Spectroscopy:

It is the branch of science which deals with the study of the interactions between matter and electromagnetic radiations.

Spectrum:- It is defined as the characteristic wavelengths of electromagnetic, ~~spectrum~~ radiations that is emitted/absorbed by an object/atom/molecule.

Spectrum
↓
Absorption spectrum   Emission spectrum

Electromagnetic Spectrum:- It consists of entire range of light; from ~~Gamma~~ Cosmic rays to radio waves.
(Cosmic rays, γ-rays, X-ray, UV, Visible, IR, Microwave, Radiowave)

Atomic Spectra:- The spectrum of electromagnetic radiation observed ~~when~~ by absorbing/emitting during transitions of electrons between atomic energy levels.

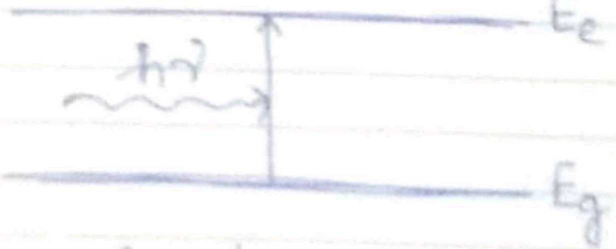
Molecular Spectra:- This is observed when the transition of electrons occurs between the molecular energy levels.

Origin of a Spectrum

Let us consider two molecular energy levels of an atom/molecule. The one with lower energy level is called ground state energy level (E_g) and one with higher energy is called excited state energy level (E_e).

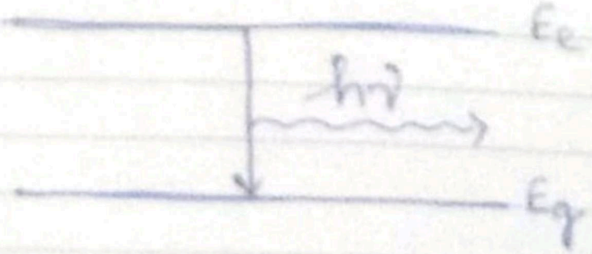
Spectrum is observed when a molecule/atom undergo transition between two energy levels either by absorbing or emitting energy.

Absorption Spectrum:



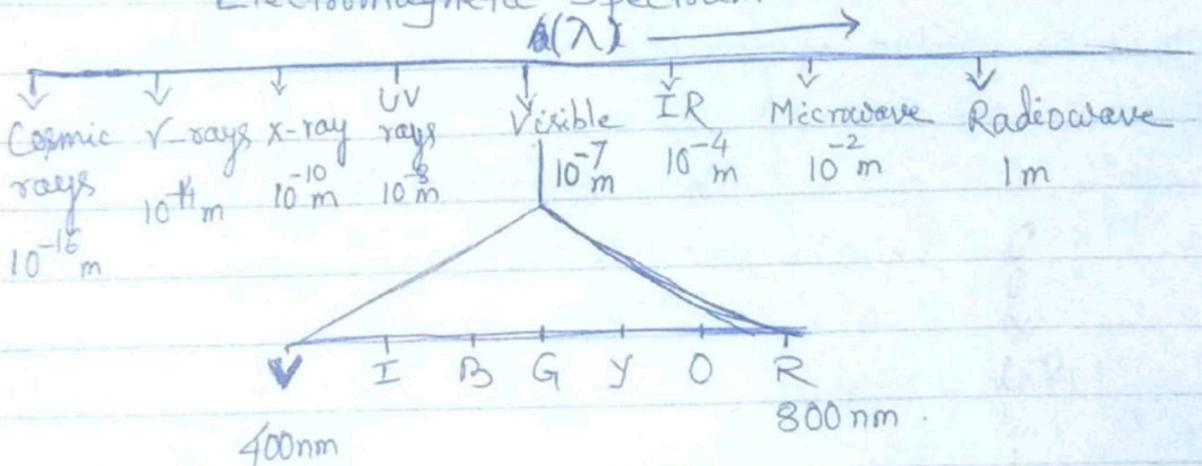
$\Delta E = E_e - E_g$

Emission Spectrum:



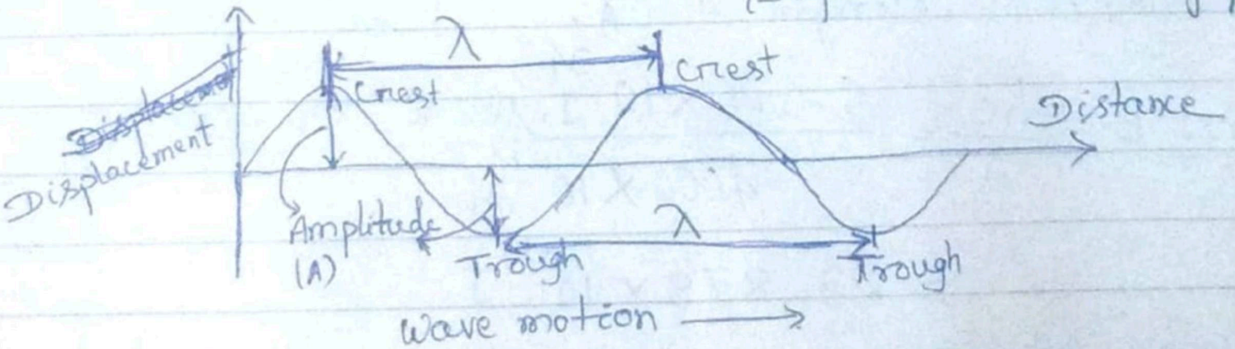
Electromagnetic Spectrum:~ The arrangement of all types of electromagnetic radiations in order of their increasing wavelength is known as electromagnetic spectrum.

Electromagnetic Spectrum



Wave parameters:

[Displacement - Distance graph]



(i) λ = Wavelength (distance between the two adjacent crests or troughs

Units = Å, m, nm, μm, pm

(ii) Wavenumber, $\bar{\nu} = \frac{1}{\lambda}$; Unit = cm^{-1}

(iii) Frequency, $\nu = \frac{c}{\lambda}$, Unit = sec^{-1} or Hz .

(It is the number of waves which can pass through a point in one second)

(iv) Energy, $E = h\nu = hc/\lambda$; Unit = Kcal, Cals, Joule

$c = 3 \times 10^{8}\ m/sec = 3 \times 10^{10}\ cm/sec$

$h = 6.626 \times 10^{-34}\ J.s$

(Planck's constant)

$1\ \mathring{A} = 10^{-10}\ m$; $1\ nm = 10^{-9}\ m$; $1\ pm = 10^{-12}\ m$

Question :- Calculate the energy associated with a light of wavelength 4000 Å.

Ans: $E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ J.sec \times 3 \times 10^{8}\ m/sec}{4000 \times 10^{-10}\ m}$

$\simeq 23.878 \times 10^{-19}\ J.$

(4)

UV- Visible Spectroscopy:

It deals with the electronic transition between the molecular orbital energy levels, when a molecule absorbs electromagnetic radiation of wavelength 200 nm to 800 nm. The wavelength of UV-radiation is 200 nm to 400 nm & that of visible radiation is 400 nm to 800 nm.

→ It is also called 'Electronic spectroscopy'.

→ It refers to 'Absorption spectroscopy'

Laws of Absorption: There are two laws:

1.) Lambert's law

2.) Beer - Lambert's law

1.) Lambert's law:~ It states that when a beam of monochromatic light passes through an absorbing medium, the rate of decrease in the intensity of radiation is proportional to the intensity of the incident radiations.

Mathematically, $-\frac{dI}{dx} = KI$ ..... (i)

$\Rightarrow -\frac{dI}{I} = k\,dx$ ..... (ii)

Integrating eq^n (ii), we get,

$\Rightarrow \boxed{I = I_0 e^{-kx}}$ ..... (iii)

I = Intensity of transmitted light

I_0 = Intensity of incident light

x = path length.

I/I_0 = Transmittance (T), k = constant

2.) **Beer-Lambert's law:-** It states that when a beam of monochromatic light passes through a homogeneous absorbing medium, the rate of decrease in the intensity of light is proportional to the intensity of the incident radiation and concentration of the solution.

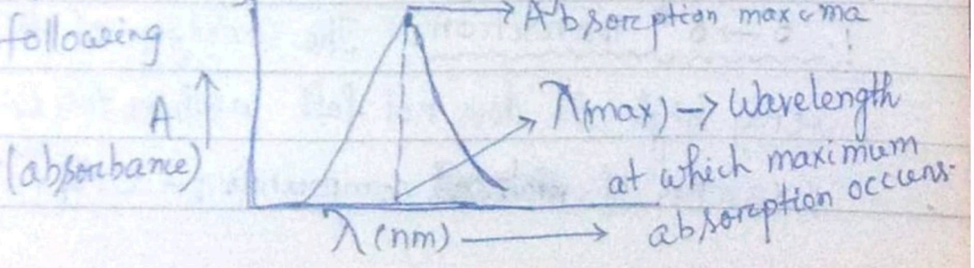
Mathematically, $\log \frac{I_0}{I} = \epsilon c x$

or, $\boxed{A = \epsilon C x}$; $A = \log \frac{I_0}{I}$

A = optical density or absorbance (A), (no unit)
I_0 = intensity of incident light
I = intensity of transmitted light
ϵ = molar extinction coefficent (Unit = lit. $mole^{-1}$. cm^{-1})
C = concentration of the solution.
x = path length (in cm)

Relation between A & T:~ $\boxed{A = -\log_{10} T = \log_{10}\left(\frac{1}{T}\right)}$

If we plot a graph by taking 'A' vs wavelength of radiation; we will get the following curve;



Limitations of Beer-Lambert's law:-

1. It is applicable to very dilute solutions.
2. The solvent used for making solutions should be transparent.
3. The solution should not contain any colloidal particle.
4. Temperature affects the absorption of radiation. On increasing the temperature, bathochromic shift (shifting of absorption towards longer wavelength) occurs.
5. Monochromatic light should be used for absorption.

Principle of UV-Visible spectroscopy:-

Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of UV/visible light to excite these electrons to higher anti-bonding molecular orbitals

There are four possible types of transitions.

Types of transitions:

1. **$\sigma \rightarrow \sigma^*$ transition:-** The energy of this transition is very high. It does not fall within the UV-Visible range

Examples of compounds :- CH_4, C_2H_6, etc

2.) $n \to \sigma^*$ transitions: Saturated compounds containing atoms with lonepaired (unpaired) electrons (called nonbonding electrons) allows this type of transitions. The energy required for this transition is less than the energy needed for $\sigma \to \sigma^*$ transitions.

Examples: CH_3Cl, CH_3OH, CH_3NH_2, etc.

3.) $\pi \to \pi^*$ transitions: Absorption bands for the organic compounds having unsaturation fall in UV-visible range. The energy required for this transition is less than the energy needed for $n \to \sigma^*$ transitions.

Examples: $H_2C=CH_2$, $HC \equiv CH$, etc.

4.) $n \to \pi^*$ transitions: This type of transition requires very less energy than other types of transitions. Increasing polarity of the solvent, $n \to \pi^*$ transitions are shifted to shorter wavelengths. (blue shift); $H_3C-\overset{O}{\overset{\|}{C}}-CH_3$, ketones, aldehydes, etc.

The energy of transitions decreases in the order;

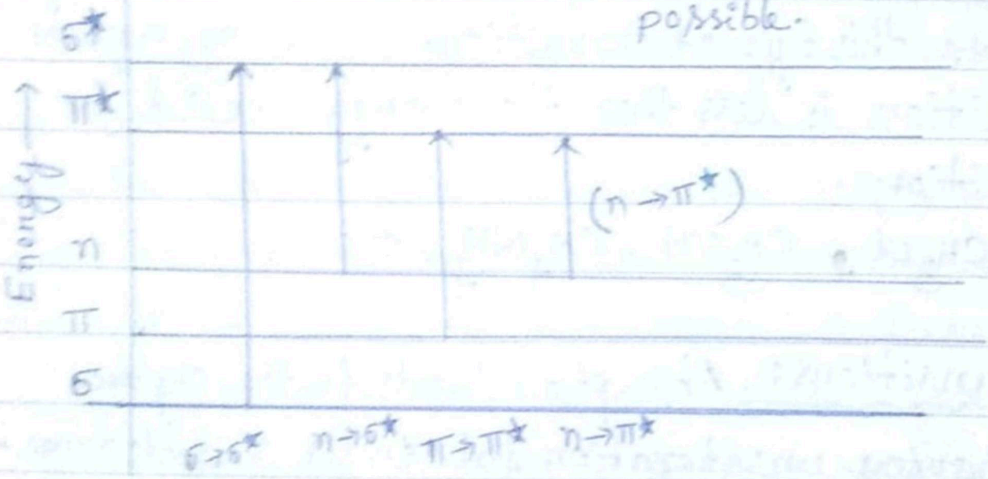
$$\sigma \to \sigma^* > n \to \sigma^* > \pi \to \pi^* > n \to \pi^*$$

$\xrightarrow{\hspace{3cm}}$ decreases

(energy of transition)

P.T.O

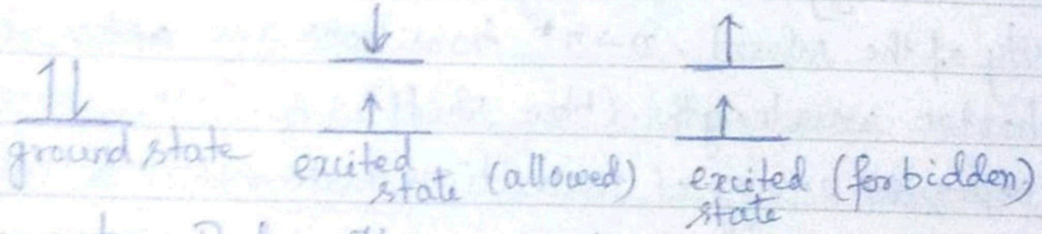
σ→π* & π→σ* transitions are forbidden transitions and only theoretically possible.



Energy level diagram.

Selection Rules:

1. Spin Rule: $\Delta S = 0$; Changes in spin multiplicity are forbidden.



2. Symmetry Rule: There must be a change in the symmetry of the complex / compound

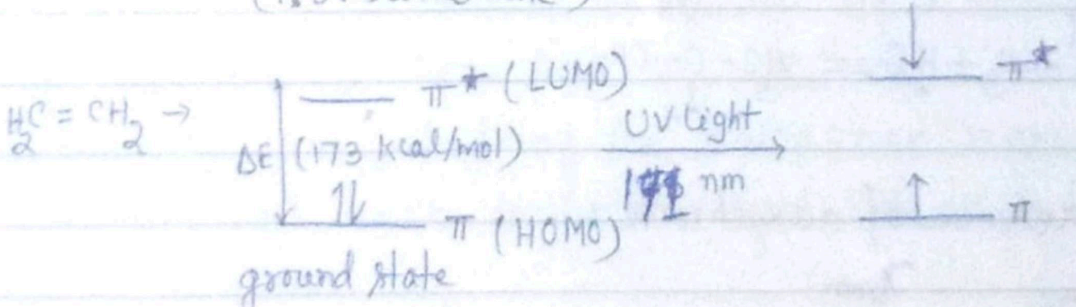
$\Delta L = 0, \pm 1$

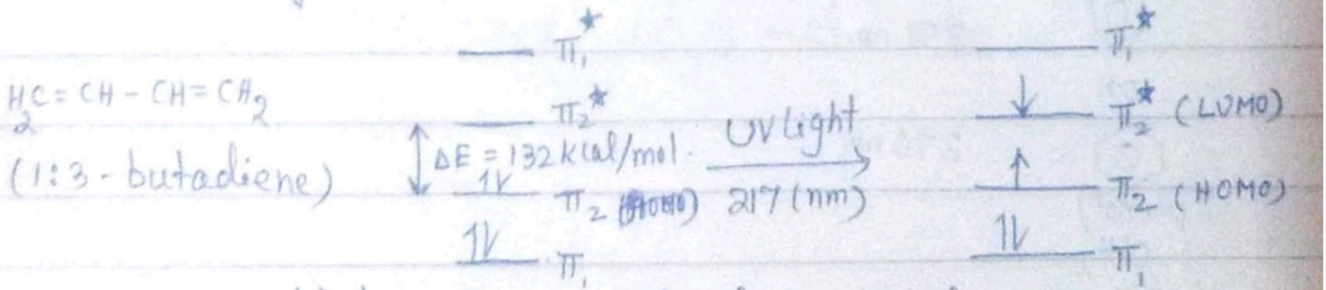
Factors affecting ~~absorption~~ absorbance:

1. Effect of conjugation:- If number of conjugated double bond is more in a compound, then the λmax value will be shifted to longer side. Less energy will be required to have electronic transitions.

Example:

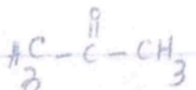
Compound	λmax (nm)
$H_2C = CH_2$ (Ethylene)	~~[illegible]~~ 171
$H_2C = CH - CH = CH_2$ (1:3-butadiene)	217



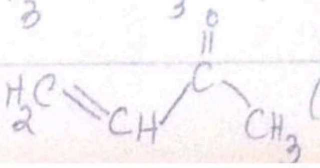


HOMO = Highest occupied molecular orbital

LUMO = Lowest unoccupied molecular orbital



$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$ → 279 nm



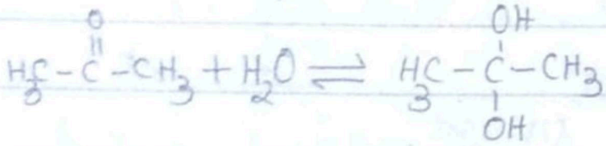
(ethyl methyl ketone ~~[illegible]~~) → 290 nm. (or But-3ene-2one) IUPAC

Number of conjugation reduces the energy gap between HOMO and LUMO.

2. Effect of Solvent:

Polarity of the solvent affects the absorption maxima of a compound.

Compound	Solvent	λmax
Acetone	n-hexane (non-polar)	279 nm
Acetone	water (polar)	264 nm

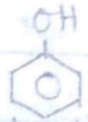


$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O \rightleftharpoons H_3C-\underset{OH}{\overset{OH}{C}}-CH_3$

3. Presence of auxochrome:

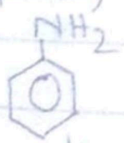
λmax

255 nm



270 nm

(phenol)



280 nm

(aniline)

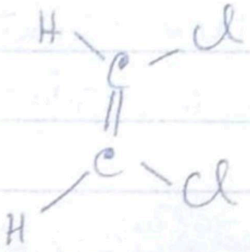
4. Steric Effect

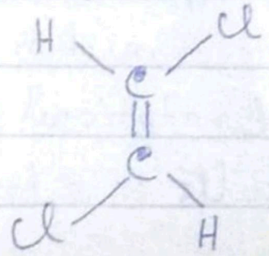
As steric effect in a molecule distorts its geometry, it disturbs conjugation. So it causes blue shift, i.e. λ_{max} value decreases.

Examples:

(1) Cis-isomer absorbs at shorter wavelength than trans-isomers.

Cis-1,2-dichloro ethylene ; Trans-1,2-dichloroethylene

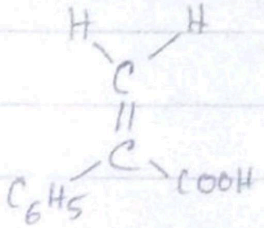




Due to steric effect ϵ_{max} occurs at shorter wavelength

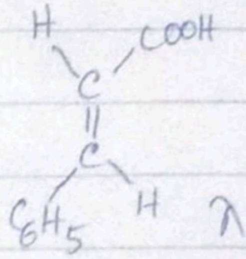
No steric effect, so ϵ_{max} occurs at longer wavelength.

(2)



$\lambda_{max} = 268\ nm$

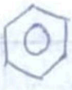
Cis - cinnamic acid

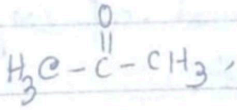


$\lambda_{max} = 272\ nm$

trans - cinnamic acid

Chromophore: It is ~~found~~ defined as any isolated part of a molecule which can absorb light in UV and visible range and ~~reflect~~ may or may not reflect colour.

Examples: $H_2C=CH_2$, , $H_2C=CH-CH=CH_2$, H_3C-Cl, etc.



$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$,

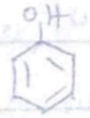
Auxochrome: It is a group of atoms which will impart a particular colour when attached to a chromophore, but alone can not act as a chromophore. It ~~w~~ can increase the intensity of colour of a chromophore by sharing its lone pair of electrons.

→ It helps in shifting the absorption maxima of a compound more towards longer side or bathochromic shift occurs.

Examples: $-\ddot{O}H$, $-NH_2$, $-NO_2$, $-Cl$, etc.

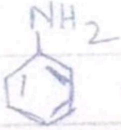
λ_{max}

→ 255 nm



→ 270 nm

phenol



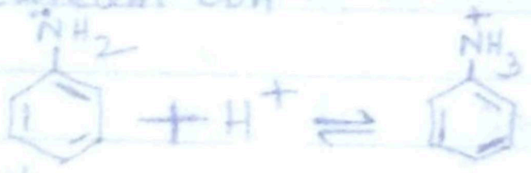
→ 280 nm

Absorption And Intensity Shifts

1. Hypsochromic Shift/Effect (Blue Shift):

It is an effect due to which the absorption maximum is shifted towards shorter wavelength due to the removal of conjugation or due to ~~by~~ the change of polarity of solvent.

Ex: ϵ_{max} (absorption maximum) occurs at 280 nm in Aniline, since lone pair electrons on 'N' atoms is in conjugation with the π-bond system of the benzene ring, but in acidic solutions, ϵ_{max} occurs at 265 nm. A blue shift occurs due to the formation of anilinium ion.



(removal of conjugation)

aniline
280 nm (λ_{max})

anilinium ion 265 nm (λ_{max})

2. Bathochromic Shift/Effect (Red Shift):-

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

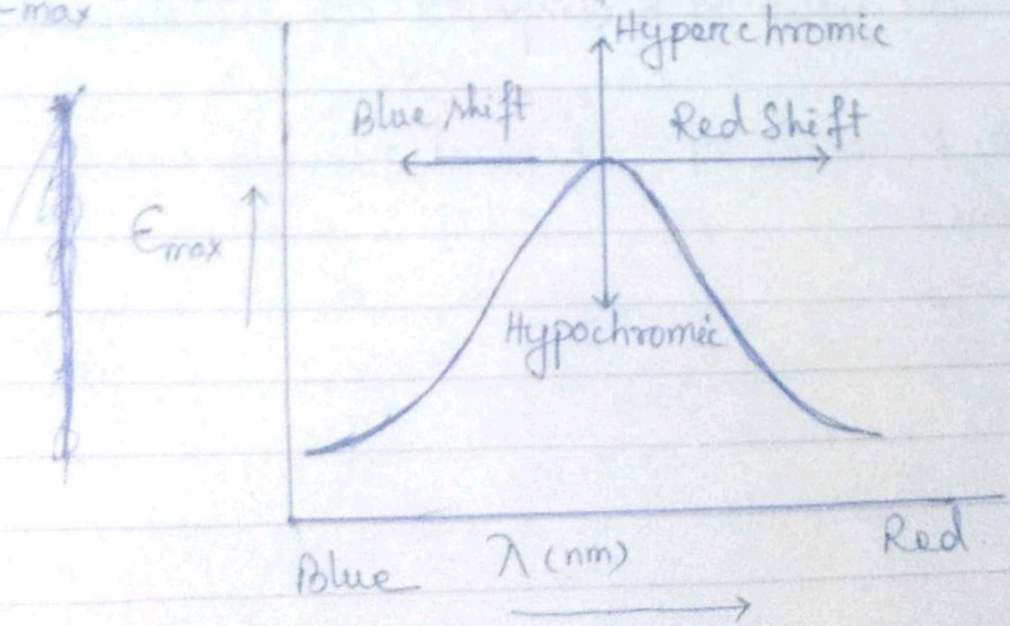
Ex: The $n \rightarrow \pi^*$ transition in acetone shows red shift when the polarity of the solvent is decreased.

Acetone in n-hexane, λ_{max} at 279 nm ; in water λ_{max} at 264 nm

3. Hyperchromic Shift/Effect: It is an effect due to which the intensity of ϵ_{max} increases.

4. Hypochromic Shift/Effect: It is an effect due to which the intensity of ϵ_{max} value decreases.

ϵ_{max} = molar extinction coefficient



Applications : (of UV-Visible spectroscopy)

1. Used in analytical chemistry for the quantitative determination of transition metal ions, conjugated organic compounds and biological macromolecules.

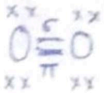
2. Detection of impurities :- It is one of the method to detect impurities in organic compound.
3. Determination of molecular weight by using Beer-Lambert's law.
4. Functional group of a compound can be identified.

5. Kinetics of a chemical reaction can be determined.

(7.1)

What are the possible types of transitions observed in the following molecules / compounds?

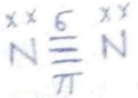
i) O_2 → Types of transitions:



$\overset{xx}{\underset{xx}{O}} \overset{\sigma}{\underset{\pi}{=}} \overset{xx}{\underset{xx}{O}}$ → $\sigma \to \sigma^*$, $n \to \sigma^*$, $\pi \to \pi^*$, $n \to \pi^*$

(x = non bonding / lone pair electron)

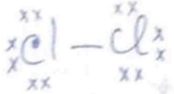
ii) N_2 →



$\overset{xx}{N} \overset{\sigma}{\underset{\pi}{\equiv}} \overset{xx}{N}$ (1 - σ bond
2 - π bonds)

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

iii) Cl_2 →



${}^{x}_{x}\overset{xx}{\underset{xx}{Cl}} - \overset{xx}{\underset{xx}{Cl}}{}^{x}_{x}$

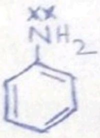
[Electronic Configuration:
$[Ne]\,3s^2 3p^5$]

Transitions: $\sigma \to \sigma^*$, $n \to \sigma^*$

iv) Benzene,

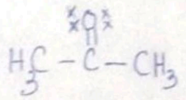
Transitions: $\sigma \to \sigma^*$, $\pi \to \pi^*$

v) Aniline ($C_6H_5NH_2$),



Transitions: $\sigma \to \sigma^*$, $\pi \to \pi^*$, $n \to \sigma^*$; (no $n \to \pi^*$)

vi) Acetone,



$H_3C-\overset{\overset{xx}{O}}{\overset{\|}{C}}-CH_3$

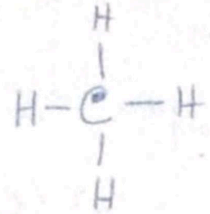
Transitions: $\sigma \to \sigma^*$, $\pi \to \pi^*$, $n \to \sigma^*$, $n \to \pi^*$

vii) H_2, H − H

Transition: $\sigma \to \sigma^*$

(7.2)

viii) CH_4 ,



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

Transition : $\sigma \rightarrow \sigma^*$.

ix) $H_2C = CH_2$; Ethylene .

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

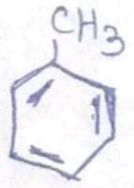
x) $H_3C-\overset{\times\times}{N}H_2$ (Methyl amine)

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

xi) $CH_3-\overset{\times\times}{\underset{\times\times}{O}}H$

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

xii) Toluene: ,



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

JANUARY
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WEDNESDAY 06
Week - 2nd • 006-359
Appointments

Questions

1. The % of transmittance of an aqueous solution of a compound is 30 %. Calculate its absorbance.

Ans: $T = 30\% = \frac{30}{100} = 0.3$

$A = \log\frac{1}{T} = \log\frac{1}{0.3} = 0.52$

2. The absorbance of an aqueous solution of a compound is 0.5. Calculate the % of transmittance.

Ans: $A = \log\frac{1}{T}$

$\Rightarrow 0.5 = \log\frac{1}{T}$

$\Rightarrow \frac{1}{T} = \text{antilog}(0.5) =$ ~~0.3162~~ 3.162

$\Rightarrow T = 0.3162$

% of Transmittance = 31.62 %

Appointments

3. The % transmittance of an aqueous solut of a compound is 20% at 25°C and 300 nm for a 4×10^{-5}M solution in a 2cm. Cell. Calculate, i) Absorbance (A); ii) The molar extinction or absorption coefficient; iii) The % of 'T' of a 2×10^{-5}M solution in a 4cm cell.

Ans: i) Absorbance, $A = \log\frac{1}{T} = \log\frac{100}{20} = 0.6$

ii) $A = \epsilon C x$

$$\Rightarrow \epsilon = \frac{A}{Cx} = \frac{0.699}{4\times10^{-5}M\times 2cm} = 8.7\times10^{3}M^{-1}Cm^{-}$$

iii) $A = \epsilon C x = 8.7\times10^{3}\times2\times10^{-5}\times4 = 0.696$

$$\Rightarrow A = \log\frac{1}{T}$$

$$\Rightarrow 0.696 = \log\frac{1}{T}$$

$$\Rightarrow \frac{1}{T} = \text{antilog}(0.696) = 4.966$$

$\Rightarrow T = 0.2$; So % of T = 20%.

4. A light of wavelength 500 nm is passed through a cell of 2 mm path length containing 10^{-3} mol / dm^3 of a compound X. If the absorbance of this solution is 0.5, calculate the molar absorption coefficient and transmittance.

Ans: $A = \varepsilon c x$

$$\Rightarrow \varepsilon = \frac{A}{cx} = \frac{0.5}{10^{-3} \times 0.2\,cm} = 2.5 \times 10^{3}\, dm^{3}\, mol^{-1}\, cm^{-1}$$

$$A = \log \frac{1}{T}$$

$$\Rightarrow 0.5 = \log \frac{1}{T}$$

$$\Rightarrow \frac{1}{T} = \text{antilog}\,(0.5) = 3.162$$

$\Rightarrow T = 0.3162$; So % of T = 31.62 % .

IR Spectroscopy

IR spectroscopy deals with the study of interaction of molecules with IR radiations.

Range of IR-radiation:

IR-radiation : **Range of wavelength** 0.8 µm to 200 µm

$(1\,\mu m = 10^{-6} m$
$= 10^{-4} cm)$

In terms of wavenumber; $(\bar{\nu} = \frac{1}{\lambda})$

Range : 12,500 cm^{-1} to 50 cm^{-1}

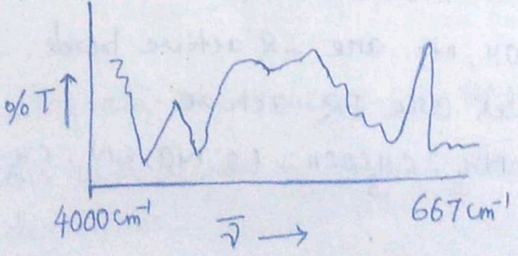
	Range
Near IR →	12500 to 4000 cm^{-1} (OR 0.8 to 2.5 µm)
IR →	4000 cm^{-1} to 667 cm^{-1} (OR 2.5 to 15 µm)
Far IR →	667 cm^{-1} to 50 cm^{-1} (OR 15 to 200 µm)

Question: wavelength of IR radiation is 2.5 µm. Find the wavenumber of IR radiation.

Ans: $\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2.5 \times 10^{-4} cm} = 4000\ cm^{-1}$

The ordinarily IR region lies between 4000 to 667 cm^{-1}, which is useful for the scientists.

IR Spectrum: It is a graph, which is plotted by taking % Transmittance Vs Wavenumber.



(2)

This spectrum gives sufficient information about the structure of a compound, presence of a functional group, etc. This spectrum consists of a large number of absorption bands.

Imp When IR-radiation is absorbed by a molecule, it causes vibration in a molecule. Due to vibration, the bonds undergo stretching and bending.

Imp So IR-spectroscopy is also called vibrational Spectroscopy.

Principle of IR-Spectroscopy:

The absorption of IR-light causes an excitation of a molecule from ground state to higher vibrational energy levels.

All molecules are not capable of absorbing IR-light but only the molecules which show change in their dipole moments, can absorb IR-light.

Imp So the molecules, whose dipole moments change with change in bond distances, are called IR-active molecules. $\left[\frac{d\mu}{dx} \neq 0\right.$, $d\mu$ = change in dipole moment, dx = change in bond distance$\left.\right]$

Examples of IR-active molecules:

$-C=O$, $N-H$, $-OH$, etc are IR active bonds.

All polar molecules are IR active.

CH_3-OH, HCl, HF, NH_3, CH_3COCH_3, CO, NO, CN, CH_3-NH_2, CH_3-Cl, etc.

On the otherhand, the molecules, whose dipole moments do not change with change in bond distances, are called IR - inactive molecules.

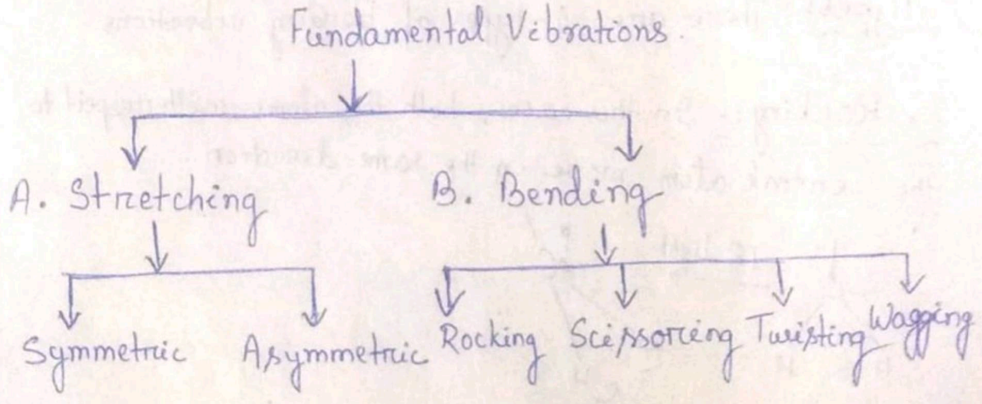
Imp
All non - polar molecules are IR - inactive.

Examples: H_2, O_2, C_6H_6, CCl_4, $CH_2=CH_2$, $CH\equiv CH$, Cl_2, etc.

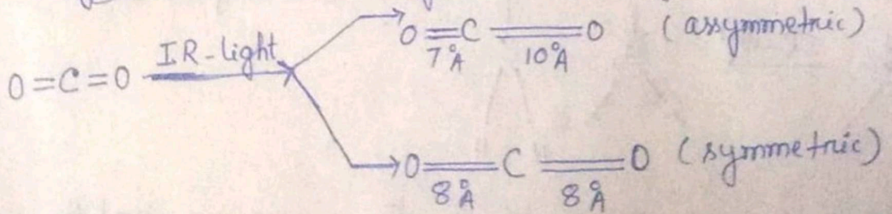
(Non - polar molecules)

Molecular Vibrations:

When IR-active molecule absorbs IR-light, vibrational energy of the molecule increases. This causes two types of fundamental vibrations:



Stretching:- In this type bond length changes, but ~~1. Symmetrical stretching:~~ bond angle remains same.



Types:

1. Symmetric stretching:- In this case, the movement of atoms with respect to central atom in a molecule is in same directions

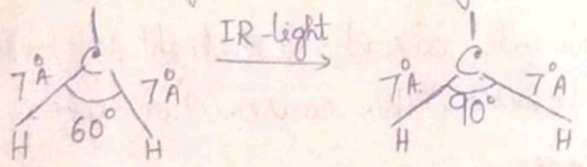
Example: $\mathrm{O{=}C{=}O} \xrightarrow{\text{IR-light}} \mathrm{O}\underset{8\mathring{A}}{=\!=}\mathrm{C}\underset{8\mathring{A}}{=\!=}\mathrm{O}$

2. Assymetric stretching: In this type, ~~one~~ the stretching of bond length is not symmetrical.

Examples: $\mathrm{O{=}C{=}O} \xrightarrow{\text{IR-light}} \mathrm{O}\underset{7\mathring{A}}{=\!=}\mathrm{C}\underset{10\mathring{A}}{=\!=\!=\!=}\mathrm{O}$

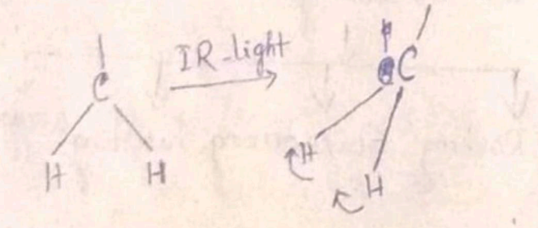
CO_2 is IR active in assymetric stretching.

B. Bending: In this case, bond angles change, but bond lengths donot change.

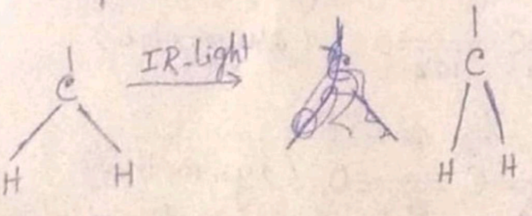


Types: There are 4-types of bending vibrations.

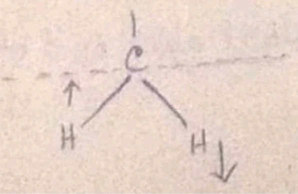
1. Rocking:- In this case, both the atoms with respect to the central atom move in the same direction.



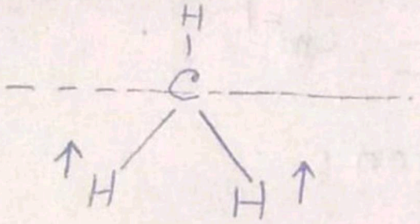
2. Scissoring:- In this case, both the atoms with respect to the central atom move towards each other. or away from each other.



3. Twisting: In this case, one atom moves up, and the other one moves down the plane w.r.t. the central atom.



4. Wagging: In this case, both the atoms move up and down w.r.t. the central atom.



Since, more energy is required to stretch one spring than to bend it, so stretching absorption of a molecular bond ~~requ~~ occurs at higher frequency as compared to bending absorption of same bond.

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \left[\text{So } E \propto \nu \text{ or } \bar{\nu} \right]$$

ν = frequency

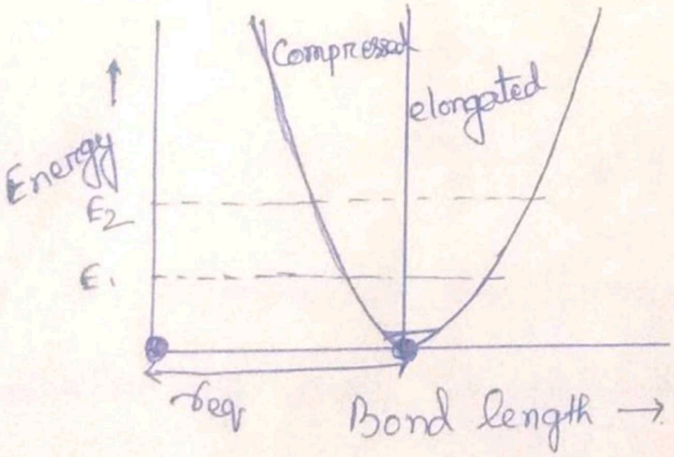
λ = wavelength

$\bar{\nu}$ = wavenumber

5.1

Vibrational energy and Frequency of vibration of a diatomic molecule:

The two atoms in a diatomic molecule will be under the influence of force of attraction (between the electrons of one atom and the nucleus of other atom) and repulsion (interelectronic and internuclear repulsion). The two atoms place themselves at a minimum distance to balance these forces and to achieve minimum energy. This minimum distance is called internuclear distance or bond length of a molecule. The internuclear distance is generally called as equilibrium distance (r_{eq}). On vibrations, this bond exhibits certain vibrational frequency which is dependent on mass of the system and force constant but independent of the extent of small distortion. This is similar to that of simple Harmonic oscillator.



Vibrational frequency: (ν)

The vibrational frequency (ν) of a bond can be calculated by using the following relation;

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

It is the measure of bond strength

Unit = gm/sec^2 or dyne/cm.

μ = Reduced mass

$$= \frac{m_1 \times m_2}{m_1 + m_2}$$, Unit = gm or kg.

m_1 = mass of one atom (1).

m_2 = mass of other atom (2).

ν = Fundamental vibrational frequency.

Unit = Sec^{-1}, Hz.

(6)

Vibrational wavenumber ($\bar{\nu}$):-

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \ \text{cm}^{-1}$$

According to the equation;

If K value increases, then both $\bar{\nu}$ & ν increase.

If μ value increases, then both $\bar{\nu}$ & ν decrease.

Questions:

1. Calculate the reduced mass of C-H bond, given $m_C = 12\,\text{amu}$, $m_H = 1\,\text{amu}$.

Ans:

$$\text{Reduced mass } (\mu) = \frac{m_1 \times m_2}{m_1 + m_2}$$

Let $m_1 = m_C = 12\,\text{amu}$
$m_2 = m_H = 1\,\text{amu}$

$$\text{So } \mu = \frac{12 \times 1}{12+1} = \frac{12}{13} = 0.9231\,\text{amu}$$

$1\,\text{amu} = 1.664 \times 10^{-24}\,\text{gm} = 1.664 \times 10^{-27}\,\text{kg}$

$$\text{So } \mu = 0.9231 \times 1.664 \times 10^{-24}\,\text{gm}$$
$$= 1.536 \times 10^{-24}\,\text{gm}$$

2. Calculate reduced mass of C-O bond, given $m_C = 12\,\text{amu}$ & $m_O = 16\,\text{amu}$.

Ans:

$$\text{Reduced mass, } \mu = \frac{12 \times 16}{12+16}\,\text{amu}$$
$$= 6.857\,\text{amu}$$
$$= 6.857 \times 1.664 \times 10^{-24}\,\text{gm}$$
$$= 11.41 \times 10^{-24}\,\text{gm}$$

(7)

3. Calculate the force constant of CO molecule, if vibration wavenumber is $3000\ cm^{-1}$. Given $m_C = 12\ amu$ & $m_O = 16\ amu$.

Ans: μ of CO $= \frac{12\times16}{(12+16)} \times 1.664\times10^{-24}\ gm$

$= 11.41\times10^{-24}\ gm$.

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

$\Rightarrow K = 4\pi^2 c^2 \mu (\bar{\nu})^2$

$= 4\times(3.14)^2 \times (3\times10^{10}\ \frac{cm}{sec})^2 \times 11.41\times10^{-24}\ gm \times (3000\ cm^{-1})^2$

$= 3644936.366\ gm/sec^2$ or $dyne/cm$.

4. Calculate the vibrational frequency and wavenumber of a $C=C$ bond, given that $K = 10\times10^5\ dyne/cm\ (erg/sec^2)$ $m_C = 12\ amu$.

Ans: $\mu = \frac{12\times12}{12+12} = \frac{12}{2} = 6\ amu$

$= 6\times1.664\times10^{-24}\ gm = 9.984\times10^{-24}\ gm$

Now, $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} = \frac{1}{2\times3.14}\sqrt{\frac{10\times10^5}{9.984\times10^{-24}}}$

$= 5.0395\times10^{3}\ sec^{-1}$

$\bar{\nu} = \frac{\nu}{c} = \frac{5.0395\times10^{3}\ sec^{-1}}{3\times10^{10}\ cm/sec} = 1679.83\ cm^{-1}$

Vebrational Energy: (E_{vib})

The vibrational energy of a chemical bond is quantized. It can be calulated by using the following equation;

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

v = vibrational quantum number.
= 0, 1, 2, 3, ...

h = Planck's constant = 6.626×10^{-34} J.s

ν = Vibrational frequency

The energy difference between the two vibrational energy level is;

$$\Delta E_{vib} = E_2 - E_1$$

$$= \left(1 + \frac{1}{2}\right) h\nu - \left(0 + \frac{1}{2}\right) h\nu \ [v = 0 \rightarrow 1]$$

$$= h\nu \ J \quad \text{------} \ (2)$$

Zero-point energy: (ZPE): It is the lowest possible energy that a molecule/quantum mechanical system may have in the ground state. The molecule constantly vibrates in the ground state, because vibrational energy is not zero in the ground state.

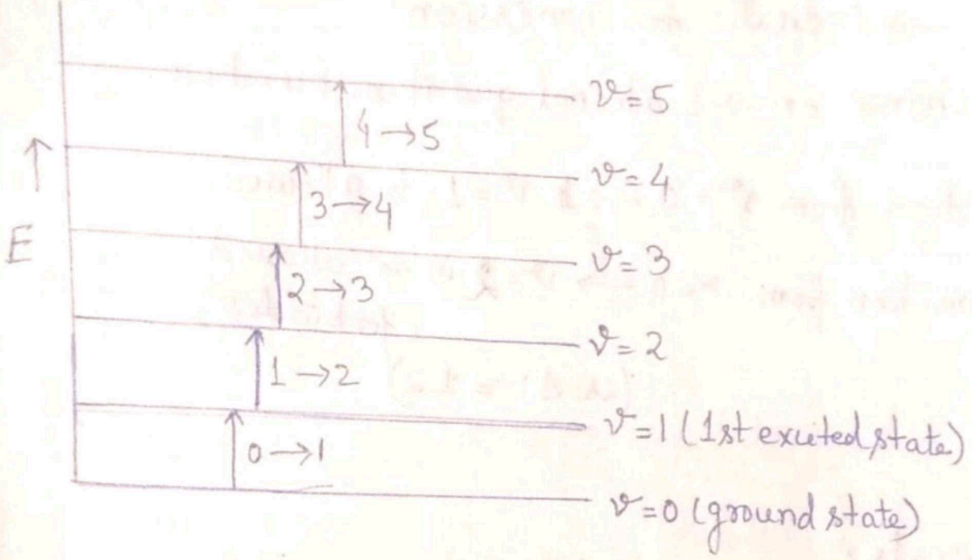
$$E_{vib} = \left(v + \frac{1}{2}\right) h\nu$$

In the ground state, $v = 0$,

$$\text{So } \boxed{E_{vib} = \frac{1}{2} h\nu \ J} \ \text{------} \ (3)$$

→ This is called 'Zero point energy'.

Energy difference between the two successive energy levels:



1. When transition occurs from $0 \to 1$

$$\Delta E_{vib} = E_1 - E_0$$
$$= \left(1+\tfrac{1}{2}\right)h\nu - \tfrac{1}{2}h\nu$$
$$= \tfrac{3}{2}h\nu - \tfrac{1}{2}h\nu$$
$$= h\nu \text{ J}$$

2. When transition occurs from $1 \to 2$

$$\Delta E_{vib} = E_2 - E_1$$
$$= \left(2+\tfrac{1}{2}\right)h\nu - \left(1+\tfrac{1}{2}\right)h\nu$$
$$= \tfrac{5}{2}h\nu - \tfrac{3}{2}h\nu$$
$$= h\nu \text{ J}$$

So all energy levels are equally spaced and Energy difference is $h\nu$.

Selection Rule:

$\Delta v = \pm 1$

$+1 \rightarrow$ indicates for absorption

$-1 \rightarrow$ indicates for emission

Δv = change in vibrational quantum number.

Transition from $v = 0 \rightarrow v = 1$ is allowed.

But transition from $v = 0 \rightarrow v = 2$ is not allowed (forbidden)

(as $\Delta v = \pm 2$)

Numericals:

1. Calculate the vibrational energy for the 1st transition state of a molecule, if vibrational frequency is 1000 sec⁻¹.

Ans: $v = 1$

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

$= (1 + \frac{1}{2}) \times 6.626 \times 10^{-34} \text{ Js} \times 1000 \text{ sec}^{-1}$

$= 9.939 \times 10^{-31} \text{ J}$

2. Calculate the zero point energy and spacing between two vibrational energy level of a molecule, if frequency of vibration is 3×10^{5} sec⁻¹.

Ans: Zero point energy $= \frac{1}{2} h\nu = \frac{1}{2} \times 6.626 \times 10^{-34} \times 3 \times 10^{5} \text{ J}$

$= 9.939 \times 10^{-29} \text{ J}$

$\Delta E_{vib} = h\nu = 2 \times 9.939 \times 10^{-29} \text{ J}$

$= 19.878 \times 10^{-29} \text{ J}$

3.) Calculate frequency of vibration, wavenumber, Zero-point energy and energy of vibration to undergo transition for CO molecule. Given $K = 1800\ kg/sec^2$ (N/m), $m_c = 12$ amu and $m_o = 16$ amu.

Ans:

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

$$\mu_{CO} = \frac{m_c \times m_o}{m_c + m_o} = \frac{12 \times 16}{12+16} \times 1.664 \times 10^{-27}\ kg$$

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

Now, i) $\nu = \frac{1}{2\pi}\sqrt{\frac{1800\ kg/s^2}{11.41 \times 10^{-27}\ kg}} = 3.971 \times 10^{14}\ s^{-1}$

ii) $\bar{\nu} = \frac{\nu}{c} = \frac{3.971 \times 10^{14}\ sec^{-1}}{3 \times 10^{10}\ cm/sec} = 1.3237 \times 10^{4}\ cm^{-1}$

iii) $ZPE = \frac{1}{2} h\nu\ J = \frac{1}{2} \times 6.626 \times 10^{-34} \times 3.971 \times 10^{14}\ J$

$$= 13.1559\cancel{8} \times 10^{-20}\ J$$

iv) $\Delta E_{vib} = h\nu = 26.3118\cancel{8} \times 10^{-20}\ J$

4. Calculate the vibrational energy of 1st excited state and force constant of HF molecule, if its frequency of oscillation is $4 \times 10^{14}\ sec^{-1}$. Given At. mass of H = 1 u & F = 19 u.

Ans: Vibrational energy of 1st excited state,

$$E_{vib} = \left(v+\frac{1}{2}\right) h\nu\ J = \left(1+\frac{1}{2}\right) \times 6.626 \times 10^{-34} \times 4 \times 10^{14}\ J \quad [v = 1]$$

$$= \frac{3}{2} \times 6.626 \times 10^{-34} \times 4 \times 10^{14}\ J = 39.756 \times 10^{-20}\ J$$

Now, $\mu_{HF} = \frac{1 \times 19}{1+19} \times 1.664 \times 10^{-24}\ gm = 1.58 \times 10^{-24}\ gm$

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

$$\Rightarrow k = 4\pi^2 \mu \nu^2 = 4 \times (3.14)^2 \times 1.58 \times 10^{-24} \times (4 \times 10^{14})^2$$

$$= 997 \times 10^4 \text{ gm/sec}^2 \text{ (or dyne/cm)}$$

Finger print Region:

The region below the wavenumber, 1500 cm^{-1} is rich in many absorptions which are caused due to bending vibrations. This region (i.e. from 500 - 1500 cm^{-1}) is known as 'Finger print region'

Some substances containing the same functional group show similar absorption above 1500 cm^{-1}, but their absorption positions differ in the finger print region.

Number of Fundamental Vibrations:

Polyatomic molecules may exhibit more than one fundamental vibrations. This resuts in many absorption bands. The number of these bands is related to the 'Degree of freedom' in a molecule.

The total number of 'degree of freedom' of a molecule consisting of '**N**' number of atoms is '3**N**'.

The total number of 'degree of freedom' includes Rotational, Translational & Vibrational degree of freedom.

Calculation: (Degree of freedom)

1. For linear molecules:- (containing 'N' atoms)

Total number of degree of freedom = 3N

Translational degree of $\text{freedom}_{(T)} = 3$

Rotational degree of $\text{freedom}_{(R)} = 2$

So Vibrational degree of $\text{freedom}_{(V)} = 3N-5$

Examples of linear molecules: HCl, HF, CO, CO_2, OCS

$CH \equiv CH$, etc.

2. For Non-linear molecules :- (Containing 'N' atoms)

Total number of degree of freedom = 3N

Translational degree of $\text{freedom}_{(T)} = 3$

Rotational degree of $\text{freedom}_{(R)} = 3$

So Vibrational degree of $\text{freedom}_{(V)} = 3N-6$

Examples of non-linear molecules: H_2O, SO_2, C_6H_6, CH_4,

$POCl_3$, etc.

Questions

Calculate translational, rotational and vibrational degree of freedom of the following molecules: CO_2, CO, HCl, C_6H_6, $CHCl_3$, H_2O

Ans:

i) CO_2: It is linear

N = 3

So total number of degree of freedom = 3N = 9

Translational degree of freedom (T) = 3

Rotational degree of freedom (R) = 2

So Vibrational degree of freedom (V) = 3N-5 = 9-5 = 4

(14)

ii) CO : It is a linear molecule

$N = 2$

So total number of degree of freedom $= 3N = 6$

$T = 3$, $R = 2$; So $V = 3N - 5 = 6 - 5 = 1$

iii) HCl : It is a linear molecule

$N = 2$

So total number of degree of freedom $= 3N = 6$

$T = 3$, $R = 2$; So $V = 6 - 5 = 1$.

iv) C_6H_6 : It is a non-linear molecule.

$N = 12$

So total number of degree of freedom $= 3N = 36$

$T = 3$, $R = 3$; So $V = 3N - 6 = 36 - 6 = 30$.

v) $CHCl_3$: It is non linear

$N = 5$

So $3N = 15$ (Total number of degree of freedom)

$T = 3$, $R = 3$; So $V = 3N - 6 = 15 - 6 = 9$

vi) H_2O : Nonlinear molecule

$N = 3$, So $3N = 9$ (Total number of degree of freedom)

$T = 3$, $R = 3$; So $V = 3N - 6 = 9 - 6 = 3$

Applications of IR Spectroscopy:

i) Identification of an organic compound; from its finger print region.

ii) Structure of a compound can be determined.

iii) Quantitative analyses of functional groups (like, $-OH$, $-COOH$, $-\overset{\overset{O}{\|}}{C}$, etc.) can be done by this spectroscopy.

iv) Types of chemical reactions can be identified.

v) Impurities present in a compound can easily be ~~identified~~ detected.

vi) Positions of the functional groups in a molecule (like, cis & trans-isomers) can be easily identified.

vii) Study of keto-enol Tautomerism can be done.

viii) Quantitative estimation of organic compounds in a mixture can be done.

Questions & Answers

(IR Spectroscopy)

1. What is the range of IR-radiations?

Ans: Range : 2.5 to 15 μm or 4000 cm^{-1} to 667 cm^{-1}

2. Name various types of bending vibrations.

Ans: These are : i) Rocking,
ii) Scissoring
iii) Twisting
iv) Wagging.

3. What do you mean by 'Finger print region'?

Ans:- The region below the wavenumber, 1500 cm^{-1} is rich in many absorptions which are caused due to bending vibrations. This region (i.e. from 500 – 1500 cm^{-1}) is known as 'Finger print region'.

4. What do you mean by fundamental vibrations?

Ans: Fundamental vibrations correspond to the first vibrational transitions from $v=0$ to $v=1$ vibrational energy level.

5. Which of the following molecules are IR-inactive?

HF, CO, N_2, H_2, O_2

Ans: N_2, H_2 & O_2 ; as they are non-polar molecules.

6. Which of the following molecules are IR-active?

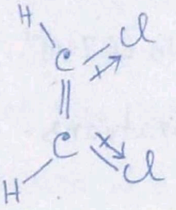
HCl, CH_4, $CH\text{-}Cl_3$, CCl_4, F_2.

Ans: HCl and $CH\text{-}Cl_3$ → They are polar molecules.

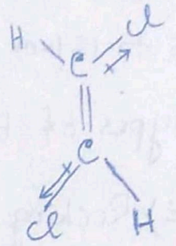
(2)

7. Cis - 1,2-dichloro ethylene is IR-active, whereas trans- 1,2-dichloro ethylene is IR-inactive. Give reason.

Ans:



Cis-1,2-dichloro ethylene has some net dipole moment, so it is IR-active



Trans-1,2-dichloro ethylene has no net dipole moment. So it is IR-inactive.

8. Mention the selection rule of vibrational spectroscopy.

Ans: $\Delta \nu = \pm 1$

9. Calculate the vibrational degree of freedom of CO_2 and CH_3Cl.

Ans: i) CO_2 → It is linear.

$n = 3$, So vibrational degree of freedom $= 3N-5$

$= 3 \times 3 - 5$

$= 4$

ii) CH_3Cl → It is non-linear

$n = 5$, So vibrational degree of freedom $= 3N-6$

$= 3 \times 5 - 6$

$= 9$

10. What is 'Zero point energy'?

Ans: It is the lowest possible energy, that a molecule has in the ground state. Since it is not '0', the molecule constantly vibrates in the ground state. In ground state, $\nu = 0$, So $E_{vib} = \frac{1}{2} h\nu$ Joule.

11.) Mention the factors, which affect vibrational frequency.

Ans: Vibrational frequency, $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$ sec^{-1} or Hz

Factors: i) Force constant, K

ii) Reduced mass.

12. The wave number of a C−H bond in a compound is 2910 cm^{-1}. Calculate its frequency of vibration.

Ans:- $\bar{\nu} = 2910\ cm^{-1}$

As, $\nu = \bar{\nu} \times C = 2910 \times 3 \times 10^{10}\ sec^{-1} = 8730 \times 10^{10}\ sec^{-1}$

13. What is the formula for calculating vibrational degree of freedom? for linear and non-linear molecules.

Ans: For linear molecules = 3N−5

For non-linear molecules = 3N−6

N = number of atoms in a molecule.

14. What is force constant of a molecule? Mention its unit.

Ans: Force constant is a measure of bond strength of a molecule.

Force constant, K of $C\equiv C > C=C > C-C$

Unit of K = g/sec^2 or dyne/cm

kg/sec^2 or N/m.

15. What is the energy difference between the two consecutive ~~energy levels~~ vibrational energy level?

Ans: $\Delta E_{vib} = h\nu$

16. Which form of stretching vibration in CO_2 molecule is IR-active?

Ans: Assymmetric stretching of CO_2 molecule is IR-active.

$O \underset{5\,Å}{=} C \underset{7\,Å}{=\!=\!=} O$, In this type net dipole moment is not zero. So it is IR-active.

Numericals:

1. The vibrational wavenumber of H–Cl bond in HCl molecule is $2900\ cm^{-1}$. Calculate the vibrational energy for the 1st excited state and force constant. ($m_H = 1u$, $m_{Cl} = 35.5u$)

Solution:

Given, $\bar{\nu} = 2900\ cm^{-1}$

So $\nu = \bar{\nu} \cdot c = 2900 \times 3 \times 10^{10} = 87 \times 10^{12}\ sec^{-1}$

$$\text{Now, } \mu_{HCl} = \frac{m_H \times m_{Cl}}{m_H + m_{Cl}} = \frac{1 \times 35.5}{1 + 35.5} \times 1.664 \times 10^{-24}\ gm$$

$$= \frac{35.5}{36.5} \times 1.664 \times 10^{-24}\ gm = 1.6184 \times 10^{-24}\ gm.$$

$$\text{Force constant, } K = 4\pi^2 \mu \nu^2$$

$$= 4 \times (3.14)^2 \times 1.6184 \times 10^{-24} \times (87 \times 10^{12})^2$$

$$= 483.107 \times 10^{3}\ g/sec^2$$

$$E_{vib} = (\nu + \tfrac{1}{2}) h\nu\ J = (1 + \tfrac{1}{2}) h\nu\ J \quad [\nu = 1, \text{ for 1st excited state}]$$

$$= \frac{3}{2} \times 6.626 \times 10^{-34} \times 87 \times 10^{12} = 864.69 \times 10^{-22}\ J$$

(5)

2. The C-H stretching vibration in chloroform ($CHCl_3$) occurs at 3000 cm^{-1}. Calculate the wavenumber of C-D stretching vibration in deutero chloroform ($CDCl_3$).
[Given $m_H = 1u$, $m_D = 2$, $m_C = 12u$, $m_{Cl} = 35.5u$]

Ans: The force constant for C-H & C-D stretching vibration is same.

$$\mu_{C-H} = \frac{12 \times 1}{12+1} u = \frac{12}{13} = 0.92 u$$

$$\mu_{C-D} = \frac{12 \times 2}{12+2} = \frac{24}{14} = 1.71 u$$

Since, $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ and k is same for C-H & C-D bond

So, for C-H bond, $\bar{\nu}_{C-H} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu_{C-H}}}$ ..... (i)

and for C-D bond, $\bar{\nu}_{C-D} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu_{C-D}}}$ ..... (ii)

~~From eqn (i) and (ii) we get~~ Taking the ratio of eqn (i) & (ii),

we get; $\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}}$

$$\Rightarrow \frac{\bar{\nu}_{C-D}}{3000} = \sqrt{\frac{0.92}{1.71}}$$

$$\Rightarrow \bar{\nu}_{C-D} = 3000 \times \sqrt{\frac{0.92}{1.71}} = 2190 \ cm^{-1}$$

3. Calculate the force constant, 'k' of O-H bond. Given, $m_O = 16$ amu, $m_H = 1$ amu and frequency of vibration $= 3 \times 10^{14} sec^{-1}$.

Ans: $\mu_{O-H} = \frac{16 \times 1}{16+1} \times 1.664 \times 10^{-24} gm = 1.566 \times 10^{-24} gm$.

$$K = 4\pi^2 \mu \nu^2 = 4 \times (3.14)^2 \times 1.566 \times 10^{-24} \times (3 \times 10^{14})^2$$
$$= 555.88 \times 10^4 \ gm/sec^2$$

4. The vibrational wavenumber of HCl molecule is 2900 cm^{-1}. Calculate the energy of transition during its vibration and the force constant. ($m_H = 1u$, $m_{Cl} = 35.5u$)

Ans: Wavenumber, $\bar{\nu} = 2900\,\text{cm}^{-1}$

$$\text{So } \nu = \bar{\nu} \times c = 2900 \times 3 \times 10^{10} = 87 \times 10^{12}\,\text{sec}^{-1}$$

Now, transitional energy, $E = h\nu$ J

$$= 6.626 \times 10^{-34} \times 87 \times 10^{12}$$

$$= 576.46 \times 10^{-22}\,\text{J}$$

$$\mu_{HCl} = \frac{1 \times 35.5}{1 + 35.5} \times 1.664 \times 10^{-24}\,\text{gm}$$

$$= \frac{35.5}{36.5} \times 1.664 \times 10^{-24}\,\text{gm}$$

$$= 1.6184 \times 10^{-24}\,\text{gm}$$

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

$$= 4 \times (3.14)^2 \times (87 \times 10^{12})^2 \times 1.6184 \times 10^{-24}\,\text{gm}$$

$$= 483107\,\text{gm/sec}^2$$

5. The vibrational wavenumber of $^1H^{37.5}Cl$ molecule is 2000 cm^{-1}. Find the value of the fundamental vibrational frequency of $^1H^{35.5}Cl$ molecule.

Ans: The force constants of $^1H^{37.5}Cl$ and $^1H^{35.5}Cl$ are same.

$$\text{Now, } \mu_{^1H^{37.5}Cl} = \frac{1 \times 37.5}{1 + 37.5}\,u = \frac{37.5}{38.5} = 0.974u$$

$$\mu_{^1H^{35.5}Cl} = \frac{1 \times 35.5}{1 + 35.5}\,u = \frac{35.5}{36.5} = 0.972u$$

$$\bar{\nu}_{^1H^{37}Cl} = 2000\,\text{cm}^{-1}; \text{ So } \nu = 2000 \times 3 \times 10^{10} = 6 \times 10^{13}\,\text{sec}^{-1}$$

Now, $\nu_{^1H^{37}Cl} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu_{^1H^{37.5}Cl}}}$ ------(i)

and $\nu_{^1H^{35.5}Cl} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu_{^1H^{35.5}Cl}}}$ ------(ii)

From eq^n (i) & (ii) we get;

$$\frac{\nu_{^1H^{37}Cl}}{\nu_{^1H^{35.5}Cl}} = \sqrt{\frac{\mu_{^1H^{35.5}Cl}}{\mu_{^1H^{37.5}Cl}}} = \sqrt{\frac{0.972}{0.974}}$$

$$\Rightarrow \frac{6\times10^{13}}{\nu_{^1H^{35.5}Cl}} = 0.032$$

$$\Rightarrow \nu_{^1H^{35.5}Cl} = \frac{6\times10^{13}}{0.032} = 1875\times10^{12}\ sec^{-1}$$

6. Calculate the zero-point energy of HCl molecule, if its force constant is $4\times10^5\ g/sec^2$. [Given $m_H = 1u$ and $m_{Cl} = 35.5u$]

Ans: $\mu_{HCl} = \frac{1\times35.5}{1+35.5} = \frac{35.5}{36.5} = 0.972\times1.664\times10^{-24}\ gm$

$= 1.6184\times10^{-24}\ gm$

Now, $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} = \frac{1}{2\times3.14}\sqrt{\frac{4\times10^5}{1.6184\times10^{-24}}} = 79.16\times10^{12}\ sec^{-1}$

So Zero point energy $= \frac{1}{2}h\nu = \frac{1}{2}\times6.626\times10^{-34}\times79.16\times10^{12}\ J$

$= 21.62\times10^{-20}\ J$

7. If the vibrational energy of CO molecule is 3.1×10^{-19} J, then calculate its force constant. [$m_C = 12u$ & $m_O = 16u$]

Ans: $E_{vib} = h\nu$; So $\nu = \frac{E}{h} = \frac{3.1\times10^{-19}}{6.626\times10^{-34}} = 4.67\times10^{14} sec^{-1}$

(8)

Now, $\mu_{CO} = \frac{12 \times 16}{12+16} \times 1.664 \times 10^{-24}$ gm

$= 11.41 \times 10^{-24}$ gm.

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

$= 4 \times (3.14)^2 \times (4.67 \times 10^{14})^2 \times 11.41 \times 10^{-24}$

$= 9813.83 \times 10^{8}$ gm/sec^2