Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Paper Code: CHC-105

Paper Title: Physical Chemistry

Unit: Molecular Spectroscopy -2

Module Name: Morse potential and dissociation energies.

Module No: 51

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Notes:

When a molecule is undergoing simple harmonic oscillations, the restoring force of the harmonic vibrations is directly proportional to the displacement and energy of the harmonic oscillator.

$$F = -k\,x \qquad\qquad V = \frac{1}{2}\,k\,x^2$$

In practice, the molecule does not always vibrate as simple harmonic oscillator this is because as displacement increases, the restoring force becomes weaker and for large amplitude of vibration, the atoms of the molecule must fall apart, i.e. the molecule must dissociate into atoms. Such real oscillator is said to be an **anharmonic oscillator.**

In 1929 P. M. Morse suggested an empirical expression for the potential energy of an anharmonic diatomic oscillator given by,

$$V(r) = D_e (1- e^{a(r-re)\ 2})$$

Where **a** is morse constant,

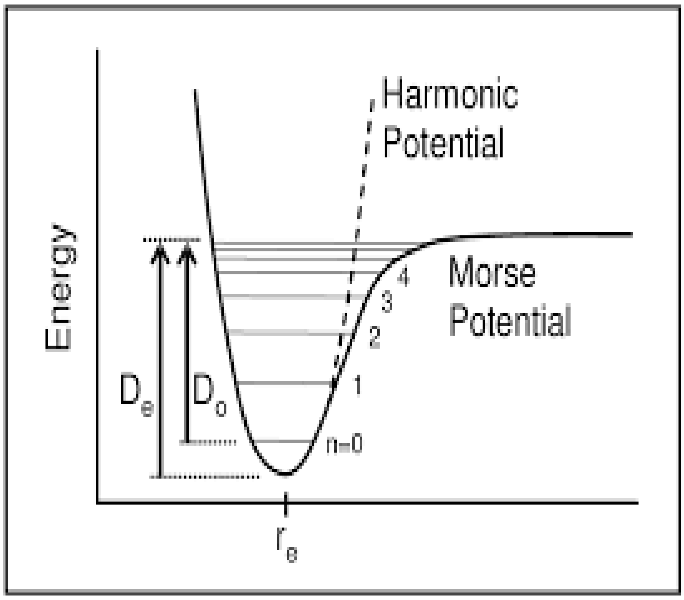
D_e is spectroscopic dissociation energy of the molecule.

Morse potential energy curve:

It may be pointed out that the dissociation energy D_e in the Morse potential energy curve is measured from the bottom of the potential well.

The experimentally measured dissociation energy D_o is the one that is measured from the ground level (v =0) to the top. Thus

$$\mathbf{D_e = D_0 + \frac{hv}{2}\ (ZPE)}$$



When the Schrödinger equation for an anharmonic oscillator is solved using the Morse potential energy, energy levels are given by:

$$\mathbf{E = (v + \frac{1}{2})\, w_e - (v + \frac{1}{2})^2\, w_e x_e \qquad (v = 0,1,2,3.....)}$$

Where $w_e x_e$ is called anharmonicity constant.

As expected $w_e x_e \ll w_e$

The consequences of anharmonicity is that the vibrational energy levels of the S.H.O. are all slightly lowered and the spacing between them is no longer constant but goes on steadily decreasing with increase in vibrational quantum number.

Also, because of anharmonicity the rule for vibrational transition is no longer $\Delta v = \pm 1$. instead , transitions corresponding to $\Delta v = \pm 2, \pm 3$ etc. are also observed in the IR spectra.

These are called first overtone, second overtone etc. respectively

The intensity of an overtone is dependent on the anharmonicity of the vibration.

Compared with highly intense fundamental vibrational frequency.

The overtones are very weak i.e. of considerably low intensity.