

**B.Sc.III / M. Sc. Sem- II, Chemistry, Paper 4, Unit II, Part A**

**Syllabus:**

**Introduction, Simple and anharmonic oscillators in vibration spectroscopy,  
diatomic-vibrating rotator**

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# Introduction

- Atoms in a molecule do not remain fixed relative positions but vibrate about some mean position.
- Consider a diatomic molecule and the spectrum which arises if its only motion is vibration.
- Energy of a vibrating diatomic molecule
  1. Fixed the atom on one axis and imagine pushing and pulling the other atom closer to or further from the first atom
  2. Pushing or pulling results in raising the energy.
  3. When the energy is minimum, the internuclear distance is referred to as the equilibrium distance  $r_e$ , or simply called as the bond length of the diatomic molecule.
  4. The compression and extension of diatomic molecule may be behave like a spring and obeys the Hooke's law  $f = -kx$  or  $f = -k(r-r_e)$  where  $f$  is the restoring force;  $k$  is the force constant, and  $r$  is the intermolecular distance.
  5. The potential energy curve is parabolic and have energy  $V(x) = \frac{1}{2} k x^2$  or  $V(r) = \frac{1}{2} k(r-r_e)^2$
  6. This model of a vibrating diatomic molecule is called as simple harmonic oscillator model.

# The Simple Harmonic Oscillator

- Potential energy is zero when  $r = r_e$
- Potential energy arises because of extension or compression of bond.
- Importantly, Potential energy is increased when degree of compression and extension will be greater but vibrational frequency will not change.
- Vibrational frequency dependent on the mass of the system and the force constant, but is independent of the amount of distortion.

- Vibrational frequency of a diatomic molecule is  $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{s}^{-1}$

- To convert vibrational frequency  $\text{s}^{-1}$  to  $\text{cm}^{-1}$ , we divided by  $c$ , velocity of light.  $\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1}$

- The Schrodinger equation for simple harmonic oscillator is  $-\frac{\hbar}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$  where  $x = r - r_e$

- The Solution of the Schrodinger equation of simple harmonic oscillator gives

the quantized vibrational energy  $E_v = \left(v + \frac{1}{2}\right) h\nu \quad \text{joules}; v = 0, 1, 2, 3, \dots \dots \dots$  And  $\nu$  in  $\text{s}^{-1}$

Where  $v$  is the **vibrational quantum number**.

# The Simple Harmonic Oscillator

- **Vibrational Energy Term:** To convert the energy from joules to  $\text{cm}^{-1}$ , energy divided by  $hc$ .

$$G(v) = E_v/hc = (v + 1/2) \nu/c = (v + 1/2) \omega_e$$

- **Zero Point Energy:** Vibrational energy  $E_v = \left(v + \frac{1}{2}\right) h\nu$

$$\text{When } v = 0, E_0 = \left(\frac{1}{2}\right) h\nu$$

The energy of the lowest vibrational level ( $v = 0$ ) of the oscillator is not zero but is equal to  $\frac{1}{2} h\nu$  joules or  $\frac{1}{2} \omega_e \text{ cm}^{-1}$ . This is called as zero point energy. It insists that the diatomic molecule must always vibrate to some extent.

- The energy levels of Simple Harmonic Oscillator are equally spaced and the spacing being equal to  $h\nu$  or  $\omega_e$ .
- **Fundamental vibrational frequency:**

The transition take place from  $v = 0$  to  $v = 1$ , the frequency corresponds to  $h\nu$  or  $\omega_e$  is called as fundamental vibrational frequency.

- **The Selection Rule for a vibrational transition:**

(1)  $\Delta v = \pm 1$

(2) Molecule must have permanent Dipole moment or change the dipole moment during the vibration.

- Homonuclear diatomic molecules are IR-inactive while heteronuclear diatomic are IR-active.

# The Anharmonic Oscillator

- Real molecules do not obey exactly the laws of simple harmonic oscillator and do not obey Hooke's Law.
- The bond between atoms is stretched for instance, there comes a point at which it will break. This is called anharmonicity.
- In 1929, P. M. Morse gave the potential energy for an anharmonic oscillator as

$V(r) = D_e [1 - \exp\{-a(r - r_e)\}]^2$  where  $a$  is a constant for a particular molecule and  $D_e$  is the dissociation energy of the molecule.

- When we use this potential energy in the Schrödinger equation for an anharmonic oscillator and solve it, then energy levels are given by
- $G(v) = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e$ ;  $v = 0, 1, 2, 3, \dots$  etc.
- $x_e$  is the anharmonic constant,  $x_e$  is always small and positive (+ 0.01), so that on increasing the vibrational levels, vibrational levels come closer.
- **Zero Point Energy for an anharmonic oscillator:** When  $v = 0$ ,  $G(0) = \frac{1}{2} \omega_e (1 - \frac{1}{2} x_e) \text{ cm}^{-1}$
- **The Selection Rule for the anharmonic oscillator:**  $\Delta v = \pm 1, \pm 2, \pm 3, \dots$

# The Anharmonic Oscillator

- The line near  $\omega_e$  ( $v = 0$  to  $v = 1$ ) is called the fundamental absorption, while those near  $2 \omega_e$  ( $v = 0$  to  $v = 2$ ) and  $3 \omega_e$  ( $v = 0$  to  $v = 3$ ) are called first and second overtones, respectively.
- **Hot Bands** :  $v = 1$  to  $v = 2$ ,  $\Delta v = +1$ ,  $\Delta G = \omega_e (1 - 4 x_e)$   $\text{cm}^{-1}$  thus weak absorption at slightly lower wavenumber than the fundamental absorption is called hot bands.

# The Diatomic Vibrating Rotator

- Rotational energies are smaller than vibrational energies, therefore a molecule always rotating in vibrational state. Hence the molecule show the rotation-vibration spectra in gaseous state.
- The rotation-vibration term  $S(J, v)$  for vibrating rotator is

$$S(J, v) = E_{\text{rotation}} + E_{\text{vibration}}$$

$$S(J, v) = BJ(J+1) + \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e \quad \text{in cm}^{-1}$$

- The Selection rule for combined rotational and vibrational transitions are the same as those for each separately;  $\Delta J = \pm 1$  and  $\Delta v = \pm 1, \pm 2, \text{etc.}$
- $\Delta S(J, v) = S(J = J', v = 1) - S(J = J'', v = 0)$

$$\Delta S(J, v) = \omega_e (1 - 2 x_e) + B(J' - J'')(J' + J'' + 1) = \omega_0 + B(J' - J'')(J' + J'' + 1)$$

Where  $\omega_0 = \omega_e (1 - 2 x_e)$

- $\Delta J = +1$  transition ,  $J' - J'' = +1$  ,  $J' = J'' + 1$  then  $\Delta S(J, v) = \omega_0 + 2B(J''+1)$ ;  $J'' = 0, 1, 2, \text{etc.}$
- $\Delta J = -1$  transition ,  $J' - J'' = -1$  ,  $J'' = J' + 1$  then  $\Delta S(J, v) = \omega_0 - 2B(J'+1)$ ;  $J' = 0, 1, 2, \text{etc.}$

Combining these expressions into:  $\Delta S(J, v) = \omega_0 + 2Bm$  in  $\text{cm}^{-1}$  ; where  $m = \pm 1, \pm 2, \text{etc.}$

- The frequency  $\omega_0$  is called as the band centre and does not appear in the spectrum.

# The Diatomic Vibrating Rotator

- Lines at low frequency corresponding to negative  $m$  ( $\Delta J = -1$ ) are referred as the P branch.
- Lines at high frequency corresponding to positive  $m$  ( $\Delta J = +1$ ) are referred as the R branch.

Lines arising from $\Delta J =$	-2	-1	0	+1	+2
Called:	O	P	Q	R	S



## Reference Books

- **Banwell, C. N., McCash, E. M., Fundamentals of molecular spectroscopy, 4<sup>th</sup> edition, Tata McGraw-Hill Publishing Co.**
- **Puri, B. R., Sharma, L. R. and Pathania, M. S., Principles of Physical Chemistry, Vishal Publishing Co.**
- **Atkins, P., Paula, J., D. and Keeler, J., Atkins' Physical Chemistry, Oxford**