

MOLECULAR SPECTRA

The study of the behavior or characteristics of a molecule when Electromagnetic radiation is interact with matter is called "Molecular Spectra."

The Spectroscopic techniques are generally used to measure the energy difference between various energy levels of molecules and to determine atomic and molecular structures.

Nature of Molecular Spectra :-

1. Molecular Spectra are band spectra.
2. It consists of a number of regularly spaced luminous bands.
3. The bands are formed by large number of closely spaced spectral lines with definite pattern.
4. The lines are crowded at the long wavelength edge, this edge is known as band head. At the other edge the lines are spacious is known as band tail.
5. The band head will be of higher intensity and tail end will be of lower intensity.

Classifications of Molecules :-

On the basis of Moment of Inertia of the molecule about the axis of rotation, the molecules are classified as,

- i) Linear molecule.
- ii) Symmetrical top molecule.
- iii) Spherical top molecule.
- iv) Asymmetric top molecule.

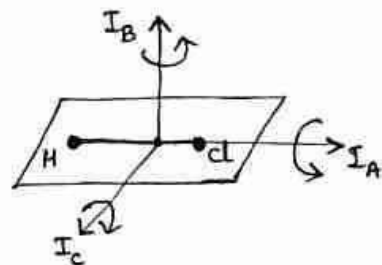
1. Linear molecules :-

The molecules in which all the atoms are arranged in a straight line.

Eg :- HCl, O-C-S (Carbon Oxy Sulphide) etc.

Consider HCl molecule whose Centre of mass lies nearest to chlorine atom as shown in figure. Let take three axis of rotation A, B, C which are mutually perpendicular to each other and passes through Centre of mass. Here axis 'A' is along the direction of bond between H^+ and Cl^- atoms, so these axis is called principle axis of rotation.

When molecule rotating about principle axis 'A', the position of H and Cl atoms does not changes, hence moment of Inertia of a molecule is approximately Zero, i.e. $I_A \approx 0$.



While the molecule rotating around axis B and C, the position of both H and Cl is changes, hence moment of Inertia about those both axis is equal and greater than I_A . Therefore, for linear molecules, $I_B = I_C, I_A \approx 0$.

2. Symmetric top molecules :-

The moment of Inertia of a molecule about principle axis of rotation is not equal to zero and the moment of Inertia about other two axis is equal, then such molecules are called as Symmetric top molecules.

$$\text{i.e. } I_B = I_C, I_A \neq 0$$

Eg :- NH_3 (Ammonia), CH_3F (Flouro methane) etc.

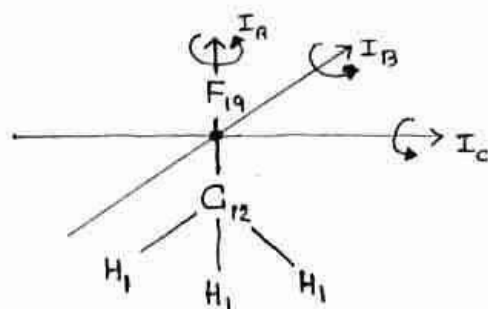
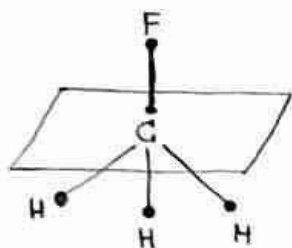
The Symmetric top molecules are classified into 2 groups:-

- i) prolate Symmetric top molecules.
- ii) oblate Symmetric top molecules.

Prolate Symmetric molecule :-

Moment of Inertia of a molecule about principle axis is not equal to zero but less than moment of Inertia's of other two axis, such molecules are prolate symmetric molecules.

Eg :- CH_3F (Fluoro methane)



When molecules rotating about principal axis 'A', position of C and F atoms are not changes its position while 3 Hydrogen atoms are changes its position. Hence $I_A \neq 0$ but very lesser.

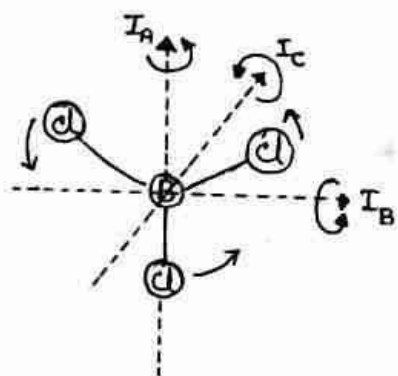
When molecules rotating about axis 'B' and 'c' all the 5 atoms are changing their relative position so $I_B = I_C$ and much higher than I_A . Therefore, for prolate molecules,

$$I_B = I_C > I_A$$

Oblate Symmetric molecules :-

Moment of Inertia of a molecule about principle axis is greater than the moment of Inertia's of other two axis of the molecule, such are known as oblate symmetric molecules.

Eg :- BCl_3 (Boron trichloride), NH_3 (Ammonia).



When molecule rotate about principle axis, the moment of Inertia about that axis is higher because all three chlorine atoms changes its position. When molecule rotate about axis 'B' and 'c', out of three chlorine

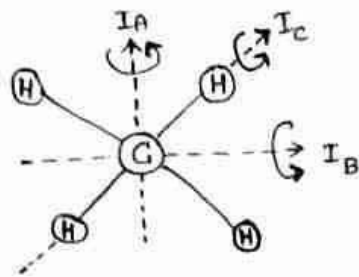
atoms only two atoms rotates in larger circumference hence moment of Inertia required is lesser than I_A . Therefore,

$$I_B = I_C < I_A$$

3. Spherical top molecules :-

Moment of Inertia of a molecule about three axis is equal then such molecules are called as Spherical top molecules.

Eg :- CH_4 (Methane)



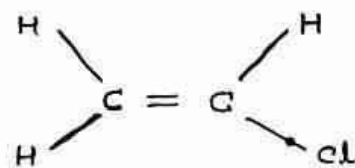
Centre of mass is in exactly on Carbon atom, hence no principle axis is exists. So when molecules rotates about the three axis all the atoms changes there relative position, hence moment of inertia of a molecule about the three axis is same.

$$\text{i.e. } I_A = I_B = I_C$$

4. Asymmetric top molecules :-

Moment of Inertia of a molecule about three axis is different then such molecules are called as Asymmetric top molecules.

Eg :- Vinyl chloride ($\text{H}_2\text{C}=\text{CHCl}$)



A molecule becomes Asymmetric top molecule if there is no proper axis of rotation. Therefore, this is the Least symmetric class of molecules.

$$\therefore I_A \neq I_B \neq I_C$$

Types of Molecular motions and Energies :-

Molecular motion is defined as movement of Constituent particles of motion in Certain direction. The degree of motion of Constituent particles is affected by temperature, because temperature is the measure of the average kinetic energy of the molecules, $\therefore E = kT$.

There are four types of molecular motion :

1. Translatory motion :-

The movement of molecules may be in a different direction, but the movement axis remains the same i.e straight line. This form of movement is called Translatory motion.

2. Rotational motion :-

The molecules rotate around the axis, this type of motion is called Rotational motion.

3. Vibrational motion :-

To and fro movement of molecule in their mean position is called Vibrational motion.

Energy of Molecule :-

The energy of a diatomic molecule is due to,

- i) the transition of electron from excited energy state to lower state within the molecule is known as Electronic energy (E_e)
- ii) the vibration of the atoms in the molecule is known as Vibrational energy (E_v).
- iii) the rotation of the molecules about the centre of mass is known as Rotational energy (E_r).
- iv) movement of molecule known as Translational energy (E_t).

thus the total energy of the molecule is the sum of E_e , E_v and E_r . i.e

$$E = E_e + E_v + E_r + E_t$$

These energies are quantized.

Born - Oppenheimer Approximation :-

It states that "the total energy associated with molecule is assumed to be sum of electronic, vibrational and rotational energies and these energies are considered to be independent on each other".

$$E_{\text{Total}} = E_{\text{vib}} + E_{\text{ele}} + E_{\text{rot}} + E_{\text{tran}}$$

the change in energy is given by

$$\Delta E_T = \Delta E_v + \Delta E_e + \Delta E_r + \Delta E_t$$

translational energy is so small that it is to be taken as continuous $\therefore \Delta E_t = 0$.

Origin of Molecular Spectra :-

The molecular spectra arises due to transitions between allowed energy states of molecules.

The transition between two energy states of a molecule as a result of absorption or emission of energy give rise to a spectral line. When molecule suffers a transition from higher energy state to lower energy state, difference of energy ΔE is emitted as radiation of frequency ν given as

$$\nu = \frac{\Delta E}{h}$$

For each allowed transition, we get one line in the spectrum of the molecule.

Types of Molecular Spectra :-

1. Pure Rotational Spectrum :-

The transitions between the rotational energy states of molecule with the emission or absorption of a photon gives pure rotational spectrum.

In this case electronic configuration of atom and vibrational state of molecule remains the same.

These spectra are in the microwave and far IR regions.

2. Rotational - Vibration Spectrum :-

If molecule remains in the ground state of electronic energies, and if there is transition between the rotational and vibrational energy levels, we get Rotational - Vibration Spectra.

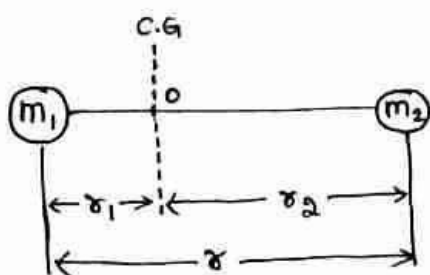
These spectrum lies near IR regions.

3. Electronic Spectrum :-

If there is transitions in the electronic, rotational and vibrational energy levels, then we get electronic spectrum.

The spectrum lies in Visible and UV regions.

Theory of Rigid Rotator :-



Consider a diatomic molecule in which m_1 and m_2 are the atomic masses of atoms. If ' r ' is a equilibrium

distance b/w atoms also known as bond length (r). Centre of mass lies at the point 'O' b/w two atoms and rotational axis is pass through Centre of mass which is perpendicular to bond length.

Moment of Inertia of i^{th} particle is $I = \sum m_i r_i^2$

\therefore Moment of Inertia of the molecule about the axis of rotation is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{----- (1)}$$

where ' r_1 ' is distance b/w axis of rotation and mass ' m_1 ' and ' r_2 ' is distance b/w axis of rotation and mass ' m_2 '.

from Centre of mass, $m_1 r_1 = m_2 r_2$ ----- (2)

Since bond length $r = r_1 + r_2$

$$\therefore r_2 = r - r_1$$

eq (2) becomes

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

$$m_1 r_1 = m_2 r - m_2 r_1$$

$$r_1 (m_1 + m_2) = m_2 r$$

$$\boxed{r_1 = \frac{m_2 r}{m_1 + m_2}} \quad \text{--- (3)}$$

$$r_1 = r - r_2$$

eq (2) becomes

$$m_1 (r - r_2) = m_2 r_2$$

$$m_1 r - m_1 r_2 = m_2 r_2$$

$$m_1 r = m_2 r_2 + m_1 r_2$$

$$\boxed{r_2 = \frac{m_1 r}{m_1 + m_2}} \quad \text{--- (4)}$$

Substitute (3) and (4) in eq (1)

$$\therefore I = \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r^2}{(m_1 + m_2)^2}$$

$$I = \frac{m_1 m_2 (m_1 + m_2) r^2}{(m_1 + m_2)^2}$$

$$I = \frac{m_1 m_2}{(m_1 + m_2)} r^2$$

$$\boxed{I = \mu r^2}$$

where $\mu = \frac{m_1 m_2}{(m_1 + m_2)}$ is reduced mass.

This equation gives moment of Inertia of diatomic molecules.

Energy levels :-

Angular momentum of rotating body is given by

$$L = I \omega$$

angular momentum of a rotating body quantum mechanically given by

$$L = \sqrt{J(J+1)} \hbar, \text{ where } \hbar = h/2\pi$$

Energy of rotating body is given by.

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

$$E = \frac{1}{2} I \omega^2 \times \frac{I}{I}$$

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

$$E = \frac{L^2}{2I} \text{ ----- (5)}$$

Substitute the value of 'L' in eqn(5), we get

$$E = \frac{J(J+1) h^2}{8\pi^2 I} \text{ ----- (6)}$$

Where $J=0, 1, 2, 3, \dots$ called Rotational quantum number.

From Planck's Law, $E = h\nu$

$$E = \frac{hc}{\lambda} = hc \cdot \frac{1}{\lambda}$$

$$E = hc \cdot \bar{\nu}$$

$$\therefore \bar{\nu} = \frac{E}{hc} = \frac{J(J+1) h^2}{8\pi^2 I hc}$$

$$\bar{\nu} = \frac{h}{8\pi^2 I c} \cdot J(J+1)$$

$$\bar{\nu} = B \cdot J(J+1)$$

The rotational energy levels of the molecules are found by using the Selection rule $\Delta J = \pm 1$.

$$\text{for } J=0, \bar{\nu}_0 = 0$$

$$J=1, \bar{\nu}_1 = 2B$$

$$\text{for } J=2, \bar{\nu}_2 = 6B$$

$$\text{for } J=3, \bar{\nu}_3 = 12B$$

$$J=4, \bar{\nu}_4 = 20B$$

$0, 2B, 6B, 12B, 20B, 30B$ are the energy levels for rotational quantum number $J=0, 1, 2, 3, 4, 5, \dots$

Energy Spectrum :-

For two successive energy levels corresponding to J and $J+1$, the energy difference is given by

$$\Delta E = E_{J+1} - E_J$$

$$\Delta E = \frac{h^2}{8\pi^2 I} (J+1)(J+2) - \frac{h^2}{8\pi^2 I} J(J+1)$$

$$\Delta E = \frac{h^2}{8\pi^2 I} (J+1) [J+2-J]$$

$$\Delta E = \frac{h^2}{4\pi^2 I} (J+1) \quad \text{and} \quad \bar{\nu} = \frac{\Delta E}{hc} = 2B(J+1)$$

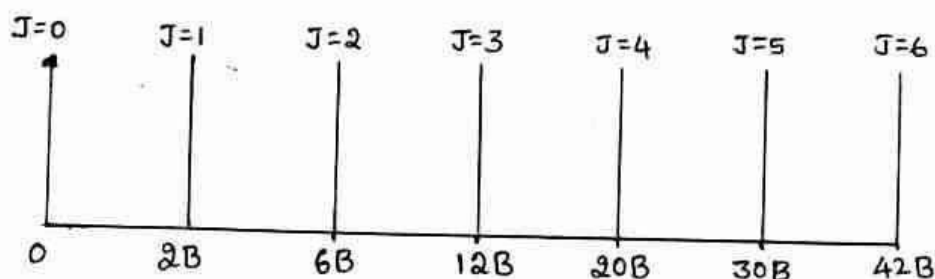
$$\therefore \bar{\nu}_{0 \rightarrow 1} = 2B(1) = 2B$$

$$\bar{\nu}_{1 \rightarrow 2} = 2B(2) = 4B$$

$$\bar{\nu}_{2 \rightarrow 3} = 2B(3) = 6B$$

$$\bar{\nu}_{3 \rightarrow 4} = 2B(4) = 8B$$

hence rotational energy spectrum of rigid diatomic molecule (rotator) consists of series of lines at $2B, 4B, 6B, 8B, \dots$ etc. These lines are equally spaced by an amount of $2B$.

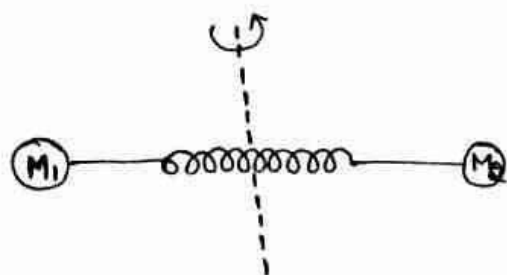


NON-RIGID ROTATOR :-

In Rigid rotator, the separation of spectral lines is equidistant by $2B$. But experimentally we saw that separation of spectral lines is decreased with increase in rotational quantum number J . This is because the distance between the atoms in a molecule i.e bond length is not constant while rotating around the axis of rotation.

When diatomic molecule is rotating about the axis of rotation, the atoms are vibrating along the bond between the atoms. Hence rotational energy of a molecule is increased as well as rotational quantum number ' J ' also increased. As a result Centrifugal force is acts on the atoms. Hence bond length ' r ' is increased, hence rotational constant ' B ' is decreased. Therefore, spacing between the spectral lines is decreased as increased in J .

In rotating diatomic molecule the atoms are connected by massless spring, such molecules which are changes its internuclear distance while rotating about axis of rotation is known as Non-rigid rotator.



Setup the Schrodinger's equation for rotational energy, then we will get

$$E_j = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 \sigma^2 K} J^2(J+1)^2 \quad \text{in Joules}$$

the frequency of energy spectrum is

$$\bar{\nu} = \frac{E_j}{hc} = \frac{h}{8\pi^2 I c} J(J+1) - \frac{h^3}{32\pi^4 I^2 \sigma^2 K c} J^2(J+1)^2$$

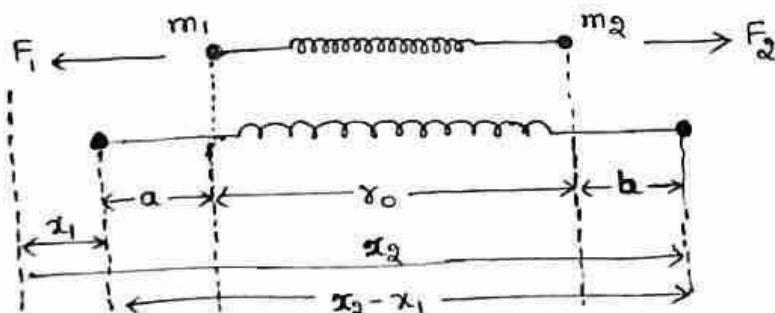
$$\bar{\nu} = B J(J+1) - D J^2(J+1)^2 \quad \text{cm}^{-1}$$

Where $D = \frac{h^3}{32\pi^4 I^2 \sigma^2 K c}$ is the Centrifugal distortion

Constant of positive quantity.

VIBRATING MOLECULE AS A HARMONIC OSCILLATOR :-

In the case of diatomic molecule, atoms are vibrating since they are connected by a spring. When the external force acting on the system is zero, molecule must be in equilibrium state i.e. atoms are in rest. \therefore Equilibrium distance b/w them is r_0 . When external force is act on the system distance b/w atoms are changed due to expansion of bond.



The displacement of the spring at any time, $x = a + b$
The length of the spring at any time is given by

$$r_0 + x = x_2 - x_1$$

$$x = x_2 - x_1 - r_0 \quad \text{--- (1)}$$

If 'k' is the force constant of the spring representing bond between two atoms, and F_1 and F_2 are the restoring forces acting on m_1 and m_2 respectively. Then, from Hooke's Law,

$$F_1 = kx \quad \text{and} \quad F_2 = -kx$$

from Newton's Second Law,

$$F_1 = m_1 a_1 = m_1 \frac{d^2 x_1}{dt^2} = kx \quad \text{--- (2)}$$

$$F_2 = m_2 a_2 = m_2 \frac{d^2 x_2}{dt^2} = -kx \quad \text{--- (3)}$$

Multiply eq (2) by m_2 and eq (3) by m_1 and then subtracting eq (2) from eq (3), we get.

$$m_1 m_2 \frac{d^2 x_2}{dt^2} - m_1 m_2 \frac{d^2 x_1}{dt^2} = -m_1 kx - m_2 kx$$

$$m_1 m_2 \left[\frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2} \right] = -kx (m_1 + m_2)$$

$$\frac{m_1 m_2}{m_1 + m_2} \left[\frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2} \right] = -kx \quad \text{--- (4)}$$

Differentiate eq (1) twice w.r.t 't' we get

$$\frac{d^2 x}{dt^2} = \frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2}$$

eq (4) becomes, $\frac{m_1 m_2}{m_1 + m_2} \frac{d^2 x}{dt^2} = -kx$

$$\mu \frac{d^2 x}{dt^2} + kx = 0$$

$$\therefore \boxed{\frac{d^2 x}{dt^2} + \frac{k}{\mu} x = 0}$$

This equation represents Simple harmonic motion, hence vibrating molecules behave as Simple harmonic oscillator. Comparing this equation with SHM equation

We have $\omega^2 = \frac{k}{\mu}$ or $\omega = \sqrt{\frac{k}{\mu}}$

$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ is the frequency of vibration.

$$\text{Wave number } (\bar{\nu}) = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Energy levels :-

When the energy of the molecule is increased, then the atoms vibrate more actively back and forth i.e. Compression and extension in the bond. The frequency of oscillation is depend only on force constant of bond and masses of atoms and independent on bond length.

Vibrational energy is also quantized and is calculated by solving Schrodinger's equation, we get

$$E_v = \left(v + \frac{1}{2}\right) h\omega_0 \quad \text{Joule.}$$

where $v \rightarrow$ vibrational quantum number.

$$E_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \frac{\omega_0}{c} \quad \text{cm}^{-1}$$

put $\frac{\omega_0}{c} = \bar{\omega}_0$, frequency in terms of wave number

$$\therefore E_v = \left(v + \frac{1}{2}\right) \bar{\omega}_0$$

The Lowest vibrational energy obtained by having $v=0$

$$\therefore E_v = \frac{1}{2} h\omega_0 \quad \text{Joules}$$

$$E_v = \frac{1}{2} \bar{\omega}_0 \quad \text{cm}^{-1}$$

It indicates that diatomic molecule do not have zero vibrational energy i.e. the atoms in the molecule can never completely at rest. The lowest possible energy must be a $\frac{1}{2} h\omega_0$ or $\frac{1}{2} \bar{\omega}_0$. It depends on strength of bond and mass of atoms.

By Selection rule, we have $\Delta v = \pm 1$

\therefore for $v=0, 1, 2, 3 \dots$, the vibrational energies be

$\frac{1}{2} \bar{\omega}_0, \frac{3}{2} \bar{\omega}_0, \frac{5}{2} \bar{\omega}_0$ in cm^{-1} or $\frac{1}{2} h\omega_0, \frac{3}{2} h\omega_0, \frac{5}{2} h\omega_0$ in Joules respectively.

$$v=3 \text{ ————— } E_3 = \frac{7}{2} \bar{\omega}_0$$

$$v=2 \text{ ————— } E_2 = \frac{5}{2} \bar{\omega}_0$$

$$v=1 \text{ ————— } E_1 = \frac{3}{2} \bar{\omega}_0$$

$$v=0 \text{ ————— } E_0 = \frac{1}{2} \bar{\omega}_0$$

PROBLEMS :-

1. In CO molecule the wavenumber difference between the successive absorption lines in the pure rotational spectrum is 384 m^{-1} . Calculate moment of Inertia of the molecule and the equilibrium bond length of the molecule.

Given :- Masses of C^{12} atoms = $1.99 \times 10^{-26} \text{ kg}$

Masses of O^{16} atoms = $2.66 \times 10^{-26} \text{ kg}$.

$$\text{w.k.t } \Delta \bar{\nu} = \frac{h}{4\pi^2 I c} = 384 \text{ m}^{-1}$$

$$\therefore I = \frac{h}{4\pi^2 c \Delta \bar{\nu}} = \frac{6.654 \times 10^{-34}}{4\pi^2 \times 3 \times 10^8 \times 384}$$

$$I = 1.456 \times 10^{-46} \text{ kg m}^2$$

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.99 \times 2.66 \times 10^{-52}}{[1.99 + 2.66] \times 10^{-26}}$$

$$\therefore \mu = 1.138 \times 10^{-26} \text{ kg}.$$

$$\text{Bond length } (r) = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.456 \times 10^{-46}}{1.138 \times 10^{-26}}} = 0.1131 \times 10^{-9} \text{ m}$$

2. The lines in the pure rotational spectrum of HCl are spaced as 20.8×10^2 per metre. Calculate moment of Inertia and the internuclear distance. Mass of proton = $1.67 \times 10^{-27} \text{ kg}$, mass of Chlorine = $58.5 \times 10^{-27} \text{ kg}$.

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.67 \times 10^{-27} \times 58.5 \times 10^{-27}}{(1.67 + 58.5) \times 10^{-27}}$$

$$\mu = 1.62 \times 10^{-27} \text{ kg}.$$

$$\Delta \bar{\nu} = \frac{h}{4\pi^2 I c} = 20.8 \times 10^2 \text{ m}^{-1}$$

$$\therefore I = \frac{6.654 \times 10^{-34}}{4\pi^2 \times 3 \times 10^8 \times 20.8 \times 10^2} = 2.689 \times 10^{-47} \text{ kg m}^2$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.689 \times 10^{-47}}{1.62 \times 10^{-27}}} = 1.286 \times 10^{-10} \text{ m}$$

3. Determine the rotational energy of CO on the quantum level $J=2$ if the equilibrium nuclear distance of CO is 1.131 \AA ($1 \text{ a.m.u} = 1.66 \times 10^{-27} \text{ kg}$).

$$\begin{aligned} \text{Reduced mass } (\mu) &= \frac{m_1 m_2}{m_1 + m_2} = \frac{16 \times 12}{16 + 12} = 6.857 \text{ a.m.u} \\ &= 6.857 \times 1.66 \times 10^{-27} \\ \mu &= 1.14 \times 10^{-26} \text{ kg} \end{aligned}$$

$$\text{Moment of Inertia } (I) = \mu r^2$$

$$I = 1.14 \times 10^{-26} \times (1.131 \times 10^{-10})^2$$

$$I = 1.46 \times 10^{-46} \text{ kg m}^2$$

$$\text{Energy } (E) = \frac{h^2 J(J+1)}{8\pi^2 I}$$

$$E = \frac{(6.654 \times 10^{-34})^2 \times 6}{8\pi^2 \times 1.46 \times 10^{-46}} = 2.30 \times 10^{-22} \text{ J}$$

4. Find the energy and angular velocity of CO molecule in the ground state. Given CO bond length = 0.113 nm and mass of atoms $m_c = 1.99 \times 10^{-26} \text{ kg}$ and $m_o = 2.66 \times 10^{-26} \text{ kg}$.

$$\text{W.K.T Energy of diatomic molecule} = \frac{J(J+1)h^2}{8\pi^2 I}$$

for ground state, $J=0$

$$\therefore E_J = 0$$

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

$$\therefore \frac{1}{2} I \omega^2 = 0$$

$$\text{Angular velocity } (\omega) = 0$$

ELECTRONIC SPECTRA :-

1. Energies of rotational and vibrational spectra are due to motion of atomic nuclei because most mass of the atom is concentrated in the nuclei.
2. In molecule, electrons are excited to higher state from ground state. The spacing of these levels is much greater than spacing of vibrational or rotational levels. The electronic transition thus involve much greater energies and gives rise to spectra of visible or UV region.
3. Electronic energy levels in a molecule are separated by energies of order of eV. Each electronic energy level may have number of vibrational energy levels, with each vibrational energy level further having number of rotational energy levels with energy separation of 10^2 eV to 10^3 eV. Thus each energy level of electronic spectra consists of large number of levels closely spaced together. Each electronic transition therefore produces a series of closely spaced lines.
4. All molecules exhibit electronic spectra, because dipole moment is always accompanied. Homonuclear molecule like N_2 , H_2 , O_2 which does not exhibit rotational or vibrational spectra because they do not possess permanent dipole moment.

Frequency of Spectra :-

When the electronic states of a molecule are excited, the total energy of the molecule in a given quantum state, is given by

$$E = E_e + E_v + E_j$$

The frequency of radiation, when transition between any two states takes place is given by

$$\nu = \frac{E_1 - E_2}{h} = \frac{E_{e1} - E_{e2}}{h} + \frac{E_{v1} - E_{v2}}{h} + \frac{E_{j1} - E_{j2}}{h}$$

$$\nu = \frac{\Delta E_e}{h} + \frac{\Delta E_v}{h} + \frac{\Delta E_j}{h}$$

$$\nu = \frac{1}{h} [\Delta E_e + \Delta E_v + \Delta E_j]$$

LUMINESCENCE :-

When molecule absorbs energy in the form a high frequency radiation and re-emits it in the form of visible light, this phenomenon is known as Luminescence.

FLOURESCENCE :-

When a molecule absorbs and emits photon simultaneously that phenomenon is known as Fluorescence.

PHOSPHORESCENCE :-

If the molecule emits light by minutes or hours after the initial absorption of photon, this type of radiation emission is Phosphorescence.

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$$\text{w.k.T } \Delta \bar{\nu} = \frac{h}{4\pi^2 I c} = 384 \text{ m}^{-1}$$

$$\therefore I = \frac{h}{4\pi^2 c \Delta \bar{\nu}} = \frac{6.654 \times 10^{-34}}{4\pi^2 \times 3 \times 10^8 \times 384}$$

$$I = 1.456 \times 10^{-46} \text{ kg m}^2$$

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.99 \times 2.66 \times 10^{-52}}{[1.99 + 2.66] \times 10^{-26}}$$

$$\therefore \mu = 1.138 \times 10^{-26} \text{ kg.}$$

$$\text{Bond length } (r) = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.456 \times 10^{-46}}{1.138 \times 10^{-26}}} = 0.1131 \times 10^{-9} \text{ m}$$

2. The lines in the pure rotational spectrum of HCl are spaced as 20.8×10^2 per metre. Calculate moment of inertia and the internuclear distance. Mass of proton = $1.67 \times 10^{-27} \text{ kg}$, mass of Chlorine = $35.5 \times 10^{-27} \text{ kg}$.

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.67 \times 10^{-27} \times 35.5 \times 10^{-27}}{(1.67 + 35.5) \times 10^{-27}}$$

$$\mu = 1.62 \times 10^{-27} \text{ kg.}$$

$$\Delta \bar{\nu} = \frac{h}{4\pi^2 I c} = 20.8 \times 10^2 \text{ m}^{-1}$$

$$\therefore I = \frac{6.654 \times 10^{-34}}{4\pi^2 \times 3 \times 10^8 \times 20.8 \times 10^2} = 2.689 \times 10^{-47} \text{ kg m}^2$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.689 \times 10^{-47}}{1.62 \times 10^{-27}}} = 1.286 \times 10^{-10} \text{ m}$$

3. Determine the rotational energy of CO on the quantum level $J=2$ if the equilibrium nuclear distance of CO is 1.131 \AA ($1 \text{ a.m.u} = 1.66 \times 10^{-27} \text{ kg}$).

$$\begin{aligned} \text{Reduced mass } (\mu) &= \frac{m_1 m_2}{m_1 + m_2} = \frac{16 \times 12}{16 + 12} = 6.857 \text{ a.m.u} \\ &= 6.857 \times 1.66 \times 10^{-27} \\ \mu &= 1.14 \times 10^{-26} \text{ kg} \end{aligned}$$

$$\text{Moment of Inertia } (I) = \mu r^2$$

$$I = 1.14 \times 10^{-26} \times (1.131 \times 10^{-10})^2$$

$$I = 1.46 \times 10^{-46} \text{ kg m}^2$$

$$\text{Energy } (E) = \frac{h^2 J(J+1)}{8\pi^2 I}$$

$$E = \frac{(6.654 \times 10^{-34})^2 \times 6}{8\pi^2 \times 1.46 \times 10^{-46}} = 2.30 \times 10^{-22} \text{ J}$$

4. Find the energy and angular velocity of CO molecule in the ground state. Given CO bond length = 0.113 nm and mass of atoms $m_C = 1.99 \times 10^{-26} \text{ kg}$ and $m_O = 2.66 \times 10^{-26} \text{ kg}$.

$$\text{W.K.T Energy of diatomic molecule} = \frac{J(J+1)h^2}{8\pi^2 I}$$

for ground state, $J=0$

$$\therefore E_J = 0$$

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

$$\therefore \frac{1}{2} I \omega^2 = 0$$

$$\text{Angular velocity } (\omega) = 0$$

5. In near IR spectrum of HCl molecule there is single intense band at 2885.9 cm^{-1} . Assuming that it is due to transition b/w vibration levels. Show that force constant $k = 480 \text{ N/m}$.

$$\text{Given :- } M_H = 1.68 \times 10^{-27} \text{ kg}$$

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

$$\therefore \text{frequency of vibration } (\nu) = \bar{\nu} c = 288590 \times 3 \times 10^8$$

$$\nu = 8.6577 \times 10^{13} \text{ Hz}$$

$$\therefore \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \Rightarrow k = 4\pi^2 \mu \nu^2$$

$$\text{reduced mass } (\mu) = \frac{M_H M_{Cl}}{M_H + M_{Cl}} = \frac{1 \times 35}{(1+35)} \times M_H$$

$$\mu = \frac{35 \times 1.68 \times 10^{-27}}{36} = 1.63 \times 10^{-27} \text{ kg}$$

$$\therefore k = 4\pi^2 \times 1.63 \times 10^{-27} \times (8.65 \times 10^{13})^2$$

$$k = 482.3 \text{ N/m}$$

6. Calculate the vibrational energy levels of an HCl molecule, assuming the force constant to be 516 N/m .

Solution :- Reduced mass $(\mu) = \frac{35}{36} \times 1.0078 \times 1.66 \times 10^{-27}$

$$\mu = 1.62 \times 10^{-27} \text{ kg}$$

$$\text{frequency } (\nu) = \frac{1}{2\pi} \sqrt{\frac{516}{1.62 \times 10^{-27}}}$$

$$\nu = 8.98 \times 10^{13} \text{ Hz}$$

Energy levels are given by $(\nu + \frac{1}{2}) h\nu$

$$\therefore E_\nu = 6.654 \times 10^{-34} \times 8.98 \times 10^{13} (\nu + \frac{1}{2}) \text{ Joules}$$

$$= 5.9 \times 10^{-20} (\nu + \frac{1}{2}) \text{ Joules}$$

for $\nu = 0$ $E_{\nu=0} = 2.95 \times 10^{-20} \text{ J} = 0.1843 \text{ eV}$

$\nu = 1$ $E_{\nu=1} = 8.85 \times 10^{-20} \text{ J} = 0.553 \text{ eV}$

$\nu = 2$ $E_{\nu=2} = 14.75 \times 10^{-20} \text{ J} = 0.921 \text{ eV}$

$\nu = 3$ $E_{\nu=3} = 20.65 \times 10^{-20} \text{ J} = 1.290 \text{ eV}$