Module - III

SPECTROSCOPIC TECHNIQUES & APPLICATIONS ①

CO- To analyze and implement the concepts of spectroscopic techniques for identification of various organic and inorganic compounds.

Topic - Defn of spectroscopy and Basic Terms :-

1. Defn of spectroscopy :-

It is the branch of science which deals with the study of the interaction of electromagnetic radiation with matter.

→ Spectroscopy divided into different types.

a) Molecular Rotational (Microwave) spectroscopy.
b) Molecular Vibrational (IR) spectroscopy.
c) Electronic (UV-Visible) spectroscopy.

Basic Terms :-

1. Electromagnetic Radiation :-

It is a form of radiant energy which has both particle as well as wave nature.

a) Wavelength :- (λ)

The distance between two adjacent crests (C-C) or troughs (T-T) in a particular wave.

→ It expressed in centimeters.

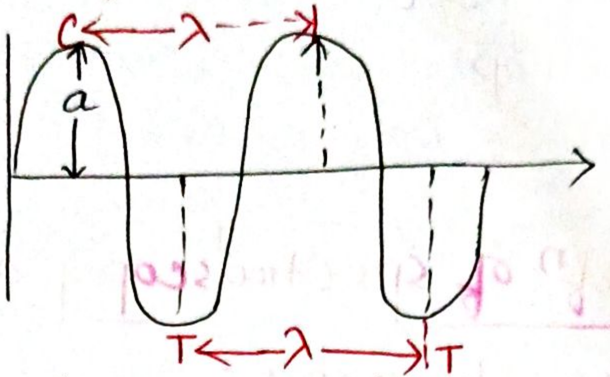
→ The units for expressing wavelength are given below.

(i) Angstrom (Å) $1Å = 10^{-8} cm = 10^{-10} m$

(ii) Nanometer (nm) or millimicron (mμ)

$1 nm = 1 m\mu = 10^{-7} cm = 10^{-9} m$

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



→ The wavelength of visible light ranges from 3800Å (violet end) to 7600Å (red end).

b) Frequency :-

The number of waves which can pass through a point in one second.

→ It is denoted by 'ν'.

→ It is expressed in cycles per second or Hertz (Hz)

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

where, c = velocity of E.M radiation $= \boxed{3 \times 10^{10}\,cm/s}$ or $\boxed{2.998 \times 10^{10}\,cm\,s^{-1}}$

Numerical :-

Q① When $\lambda = 3800\text{Å} = 3800 \times 10^{-8}\,cm$. Find λ'.

Soln :- $\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10}\,cm\,s^{-1}}{3800 \times 10^{-8}\,cm}$

$= 0.00078894 \times 10^{10} \times 10^{8}\,s^{-1}$

$$\boxed{\nu = 7.8894 \times 10^{14}\,s^{-1}}$$

② When $\lambda = 7600\text{Å} = 7600 \times 10^{-8}\,cm$. Find λ'.

$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10}\,cm\,s^{-1}}{7600 \times 10^{-8}\,cm}$

$= 0.000394473 \times 10^{10} \times 10^{8}\,s^{-1}$

$$\boxed{\nu = 3.94473 \times 10^{14}\,s^{-1}}$$

ⓒ velocity :-

The distance travelled by a wave in one second.

→ It denoted by 'c'.

→ Speed of light is $2.998 \times 10^{10} \, cm s^{-1}$ or $3 \times 10^{8} \, m s^{-1}$.

ⓓ Wave number :-

The total number of waves in a length of one-centimetre

(or)

→ It is reciprocal of wavelength.

→ It is expressed in per centimetre or cm^{-1}.

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

ⓔ Energy :-

Energy of a wave can be calulated by applying Planck relation.

$$\boxed{E = h\nu}$$

where h = planck's constant

$$\boxed{E = h\frac{c}{\lambda}}$$

$= 6.626 \times 10^{-34} \, Js$

$= 6.626 \times 10^{-34} \, Kg m^{2} s^{-1}$

$= 6.628 \times 10^{-27} \, ergs$.

Numerical :-

Calculate the frequency (ν) of radiation whose wavelength is 400nm. Express this wavelength in wave number.

Soln :- $\lambda = 400nm = 400 \times 10^{-7} \, cm$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10} \, cm/s}{400 \times 10^{-7} \, cm} = 0.0075 \times 10^{10} \times 10^{7} \, s^{-1}$$

$$= 0.0075 \times 10^{17} \, s^{-1}$$

$$\boxed{\nu = 7.5 \times 10^{14} \, s^{-1}}$$

$$\boxed{\bar{\nu} = \frac{1}{\lambda}} = \frac{1}{400 \times 10^{-7} \, cm} = 0.0025 \times 10^{7} \, cm^{-1} = \boxed{2.5 \times 10^{4} \, cm^{-1}}$$ Ans

1. (Microwave) Spectroscopy or Rotational Spectroscopy :-

Basic Principle :-

→ Microwave Region : 10 to 10^{-2} cm .

→ This region lies between far infrared and radio freqeency region .

→ The microwave spectroscopy deals with Pure rotational motion of molecule it is known as Rotational spectroscopy .

Theory of Spectroscopy :-

→ Due to rotation of charged molecule induced electric field is produced which interacts with electric field component of microwave radiation .

→ Molecules like HCl , CH_3Cl are having dipole moment and their interaction will give rise to a spectrum .

→ When tranition offers in rotational energy level when energy is absorbed and peak appears in rotational spectra of that molecule .

Microwave Active & Inactive molecules :-

→ If molecule are not having Permanent dipole moment is called microwave inactive .

Ex - H_2 , N_2 , O_2 , Cl_2 , OCS etc .

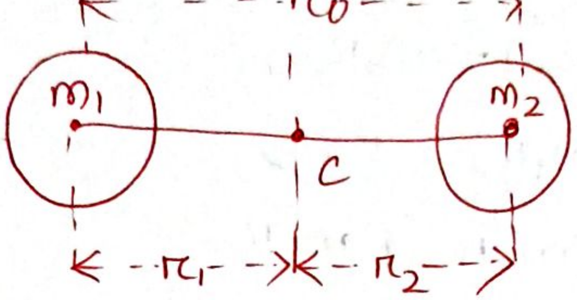
→ If molecules are having Permanent dipole moment is called microwave active .

Ex - HCl , HF , CO, CN , CH_3Cl etc .

Topic :-

Application of Rotational spectroscopy :-

For Diatomic molecules :-



Consider a rigid diatomic mass m_1 and m_2.
Bond length is $r_0 = r_1 + r_2$.
Consider, the centre of mass is at 'c'.
Rotations of this molecule are with respect to the two axis.
So, The centre of mass is defined as,

$$m_1 r_1 = m_2 r_2 \quad \text{------} \quad (i)$$

The moment of inertia is,

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

$$= m_1 r_1 r_1 + m_2 r_2 r_2 \quad [m_1 r_1 = m_2 r_2]$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$I = r_1 r_2 (m_2 + m_1) \quad \text{---} \quad (ii)$$

Since, we know that,

$$r_0 = r_1 + r_2 \quad \text{------} \quad (iii)$$

$$r_1 = r_0 - r_2 \quad \text{------} \quad (iv)$$

$$r_2 = r_0 - r_1 \quad \text{------} \quad (v)$$

Now, $m_1 r_1 = m_2 r_2$

$$= m_2 (r_0 - r_1) \quad \left[\text{Substituting eq}^n \text{ (v)}\right]$$

$$\Rightarrow m_1 r_1 = m_2 r_0 - m_2 r_1$$

$$\Rightarrow m_1 r_1 + m_2 r_1 = m_2 r_0$$

$$\Rightarrow \boxed{r_1 = \frac{m_2 r_0}{m_1+m_2}} \text{ ---- (vi)}$$

Now, substituting the value of 'r_1'

$$m_1 r_1 = m_2 r_2$$

$$\Rightarrow m_1(r_0 - r_2) = m_2 r_2$$

$$\Rightarrow m_1 r_0 - m_1 r_2 = m_2 r_2$$

$$\Rightarrow m_1 r_0 = m_1 r_2 + m_2 r_2$$

$$\Rightarrow m_1 r_0 = r_2 (m_1 + m_2)$$

$$\Rightarrow r_2 (m_1 + m_2) = m_1 r_0$$

$$\Rightarrow \boxed{r_2 = \frac{m_1 r_0}{m_1+m_2}} \text{ --- (vii)}$$

Now, substituting the value of r_1 & r_2 in eqn (ii)

$$I = r_1 r_2 (m_2 + m_1)$$

$$= \frac{m_2 r_0}{m_1+m_2} \times \frac{m_1 r_0}{\cancel{m_1+m_2}} (\cancel{m_2+m_1})$$

$$= \left(\frac{m_1 m_2}{m_1+m_2}\right) r_0^2$$

$$\boxed{I = \mu r_0^2} \quad \text{where } \mu = \frac{m_1 m_2}{m_1+m_2}.$$

μ = Reduced masses

m_1 = mass of one atom

m_2 = mass of another atom

r_0 = Bond length or distance from one atom to another.

Topic:- Rotational spectroscopy of linear rigid rotor molecule :-

A diatomic molecule is assumed to be a linear rigid rotor. that, its internuclear distance doesnot change during rotational motion.

Let the angular momentum is 'L' of a rotating molecule is 'Iw'.

Where, 'w' is the angular velocity in radian s/s.

Angular momentum is quantised.

$$L = \sqrt{J(J+1)}\frac{h}{2\pi} \quad \text{------} (i)$$

Where, $J = 0, 1, 2, 3$ ----- (Rotational quantum no)

The energy E_J of a rotating molecule.

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

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

$$= \frac{L^2}{2I} \quad \text{--} (ii)$$

Substituting the value of 'L' in eqn (i)

$$\boxed{E_J = J(J+1)\frac{h^2}{8\pi^2 I}} \quad \text{-----} (iii)$$

Where E_J = Energy in Joules.

h = Planck constant = 6.626×10^{-34} Js.

I = Moment of inertia in Kgm^2

J = Rotational quantum number.

It is customary to express the energy difference between two rotational levels as wave no. is the reciprocal of wavelength $\frac{1}{\lambda}$ and expressed in cm^{-1}.

Hence, dividing eqn (iii) by hc.

$$\frac{E_J}{hc} = J(J+1)\frac{h}{8\pi^2 Ic} \quad \text{- - - - (iv)}$$

Now, further simplifies,

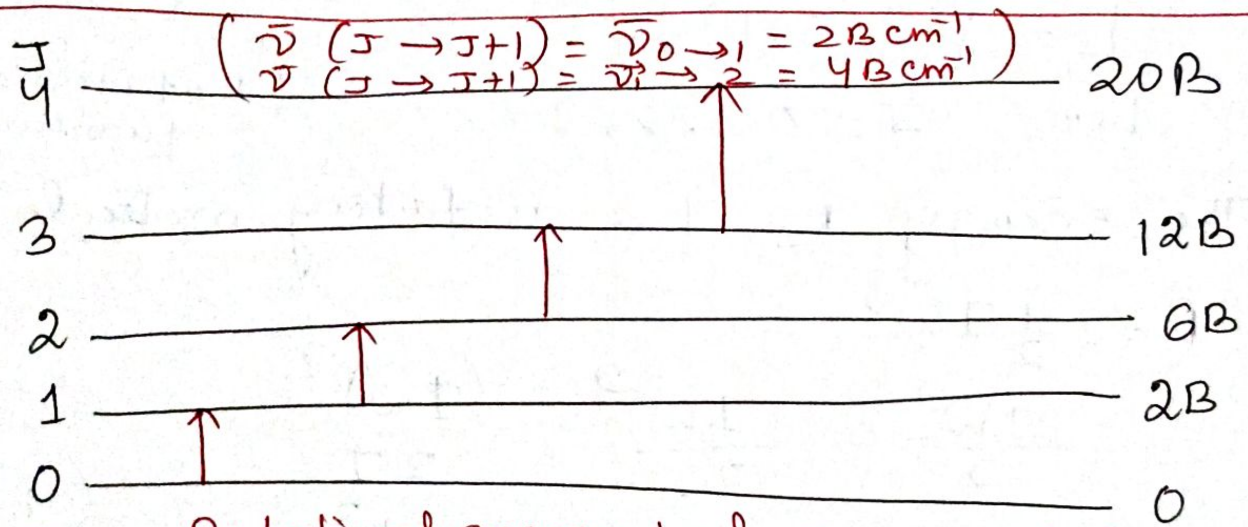
$$\boxed{B = \frac{h}{8\pi^2 Ic}} \ (\text{cm}^{-1}).$$

Hence, eqn (iv) reduces to,

$$\boxed{\frac{E_J}{hc} \text{ or } \bar{\nu} = BJ(J+1)\ \text{cm}^{-1}}.$$

Where, J = 0, 1, 2, 3 ......

The wave no. for different levels will be 0, 2B, 6B, 12B, 20B, 30B.



$$\left(\begin{array}{l}\bar{\nu}(J\rightarrow J+1) = \bar{\nu}_{0\rightarrow 1} = 2B\,\text{cm}^{-1} \\ \bar{\nu}(J\rightarrow J+1) = \bar{\nu}_{1\rightarrow 2} = 4B\,\text{cm}^{-1}\end{array}\right)$$

Fig:- Rotational energy levels of a rigid diatomic molecule and the allowed transitions.

Selection rule:- $\boxed{\Delta J = \pm 1}$

J = 0, Ground state

J = 1, Excited state

For $\boxed{B(\text{Joules}) = \frac{h^2}{8\pi^2 I}}$ For $\boxed{(B(\text{Hz})) = \frac{h}{8\pi^2 I}}$

$\boxed{\bar{\nu} = \frac{\Delta E}{hc}\ \text{cm}^{-1}}$ $\boxed{B\,\text{cm}^{-1} = \frac{h}{8\pi^2 Ic}}$.

$\boxed{\mu = \frac{m_1 m_2}{m_1 + m_2}}$ The atomic mass unit is equivalent to $\boxed{1.66 \times 10^{-27}\,\text{kg}}$.

Topic:- Numerical (Rotational spectroscopy)

Q① Calculate the reduced mass of HF molecule (rigid typ).

Soln:- $m_1(H) = 1.0078$ amu

$m_2(F) = 18.9984$ amu

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{1.0078 \times 18.9984 \text{ amu}}{1.0078 + 18.9984 \text{ amu}}$$

$$= \frac{19.14658752 \text{ amu}}{20.0062} = 0.957032 \text{ amu}$$

$$= 0.957 \times 1.66 \times 10^{-27} \text{kg}$$

$$\boxed{\mu = 1.58862 \times 10^{-27} \text{ kg}}$$

Q② Calculate the reduced mass for isotopic diatomic molecule, $^1H\,^{35}Cl$.

Soln:- $^1H(m_1) = 1.0078$ amu , $^{35}Cl(m_2) = 34.9689$ amu

$$\mu = \frac{1.0078 \times 34.9689}{1.0078 + 34.9689} \times 1.66 \times 10^{-27} \text{ kg}$$

$$= \frac{35.2416}{35.9767} \times 1.66 \times 10^{-27} \text{ kg}$$

$$= 0.979568 \times 1.66 \times 10^{-27} \text{ kg}$$

$$\boxed{\mu = 1.6267 \times 10^{-27} \text{ kg}}$$

Q③ Calculate the reduced mass for $^2H\,^{35}Cl$.

Soln:- $^2H(m_1) = 2.0141$ amu , $^{35}Cl(m_2) = 34.9689$ amu

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{2.0141 \times 34.9689}{2.0141 + 34.9689} \times 1.66 \times 10^{-27} \text{ kg}$$

$$= \frac{70.43086149 \text{ amu}}{36.983} = 1.9044 \times 1.66 \times 10^{-27} \text{ kg}$$

$$= 3.1623 \times 10^{-27} \text{ kg}$$

$$\boxed{\mu = 3.1623 \times 10^{-27} \text{ kg}}$$

Q④ The HF molecule (rigid type) has bond length, $r_0 = 1.10 \times 10^{-10}$ m. Calculate its rotational constant in Joules. ⑩

Soln: $r_0 = 1.10 \times 10^{-10} m$, $m_1 = 1.0078$ amu

$m_2 = 18.9984$ amu

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.0078 \times 18.9984}{1.0078 + 18.9984}$$

$$= \frac{19.1465}{20.0062} \times 1.66 \times 10^{-27} kg$$

$$= 0.957 \times 1.66 \times 10^{-27}$$

$$\boxed{\mu = 1.58862 \times 10^{-27} kg}$$

$$I = \mu r_0^2$$

$$= 1.5886 \times 10^{-27} kg \times (1.10 \times 10^{-10} m)^2$$

$$= 1.922206 \times 10^{-27} \times 10^{-20} \, kgm^2$$

$$\boxed{I = 1.9222 \times 10^{-47} \, Kgm^2}$$

$$B(\text{Joule}) = \frac{h^2}{8\pi^2 I}$$

$$= \frac{(6.626 \times 10^{-34})^2 (Js)^2}{8 \times 3.14 \times 3.14 \times 1.9222 \times 10^{-47} \, Kgm^2}$$

$$= \frac{43.903876 \times 10^{-68} \, J^2 s^2}{151.6169 \times 10^{-47} (Kgm^2)}$$

$$= 0.2895709 \times 10^{-68} \times 10^{47} \frac{(\cancel{Kg}\cancel{m^2} s^{-2} s)^2}{\cancel{Kg}\cancel{m^2}}$$

$$= 0.28957 \times 10^{-21} \, kg m^2 s^{-2}$$

$$\boxed{B = 0.289 \times 10^{-21} J.}$$

Ans

Topic :- Vibrational (IR) spectroscopy :-

Basic Principle :-

→ It is a type of spectroscopy used to analysis of infrared light interacting with a molecule

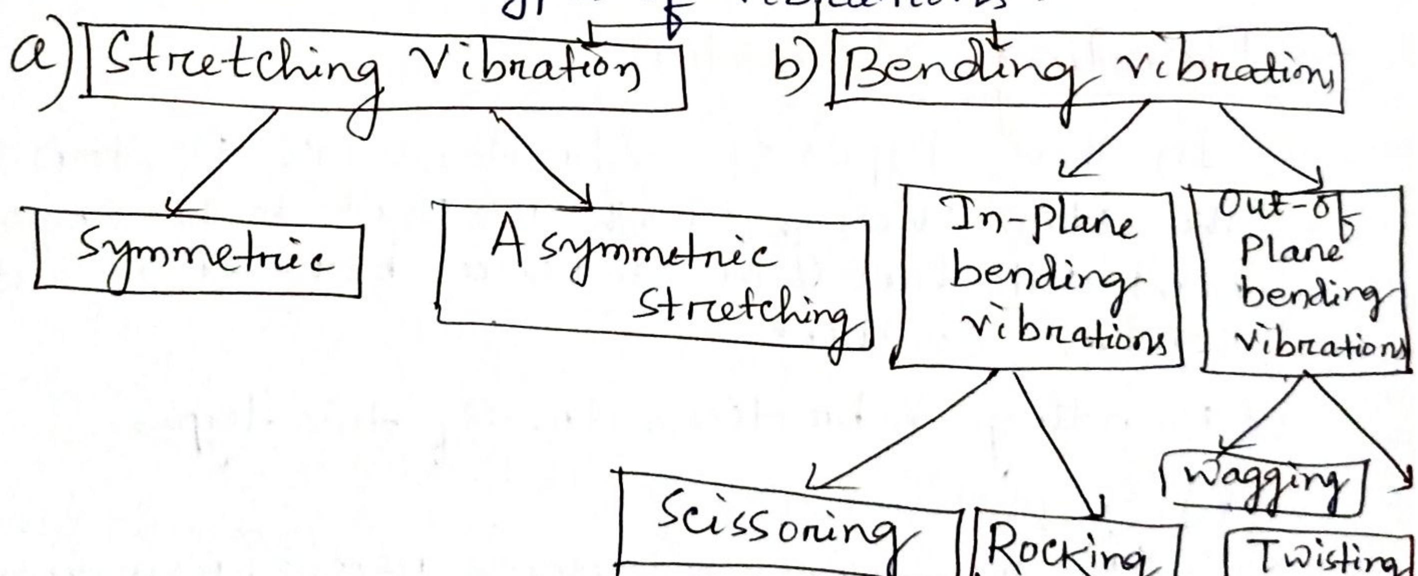
→ It measures the vibrations of atoms & based on this it is possible to determine the functional groups.

→ Generally, stronger bonds and light atoms will vibrate at a high stretching freqeency (wave no).

Application :-

Types of vibration :- Flow chart diagram.

There are two types of vibrations.



Types of vibration :-

a) Stretching vibration :-

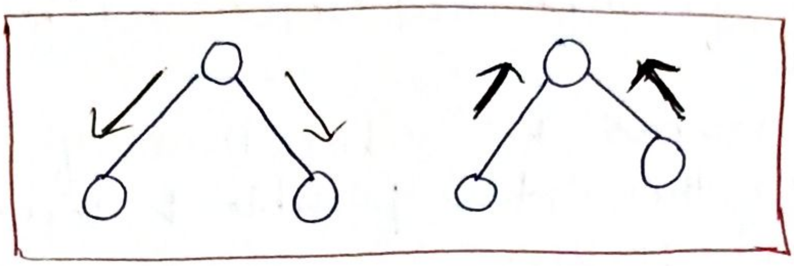
In this type of vibrations, the distance between the atoms increases or decreases but the atoms remain in the same bond axis.

→ Stretching vibration can be two types.

a) symmetric stretching b) Asymmetric stretching

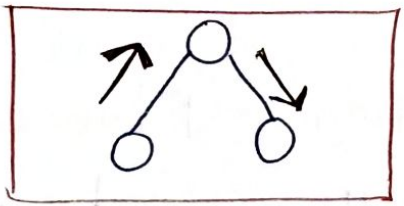
a) Symmetric stretching :-

In symmetric stretching, the movement of the atoms with respect to a particular atom is in the same direction.



b) Asymmetric stretching :-

In these vibrations, one atom approaches the central atom and the other departs from it.



→ Bending vibration :-

In these types of vibrations, the position of the atom changes with respect to the original bond axis but the distance between the atoms remains constant.

→ Bending vibrations are of two types.

(i) In-plane vibrations :-

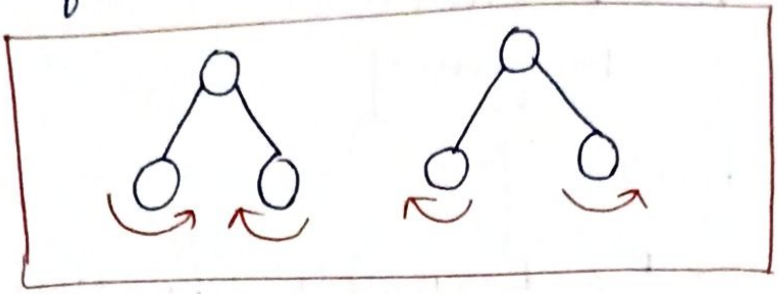
In this type, the atoms remain remain in the same plane as the nodal plane of the system.

(ii) Out-of-Plane bending vibrations :-

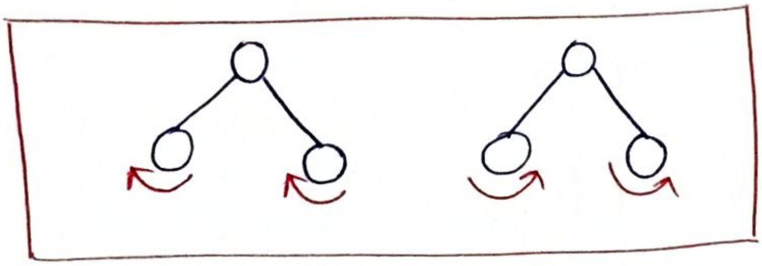
The atoms move out of the nodal plane with respect to the central atom. These are again two types.

In-plane bending vibrations :-

(i) **Scissoring :-** In this type, the two atoms approach each other and move away like the two arms of a scissors.

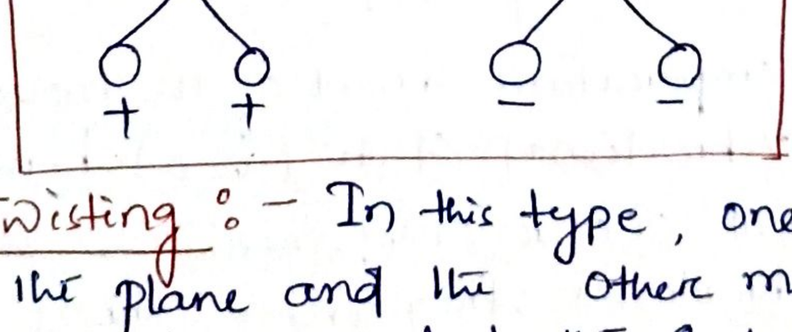


(ii) **Rocking :-** In this type, both the atoms move in the same direction.

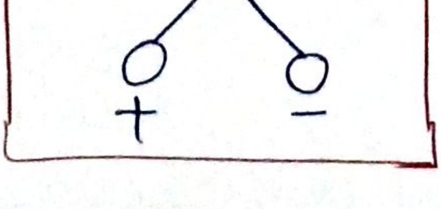


Out-of plane bending vibrations :-

(i) **Wagging :-** In this type, both the atoms swing - up and down with respect to the central atom.



(ii) **Twisting :-** In this type, one atom moves up the plane and the other moves down the plane with respect to the central atom.



Vibrational Frequency :-

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

Where, K is the force constant.
μ = Reduced mass.
ν = frequency.

$$\boxed{E_v = h\omega_{osc}}$$

Where, E_v = Energy of vibration.
ω_{osc} = Frequency of ossilation.

$$\boxed{K = 4\pi^2\omega_{osc}^2\mu}$$

Selection Rule :-

$$\boxed{\Delta v = \pm 1}$$

→ The +ve sign indicates absorption spectra.

→ The -ve sign indicates emission spectra. Hence, transition from any v to v+1 level will give the same energy change and hence only one line is expected.

→ At room temperature most of the molecules are in ground vibrational state ($v=0$). hence the transitions will occur only from $v=0$ to $v=1$ and the vibrational frequency corresponding to this is the fundamental vibrational frequency.

Topic- Numerical :- (Vibrational spectroscopy)

Q① The frequency of oscillation of HF is 4.12×10^{14} Hz. Calculate the energy of vibration and its force constant.

Soln:- $\mu = \dfrac{1.0078 \times 18.9984}{1.0078 + 18.9984} \times 1.66 \times 10^{-27}$ kg

$= 1.5887 \times 10^{-27}$ kg

$\omega_{osc} = 4.12 \times 10^{14}$ Hz or s^{-1}.

$E_v = h\omega_{osc}$

$= 6.626 \times 10^{-34}$ Js $\times 4.12 \times 10^{14}$ s^{-1}

$= 27.29912 \times 10^{-20}$ J

or

$\boxed{E_v = 2.73 \times 10^{-19} \text{ J}.}$

Now, $K = 4\pi^2 \omega_{osc}^2 \mu$

$= 4 \times (3.14)^2 \times (4.12 \times 10^{14} s^{-1})^2 \times 1.5887 \times 10^{-27}$ kg

$= 1063.54437 \times 10^{28} \times 10^{-27}$ kg s^{-2}

$\boxed{K = 10635 \text{ kg } s^{-2}}$

or

$\boxed{K = 10635 \text{ N} m^{-1}}$ Ans

Q② Calculate the vibrational absorption frequency of the carbonyl, $>C=O$ group. If the force constant for the double bond is 1×10^{6} dynes cm^{-1}.

Sol^n:- Mass of O_2 atom $= 2.65 \times 10^{-23} g$ (approx)

Mass of Carbon atom $= \frac{12}{6.023 \times 10^{23}} = 2 \times 10^{-23} g$ (approx)

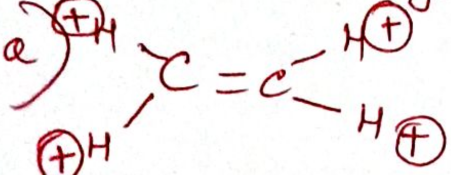
$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$$\bar{\nu} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10} cm s^{-1}}\sqrt{\frac{1 \times 10^{6}}{\frac{2.65 \times 10^{-23} \times 2 \times 10^{-23}}{2.65 \times 10^{-23} + 2 \times 10^{-23}}}}$$

$$\boxed{\bar{\nu} = 1581 cm^{-1}}$$

Q③ Indicate whether the following vibrations will which type of vibration follows.

a)



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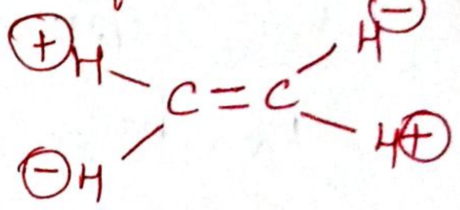
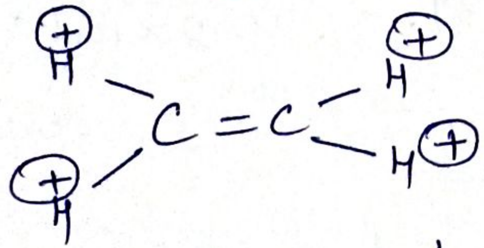
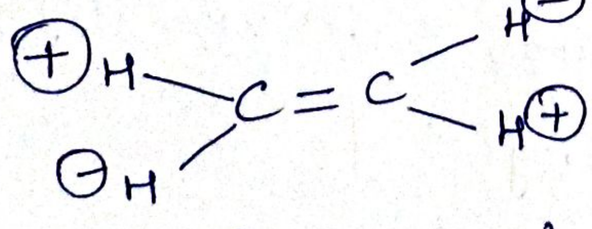


Sol^n:- a)



It shows 'wagging' type of vibration.
i.e, out-of plane bending vibrations.

b)



It shows 'twisting' type of vibration
i.e, also out-of plane bending vibration.

Topic :- Applications of (IR) vibrational spectroscopy :- (CO4)

a) Identification of an organic compound :-

The molecule containing the same functional groups may have similar absorptions above 1500cm⁻¹ but their spectra differ significantly in the finger print region.

(b) Structure determination :-

The IR spectra of amino acids exhibit bands for ionised Carboxylic acids and amine salts but no band for free amino and Carboxylic groups is observed. Thus, we conclude that the amino acids exist as zwitter ions.

$$H_3N^+ - CH_2 - COO^-$$

For the same molecular formula, different isomers can be proposed and their identify can be established with the help of IR spectra.

ⓒ Detection of impurities :-

The presence of impurities can be detected if they absorb in the region where the sample does not show any absorption.

d) Distinction between Inter and Intramolecular Hydrogen Bonding :-

Intramolecular hydrogen bonding has no effect of dilution but Intermolecular hydrogen bonding shows the change in absorption pattern of the sample if diluted with non-polar solvents.

e) Kinetic study on reactions :-

→ It helps to follow the progress of chemical reaction.

f) Others :-

It also helps to study the structure of complex molecules, Keto-enol tautomerism, Stability of conformers and optical isomerism etc.

Regular ② ⓕ

Topic :-

3. UV-Visible spectroscopy :-

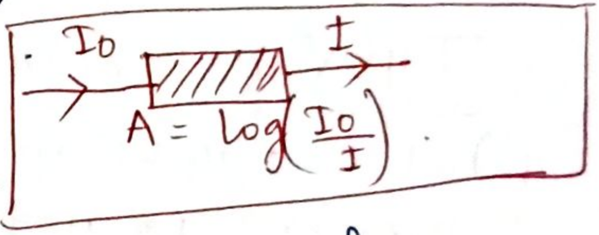
② ⓑ Back

Principle :-

(i) It is the branch of spectroscopy that deals with the transitions of electrons between the electronic energy levels.

(ii) UV-region (200 - 380 nm)
Visible-region (380 - 760 nm)

(iv) It is also called electronic spectroscopy as it involves the promotion of electrons (σ, π, n) from the ground state to higher energy states.



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

Law of absorption :-

Two fundamental laws govern the absorption of light by molecules. These are,

a) Lambert's Law   b) Beer's Law.

a) Lambert's Law :-

According to Lambert, Absorbance is directly proportional to the length of the sample.

Mathematically, $A \propto l$

$$\boxed{A = \epsilon l} \quad \text{---} (i).$$

b) Beer's Law :-

According to Beer', Absorbance is directly Proportional to the concentration of the sample.

Mathematically,

$$A \propto C$$

$$\boxed{A = \epsilon C} \quad \text{---} \quad (ii)$$

Combining both eqn (i) & (ii)

$\boxed{A = \epsilon C l}$. This is Beer's-Lambert's Law.

Where A = Absorbance
C = concentration of sample
l = length of the sample where it keept.

Types of Electronic Tranitions :-

(i) When a molecule absorbs UV-visible light, its electrons promoted from the ground state to a higher energy state.

(ii) The electrons in the bonding molecular orbitals like, σ-orbital, π-orbital & σ* & π*

The following types of electronic tranitions are possible :-

→ 4 types such as σ-σ*, n-σ*, π-π*, n-π*.

(i) $\boxed{\sigma\text{-}\sigma^* \text{ tranitions}}$:-

(a) The σ-bonded e⁻ are held firmly in the molecule Hence, the tranition from σ-σ* reqeine large amount of energy.

(b) Therefore, they occur in the far-UV region (150nm, high energy).

c) Ex - Methane, Propane - - .

(ii) **$n-\sigma^*$ transition** :-

→ This type of transitions occurs in saturated compounds with one heteroatom having unshared pairs of e^- (n-electrons) like alcohol, ethers, amines, Ketones, aldehydes.

→ The energy required for these transitions is lesser than the energy required for $\sigma-\sigma^*$.

→ Ex- H_2O absorbs at 167 nm, Methyl-alcohol at 174 nm, Methylchloride (169 nm).

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

→ These transitions take place in compounds containing (= bond) & (≡ bonds).

→ The excitation of π-electrons requires lesser energy; hence, they occur at longer wavelength.

→ In unconjugated alkenes, absorption bands appear around (170-190 nm).

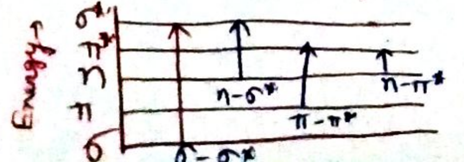
(iv) **$n-\pi^*$ transitions** :-

→ In these transitions, the electrons of the unshared electron pair on the heteroatom is excited to π^* anti-bonding orbital.

→ As non-bonding e^- are loosely held, these require least energy and occur at larger wavelengths

→ They occur in unsaturated compounds with heteroatoms having unshared Pairs of e^- like C=O, C=S.

→ The relative energies required for the various transitions follow the order. $\boxed{\sigma\to\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*}$



1. Chromophore :-

Defn :- A Chromophore considered as any system responsible for imparting colour to a compound.

→ It is an isolated covalently bonded group that shows a characteristic absorption in the UV-visible region.

→ It is two types :-

a) Those which contain 'π' electron and undergo $\pi-\pi^*$ transitions.
Ex - $(C=C)$, $(-C\equiv C-)$.

b) Those which contain both 'π' electrons and non-bonding electrons. They undergo, $\pi\to\pi^*$ & $n\to\pi^*$ transitions.
Ex - $>C=O$, $-C\equiv N$, $-\ddot{N}=\ddot{N}-$ ....

2. Auxochromes :-

Defn :- Any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength).

→ It is a saturated group which when attached to a chromophore, changes its intensity as well as wavelength.
Ex → $-OH$, $-NH_2$ and $-Cl$.

Ex → Benzene absorbs at 255 nm with $\epsilon_{max} = 203$.
→ Aniline absorbs at 280 nm with $\epsilon_{max} = 1430$.
Hence, Amino group $(-NH_2)$ is a auxochrome.

Absorption & Intensity shifts :-

a) **Bathochromic Shift (red-shift) :-**

Absorption maximum shift towards a longer wavelength.

Ex- Carbonyl compounds shows this when polarity of the solvent decreases.

b) **Hypsochromic shift (blue shift) :-**

Absorption maximum towards shorter wavelength.

c) **Hyperchromic shift :-**

Intensity of absorption maximum increases
Emax increases.

d) **Hypochromic shift :-**

Intensity of absorption maximum decreases due to Emax decreases.

Application :-

1. **Extent of conjugation :-**

The greater the extent of conjugation the longer is the absorption wavelength.

Ex- Ethylene absorbs → 170 nm ($\pi \rightarrow \pi^*$)
Butadiene (=) ⟶ 217 nm
Lycopene absorbs (454 nm) imparts red colour to tomatoes.

2. **Determination of geometrical isomers :-**

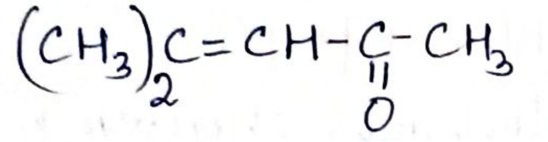
Cis-isomers absorbs at a shorter wavelength when, compared to the trans-isomers.

Ex- Cis-stilbene absorbs at 280 nm.
- Trans-stilbene absorbs at 295 nm.

3. Identification of unknown compounds :-

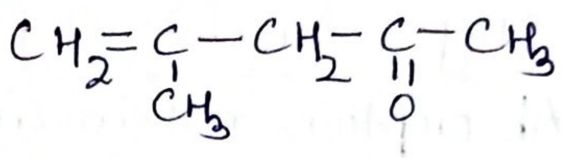
→ Identical spectra reveal identical structure and if the spectra is different, then the structure is different.

4. Distinction between conjugated and non-conjugated compounds :-



$(CH_3)_2C=CH-\underset{\underset{O}{\|}}{C}-CH_3$

(a)



$CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

(b)

λmax longer because, C=O group is in conjugation with the double bond.

5. Detection of impurities :-

→ Benzen shows 280nm spectra $\epsilon_{max} = 230$.

→ Ethanol is transparent.

6. Detection of hydrogen bonding :-

It can be detected on the basis of the shift absorbed in polar solvents.

7. Quantitative analysis :-

Beer-lambert's law,

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

Numerical :-

Q① For a solution of camphor in hexane in a 5cm cell, the absorbance 'A' was found to be 2.52 at 295 nm with $\epsilon_{max} = 14$. What is the concentration of camphor?

Soln:- Given data :-

$A = 2.52$

$c = ?$

$\epsilon = 14$

$l = 5\,\text{cm}$

Now, According to formula:-

$$A = \epsilon c l$$

$$c = \frac{A}{\epsilon l}$$

$$= \frac{2.52}{14 \times 5} = \frac{2.52}{70} = 0.036\ \text{mol}$$

Q② The % transmittance of an aq. soln at 25°C and 250 nm is 19.2 % with concentration of 5×10^{-4} M in a 1cm cell. Calculate,

a) absorbance (A)

b) The molar absorption co-efficient (ϵ).

Soln:- (i) $A = \log\left(\frac{I_0}{I}\right) = \log\left(\frac{100}{19.2}\right)$

$$= \log(5.20)$$

$$\boxed{A = 0.716}$$

(ii) $\epsilon = \frac{A}{cl} = \frac{0.716}{1 \times 5 \times 10^{-4}} = \frac{0.716 \times 10^{4}}{5}$

$$= 0.1432 \times 10^{4}\ \text{cm}^{-1}\,\text{m}^{-1}$$

$$\boxed{\epsilon = 1.432 \times 10^{3}\ \text{cm}^{-1}\,\text{m}^{-1}}$$

③ Compound 'x' exhibits ϵ of $245 m^2 mol^{-1}$. What concⁿ of 'x' in a solution will cause a 25% decrease in the intensity of 450 nm. When the solution is placed in a 0.01m absorption cell?

Solⁿ:- Let $I_0 = 100\%$ $\quad l = 0.01m$ or $10^{-2}m$

$I = 75\%$

Now, $A = \epsilon c l$

$$\Rightarrow \log\left(\frac{I_0}{I}\right) = \epsilon c l$$

$$\Rightarrow c = \frac{\log(I_0/I)}{\epsilon l}$$

$$= \frac{\log(100/75)}{245 m^2 mol^{-1} \times 10^{-2} m}$$

$$= \frac{0.1249387366}{245 \times 10^{-2}}$$

$$= \frac{0.000509}{10^{-2}} = \boxed{0.0510 \; mol \, m^{-3}}$$ Ans

Q④ A solution of thickness 2cm transmits 40% incident light. Calculate the concⁿ of the solⁿ.
Given, $\epsilon = 6000 \; mol^{-1} cm^{-1}$.

Solⁿ:- $A = \log\left(\frac{I_0}{I}\right) = \log\left(\frac{100}{40}\right) = \log(2.5) = 0.3979$
$= 0.398$

$\epsilon = 6000 \; mol^{-1} cm^{-1}$.
$l = 2cm$
$c = ?$

$A = \epsilon c l$

$$\Rightarrow c = \frac{A}{\epsilon l} = \frac{0.398}{6000 \times 2 \cancel{cm} \times mol^{-1} \cancel{cm^{-1}}}$$

$$= \frac{0.398}{12000 \; mol^{-1}} = \boxed{3.316 \times 10^{-5} \; mol}$$

Ans