ROTATIONAL SPECTROSCOPY
(Microwave Spectroscopy)

Rotation of molecules:

The microwave region is concern with study of rotating molecules. The rotation of the 3D body is quite complex and can be resolved into rotational components about three mutually perpendicular directions through the centre of gravity. Thus a body has three principal moment of inertia about each axis designated as I_X, I_Y and I_Z.

1. **Linear Molecules**

   All the atoms are arranged in a straight line such as H - Cl, O=C=S

   The three directions of rotations are

   a. Along the bond axis

   b. End over end rotation in the plane of paper (I_Y)

   c. End over end rotation perpendicular to the plane of paper (I_Z)

   I_X is very small and can be neglected but $I_Y = I_Z$

2. **Symmetric Top Molecules** :

   In this case the end over end rotation in the plane and out of the plane of paper are identical & the rotation along main axis not negligible

   It is called oblate symmetric Top when $I_Y = I_Z < I_X$ EX : $CHCl_3$, CHF_3, CHI_3

   It is called prolate symmetrical Top when $I_Y = I_Z > I_X$ Ex : NH_3, BF_3 etc

3. **Spherical Top Molecules :**

   When a molecule has three Moment of Inertia are identical it is called spherical top molecules. $I_X = I_Y = I_Z$, Ex : CH_4, CCl_4

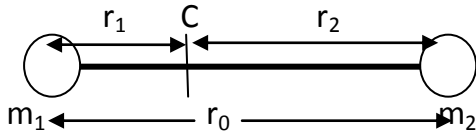   Since they are non-polar, hence no rotational spectra are observed.

4. **Asymmetric Top Molecules**

   In this case the 3 MI are different $I_X \neq I_Y \neq I_Z$ Ex : H_2O, SO_2, $CH_2=CHCl$

Rotational Spectra of Rigid Molecules

RIGID DIATOMIC MOLECULES

Let us consider a diatomic molecule consisting of atoms with masses m_1 and m_2 joined by a rigid bar (bond length r_0)

$r_0 = r_1 + r_2$ ---------------------------- (1)

where r_1 and r_2 are the axis of rotation from 'C' the centre of gravity.

$\Rightarrow m_1r_1 = m_2r_2$ ---------------------------- (2)

Moment of inertia about C is given by

$I = m_1r_1{}^2 + m_2r_2{}^2$

$\quad = m_1r_1r_1 + m_2r_2r_2$

$\quad = m_2r_2r_1 + m_1r_1r_2$ (putting $m_1r_1 = m_2r_2$)

$I = r_1r_2 (m_1+m_2)$ ---------------------------- (3)

From equation (1) and (2)

$m_1r_1 = m_2r_2$

$\qquad = m_2(r_0 - r_1)$

$\Rightarrow r_1 = \dfrac{m_2\ r_0}{m_1+m_2}$

$\Rightarrow r_2 = \dfrac{m_1r_0}{m_1+m_2}$

From Equation (3), $I = r_1r_2 (m_1+m_2)$

$\qquad = \dfrac{m_2r_0}{m_1+m_2} \text{X} \dfrac{m_2r_0}{m_1+m_2} (m_1 + m_2)$

$\qquad = \dfrac{m_1m_2}{m_1+m_2} r_0{}^2$

$\qquad I = \mu r_0{}^2$ ---------------------------- (4)

Where: μ = Reduced Mass

By the use of the Schrodinger's wave equation the rotational energy level of a rigid diatomic molecule is given by

$E_J = \dfrac{h^2}{8\pi^2 I} J(J + 1)$ Joules   ---------------------------- (5)

Where J = 0,1,2,3 .... are called as rotational quantum number

h= Planck's Constant,   I = Moment of Inertia

The energy can also be expressed in the terms of frequency or wave number

$E = h\nu \Rightarrow \dfrac{hC}{\lambda} \Rightarrow hC\bar{\nu} \Rightarrow \bar{\nu} = \dfrac{E}{hC}$

Thus $\qquad \nu = \dfrac{E_J}{h} = \dfrac{h}{8\pi^2 I} J(J+1)$ Hz

and $\qquad \bar{\nu} = \dfrac{E_J}{hC} = \dfrac{h}{8\pi^2 IC} J(J+1)$ Cm^{-1}

Now $\qquad \bar{\nu} = B J(J+1)$ Cm^{-1}

Where $\qquad B = \dfrac{h}{8\pi^2 IC}$ Cm^{-1} = Rotational Constant

When $\qquad$ J=0 , $\qquad\qquad \bar{\nu} = B J(J+1)$ Cm$^{-1} = 0$ it the ground state

$\qquad$ J=1 , $\qquad\qquad \bar{\nu} = B J(J+1)$ Cm$^{-1} = 2$ B Cm^{-1}

$\qquad$ J=2 , $\qquad\qquad \bar{\nu} = B J(J+1)$ Cm$^{-1} = 6$ B Cm^{-1}

$\qquad$ J=3 , $\qquad\qquad \bar{\nu} = B J(J+1)$ Cm$^{-1} = 12$ B Cm^{-1} and so on

There comes appoint at which centrifugal force of a rapidly rotating diatomic molecule is greater than the strength of bond & the molecule is disrupted. But this point does not reach at normal temperature.

In order to obtain rotational spectra a molecule jumps from J=0 to J=1, the energy absorbed will be $\Delta\bar{\nu} = \bar{\nu}_{J=1} - \bar{\nu}_{J=0} = 2B\text{-}0 = 2B$ Cm^{-1}

Similarly $\qquad \Delta\bar{\nu}_{J=1 \to J=2} = \bar{\nu}_{J=2} - \bar{\nu}_{J=1} = 6B \text{ - } 2B = 4B$ Cm^{-1}

In general $\qquad \Delta\bar{\nu}_{J=J \to J=J+1} = \bar{\nu}_{J=J+1} - \bar{\nu}_{J=J} = 2B J(J+1)$ Cm^{-1}

Thus stepwise raising of rotational energy result of absorption spectra consisting of series of lights at 2B, 4B, 6B Cm^{-1} etc

The separation between lines is 2B cm^{-1}.

SELECTION RULE

1. The Molecule has permanent dipole moment
2. The transition between adjacent state is allowed i.e. $\Delta J = \pm 1$

Hence transition from $\qquad$ J=0 to J=1

$\qquad\qquad\qquad\qquad$ J=1 to J=2

$\qquad\qquad\qquad\qquad$ J=2 to J=3 and so on are allowed

And transition from $\qquad$ J=0 to J=2,3,4....

$\qquad\qquad\qquad\qquad$ J=1 to J=3,4,5... etc are forbidden (not allowed)

LINEAR POLYATOMIC MOLECULES

These are treated as diatomic molecule. In this case the energy of the molecule is

$E_J = BhC\ J(J + 1)$ Joule   and

$\bar{v} = B\ J(J + 1)\ Cm^{-1}$

Where $B = \dfrac{h}{8\pi^2 IC}\ Cm^{-1}$

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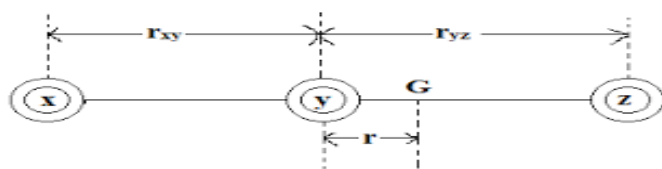
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J=1 to J=2

J=2 to J=3 and so on are allowed

And transition from   J=0 to J=2,3,4....

J=1 to J=3,4,5... etc are forbidden (not allowed)

Calculation of Moment of Inertia of linear polyatomic molecule

Let us consider a linear triatomic molecule XYZ . m_X, m_y and m_z are the masses of the atoms X, Y and Z respectively. The centre of gravity is at G. The bond distances are r_{xy} and r_{yz}. r is the distance between centre gravity and atom Y.

The conservation of Moment of Inertia states that

$m_X\ (r_{XY} + r) + m_Y\ r = m_Z\ (r_{YZ}\text{-}r)$

$\Rightarrow r = \dfrac{m_z\ r_{YZ} - m_x\ r_{XY}}{m_X + m_Y + m_z}$

The moment of Inertia of a molecule about the axis passing through the centre of mass i.e bond axis will be

$I = m_x(r_{XY} + r)^2 + m_Y r^2 + m_z(r_{YZ} - r)^2$

$$= \frac{m_x m_Y\ r_{xy}{}^2 + m_x m_Z\ (r_{xy} + r_{yz})^2 + m_Z m_Y\ r_{yz}{}^2}{m_X + m_Y + m_z}$$

4

VIBRATIONAL SPECTROSCOPY

DIATOMIC MOLECULES

In case of a molecule the atoms are held together & has mean inter nuclear distance as a result of attraction of nucleus of one atom and electron cloud of other atom and vice versa at the same time there is repulsion of two nuclei and two charge clouds.

The attractive force try to bring atoms closer and repulsive force try to take atoms away. As a result the bond behaves like a spring and behaves Hooke's Law.

$$F = -K(r - r_e) \text{ ------------------ (1)}$$

F = Restoring force
K = Force Constant
r = Inter nuclear distance
r_e = Equilibrium distance

The quantum mechanical model consists of the potential energy given by

$$E = \frac{1}{2}K(r - r_e)^2 \text{ ------------------ (2)}$$

If E=0 then $r = r_e$ and with higher there is higher rate of compression and expansion of the bond and has certain vibrational frequency depends upon the mass of the system & force constant. It is given by

$$\omega = \frac{1}{2\pi}\sqrt{K/\mu} \text{ Hz ------------------ (3)}$$

Where : ω = Frequency of Oscillation
K = Force Constant
μ = Reduced Mass

Converting energy into spectroscopic units cm^{-1}, we have

$$\bar{\omega} = \frac{1}{2\pi C}\sqrt{K/\mu} \text{ cm}^{-1} \text{ ------------------ (4)}$$

Vibrational energy is also quantised & can be calculated as

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

Where: v =0,1,2,3,4,........ = Vibrational quantum number

$$\bar{V} = \left(v + \frac{1}{2}\right)\bar{\omega} \text{ cm}^{-1}$$

When, $v = 0$ $\quad \bar{V} = \frac{1}{2}\bar{\omega}$ cm^{-1} and E = ½ hω joules

So, the diatomic molecule can never have zero vibrational energy at rest relating to each other & the quantity ½ hω joule or ½ $\bar{\omega}$ cm^{-1} is known as **Zero Potential Point** or **Zero Point Energy**.

SELECTION RULE

1. The Molecule should change dipole moment with vibration.
2. The transition between adjacent state is allowed i.e. $\Delta v = \pm 1$
   $\Delta v = +1 \rightarrow$ Absorption of Energy
 $\Delta v = -1 \rightarrow$ Emission of Energy
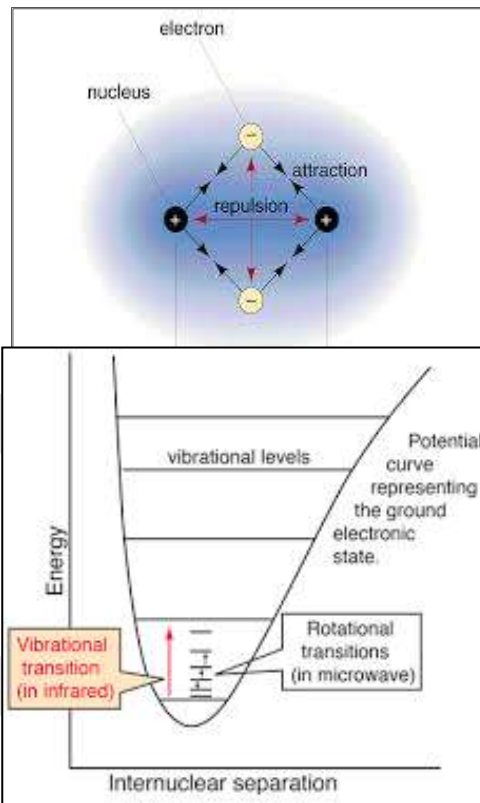
VIBRATIONAL SPECTRA

From the selection rule we can calculate the spectral line as

$$\Delta \bar{v}_{(v+1) \to v} = ((v + 1 + 1/2))\,\bar{\omega} - ((v + 1/2))\,\bar{\omega} = \bar{\omega} \text{ cm}^{-1}$$

Since the vibrational energy level are equally spaced the transition between any two neighbouring state will give rise same energy change.

The transition energy equal to the natural vibrational frequency $\bar{v}_0$, thus the dipole oscillates in the frequency $\bar{v}_0$ must interact with the light of the same frequency $\bar{v}_0$ is called as **fundamental frequency of vibration**.
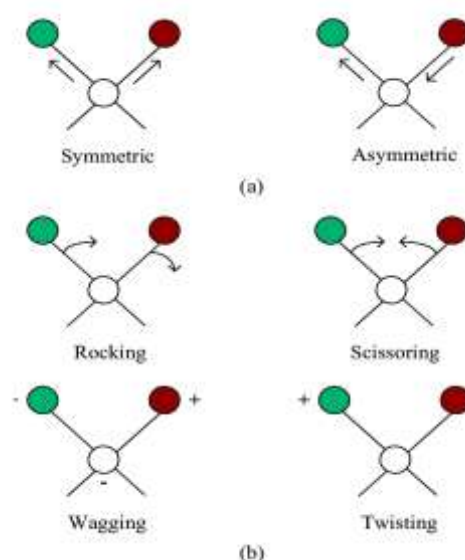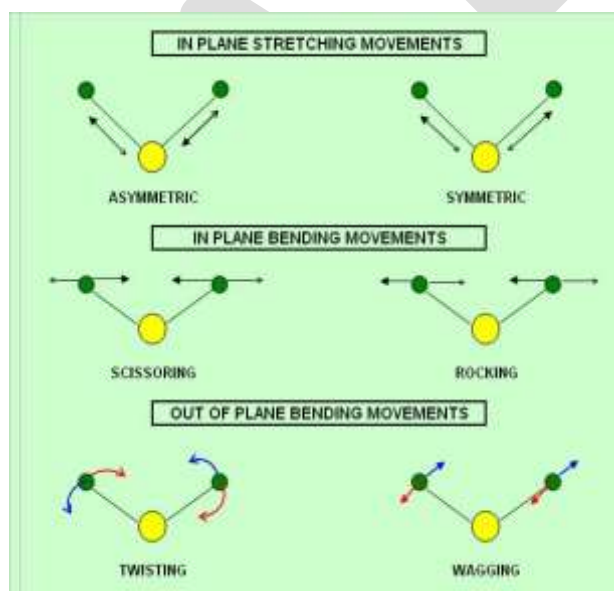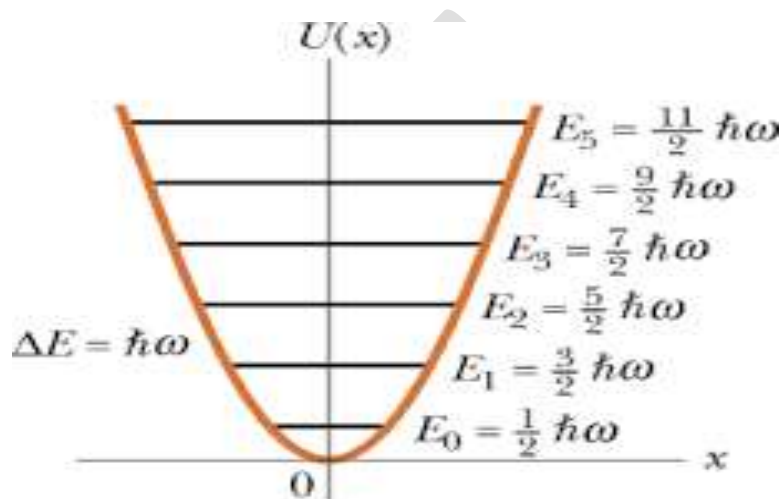
TYPES OF MOLECULAR VIBRATIONS

ASSIGNMENTS

1. Set up and solve the Schrodinger wave equation for a particle in an infinite one dimensional Box. With potential box with zero inside the box. Normalized the wave function.

2. Write the application of Schrodinger equation to particle in one dimensional box.

3. Explain Lambert-Beer's law. Define Auxochrome & chromophore. A light of wave length 400 nm is passed through a cell of 2 mm path length containing 10^{-3} mol dm^{-3} of compound X. If absorbance of this solution is 0.5. Calculate molar absorption co-efficient and transmittance.

4. State and explain Beer-Lambert's law. Explain various type of electronic transition occurs in UV spectroscopy with Example.

5. The vibration spectrum of HCl gas exhibits an absorption band cantered 2885 cm^{-1}. Calculate the force consent of the bond of HCl molecules. (mass of H =1.0078u, Cl=35.4993u)

6. What do you mean by auxochrome & chromophore? Discuss the various types of shift in UV-spectroscopy.

7. Calculate moment of inertia and rotational constant of HF molecule having bond distance 92pm.

8. Which type of molecules exhibit infra-red Spectra? Calculate the vibration energy and force constant of HF if its vibrational frequency is 3.0×10^{14} Hz

Short Questions with Answers

1. What do you mean by auxochrome? Explain how an Auxochrome exert a Bathochrome shift on a chromophore such as an ethylene bond.

Ans:-An Auxochrome is an auxiliary group which interacts with chromophore causing Bathochrome shift. Typical examples are:-NH_2 – OH, and –Cl.

The unshared electron on the heteroatom of an auxochrome becomes part of an extended π system by interacting with π-electron of olefinic system.This interaction has the effect of lowering the energy in both π and π^* orbital and consequently the $\pi \rightarrow \pi^*$ energy gas decreases resulting in a redshift.

2. Define chromophore and identify the chromophore group in the following compound.
a) Toluene b) Butanone

Ans:-A chromophore is a functional group which is responsible for electronic absorption.
The chromophoric group present in compound.
a)   Toluene   : $-C_6H_5$
b)   Butanone   : $>C = O$

3. Acetone absorb at 279 nm in hexane where as values λ max of it in water is 269.5 nm Explain.
Ans:-The blue shift results from hydrogen bond which lowers the energy of the n-orbital in water.

7

4. Write the selection rule of rotational spectrum and define the term used there in.

Ans:-The selection Rule for rotational spectrum is the molecule has permanent dipole moment
The transition between adjacent state is given by
$\Delta J = \pm 1$
For absorption of radiation $\Delta J = +1$
For emission of radiation $\Delta J = -1$

5. Which of the molecules exhibit rotational spectrum? H_2, NH_3, H_2O, Benzene, CO_2.

Ans:-To exhibit a pure rotational spectrum, a molecule must possess a permanent dipole moment. Thus, only HN_3 and H_2O molecules have permanent dipole moment. Hence, NH_3 and H_2O exhibit pure rotational spectrum. Note that H_2, CO_2 and benzene molecules do not have permanent dipole moment and hence these molecules do not exhibit pure rotational spectrum.

6. Define red and blue shifts in UV- visible spectra.
Ans:-It is the effect by virtue of which the absorption is shifted towards longer wavelength. This shift is called as red shift. & it is the effect by virtue of which the absorption shifts toward shorter wavelength or blue colour. It is called as hypso chromic shift.

7. Some of the fundamental vibrations and IR Active while others are not. Explain?
Ans:- Infra-red light is absorbed only when a molecule of substance under examination undergoes a net change of dipole moment.Total symmetry about a bond eliminates certain bonds and thus the number of bands which appear does not agree with the number of fundamental vibrations.Clearly,some of the fundamental vibrations in infra-red are active and some are inactive.

8. Write down the vibrational degree of freedom for Linear and non-Linear molecule.
Ans:-In non-linear molecules, three degrees of freedom describe rotation and another three describe translational. The remaining (3n-6) are the vibrational degrees of freedom. But in linear molecules, there are only two degree of rotation.

9. Write the selection rule for Vibrational Spectroscopy.
Ans:-The molecule should change in dipole moment with vibration.
$\Delta v = \pm 1$, $\nabla v = +1$ (Absorption of energy), $\nabla v = -1$(Emission of energy)

10. Calculate the wave length of an electron moving with the 4.55×10^{-25} j of kinetic energy.

Ans:- $KE = \frac{1}{2}mv^2 = 4.55 \times 10^{-25}$J $\quad V = \left\{ \frac{2 \times 4.55 \times 10^{-25}J}{9.1 \times 10^{-31}kg} \right\}^{\frac{1}{2}} = 10^3 ms^{-1}$
De Broglie equation, $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} Js}{9.1 \times 10^{-31}kg \times 10^3 ms^{-1}} = 7.281 \times 10^{-7}$m.

11. Two energy level are separated in wave number by 400 cm^{-1}. Covert this energy into joule.

Ans:- $\bar{v} = 400$ cm-1
$\Delta E = hv = \frac{hc}{\lambda} = hc\bar{v} = 6.626 \times 10^{-34}$ JS x 3 x 10^8 cm/sec x 400 cm^{-1} = 7.9512 X 10^{-21} joules

12. Write the physical significance of $\Psi \& \Psi^2$.
Ans:- Wave function Ψ is a state function which has no physical significance except that it represents the amplitude of waves. Many values of wave function Ψ obtained from the Schrödinger's equation have no significance. According to Born interpretation, wave function Ψ for stationary states is the Eigen function, which corresponds to the definite values of total energy E called Eigen values. Ψ Must have the following restrictions imposed by born interpretation. Ψ^2 is the probability of finding electron.

13. Write the one-dimensional time-independent Schrodinger equation.

Ans:- $\dfrac{\partial^2 \Psi}{\partial x^2} + \dfrac{8\pi^2 m}{h^2}(E-V)\Psi = 0$

14. Write the Schrodinger's 3-dimensional wave equation and define the terms.

Ans:- :- $\dfrac{\partial^2 \Psi}{\partial x^2} + \dfrac{\partial^2 \Psi}{\partial y^2} + \dfrac{\partial^2 \Psi}{\partial z^2} + \dfrac{8\pi^2 m}{h^2}(E-V)\Psi = 0$

15. Calculate the uncertainty in velocity of a cricket ball with mass 100 gm, if uncertainty in position is 1 cm.

Ans:- m= 100 gm , $\Delta x = 1cm$.

$\Delta x.\, \Delta v = \dfrac{h}{4\pi m} \Rightarrow \Delta v = \dfrac{h}{4\pi m.\Delta x} = \dfrac{6.626\times 10^{-27}}{4\times 3.14\times 100\times 1} = 5.2\times 10^{-29}$ cm/sec