P.G. Sem III : core course X

Unit II

Population of vibrational Energy levels

The population of vibrational energy levels is governed by Boltzmann's distribution equation —

gf

n_1 = No. of molecules in vib. level $v = 1$

n_0 = " " " " " " $v = 0$

• Then

$$\frac{n_1}{n_0} = e^{-\Delta E/kT}$$

As. $\Delta E >> kT$

$$\therefore \frac{n_1}{n_0} = \frac{1}{99}$$

i.e. At ordinary temperature about 99% molecules occupy $v = 0$ vibrational level. Hence as $\Delta v = \pm 1$, transition involved " is

$$v = 1 \leftarrow v = 0$$

Calculation of force constant

Let

λ = wavelength of radiation absorbed

$\therefore \bar{\nu} = \frac{1}{\lambda}$

Transition involved is

$v=1 \leftarrow v=0$

Since, fundamental vibrational frequency

$$\nu_0 = \frac{1}{2\pi}\sqrt{K/\mu} \ \sec^{-1}$$

or $$\bar{\nu}_0 = \frac{1}{2\pi c}\sqrt{K/\mu} \ cm^{-1}$$

As for absorption of radiation

$$\bar{\nu} = \bar{\nu}_0$$

$$\therefore \bar{\nu} = \frac{1}{\lambda} = \frac{1}{2\pi c}\sqrt{K/\mu} \ cm^{-1}$$

or $$\bar{\nu}^2 = \frac{1}{4\pi^2 c^2} \cdot \frac{K}{\mu}$$

or $$K = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

(force constant)

Anharmonicity

Real molecules do not exactly obey the law of simple harmonic motion (S.H.M) and bonds in real molecules are not homogeneous as such Hooke's law is exactly obeyed. For small ~~extn~~ extention and compression a real bonds may be taken as perfectly elastic and obey Hooke's law and potential energy rises parabolically. But at large extensions Hooke's law is not exactly obeyed. Also when greatly streached the bond is much destroyed and further extension become easy. The restoring force goes on decreasing and at large extensions it almost become zero. Therefore potential energy rises more and more slowly and stops to increase with further extensions. In compression the repulsive forcess due to nucleus— nucleus and electron - electron repulsion become ~~lag~~ large.

As a result the bond is not compressed further and rise in potential energy curve gets steeper (उच्चा ढलुआ). Real molecules thus undergo anharmonic extensions and compressions. These molecules are therefore called anharmonic oscillator and this property of real molecule is known as anharmonicity. Potential energy curve for such molecule as —

$\Delta v = \pm 1, \pm 2, \pm 3 \ldots$