

UNIT - IV

Molecular Spectra

• Salient Features of Rotational Spectra:

Pure rotational molecular spectra arise from transitions between the rotational energy levels on the absorption of radiations falling in the microwave region. These spectra are shown by molecules which possess a permanent dipole moment, e.g., HCl, CO, HF etc.

Homonuclear diatomic molecules such as H_2 , O_2 , N_2 etc, and linear polyatomic molecules such as CO_2 , which do not have a dipole moment, do not show rotational (microwave) spectra.

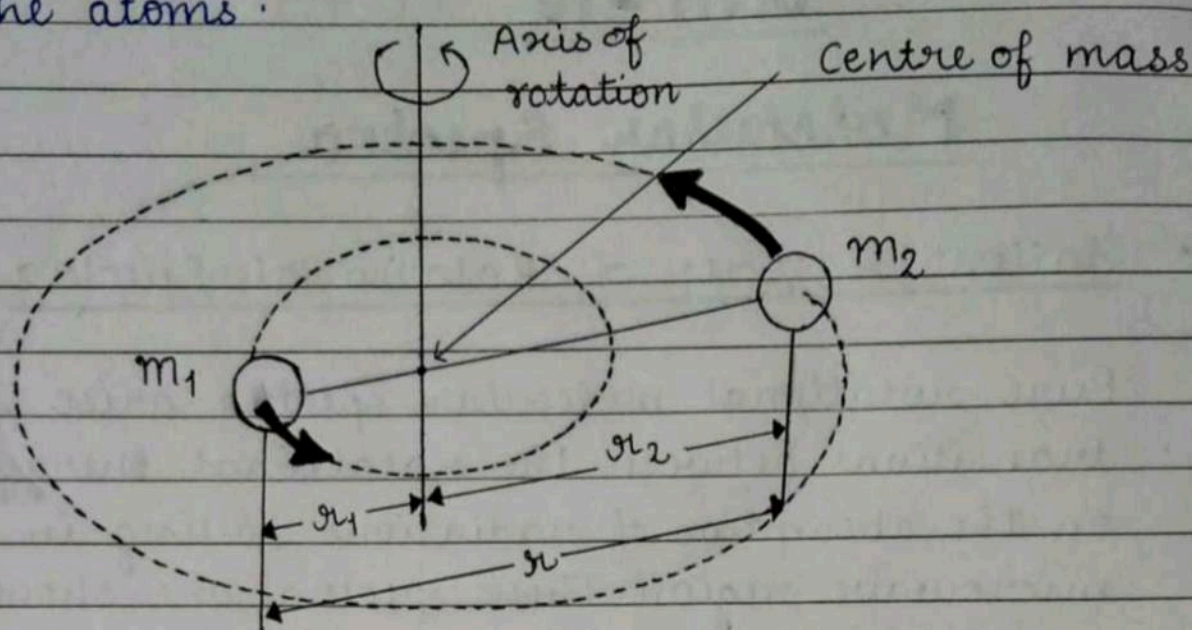
Rotational (microwave) spectra occur in spectral range of $1-100\text{ cm}^{-1}$.

• Rotational (Microwave) Spectra of Diatomic Molecules: [Diatomic molecule as a Rigid Rotator]

A rotating diatomic molecule with fixed inter-nuclear separation (bond length) is a Rigid rotator.

Consider a diatomic molecule in which ' m_1 ' and ' m_2 ' are the masses of the atoms and ' r ' is the equilibrium bond length, rotating about an axis passing through its centre of mass and perpendicular to the line joining

the atoms.



The moment of inertia of the molecule about the axis of rotation is given by-

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

Here, r_1 and r_2 are the distances of m_1 and m_2 , respectively from the centre of mass.

From the definition of centre of mass,

$$(m_1 + m_2) r_1 = m_1 \times 0 + m_2 r \quad \left\{ \begin{array}{l} \text{Taking mass } m_1 \\ \text{as origin} \end{array} \right.$$

$$\therefore r_1 = \frac{m_2 r}{m_1 + m_2}$$

Further, $r = r_1 + r_2$

$$\therefore r_2 = r - r_1$$

$$r_2 = r - \frac{m_2 r}{m_1 + m_2}$$

$$\text{So, } r_2 = \frac{m_1 r}{m_1 + m_2}$$

Putting these values of r_1 and r_2 in eqs(1),

$$I = m_1 \left[\frac{m_2 r}{m_1 + m_2} \right]^2 + m_2 \left[\frac{m_1 r}{m_1 + m_2} \right]^2$$

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

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

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

$$\text{So, } \boxed{I = \mu r^2}$$

Here, $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the molecule.

Classically, the angular momentum L of a rotating molecule is given by-

$$L = I\omega$$

where, ω is the angular velocity of molecule.

However, quantum mechanically the angular momentum is quantised and is given by-

$$L = \frac{\sqrt{J(J+1)} \hbar}{2\pi} \quad ; J = 0, 1, 2, 3 \dots$$

where, J is the rotational quantum number.

The energy of a rotating molecule is given by-

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

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

$$E = \frac{1}{2I} L^2 = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

$$\therefore E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1) \text{ Joule}$$

where, $J = 0, 1, 2, 3 \dots$

Thus, the rotating diatomic molecule (Rigid Rotator) can have a discrete set of energy levels.

• Rotational Spectrum:

The expression for the rotational energy of a diatomic molecule is,

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

; $J = 0, 1, 2, 3 \dots$

where, J is the rotational quantum number.

Now, in terms of wave number, the energy equation can be written as,

$$F(J) = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1)$$

Let us put $\frac{h}{8\pi^2 Ic} = B$, known as 'Rotational constant'. Then

$$F(J) = BJ(J+1)$$

Substituting $J = 0, 1, 2, 3, \dots$, we get

$$F(J) = 0, 2B, 6B, 12B, 20B, 30B, \dots$$

Thus, we have a series of discrete rotational energy levels whose spacing increase with increasing J .

¹³
The transitions between the rotational energy levels, i.e., the rotational transitions for a rigid diatomic molecule are governed by the selection rule,

$$\Delta J = \pm 1$$

i.e., only those transitions are allowed in

which the rotational quantum number changes by unity. The (+) sign refers to absorption and (-) sign refers to emission of radiation. Rotational (Microwave) spectra are usually observed as absorption spectra so that the selection is $\Delta J = +1$.

For a transition taking place from J to $J+1$, the wave number ($\bar{\nu}$) of absorbed radiation is given by-

$$\bar{\nu}_{J \rightarrow J+1} = F(J+1) - F(J)$$

$$\bar{\nu}_{J \rightarrow J+1} = B(J+1)(J+2) - BJ(J+1)$$

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

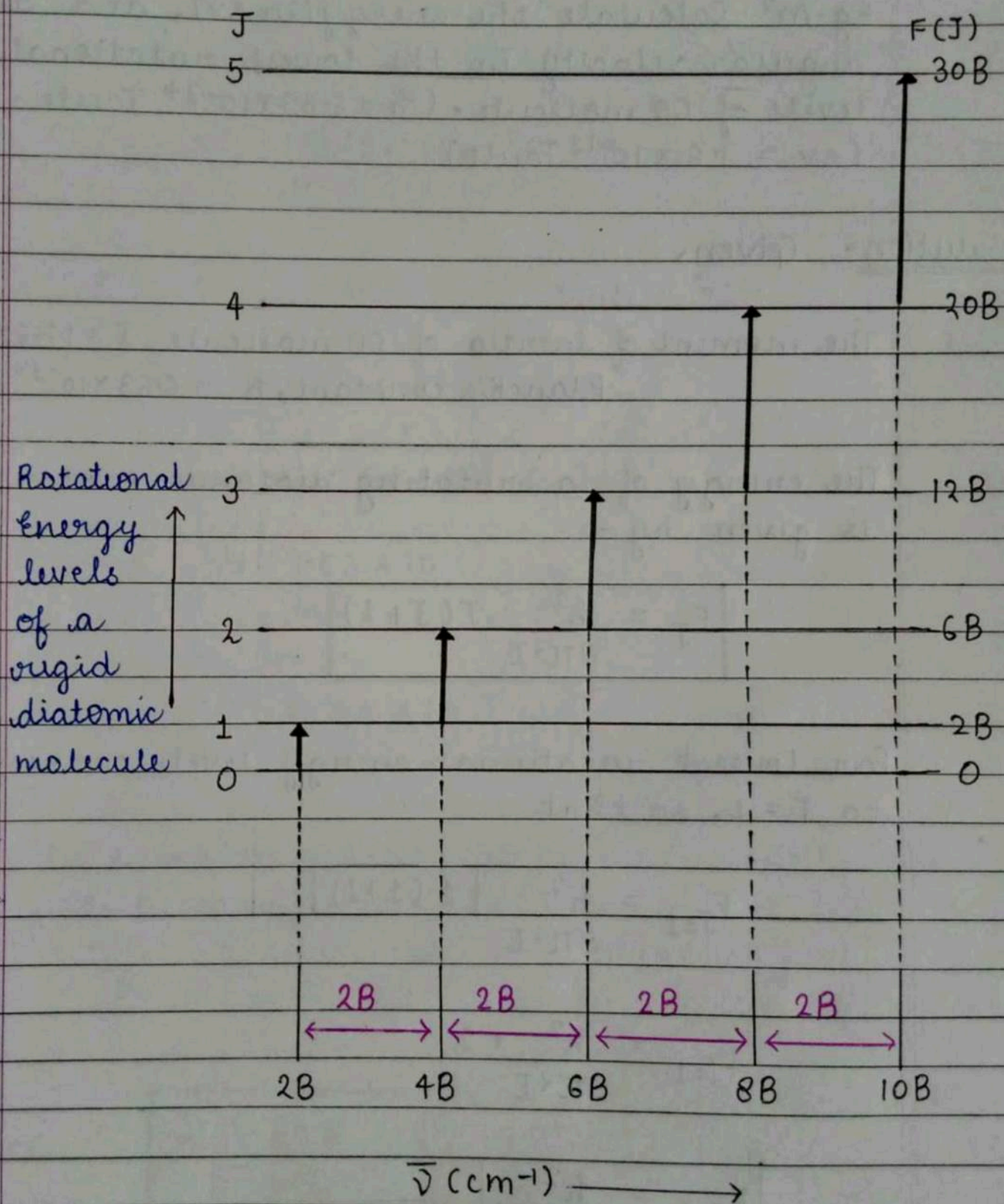
Substituting $J = 0, 1, 2, 3, \dots$, we have,

$$\begin{aligned} \bar{\nu}_{0 \rightarrow 1} &= 2B \\ \bar{\nu}_{1 \rightarrow 2} &= 4B \\ \bar{\nu}_{2 \rightarrow 3} &= 6B \\ \bar{\nu}_{3 \rightarrow 4} &= 8B \end{aligned} \quad \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \begin{array}{l} 2B \\ 2B \\ 2B \end{array} \quad \text{and so on.}$$

----- etc

Thus, the rotational spectrum of a rotating

diatomic molecule (Rigid Rotator) consist of a series of equidistant spectral lines with constant separation $2B$.



Rotational spectrum of a Rigid rotator

• NUMERICALS :

- 1.) The moment of inertia of CO molecule is $1.46 \times 10^{-46} \text{ Kg-m}^2$. Calculate the energy (in eV), and the angular velocity in the lowest rotational energy level of CO molecule. ($h = 6.63 \times 10^{-34} \text{ Joule-sec}$); $1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joule}$)

Solution- Given,

The moment of inertia of CO molecule, $I = 1.46 \times 10^{-46} \text{ Kg-m}^2$
Planck's constant, $h = 6.63 \times 10^{-34} \text{ Joule-sec}$

The energy of a rotating diatomic molecule is given by-

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

For lowest rotational energy level corresponds to $J=1$, so that

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

$$E_{J=1} = \frac{h^2}{8\pi^2 I} \times 2$$

$$E_{J=1} = \frac{h^2}{4\pi^2 I}$$

Substituting the given values of h and I , we have:

$$E_{J=1} = \frac{(6.63 \times 10^{-34})^2}{4 \times (3.14)^2 \times (1.46 \times 10^{-46})} \text{ Joule}$$

$$E_{J=1} = \frac{43.956 \times 10^{-68}}{57.576 \times 10^{-46}} \text{ Joule}$$

$$E_{J=1} = 0.763 \times 10^{-22} \text{ Joule}$$

$$E_{J=1} = 7.63 \times 10^{-23} \text{ Joule}$$

$$\text{Now, } 1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joule}$$

$$\therefore E_{J=1} = \frac{7.63 \times 10^{-23}}{1.6 \times 10^{-19}} \text{ eV}$$

$$E_{J=1} = 4.77 \times 10^{-4} \text{ eV}$$

Ans

The angular velocity of CO molecule in the lowest energy level ($J=1$) is -

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

or,

$$\omega = \sqrt{\frac{2E}{I}}$$

$$\omega = \sqrt{\frac{2 \times 7.63 \times 10^{-23} \text{ Joule}}{1.46 \times 10^{-46} \text{ Kg-m}^2}}$$

$$\omega = \sqrt{10.45 \times 10^{23}}$$

$$\omega = \sqrt{1.045 \times 10^{24}}$$

$$\omega = 1.02 \times 10^{12}$$

$$\omega = 1.02 \times 10^{12} \text{ rad/sec}$$

Ans

- 2.) The $J=0 \rightarrow J=1$ absorption line in CO occurs at a frequency of 1.153×10^{11} cycles/sec. Calculate the moment of inertia and the internuclear separation of CO molecule. ($h = 6.63 \times 10^{-34}$ Joule-sec, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$)

Solution- Given,

Frequency of Absorption line of CO molecule, ν
 $= 1.153 \times 10^{11} \text{ cycles/sec}$

Avogadro's Number, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

Planck's constant, $h = 6.63 \times 10^{-34} \text{ Joule-sec}$

The energy of a rotating diatomic molecule is given by -

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

The energy separation between $J=0$ and $J=1$ level is,

$$\Delta E = E_{J=1} - E_{J=0}$$

$$\Delta E = \frac{h^2}{8\pi^2 I} [1(1+1)] - 0$$

$$\Delta E = \frac{h^2}{8\pi^2 I} \times 2$$

$$\Delta E = \frac{h^2}{4\pi^2 I}$$

The frequency ν absorbed in transition $J=0 \rightarrow J=1$ is,

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

$$\nu = \frac{h^2}{4\pi^2 I} \times \frac{1}{h}$$

$$\nu = \frac{h}{4\pi^2 I}$$

$$\therefore I = \frac{h}{4\pi^2 \nu}$$

Substituting the given values of h and ν , we have;

$$I = \frac{6.63 \times 10^{-34} \text{ J-sec}}{4 \times (3.14)^2 \times (1.153 \times 10^{11} \text{ sec}^{-1})}$$

$$I = \frac{6.63 \times 10^{-34}}{45.35 \times 10^{11}}$$

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

Ans

The reduced mass of CO molecule is given by,

$$\mu_{CO} = \frac{(m_C/N_A) \times (m_O/N_A)}{(m_C/N_A) + (m_O/N_A)}$$

$$\mu_{CO} = \frac{m_C m_O}{m_C + m_O} \times \frac{1}{N_A}$$

Taking, $m_C = 12 \text{ gm mol}^{-1}$ (For carbon)
 $m_O = 16 \text{ gm mol}^{-1}$ (For oxygen)

$$\mu_{CO} = \frac{(12 \text{ gm mol}^{-1} \times 16 \text{ gm mol}^{-1})}{(12 \text{ gm mol}^{-1} + 16 \text{ gm mol}^{-1})} \times \frac{1}{6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$\mu_{CO} = \frac{192 \text{ gm}^2 \text{ mol}^{-2}}{28 \text{ gm mol}^{-1}} \times \frac{1}{6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$\mu_{CO} = 1.14 \times 10^{-23} \text{ gm}$$

$$\mu_{CO} = 1.14 \times 10^{-26} \text{ kg}$$

Therefore, the internuclear separation (bond length)

of CO molecule is given by-

$$r = \sqrt{\frac{I}{M_{CO}}} \quad \left\{ \because I = Mr^2 \right.$$

$$r = \sqrt{\frac{1.46 \times 10^{-46} \text{ kg-m}^2}{1.14 \times 10^{-26} \text{ kg}}}$$

$$r = \sqrt{\frac{1.46}{1.14} \times 10^{-20}}$$

$$r = 1.13 \times 10^{-10} \text{ m}$$

$$r = 1.13 \text{ \AA}$$

Ans

- (3). The pure rotational (microwave) spectrum of the gaseous molecule CN consists of a series of equally spaced lines separated by 3.7978 cm^{-1} . Calculate the internuclear distance of the molecule. The molar masses are: $^{12}\text{C} = 12.011$ and $^{14}\text{N} = 14.007 \text{ g mol}^{-1}$.

Solution Given,

The separation between equally spaced lines
 $= 2B = 3.7978 \text{ cm}^{-1}$

$$\therefore B = \frac{3.7978 \text{ cm}^{-1}}{2}$$

$$B = 1.8989 \text{ cm}^{-1}$$

Rotational constant, $B = \frac{h}{8\pi^2 I c} \text{ cm}^{-1}$

So, $I = \frac{h}{8\pi^2 B c}$

where,

h = Planck's constant
($6.63 \times 10^{-34} \text{ J-sec}$)

c = speed of light
($3 \times 10^{10} \text{ cm/sec}$)

$$I = \frac{6.63 \times 10^{-34} \text{ J-sec}}{8 \times (3.14)^2 \times (1.8989 \text{ cm}^{-1}) \times (3 \times 10^{10} \text{ cm/sec})}$$

$$I = \frac{6.63 \times 10^{-34}}{449.337 \times 10^{10}}$$

$$I = 1.47 \times 10^{-46} \text{ Kg-m}^2$$

The reduced mass of CN molecule is given by,

$$M_{CN} = \frac{(m_C / N_A) \times (m_N / N_A)}{(m_C / N_A) + (m_N / N_A)}$$

$$M_{CN} = \frac{m_C m_N}{m_C + m_N} \times \frac{1}{N_A}$$

Given, $m_C = 12.011 \text{ gm mol}^{-1}$ (for carbon)
 $m_N = 14.007 \text{ gm mol}^{-1}$ (for nitrogen)

where, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$ (Avogadro's number)

$$M_{CN} = \frac{(12.011 \text{ gm mol}^{-1} \times 14.007 \text{ gm mol}^{-1})}{(12.011 \text{ gm mol}^{-1} + 14.007 \text{ gm mol}^{-1})} \times \frac{1}{6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$M_{CN} = \frac{168.238 \text{ gm}^2 \text{ mol}^{-2}}{26.018 \text{ gm mol}^{-1}} \times \frac{1}{6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$M_{CN} = 1.0737 \times 10^{-23} \text{ gm}$$

$$M_{CN} = 1.0737 \times 10^{-26} \text{ kg}$$

Therefore, internuclear distance of CN molecule is given by -

$$r = \sqrt{\frac{I}{M_{CN}}}$$

$$\left\{ \because I = Mr^2 \right.$$

$$r = \sqrt{\frac{1.47 \times 10^{-46} \text{ kg-m}^2}{1.0737 \times 10^{-26} \text{ kg}}}$$

$$r = \sqrt{\frac{1.47 \times 10^{-20}}{1.0737}}$$

$$r = 1.1717 \times 10^{-10} \text{ m}$$

$$r = 117 \text{ pm}$$

Ans

- Salient features of Vibrational - Rotational Spectra :

Vibrational-rotational molecular spectra arise from transitions between the vibrational energy levels of a molecule on the absorption of radiation belonging to the infrared region. Like pure rotational spectra, the vibrational-rotational spectra are obtained only for molecules having permanent dipole moments; such as heteronuclear diatomic molecules. When the (unlike) nuclei of such a molecule vibrate relative to each other, the internuclear distance changes. Hence the dipole moment changes periodically with the frequency of vibration 'vosc' of the molecule.

Vibrational-rotational spectra occur in the spectral range of $500 - 4000 \text{ cm}^{-1}$.

- Vibrational (Infrared) Spectra of Diatomic Molecule :

A diatomic molecule with atomic masses ' m_1 ' and ' m_2 ' joined by a chemical bond vibrates as a one dimensional simple Harmonic oscillator (S.H.O). The masses ' m_1 ' and ' m_2 ' vibrate back and forth relative to their centre of mass in opposite directions. The two masses reach the extreme of their respective motions at the same time.

The vibrational frequency of the molecule (oscillator) is given by-

$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \text{ sec}^{-1}$$

Where, K is the force constant of spring and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the molecule (oscillator).

The potential energy of the simple harmonic as a function of displacement from the equilibrium configuration is given by-

$$V(x) = \frac{1}{2} K (r - r_e)^2 = \frac{1}{2} K x^2$$

where, $x = (r - r_e)$ is the displacement, r_e being the equilibrium bond length.

The Schrodinger wave equation for the oscillator would be,

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 \mu}{h^2} \left(E - \frac{1}{2} K x^2 \right) \psi = 0$$

The solution of the Schrodinger equation for the simple harmonic oscillator gives the quantized vibrational energy levels.

$$E_v = h\nu_{\text{osc}} \left(v + \frac{1}{2} \right)$$

where, v is the vibrational quantum number which can take the integral values:

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

Hence, the vibrational energy levels are quantized and equally spaced, the spacing being equal to $h\nu_{\text{osc}}$.

NOTE: The energy of the lowest vibrational level of the oscillator is not zero but it equal to $\frac{1}{2} h\nu_{\text{osc}}$; this is called Zero point energy.

• Spectrum:

The energy in wave number unit m^{-1} or cm^{-1} is,

$$G(v) = \frac{E}{hc} = \frac{h\nu_{\text{osc}}}{hc} \left(v + \frac{1}{2} \right)$$

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

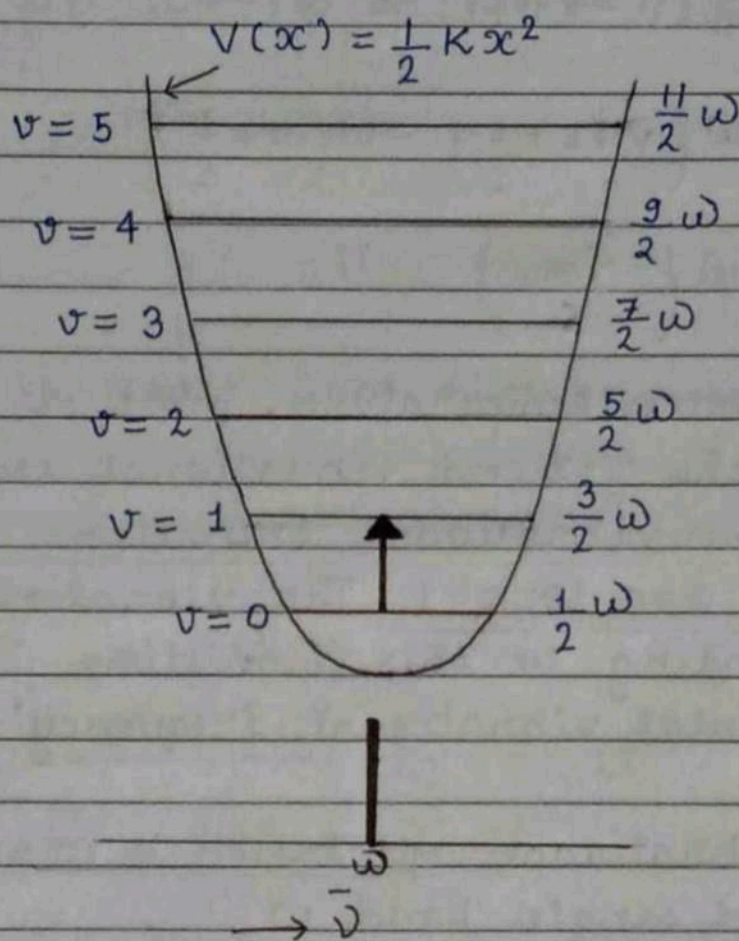
ν_{osc} is the frequency in wavenumber unit, cm^{-1} and is known as Vibrational constant ω .

$G(v)$ is called the vibrational term

Substituting $v = 0, 1, 2, 3, \dots$, we get

$$G(v) = \frac{1}{2}\omega, \frac{3}{2}\omega, \frac{5}{2}\omega, \frac{7}{2}\omega, \dots$$

Thus, we have a series of equispaced discrete vibrational levels, the common separation being ω .



- Equispaced discrete vibrational levels -

The selection rule for a vibrational transition (i.e., transitions between vibrational energy levels) in the simple harmonic oscillator is,

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

Vibrational spectrum is usually observed as absorption spectra so the selection rule is $\Delta v = +1$, i.e.; the vibrational quantum number (v) changes by unity. Using the selection rule, the

frequency of the vibrational transition is given by -

$$\begin{aligned}\bar{\nu} &= G(v \rightarrow v+1) = G(v+1) - G(v) \\ &= \omega \left(v+1 + \frac{1}{2} \right) - \omega \left(v + \frac{1}{2} \right) \\ \bar{\nu} &= \omega \left(= \frac{\nu_{osc}}{c} \right)\end{aligned}$$

At the room temperature, most of the molecules are in the ground vibrational state ($v=0$) so the main vibrational transition in absorption is from $v=0$ to $v=1$. The vibrational frequency corresponding to this transition is called 'fundamental vibrational frequency'.

Thus, vibrational spectrum is expected to consist of single band ω .

• NUMERICALS:

1. The force constant of the bond in CO molecule is 1870 N/m . Find the energy of the lowest vibrational level. The reduced mass of CO molecule $1.14 \times 10^{-26} \text{ kg}$. Given: $h = 6.63 \times 10^{-34} \text{ J-sec}$, $1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joule}$.

Solution Given -

Force constant, $K = 1870 \text{ N/m}$

Planck's constant, $h = 6.63 \times 10^{-34} \text{ Joule-sec}$

Reduced mass of CO molecule, $\mu = 1.14 \times 10^{-26} \text{ kg}$

The frequency of vibration of CO molecule is,

$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

Substituting the value of K and μ , we have,

$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{1870 \text{ N/m}}{1.14 \times 10^{-26} \text{ kg}}}$$

$$\nu_{\text{osc}} = \frac{1}{2 \times 3.14} \sqrt{\frac{1870 \times 10^{26}}{1.14}}$$

$$\nu_{\text{osc}} = \frac{1}{6.28} \sqrt{1640.3 \times 10^{26}}$$

$$\nu_{\text{osc}} = \frac{40.50 \times 10^{13}}{6.28}$$

$$\nu_{\text{osc}} = 6.45 \times 10^{13} \text{ sec}^{-1}$$

The vibrational energy of a diatomic molecule (oscillator) is given by,

$$E_v = h\nu_{\text{osc}} \left(v + \frac{1}{2} \right) \quad ; v = 0, 1, 2, 3, \dots$$

The lowest vibrational level corresponds to $v=0$, its energy is -

5/10/20

$$E_{v=0} = \frac{h\nu_{osc}}{2} \left(0 + \frac{1}{2} \right)$$

$$E_{v=0} = \frac{1}{2} h\nu_{osc}$$

$$E_{v=0} = \frac{1}{2} \times 6.63 \times 10^{-34} \text{ Joule-sec} \times 6.45 \times 10^{13} \text{ sec}^{-1}$$

$$E_{v=0} = \frac{42.76 \times 10^{-21}}{2}$$

$$E_{v=0} = 21.4 \times 10^{-21} \text{ Joule}$$

$$\text{Now, } 1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joule}$$

$$\therefore E_{v=0} = \frac{21.4 \times 10^{-21}}{1.6 \times 10^{-19}} \text{ eV}$$

$$E_{v=0} = 0.134 \text{ eV}$$

Ans

Lec-15

- (2). Assume that the H_2 molecule behaves like a harmonic oscillator with a force constant $K = 573 \text{ N/m}$ and find the vibrational quantum number corresponding to its 4.50 eV dissociation energy. Given: mass of hydrogen atom $= 1.67 \times 10^{-27} \text{ kg}$
 $h = 6.63 \times 10^{-34} \text{ Joule-sec}$.

Solution - Given -Force constant, $K = 573 \text{ N/m}$ Its dissociation energy, $E_v = 4.50 \text{ eV}$ Planck's constant, $h = 6.63 \times 10^{-34} \text{ Joule-sec}$ mass of hydrogen atom $= 1.67 \times 10^{-27} \text{ kg}$

The frequency of oscillation of the molecule is given by -

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{K}{M}}$$

The reduced mass of H_2 molecule,

$$M_{H_2} = \frac{m_H m_H}{m_H + m_H} = \frac{m_H^2}{2m_H} = \frac{1}{2} m_H$$

$$M_{H_2} = \frac{1}{2} \times (1.67 \times 10^{-27} \text{ kg})$$

$$M_{H_2} = 0.835 \times 10^{-27} \text{ kg}$$

Substituting the values of K and M , we have;

$$\therefore \nu_{osc} = \frac{1}{2 \times 3.14} \sqrt{\frac{573 \text{ N/m}}{0.835 \times 10^{-27} \text{ kg}}}$$

$$\nu_{osc} = \frac{1}{6.28} \sqrt{686.22 \times 10^{27}}$$

$$\nu_{osc} = \frac{1}{6.28} \sqrt{68.62 \times 10^{28}}$$

$$\nu_{osc} = \frac{8.28}{6.28} \times 10^{14}$$

$$\nu_{osc} = 1.32 \times 10^{14} \text{ sec}^{-1}$$

The vibrational energy of the H_2 molecule is,

$$E_v = h\nu_{osc} \left(v + \frac{1}{2} \right)$$

$$E_v = (6.63 \times 10^{-34} \text{ J}\cdot\text{sec}) (1.32 \times 10^{14} \text{ sec}^{-1}) \left(v + \frac{1}{2} \right)$$

$$E_v = 8.75 \times 10^{-20} \left(v + \frac{1}{2} \right) \text{ Joule}$$

$$E_v = \frac{8.75 \times 10^{-20}}{1.6 \times 10^{-19}} \left(v + \frac{1}{2} \right) \text{ eV} \quad \left\{ \because 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J} \right.$$

$$E_v = 0.547 \left(v + \frac{1}{2} \right) \text{ eV}$$

Substituting the value of E_v , we have;

$$4.50 \text{ eV} = 0.547 \left(v + \frac{1}{2} \right) \text{ eV}$$

$$\frac{v + \frac{1}{2}}{2} = \frac{4.50}{0.547}$$

$$v + \frac{1}{2} = 8.22 - \frac{1}{2}$$

$$v = 7.72 \approx 8$$

$$v = 8$$

Thus, the vibrational quantum number = 8

Ans

- (3). The force constant of a vibrating HCl molecule is 480 N/m . Find the energy difference between the lowest and the first vibrational level of HCl. Given: $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$, $h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joule}$$

Is the HCl molecule likely to be found in the first excited vibrational state at Room temperature

Given: Boltzmann constant $K = 1.38 \times 10^{-23} \text{ J/K}$

Solution Given:

Force constant of a vibrating HCl molecule, $K = 480 \text{ N/m}$

Avogadro's number, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

Planck's constant, $h = 6.63 \times 10^{-34} \text{ Joule-sec}$

Boltzmann constant $K = 1.38 \times 10^{-23} \text{ J/K}$

The frequency of vibration of the molecule is given by-

$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{K}{M}}$$

The reduced mass of HCl molecule is,

$$M_{\text{HCl}} = \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}}$$

Taking, $m_{\text{H}} = 1 \text{ gm mol}^{-1}$ (For Hydrogen)
 $m_{\text{Cl}} = 35 \text{ gm mol}^{-1}$ (For chlorine)

$$M_{\text{HCl}} = \frac{1/N_A \cdot 35/N_A}{1/N_A + 35/N_A}$$

$$M_{\text{HCl}} = \frac{1 \times 35 \times 1}{1 + 35} \times \frac{1}{N_A}$$

$$\mu_{HCl} = \frac{35}{36} \times \frac{1}{6.023 \times 10^{23}}$$

$$\mu_{HCl} = \frac{35}{216.8} \times 10^{-23}$$

$$\mu_{HCl} = 1.61 \times 10^{-24} \text{ gm}$$

$$\mu_{HCl} = 1.61 \times 10^{-27} \text{ kg}$$

$$\therefore \nu_{osc} = \frac{1}{2 \times 3.14} \sqrt{\frac{480 \text{ N/m}}{1.61 \times 10^{-27} \text{ kg}}}$$

$$\nu_{osc} = \frac{1}{6.28} \sqrt{298.13 \times 10^{27}}$$

$$\nu_{osc} = \frac{1}{6.28} \sqrt{29.81 \times 10^{28}}$$

$$\nu_{osc} = \frac{5.45}{6.28} \times 10^{14}$$

$$\nu_{osc} = 0.87 \times 10^{14} \text{ sec}^{-1}$$

The vibrational energy of a diatomic molecule is,

$$E_v = h\nu_{osc} \left(v + \frac{1}{2} \right)$$

The energy difference between the lowest ($v=0$) and the first excited ($v=1$) vibrational levels of HCl molecule is,

$$\Delta E = E_{v=1} - E_{v=0}$$

$$\Delta E = h\nu_{osc} \left(1 + \frac{1}{2}\right) - h\nu_{osc} \left(0 + \frac{1}{2}\right)$$

$$\Delta E = \frac{3}{2} h\nu_{osc} - \frac{1}{2} h\nu_{osc}$$

$$\Delta E = h\nu_{osc}$$

Substituting the values of h and ν_{osc} , we have;

$$\Delta E = (6.63 \times 10^{-34} \text{ J-sec}) \times (0.87 \times 10^{14} \text{ sec}^{-1})$$

$$\Delta E = 5.768 \times 10^{-20} \text{ Joule}$$

$$\Delta E = \frac{5.768 \times 10^{-20}}{1.6 \times 10^{-19}} \text{ eV}$$

$$\left\{ \because 1 \text{ eV} = 1.6 \times 10^{-19} \text{ J} \right.$$

$$\Delta E = 0.36 \text{ eV}$$

This is required energy for the molecule to rise to the first excited state.

The thermal energy of a molecule is of the order of KT , where K = Boltzman constant ($1.38 \times 10^{-23} \text{ J/K}$) at room temperature, $K = 300 \text{ K}$

Then, energy is -

$$KT = \frac{(1.38 \times 10^{-23} \text{ J/K})}{300 \text{ K}} = 4.14 \times 10^{-21} \text{ Joule}$$

$$KT = \frac{4.14 \times 10^{-21}}{1.6 \times 10^{-19}} \text{ eV}$$

$$\left\{ \because 1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joule} \right.$$

$$KT = 0.026 \text{ eV}$$

Thus, at room temperature, collisions of molecules can transfer only 0.026 eV of kinetic energy to the internal energy, which is insufficient to excite even the $(v=1)$ state (the required energy is 0.036 eV). Hence, the HCl molecule is not likely to be found vibrating in its first vibrational excited state at room temperature.

Ans

- (4). Calculate the amplitude of vibration in the line $v=0$ level of the molecule CO which has a stiff bond of 1870 N/m . Given: $h = 6.63 \times 10^{-34} \text{ J-s}$
 $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

Solution - Given :

Force constant, $K = 1870 \text{ N/m}$

Avogadro number, $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

Planck's constant, $h = 6.63 \times 10^{-34} \text{ J-sec}$

Let ' x_0 ' be the maximum displacement (amplitude) from the equilibrium position. The potential energy $x = x_0$ is equal to vibrational energy of the $(v=0)$ level, i.e.; zero point energy. Thus

$$\frac{1}{2} K x_0^2 = E_v$$

$$\frac{1}{2} K x_0^2 = h \nu_{\text{osc}} \left(0 + \frac{1}{2} \right)$$

$$\frac{1}{2} K x_0^2 = \frac{1}{2} h \nu_{\text{osc}}$$

$$\frac{h\nu_{\text{osc}}}{K} = x_0^2$$

$$x_0 = \sqrt{\frac{h\nu_{\text{osc}}}{K}} \quad \text{----- (i)}$$

$$\text{Now, } \nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{K}{M}}$$

The reduced mass of CO molecule is given by,

$$M_{\text{CO}} = \frac{m_{\text{C}} m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}}$$

Taking,

$$m_{\text{C}} = 12 \text{ gm mol}^{-1} \quad (\text{for carbon})$$

$$m_{\text{O}} = 16 \text{ gm mol}^{-1} \quad (\text{for oxygen})$$

$$M_{\text{CO}} = \frac{12/\text{NA} \cdot 16/\text{NA}}{12/\text{NA} + 16/\text{NA}}$$

$$M_{\text{CO}} = \frac{12 \times 16 \times 1}{12 + 16 \text{ NA}}$$

$$M_{\text{CO}} = \frac{192 \times 1}{28 \times 6.023 \times 10^{23}}$$

$$M_{\text{CO}} = 1.14 \times 10^{-23} \text{ gm}$$

$$M_{\text{CO}} = 1.14 \times 10^{-26} \text{ kg}$$

$$\therefore \nu_{\text{osc}} = \frac{1}{2 \times 3.14} \times \sqrt{\frac{1870 \text{ N/m}}{1.14 \times 10^{-26} \text{ kg}}}$$

$$v_{osc} = \frac{1}{6.28} \sqrt{1640.3 \times 10^{26}}$$

$$v_{osc} = \frac{40.50 \times 10^{13}}{6.28}$$

$$v_{osc} = 6.45 \times 10^{13} \text{ sec}^{-1}$$

Putting this value of v_{osc} , and the given value of h and k in eq. (i), we get

$$x_0 = \sqrt{\frac{(6.63 \times 10^{-34} \text{ J-sec}) \times (6.45 \times 10^{13} \text{ sec}^{-1})}{1070 \text{ N/m}}}$$

$$x_0 = \sqrt{\frac{42.76 \times 10^{-21}}{1070}}$$

$$x_0 = \sqrt{0.2286 \times 10^{-21}}$$

$$x_0 = \sqrt{0.2286 \times 10^{-22}}$$

$$x_0 = 0.478 \times 10^{-11} \text{ m}$$

$$x_0 = 4.78 \times 10^{-12} \text{ m}$$

$$x_0 = 4.78 \times 10^{-2} \text{ \AA}$$

Ans

(5). find the amplitude of vibration of HCl molecule

in the first excited vibrational level. The force constant K of the vibrating HCl molecule is 480 N/m , and its reduced mass is $1.63 \times 10^{-27} \text{ kg}$.
 Given: ($h = 6.63 \times 10^{-34} \text{ Joule-sec}$);

Solution Given -

Force constant, $K = 480 \text{ N/m}$

Reduced mass of HCl molecule, $\mu = 1.63 \times 10^{-27} \text{ kg}$

Planck's constant, $h = 6.63 \times 10^{-34} \text{ Joule-sec}$

Let ' x_0 ' be the maximum displacement (amplitude) from the equilibrium position. The potential energy at $x = x_0$ is equal to vibrational energy of the ($v=1$) state.

$$\text{i.e.; } \frac{1}{2} K x_0^2 = E_v$$

$$\frac{1}{2} K x_0^2 = h \nu_{\text{osc}} \left(1 + \frac{1}{2} \right)$$

$$\frac{1}{2} K x_0^2 = \frac{3}{2} h \nu_{\text{osc}}$$

$$x_0^2 = \frac{3 h \nu_{\text{osc}}}{K}$$

$$x_0 = \sqrt{\frac{3 h \nu_{\text{osc}}}{K}} \quad \text{----- (1)}$$

$$\text{Now, } \nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

$$\nu_{osc} = \frac{1}{2 \times 3.14} \sqrt{\frac{480 \text{ N/m}}{1.62 \times 10^{-27} \text{ Kg}}}$$

$$\nu_{osc} = \frac{1}{6.28} \sqrt{296.2 \times 10^{27}}$$

$$\nu_{osc} = \frac{1}{6.28} \sqrt{29.62 \times 10^{28}}$$

$$\nu_{osc} = \frac{5.44 \times 10^{14}}{6.28}$$

$$\nu_{osc} = 0.87 \times 10^{14} \text{ sec}^{-1}$$

Putting this value of ν_{osc} , and the given value of h and K in equ (i), we get,

$$x_0 = \sqrt{\frac{3 \times (6.63 \times 10^{-34} \text{ J-sec}) \times (0.87 \times 10^{14} \text{ sec}^{-1})}{480 \text{ N/m}}}$$

$$x_0 = \sqrt{\frac{17.30 \times 10^{-20}}{480}}$$

$$x_0 = \sqrt{0.360 \times 10^{-20}}$$

$$x_0 = 0.190 \times 10^{-10} \text{ m}$$

$$x_0 = 0.190 \text{ \AA}$$

Thus, the amplitude of vibration of HCl molecule in the first excited level is = $0.190 \text{ \AA}$

Ans

• Variation of vibrational frequency:

The vibrational frequency of a molecule, assumed as harmonic oscillator is given by,

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{K}{M}}$$

The reduced mass M is different for different isotopes. K is force constant of the bond between atoms and relates to strength of the bond. For a single bond, it is approximately $5 \times 10^2 \text{ Kg} \left(\frac{\text{N}}{\text{m}} \right) \text{ Sec}^2$. It becomes double and triple for the double and triple bond respectively.

Question: Evaluate the ratio of fundamental oscillation frequencies of HCl and DCl.

Answer- The vibrational frequency of a molecule -

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{K}{M}}$$

Here,

M is reduced mass of molecule

K is force constant

For HCl,

$$\nu_{HCl} = \frac{1}{2\pi} \sqrt{\frac{K}{M_{HCl}}}$$

For DCl,

$$\nu_{DCl} = \frac{1}{2\pi} \sqrt{\frac{K}{M_{DCl}}}$$

$$\therefore \frac{v_{HCl}}{v_{DCl}} = \sqrt{\frac{M_{DCl}}{M_{HCl}}}$$

$$M_{HCl} = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{1/N_A \cdot 35/N_A}{1/N_A + 35/N_A} = \frac{35}{36} \times \frac{1}{N_A} \text{ gm}$$

and

$$M_{DCl} = \frac{m_D m_{Cl}}{m_D + m_{Cl}} = \frac{2/N_A \cdot 35/N_A}{2/N_A + 35/N_A} = \frac{70}{37} \times \frac{1}{N_A} \text{ gm}$$

Here, N_A is Avogadro's number.

$$\text{Therefore, } \frac{v_{HCl}}{v_{DCl}} = \sqrt{\frac{70}{37} \times \frac{36 N_A}{35}}$$

$$\frac{v_{HCl}}{v_{DCl}} = \sqrt{\frac{72}{37}} = 1.9459$$

$$\therefore \frac{v_{HCl}}{v_{DCl}} = 1.39$$

$$\text{and } \frac{v_{DCl}}{v_{HCl}} = \frac{1}{1.39} = 0.71$$

• Molecular Spectra:

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

The molecular spectra arise from three types

transitions: rotational, vibrational and electronic transitions. The transition between two energy orbits of a molecule, as a result of absorption or emission of energy will give rise to a spectral line of the spectra.

- The various types of a spectra given by a molecule the regions in which these spectra lie on absorption of radiation, are listed below:

(i). Rotational (Microwave) Spectra:

Rotational Spectra arise from transitions between the rotational energy levels of a gaseous molecule on the absorption of radiations falling in the microwave region. These Spectra are shown by molecules which possess (have) a permanent dipole moment, eg; HCl, CO₂, H₂O vapour, NO etc. [Heteronuclear molecules].

Homonuclear diatomic molecules such as H₂, Cl₂ etc, and linear polyatomic molecules such as CO₂, which do not have a dipole moment, do not show rotational spectra.

Rotational Spectra occur in the spectral range of 1-100 cm⁻¹

(ii). Vibrational and Vibrational-Rotational (Infrared) Spectra:

These spectra result from transitions between the vibrational energy levels of a molecule on

the absorption of radiations falling in Infrared region. IR spectra are shown by the molecules when vibrational motion is accompanied by a change in the dipole moment of the molecule.

Like pure rotational spectra, the vibrational-rotational spectra are obtained only by molecules having permanent dipole moment such as heteronuclear diatomic molecules. Homonuclear diatomic molecules like H_2 , O_2 , N_2 which have zero dipole moment for all internuclear separations, fail to interact with radiation, and so give no vibrational spectra.

The spectra occur in the spectral range of $500-4000\text{ cm}^{-1}$

iii) Electronic Spectra:

Electronic Spectra arise from electronic transitions in a molecule by absorption of radiations falling in the visible and ultraviolet regions. Since electronic transitions in a molecule are accompanied by vibrational and rotational transitions, the electronic spectra of a molecule are highly complex.

All diatomic molecules exhibit electronic spectra. Homonuclear molecules (H_2 , N_2 , O_2) which give neither rotational nor vibrational-rotational spectra because they do not have permanent dipole moments, give electronic spectra.

Raman Effect :

When a strong beam of visible or ultraviolet line - Spectral line illuminates a gas, a liquid, or a transparent crystal, a small fraction of light is scattered in all directions. The spectrum of the scattered light is found to consist of lines of the same frequencies as the incident beam (Rayleigh lines or Exciting lines), and also certain weak lines of changed frequencies. These additional lines are called 'Raman lines'

The Raman lines corresponding to each exciting [Rayleigh] line occur symmetrically on both sides of the exciting line. The lines on the low-frequency side of the exciting line are called Stokes lines, while those on the high-frequency side are called Anti-stokes line.

This phenomenon is called 'Raman effect'

• Characteristic of Raman Lines:

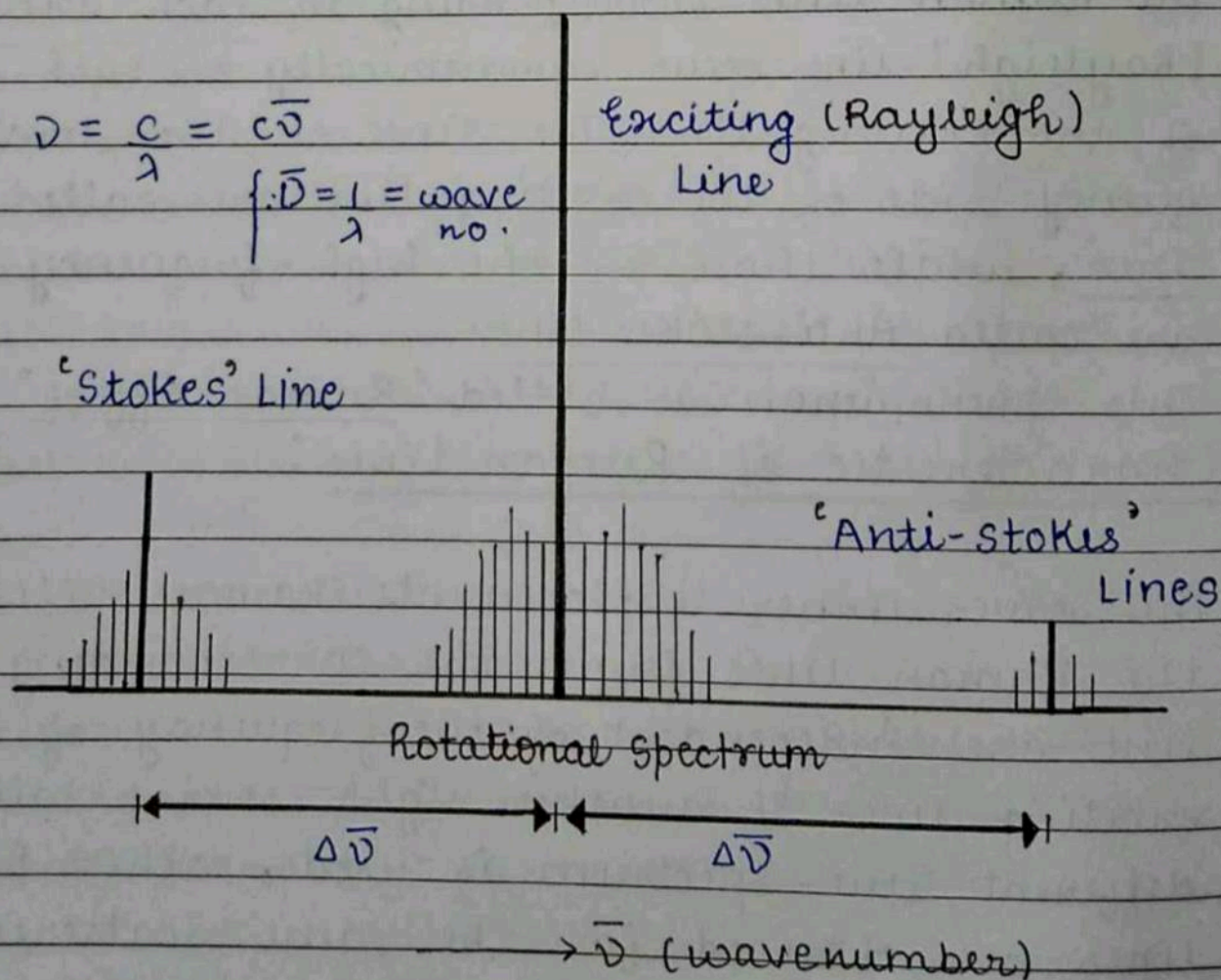
- 1) The wavenumber displacements (Raman shift) $\Delta \bar{\nu}$ of the Raman lines from the corresponding exciting line are independent of the frequency of the exciting line. If another light source with a different line-spectrum is used, other Raman lines are obtained for the same scattering substance. However, the displacement from the exciting lines are the same. Thus, the Raman displacements are characteristics of the scattering

substance.

- 2). The Stokes lines are found to be more intense than the Anti-Stokes lines.
- 3). The Raman lines are symmetrically displaced about the parent line (exciting line).

• Vibrational and Pure Rotational Raman Spectra:

A typical Raman Spectrum is shown in figure.



It has two characteristics -

- i). Under low resolution, there is one Stokes Raman line, and one Anti-Stokes Raman line, each having the same wave number displacement, ' $\Delta\bar{\nu}$ ', with respect to exciting (Rayleigh) line. This is 'Vibrational Raman Spectrum'.
- ii). Under high resolution, the exciting (Rayleigh) line is found to have both sides close, approximately equidistant lines. This is 'Pure Rotational Spectrum'.

NUMERICALS:

- 1). With exciting line $2536 \text{ \AA}$ a Raman line for a sample is observed at $2612 \text{ \AA}$. Calculate the Raman Shift in cm^{-1} .

Solution - Given:

Wavelength of exciting line, $\lambda_{\text{exciting}} = 2536 \text{ \AA}$

Wavelength of Raman line, $\lambda_{\text{Raman}} = 2612 \text{ \AA}$

The wavenumber of the exciting line is,

$$\bar{\nu}_{\text{exciting}} = \frac{1}{\lambda_{\text{exciting}}}$$

$$\bar{\nu}_{\text{exciting}} = \frac{1}{2536 \times 10^{-8} \text{ cm}}$$

$$\bar{\nu}_{\text{exciting}} = 39432 \text{ cm}^{-1}$$

and wavenumber of Raman line is,

$$\bar{\nu}_{\text{Raman}} = \frac{1}{\lambda_{\text{Raman}}}$$

$$\bar{\nu}_{\text{Raman}} = \frac{1}{2612 \times 10^{-8} \text{ cm}}$$

$$\bar{\nu}_{\text{Raman}} = 38285 \text{ cm}^{-1}$$

Therefore, the Raman shift (wavenumber displacement) is,

$$\Delta\bar{\nu} = \bar{\nu}_{\text{exciting}} - \bar{\nu}_{\text{Raman}}$$

$$\Delta\bar{\nu} = 39432 \text{ cm}^{-1} - 38285 \text{ cm}^{-1}$$

$$\Delta\bar{\nu} = 1147 \text{ cm}^{-1} \quad \underline{\text{Ans}}$$

- 2). The exciting line in an experiment is $5460 \text{ \AA}$ and the Stokes line is at $5520 \text{ \AA}$. Find the wavelength of the anti-Stokes line.

Solution- Given:

Wavelength of exciting line, $\lambda_{\text{exciting}} = 5460 \text{ \AA}$
 $= 5460 \times 10^{-8} \text{ cm}$

Wavelength of Stokes line, $\lambda_{\text{Stokes}} = 5520 \text{ \AA}$
 $= 5520 \times 10^{-8} \text{ cm}$

The wavenumber of exciting line is,

$$\bar{\nu}_{\text{exciting}} = \frac{1}{\lambda_{\text{exciting}}}$$

$$\bar{\nu}_{\text{exciting}} = \frac{1}{5460 \times 10^{-8} \text{ cm}}$$

$$\bar{\nu}_{\text{exciting}} = 18315 \text{ cm}^{-1}$$

and the wavenumber of stokes line is,

$$\bar{\nu}_{\text{stokes}} = \frac{1}{\lambda_{\text{stokes}}}$$

$$\bar{\nu}_{\text{stokes}} = \frac{1}{5520 \times 10^{-8} \text{ cm}}$$

$$\bar{\nu}_{\text{stokes}} = 18116 \text{ cm}^{-1}$$

Therefore, Raman shift (wavenumber displacement) is,

$$\Delta \bar{\nu} = \bar{\nu}_{\text{exciting}} - \bar{\nu}_{\text{stokes}}$$

$$\Delta \bar{\nu} = 18315 \text{ cm}^{-1} - 18116 \text{ cm}^{-1}$$

$$\Delta \bar{\nu} = 199 \text{ cm}^{-1}$$

As the stokes and anti-stokes line have the same wavenumber displacement with respect to exciting line. The wavenumber of the anti-stokes line is -

$$\bar{\nu}_{\text{anti-stokes}} = \bar{\nu}_{\text{exciting}} + \Delta \bar{\nu}$$

$$\bar{\nu}_{\text{Anti-stokes}} = 181315 \text{ cm}^{-1} + 199 \text{ cm}^{-1}$$

$$\bar{\nu}_{\text{Anti-stokes}} = 18514 \text{ cm}^{-1}$$

Corresponding wavelength is,

$$\lambda_{\text{Anti-stokes}} = \frac{1}{\bar{\nu}_{\text{Anti-stokes}}}$$

$$\lambda_{\text{Anti-stokes}} = \frac{1}{18514 \text{ cm}^{-1}}$$

$$\lambda_{\text{Anti-stokes}} = 5.4013 \times 10^{-5} \text{ cm}$$

$$\lambda_{\text{Anti-stokes}} = 5401 \text{ \AA}$$

Ans.

- 3). A substance shows a Raman line at $4567 \text{ \AA}$ when exciting line $4358 \text{ \AA}$ is used. Deduce the positions of Stokes and anti-stokes lines for the same substance exciting line $4047 \text{ \AA}$ is used.

Solution - Given:

$$\text{wavelength of Raman line, } \lambda_{\text{Raman}} = 4567 \text{ \AA} = 4567 \times 10^{-8} \text{ cm}$$

$$\text{wavelength of exciting line, } \lambda_{\text{exciting}} = 4358 \text{ \AA} = 4358 \times 10^{-8} \text{ cm}$$

$$\text{wavelength of another exciting line, } \lambda_{\text{exciting}} = 4047 \text{ \AA}$$

The wavelength of the exciting line is,

$$\bar{\nu}_{\text{exciting}} = \frac{1}{\lambda_{\text{exciting}}}$$

$$\bar{\nu}_{\text{exciting}} = \frac{1}{4358 \times 10^{-8} \text{ cm}}$$

$$\bar{\nu}_{\text{exciting}} = 22946 \text{ cm}^{-1}$$

and wavelength of Raman line is,

$$\bar{\nu}_{\text{Raman}} = \frac{1}{\lambda_{\text{Raman}}}$$

$$\bar{\nu}_{\text{Raman}} = \frac{1}{4567 \times 10^{-8} \text{ cm}}$$

$$\bar{\nu}_{\text{Raman}} = 21896 \text{ cm}^{-1}$$

Therefore, the Raman shift (wavenumber displacement) is,

$$\Delta \bar{\nu} = \bar{\nu}_{\text{exciting}} - \bar{\nu}_{\text{Raman}}$$

$$\Delta \bar{\nu} = 22946 \text{ cm}^{-1} - 21896 \text{ cm}^{-1}$$

$$\Delta \bar{\nu} = 1050 \text{ cm}^{-1}$$

Now, the wavenumber of another exciting line is,

$$\bar{\nu}_{\text{exciting}} = \frac{1}{\lambda_{\text{exciting}}}$$

$$\bar{\nu}_{\text{exciting}} = \frac{1}{4047 \times 10^{-8} \text{ cm}^{-1}}$$

$$\bar{\nu}_{\text{exciting}} = 24710 \text{ cm}^{-1}$$

Therefore, the wavenumber for the stokes and anti-stokes line are;

$$= \bar{\nu}_{\text{exciting}} \pm \Delta \nu$$

$$\begin{aligned} \text{Stokes line, } \bar{\nu}_{\text{stokes}} &= \bar{\nu}_{\text{exciting}} - \Delta \nu \\ &= 24710 \text{ cm}^{-1} - 1050 \text{ cm}^{-1} \\ &= 23660 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Anti-stokes line, } \bar{\nu}_{\text{anti-stokes}} &= \bar{\nu}_{\text{exciting}} + \Delta \nu \\ &= 24710 \text{ cm}^{-1} + 1050 \text{ cm}^{-1} \\ &= 25760 \text{ cm}^{-1} \end{aligned}$$

The corresponding wavelengths are-

$$\lambda_{\text{stokes}} = \frac{1}{\bar{\nu}_{\text{stokes}}}$$

$$\lambda_{\text{stokes}} = \frac{1}{23660 \text{ cm}^{-1}}$$

$$\lambda_{\text{stokes}} = 4.2265 \times 10^{-5} \text{ cm}$$

$$\lambda_{\text{stokes}} = 4226.5 \text{ Å}^{\circ}$$

and $\lambda_{\text{Anti-stokes}} = \frac{1}{\nu_{\text{Anti-stokes}}}$

$$\lambda_{\text{Anti-stokes}} = \frac{1}{25760 \text{ cm}^{-1}}$$

$$\lambda_{\text{Anti-stokes}} = 3.882 \times 10^{-5} \text{ cm}$$

$$\lambda_{\text{Anti-stokes}} = 3882 \text{ \AA}$$

Thus, $\lambda_{\text{stokes}} = 4226.5 \text{ \AA}$

$$\lambda_{\text{Anti-stokes}} = 3882 \text{ \AA}$$

Ans