

Vibrational spectra of diatomic molecules

Pure vibrational spectra of diatomic molecules lies in near-infrared region of the electromagnetic spectrum. To deal with the theory, the molecules are treated as harmonic oscillator. The potential energy function is given by

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

where k is the force constant, r_e is the equilibrium internuclear distance, and x is the displacement of the oscillator from the equilibrium position. The Schrödinger wave equation for motion is given by

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

where μ = reduced mass of diatomic molecule

Substituting $\alpha = \frac{8\pi^2\mu E}{h^2}$ and $\beta = \sqrt{\frac{4\pi^2\mu k}{h^2}}$, we get

$$\frac{d^2\psi}{dx^2} + (\alpha - \beta^2 x^2) \psi = 0$$

Let us introduce a dimensionless independent variable

$$\xi = \sqrt{\beta} x$$

So that $\frac{d^2}{dx^2} = \beta \frac{d^2}{d\xi^2}$

Then we have

$$\beta \frac{d^2\psi}{d\xi^2} + \left(\alpha - \beta^2 \frac{\xi^2}{\beta} \right) \psi = 0$$

$$\text{or } \frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2 \right) \psi = 0 \quad \text{--- (I)}$$

Let us take the solution of following form

$$\psi(\xi) = C U(\xi) e^{-\xi^2/2} \quad \text{--- (II)}$$

Making the substitution in eq. (I), we get

$$\frac{d^2U}{d\xi^2} - 2\xi \frac{dU}{d\xi} + \left(\frac{\alpha}{\beta} - 1 \right) U = 0$$

If we replace $\frac{\alpha}{\beta} - 1$ by 2ν then the equation becomes Hermite differential equation & we may put $U(\xi) = H_\nu(\xi)$. Then

$$\frac{d^2 H_\nu(\xi)}{d\xi^2} - 2\xi \frac{dH_\nu(\xi)}{d\xi} + 2\nu H_\nu(\xi) = 0$$

This shows that the solution of equation (1) is obtained by replacing $U(\xi)$ by the Hermite polynomial $H_\nu(\xi)$ in eqn (1). That is

$$\Psi(\xi) = C H_\nu(\xi) e^{-\xi^2/2}$$

These solutions are acceptable only for $\nu = 0, 1, 2, \dots$. The restrictions on ν gives a corresponding restriction on E . We have

$$\frac{\alpha}{\beta} = 2\nu + 1$$

$$\text{or } \frac{8\pi^2 \mu E / h^2}{2\pi \sqrt{\mu k} / h} = 2\nu + 1 = 2\left(\nu + \frac{1}{2}\right)$$

$$\text{or } E = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left(\nu + \frac{1}{2}\right)$$

But $\frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \nu_{\text{osc}}$ (classical frequency of oscillator)

$$\therefore E = h \nu_{\text{osc}} \left(\nu + \frac{1}{2}\right)$$

This gives the allowed energies for the harmonic oscillator. ν is called the vibrational quantum no. which can take the integral values $0, 1, 2, 3, \dots$

A special feature of the quantum mechanical oscillator is the existence of zero point energy $\frac{1}{2} h \nu_{\text{osc}}$.

Let us now investigate the expected spectra of such an oscillator. The vibrational terms (energy in wave no ^{unit} m^{-1} or cm^{-1}) are

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

$\frac{v_{0e}}{c}$ is the classical frequency in wave no. unit and c is known as vibrational constant denoted by ω . Thus

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

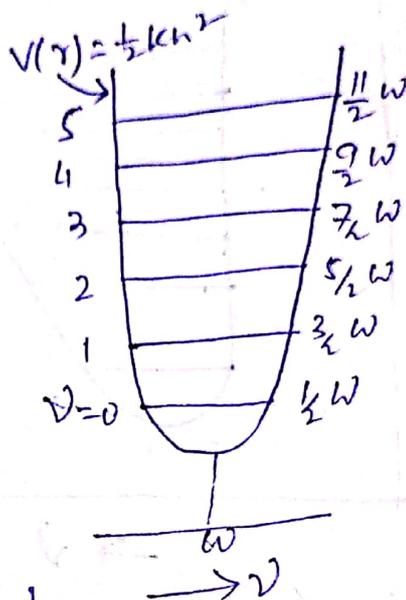
Putting $v=0, 1, 2, 3, \dots$ we get

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

Thus we have a series of equispaced discrete vibrational ~~to~~ levels, the common separation being ω (fig)

When transition takes place between an upper level v' & a lower level v'' , the wave no. of the emitted or absorbed radiation is

$$\begin{aligned} \nu &= G(v') - G(v'') \\ &= \omega(v' + \frac{1}{2}) - \omega(v'' + \frac{1}{2}) \end{aligned}$$



Now, for harmonically oscillating molecule of dipole moment M , the matrix element is found to be non-vanishing only when

$$\frac{dM}{dr} \neq 0 \quad \text{and} \quad \Delta v = \pm 1$$

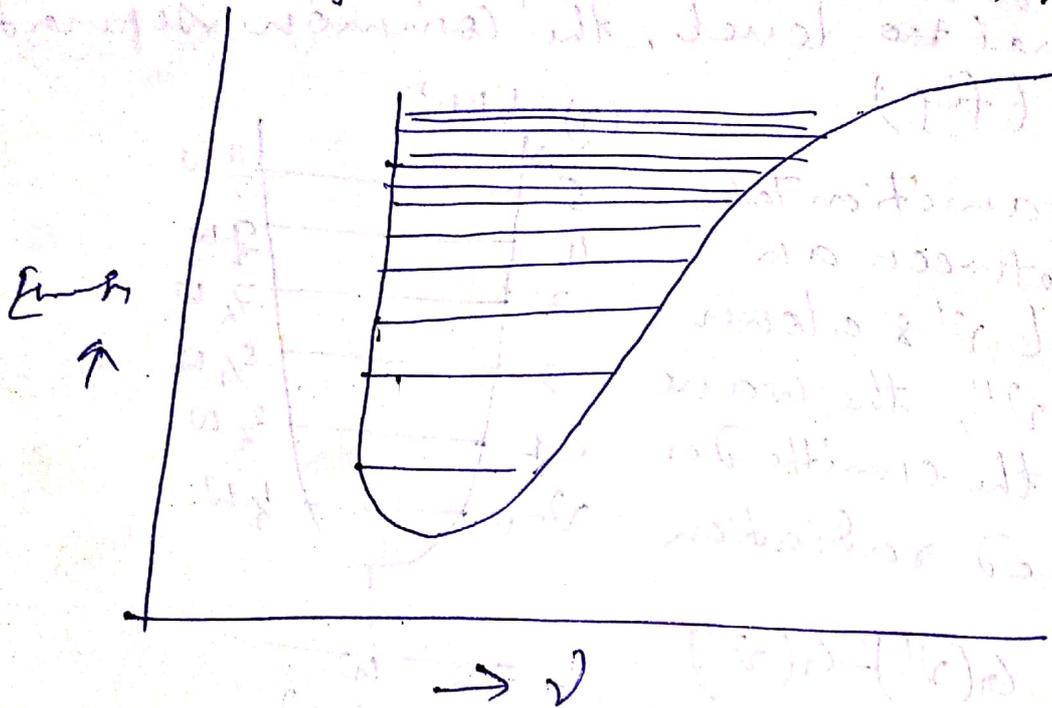
i.e., the vibrational transition can only occur when the molecule has a permanent dipole moment which changes with distance.

Further, the selection rule $\Delta v = \pm 1$ gives

$$v' = v'' + 1$$

The vibrational spectrum is expected to consist of a single band at ω .

The actual infra-red spectrum is, however found to consist of an intense band at ω plus a no. of weak bands (overtones). The selection rule $\Delta v = \pm 1$ is not strictly obeyed. This is attributed to the fact that for an actual molecule the potential energy curve is not perfectly parabolic rather as shown in fig



It is called Morse Potential Curve because P. M. Morse explained it as due to anharmonicity.