

*. UNIT-II

*. Vibrational spectra:-

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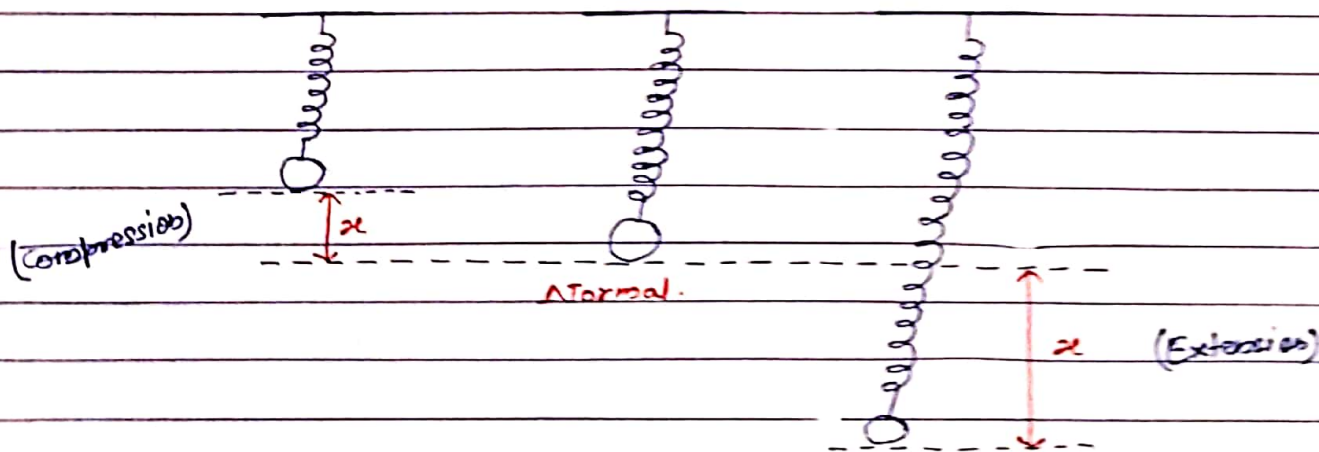
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*. Introduction:-

The absorption spectrum in the infrared region represents the promotion of a molecule from its lowest vibrational level to the most higher one. The correlation of experimental absorption with theoretical difference in the energy level yields information on the flexibility of the bond undergoing vibrations motions. Flexibility means the relative consequences with which the bond length and bond angle of the molecule can be distorted from the equilibrium configuration. These spectra occurs in the spectral range of $500 - 4000 \text{ cm}^{-1}$.

*. classical expression for the frequency of harmonic vibration of a Diatomic molecule:-

[Vibrational Frequency] :-



A/c to Hook's law

$$f = -K \cdot x \quad \text{--- (1)}$$

where, K is a constant known as force constant.

x = Amount of displacement the -ve sign of the expression indicates that the force is a restoring force and thus has a direction opposite to that of the displacement.

Since, $x = A \cos 2\pi \nu_0 t$.

[Periodic motion eqs]

A/c to Newton's 2nd law -

$$f = m \cdot a$$

$$\text{or } f = m \cdot \frac{d^2 x}{dt^2} \quad \text{--- (1)}$$

On comparing eqs - (1) and (2) we get -

$$-kx = m \frac{d^2 x}{dt^2}$$

Now, putting the value of x in the above expression we get -

$$-k(A \cos 2\pi \nu_0 t) = m \cdot A \frac{d^2 x}{dt^2} (\cos 2\pi \nu_0 t)$$

$$-k(A \cos 2\pi \nu_0 t) = m \cdot A \frac{d}{dt} \left[\frac{d}{dt} (\cos 2\pi \nu_0 t) \right]$$

$$-k(A \cos 2\pi \nu_0 t) = -2\pi \nu_0 m \cdot A \frac{d}{dt} (\sin 2\pi \nu_0 t)$$

$$-k(A \cos 2\pi \nu_0 t) = -4\pi^2 \nu_0^2 m (A \cos 2\pi \nu_0 t)$$

$$k = 4\pi^2 \nu_0^2 m$$

$$\nu_0^2 = \frac{1}{4\pi^2} \times \frac{k}{m}$$

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \text{ Hz.}$$

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \cdot \text{Hz.}$$

where μ = reduced mass which is equal to -

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\therefore \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz.}$$

ν_0 = Vibrational frequency.

The above expression is the required characteristic frequency at which atoms of a diatomic molecule under go harmonic vibrations.

To convert this frequency to wave number, we divide by the velocity of light 'c' expressed in cm^{-1} . Thus the above expression becomes equal to -

$$E_0 = \bar{\nu}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

$$E_0 = \bar{\nu}_0 = \text{Wave no.}$$

*. Potential energy of Harmonic Vibrations of a Diatomic molecules:-

The potential energy of a system can be evaluated from the expression as -

$$V = \int_0^x K \cdot x \, dx$$

$$V = K \int_0^x x \, dx$$

$$V = K \cdot \frac{x^2}{2}$$

$$V = \frac{1}{2} K x^2 \quad \text{--- (1)}$$

We know that $K = 4\pi^2 \nu_0^2 m$

Now putting the value of K in the eqⁿ (1) we get

$$V = \frac{1}{2} \times 4\pi^2 \nu_0^2 m \cdot x^2$$

$$V = 2\pi^2 \nu_0^2 m \cdot x^2$$

$$V = 2\pi^2 \nu_0^2 x^2 \mu$$

$$[\because m = \mu]$$

Thus the vibrational energy

$$V = 2\pi^2 \nu_0^2 A^2 \mu$$

where, $A = x$

* Vibrational Energy

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Vibrational energy are quantised. But the classical expression includes the term 'A' i.e. the Amplitude giving any value of vibrational energy which is not acceptable. So, the quantised energies is calculated with the help of Schrodinger equation -

$$\nabla^2 \psi + \frac{8\pi^2 \mu}{h^2} (E - V) \psi = 0$$

$$\text{where } V = \frac{1}{2} kx^2$$

Thus, the solution of the equation gives -

$$E_v = \left(v + \frac{1}{2}\right) h\nu \text{ Joules.}$$

$$\text{where } v = 0, 1, 2, 3, \dots$$

called the vibrational quantum no.

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

$$\therefore E_v = \left(v + \frac{1}{2}\right) \bar{\nu} \text{ cm}^{-1} \quad [\text{where } \bar{\nu} = hc\nu]$$

* Energy level diagram:-

$$\text{Since, } v = 0$$

$$E_0 = \frac{1}{2} h\nu$$

$$v = 1$$

$$E_1 = \frac{3}{2} h\nu$$

$$v = 2$$

$$E_2 = \frac{5}{2} h\nu$$

Conclusions:-

- (i). The energy levels are equally spaced i.e. The difference between the two nearest level is the same throughout and has a value of $h\nu \text{ cm}^{-1}$.

(ii). The lowest vibrational energy ($v=0$) is not zero as in the case of classical vibration but has a value of $\frac{1}{2} h\bar{\nu}$.

Since, $E_v = (v + \frac{1}{2}) \bar{\nu} \text{ cm}^{-1}$

$$E_v = (v + \frac{1}{2}) \bar{\omega}_{0se} \text{ cm}^{-1}$$

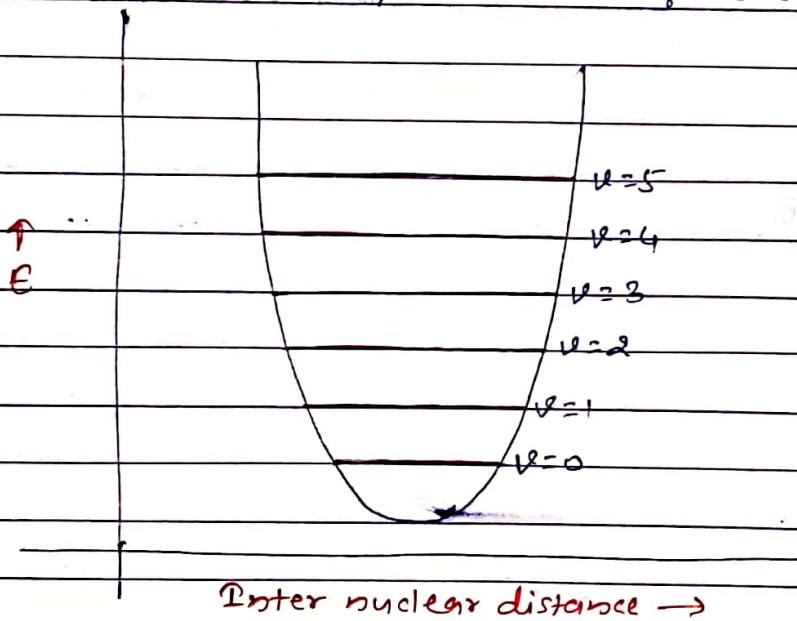
at, $v=0$

$$\therefore \bar{\nu} = \bar{\omega}_{0se}$$

$$E_v = (0 + \frac{1}{2}) \bar{\nu} \text{ cm}^{-1}$$

$$\therefore E_v = \frac{1}{2} \bar{\nu} \text{ cm}^{-1}$$

Schematic representation of energy level -



\therefore Vibrational energy levels for a diatomic molecule undergoing SHM.:-

[SHM = Simple Harmonic Motion]

This lowest energy is known as zero point energy (ZPE).

This means that the atoms in a molecule can never be completely at rest relative to each other.

In classical mechanics the minimum vibrational energy which a diatomic molecule can possess is zero i.e. the atoms can be at rest relative to each other.

The zero point energy is just half of the energy difference between the two nearest vibrational energy levels. It may be noted that both these quantities depends on the strength of the chemical bond and the atomic masses.

*. Resonance Condition :—

$$E_{v+1 \rightarrow v} = \left(v + \frac{1}{2} + 1\right) \bar{\nu} - \left(v + \frac{1}{2}\right) \bar{\nu} \quad \text{cm}^{-1}$$

$$E_{v+1 \rightarrow v} = \left(v + \frac{3}{2}\right) \bar{\nu} - \left(v + \frac{1}{2}\right) \bar{\nu} \quad \text{cm}^{-1}$$

$$E_{v+1 \rightarrow v} = \cancel{v\bar{\nu}} + \frac{3}{2}\bar{\nu} - \cancel{v\bar{\nu}} - \frac{1}{2}\bar{\nu} \quad \text{cm}^{-1}$$

$$E_{v+1 \rightarrow v} = \frac{3}{2}\bar{\nu} - \frac{1}{2}\bar{\nu} \quad \text{cm}^{-1}$$

$$E_{v+1 \rightarrow v} = \bar{\nu} \quad \text{cm}^{-1}$$

where, $\boxed{\bar{\nu} = hc\omega}$