Infrared spectroscopy or vibrational spectroscopy:-

Atoms in a molecule don't remain in fixed relative positions but do vibrates about some mean position.

The compression and extension of a bond obeys Hook's law where the restoring force F

$$F = -k(r - r_{eq})$$

where k is the force constant of the bond and r_{eq}, the eq^n internuclear distance.

The energy curve is parabolic and has the form

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

The classical oscillation frequency

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{Joules,}$$

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

Spectrum of a simple harmonic oscillator:-

Vibration energies are quantised and the vibration energy for a simple harmonic oscillator may be calculated from the schrödinger eq^n.

$$E_v = (v + \tfrac{1}{2})h\,\omega_{osc} \quad \text{Joules}$$

or

$$E_v = \frac{E_v}{hc} = (v + \tfrac{1}{2})\frac{\omega_{osc}}{c} \quad cm^{-1}$$

$$E_v = (v + \tfrac{1}{2})\bar{\omega}_{osc} \quad cm^{-1}$$

where vibrational quantum no. $v = 0, 1, 2, 3 \dots$ etc.

When $v = 0$, $E_v = \tfrac{1}{2}\bar{\omega}_{osc} \, cm^{-1}$. This is known as the zeropoint energy and depends only on the classical vibrational frequency and hence on the strength of the chemical bond and the atomic masses.

Selection rule for a simple harmonic osc. undergoing vibrational changes is $\Delta v = \pm 1$.

A spectrum will be at observed only for hetero nuclear molecules where vibration leads in change in dipole moment.
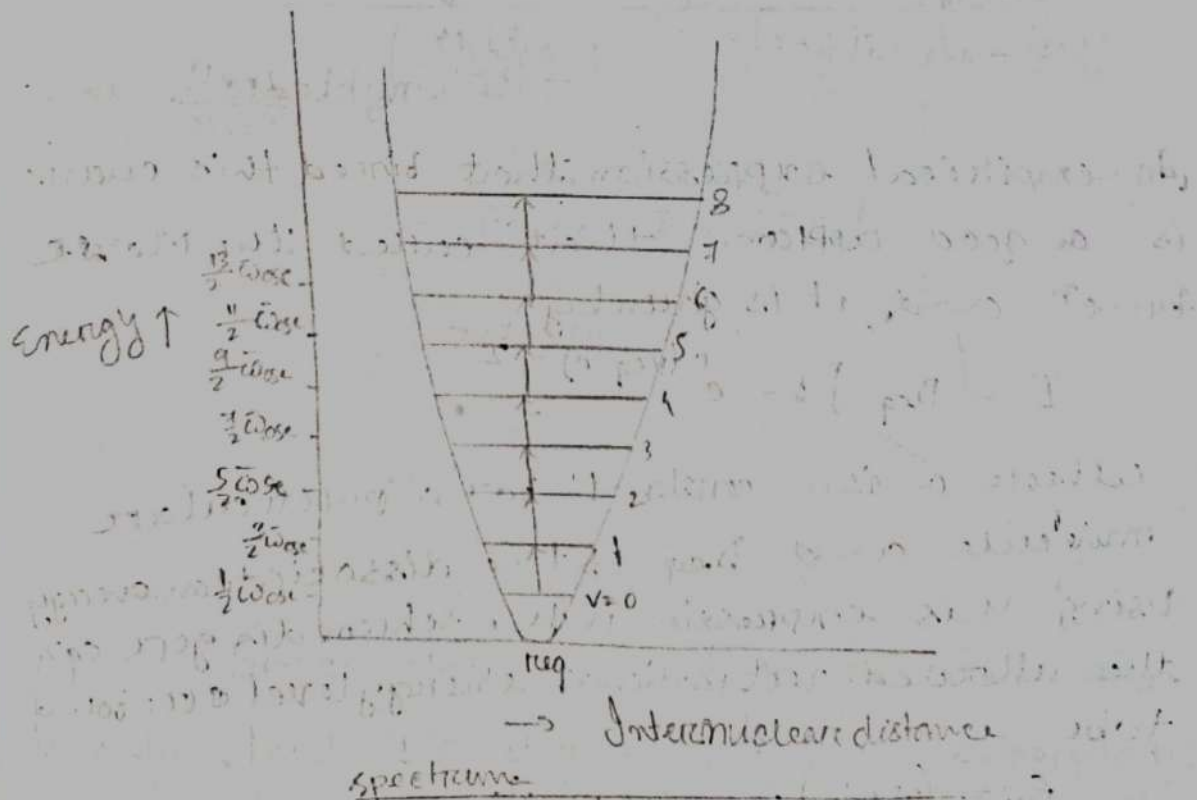
The wavenumber of the radiation absorbed for the transition from v to v_{+1},

$$\bar{v}_{v - v_{+1}} = \varepsilon_{v_{+1}} - \varepsilon_v$$

$$= \left(v_{+1} + \frac{1}{2}\right)\bar{\omega}_{osc} - \left(v + \frac{1}{2}\right)\bar{\omega}_{osc}.$$
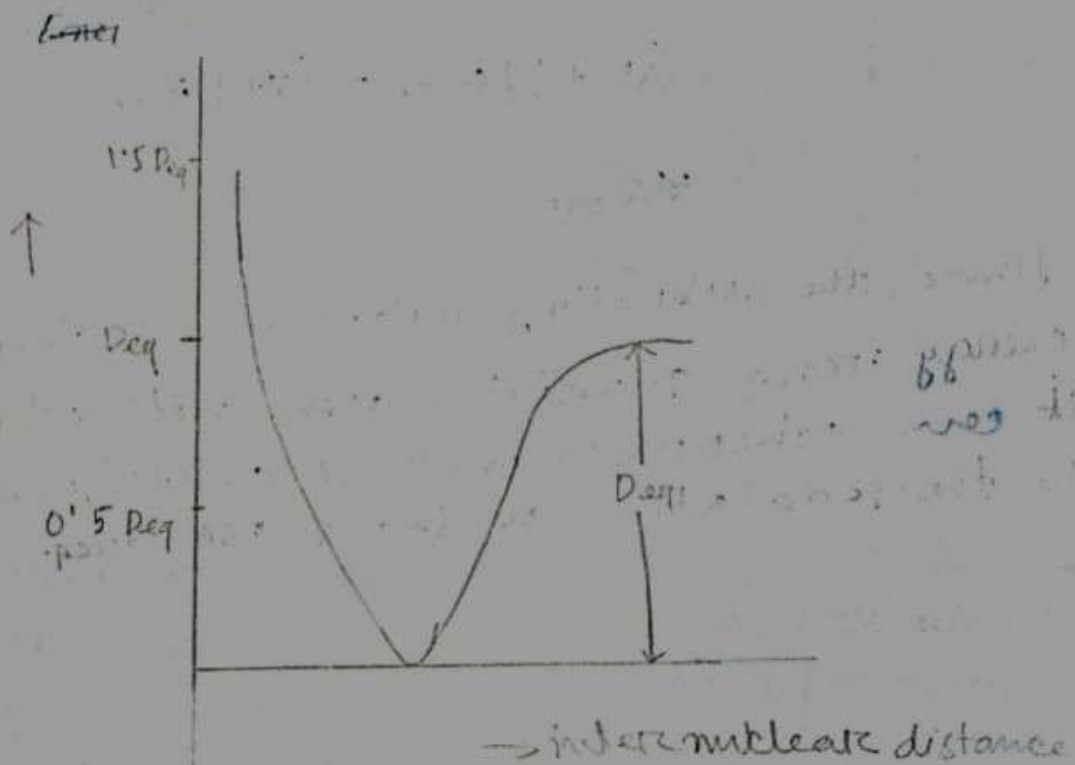
$$= \text{✻} \bar{\omega}_{osc}$$

Hence, the vibrating molecule will absorb energy from radiation from with which it can coherently interact and this must be the radiation of its own osc. freq.

Energy ↑

$\frac{13}{2}\bar{\omega}_{osc}$
$\frac{11}{2}\bar{\omega}_{osc}$
$\frac{9}{2}\bar{\omega}_{osc}$
$\frac{7}{2}\bar{\omega}_{osc}$
$\frac{5}{2}\bar{\omega}_{osc}$
$\frac{3}{2}\bar{\omega}_{osc}$
$\frac{1}{2}\bar{\omega}_{osc}$

8
7
6
5
4
3
2
1
$v = 0$

req

→ Internuclear distance

spectrum

→ $\bar{v}$

Anharmonic oscillator:-

Real molecules donot obey laws of simple harmonic motion as the bond betn atoms break and molecules dissociates into atoms if the bond is stretched beyond the point of the

The shape of energy curve of a diatomic molecule is shown in the figure.

An empirical expression that fitted this curve is a good appror. that called the Morse funcn and it is given by

$$E = D_{eq} \left[1 - e^{a(r_{eq}-r)} \right]^2$$

where a is a constant for a particular molecule and D_{eq} is the dissociation energy. Using this expression in the schroedingere eqn the allowed vibrational energy level are found to be

$$E_v = \left(v + \frac{1}{2} \right) \bar{\omega}_e - \left(v + \frac{1}{2} \right)^2 \omega_e x_e \quad \text{cm}^{-1}$$

Where vibrational quantum number

$$v = 0, 1, 2 \cdots$$

$\bar{\omega}e$ is the oscilation frequency, and x_e the enharmonic constant which for bond streching vibration is small and positive (0·01)

The vibrational level crowd closly togetherr with increasing v.

The selection rule for anharmonic oscilator is

$dv = \pm 1, \pm 2, \pm 3 \ldots$ i·e, all transition are allowed.

It If the spacing betn the line is the order of 10^3 than the number of mol in $v=1$ state compared to $v=0$ state is given by the botzman distribution.

$$\frac{N_{v=1}}{N_{v=0}} = e^{\left(-E_v/kT\right)}$$

$$\frac{N_{v=1}}{N_{v=0}} = e^{\left(-\frac{ch\bar{\omega}_{ose}}{kT}\right)}$$

$E_v = (1+\frac{1}{2})h\bar{\omega}ose$

$= he\bar{\omega}ose$
$= hc\omega ose$

$E = (1+\frac{1}{2})h\omega ose - (1+\frac{1}{2})$.

$$= e^{\left(-\frac{3\times 10^{10} cm\,s^{-1} \times 10^3\, cm^{-1}}{1·38\times 10^{-23} J k^{-1} \times 300 K}\right)}$$

$$= e^{-\,0072\times 10}$$

$\approx \,·01$

Since the population of $v=1$ state is only about 1% of the ground state population then to a good approximation we can restrict ourselb to the 3 transitions.

① $v=0 \longrightarrow v=1$. $dv=+1$. with considerably intensity.

$$d\epsilon = \epsilon_{v=1} - \epsilon_v$$

$$= \tfrac{3}{2}\bar{\omega}e - \tfrac{9}{4}\bar{\omega}e\chi e - \tfrac{1}{2}\bar{\omega}e + \tfrac{1}{4}\bar{\omega}e\chi e$$

$$= \bar{\omega}e - 2\omega e\chi e$$

$$d\epsilon = \bar{\omega}e(1 - 2\chi e)\,cm^{-1}.$$

② $v=0 \longrightarrow v=2 \quad dv = +2$ with small intensity.

$$d\epsilon = (2+\tfrac{1}{2})\bar{\omega}e - (2+\tfrac{1}{2})^2\bar{\omega}e\chi e - (0+\tfrac{1}{2})\bar{\omega}e + (0+\tfrac{1}{2})^2\bar{\omega}e\chi e$$

$$= \tfrac{5}{2}\bar{\omega}e - \tfrac{25}{4}\bar{\omega}e\chi e - \tfrac{1}{2}\bar{\omega}e + \tfrac{1}{4}\bar{\omega}e\chi e.$$

$$= 2\bar{\omega}e - 6\bar{\omega}e\chi e$$

$$= 2\bar{\omega}e(1 - 3\chi e)\,cm^{-1}$$

③ $v=0 \longrightarrow v=3. \quad dv = +3.$ with negligible intensity

$$d\epsilon = \tfrac{7}{2}\bar{\omega}e - \tfrac{49}{4}\bar{\omega}e\chi e - \tfrac{1}{2}\bar{\omega}e +$$

$$d\epsilon = 3\omega e(1 - 4\chi e)\,cm^{-1}$$

Since $\chi e \approx 0.01$, the 3 spectral lines lie very close to $\bar{\omega}e$, $2\bar{\omega}e$ and $3\bar{\omega}e$.

The line near $\bar{\omega}e$ is called fundamental absorption while those near $2\bar{\omega}e$ and $3\bar{\omega}e$ are called 1s and 2nd second overtion.

If the temperature is raised or if the vibration has low frequency the population of $v=1$ state may become appreciable and transitions from $v=1$ to $v=2$ will have intensity of about 10% of the fundamental. such weak absorption are called that band. since high temp^r is one on conditi-

for their occurrence and occurs at a wave number

$$\overline{v_0} \longrightarrow \overline{v}$$

$$\overline{v}_{v=1 \to v=2} = E_{v=2} - E_{v=1}.$$

$$= \overline{\omega}(1-$$

$$= \frac{5}{2}\overline{\omega}e - \frac{25}{4}\overline{\omega}e\,x_e - \frac{3}{2}\overline{\omega}e - \frac{9}{4}\overline{\omega}e\,x_e.$$

$$= \overline{\omega}e\,(1 - 4x_e)\ cm^{-1}.$$

It occurs in a slightly lower wavenumber than the fundamental and its nature may be confirmed by raising the temperature of sample when a true hot band increases in intensity.

that Calculation of force const.

The force constant of a bond can be calculated from the expression $\overline{\omega}k = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ cm^{-1}.$

. knowing $\overline{\omega}$ from an its IR spectrum the value of k may be determined.

__Pr__

The IR spectra of HCl shows intense absorption at & 2886 cm⁻¹, a weaker one at 5668 cm⁻¹ and a very weak one at 8347 cm⁻¹! Find the force constant of the bond in HCl. (Nm⁻¹)

__sol__

$$\Delta E_1 = 2886\ cm^{-1} \qquad \Delta E_2 = 5668\ cm^{-1}$$

$$\Rightarrow \overline{\omega}e(1-2x_e) = 2886 \qquad 2\overline{\omega}e(1-3x_e) = 5668.$$

$$= \overline{\omega}e = \frac{2886}{1-2x_e} \qquad \Rightarrow 2\times\frac{2886}{1-2x_e}(1-3x_e) = 5668.$$

$$\Rightarrow 5772\,(1-3x_e) = 5668\,(1-2x_e)$$

$$\Rightarrow 5772 - 17316\,x_e = 5668 - 11336\,x_e$$

$$\Rightarrow -5920\,x_e = -5 - 104.$$