence of F.G in an org. compound

3. To study Keto - enol tautomerism

(4) To study geometrical isomerism

(5) To detect impurity in a compound

(6) To study the interaction between solute & solvent

(7) To study Isotope effect on the vibrational frequency

(8) To differentiate between the two compounds of same family

(9) To differentiate between intermolecular & intramolecular H-bonding

(10) It is very useful in the study of synthesis of nanoparticles