INFRA-RED SPECTROSCOPY

Vibrational spectra of diatomic molecules

THE SIMPLE HARMONIC OSCILLATOR :

Atoms in a molecule do not remain in fixed positions, but vibrate about some mean position. The compression and extension of a bond can be assumed to be similar to the behaviour of a spring obeying Hooke's law,

$$f = -kx$$ ——①

where f is the restoring force, and x is the displacement from mean position, k is the force constant.

In case of the molecule, eqⁿ ① can be written as,

$$f = -k(r - r_{eq})$$ ——②

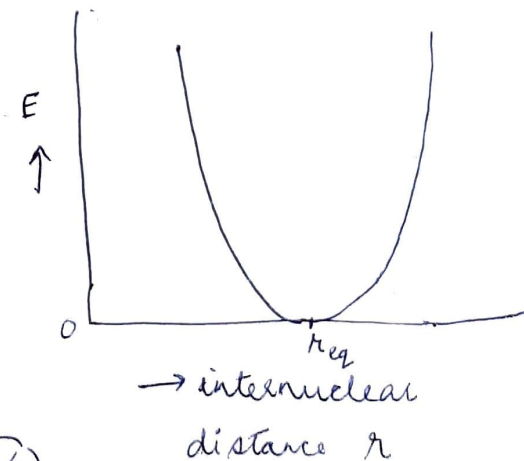where r is the internuclear distance and r_{eq} is the equilibrium internuclear distance, or bond length.

The energy is given by,

$$E = \frac{1}{2}k(r - r_{eq})^2$$ ——③

This is the eqⁿ of a parabola and the zero of the curve is at $r = r_{eq}$.

An elastic bond has an intrinsic vibrational frequency ω_{osc} which depends on the mass of the system and force constant, and is given by,

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad Hz$$ ——④

where μ is the reduced mass of the system. Eqn (4) can be written in terms of wave number as,

$$\bar{\omega}_{osc} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad cm^{-1} \quad -(5)$$

Here, c is the velocity of light expressed in $cm\,s^{-1}$.

$$\boxed{\begin{array}{l} \omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \\ c = \lambda\, \omega_{osc} \\ \Rightarrow \bar{\omega}_{osc} = \frac{1}{\lambda} = \frac{\omega_{osc}}{c} \\ \qquad = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \end{array}}$$

Now, vibrational energies are quantized, and the allowed vibrational energies of a simple harmonic oscillator can be obtained from the solution of the Schrodinger eqn as,

$$E_v = \left(v + \frac{1}{2}\right) h\,\omega_{osc} \quad \text{joules} \quad (v = 0, 1, 2, \cdots) \quad -(6)$$

v is called the vibrational quantum number.

Eqn (6) can be written in terms of wave number as

$$E_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \bar{\omega}_{osc} \quad cm^{-1} \quad -(7) \qquad \bar{\omega}_{osc} = \frac{\omega_{osc}}{c}$$

The energy of the lowest vibrational level, $v = 0$ is,

$$E_0 = \frac{1}{2} h\,\omega_{osc} \quad J\, \left[\, from\ eq^n\ (6)\,\right]$$

or $\quad E_0 = \frac{1}{2} \bar{\omega}_{osc} \quad cm^{-1} \left[\, from\ eq^n\ (7)\,\right]$

This means that a molecule can never have zero vibrational energy. The quantity $\frac{1}{2} h\,\omega_{osc}$ joules or $\frac{1}{2} \bar{\omega}_{osc}\ cm^{-1}$ is known as the zero-point energy. It depends on the strength of the chemical bond and the atomic masses. [from eqn (4) and (5)]

Selection rule : $\qquad \Delta v = \pm 1$

Besides, a spectrum will be observed only when

the vibration can interact with a the radiation, i.e. if the vibration involves a change in dipole moment of the molecule.

Therefore, vibrational spectra will be observed only in heteronuclear diatomic molecules.

[homonuclear diatomic molecules have no dipole moment].

Energy of vibrational transitions : For emission from $v+1$ to v level,

$$E_{v+1 \to v} = \left(v + \tfrac{1}{2} + 1\right) \bar{\omega}_{osc} - \Phi\left(v + \tfrac{1}{2}\right) \bar{\omega}_{osc} \quad cm^{-1}$$

$$= \bar{\omega}_{osc} \quad cm^{-1}$$

~~This~~ ∨ Similarly, for absorption,

$$E_{v \to v+1} = \bar{\omega}_{osc} \quad cm^{-1}$$

This is independent of v, i.e. transitions between any two neighbouring levels will give rise to the same energy change.