Due to the above mentioned reasons,

oscillator

Vibrating Diatomic Molecule as Anharmonic Oscillator

Real molecules do not obey exactly the laws of simple harmonic motion. The bonds in real molecules are known as real bonds. Although, for small expressions, and extensions, real bonds may be considered to be perfectly elastic, obeying Hooke's law, yet at larger distortions they deviate from the behaviour of Hooke's law.

Fig. 3.4 shows the energy curve for a typical diatomic real molecule which behaves as anharmonic oscillator and undergoes extensions and compressions. In the same figure, a dotted parabola is there which is due to an ideal diatomic molecule obeying ideal simple harmonic motion.

In order to explain the energy curve due to a real molecule, P.M. Morse invented a purely empirical expression known as Morse function which is as follows : (3.21)

$$E = D_{eq}[1-e^{a/r_{eq}-r)}]^2$$

where D_{eq} = the dissociation energy for a particular molecule

a = a constant for a particular diatomic molecule and

r_{eq} = the value of internuclear distance which corresponds to a minimum of Morse curve.

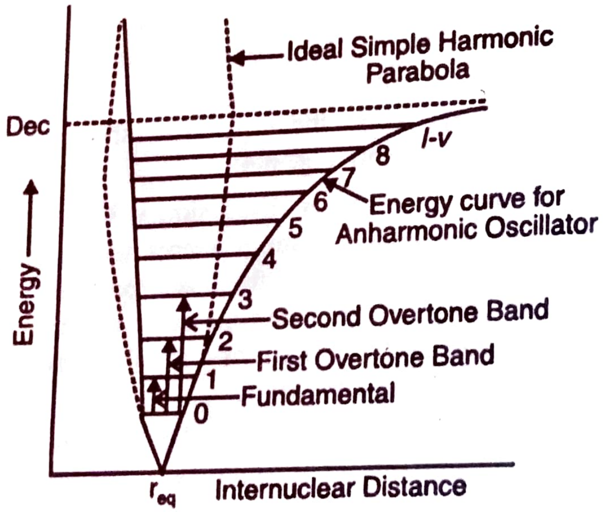

Fig. 3.4

When equation (3.21) is used in the Schrodinger's equation, the values of allowed vibrational energy levels are as follows :

$$E_v=(v+½)\, hc\,\overline{w}_e-(v+½)^2hcx\, w_e+(v+½)^3\, hcy\,\overline{w}_e+... \tag{3.22}$$

where $\overline{w}_e$ =equilibrium frequency of the molecule expressed in wave numbers, and, $x,y,...$= the anharmonic constants.

The selection rules for all the transitions in anharmonic oscillator may be given as :

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

for these transitions in which

(i) v=1 to v=0 gives fundamental band.

(ii) v=2 to v=0 gives first overtone (second anharmonic)

(iii) v=3 to v=0 gives second overtone (third anharmonic), etc.

The energy change when a transition results from an upper level v' to the lower level v" will be given by

$$E'_v - E''_v = (v' - v'')\, hc\, \bar{w}_e - \{v'(v'+1) - v''(v''+1)]\, xhc\, \bar{w}_e \tag{3.23}$$

The frequency of such resulting radiation will be

$$\bar{v}_v = (E'_v - E''_v)/hc \tag{3.24}$$

or

$$\bar{v}_v = (v' - v'')\bar{w}_e - \{v\,(v'+1) - v''+1]\, x\bar{w}_e$$

The vibrational quantum number in the final state is always zero from which follows that

$$\bar{v}_{v\rightarrow 0} = v\bar{w}_e - \{v(v+1)x]\bar{w}_e \tag{3.25}$$

$$= [1 - (v+1)x]v\bar{w}_e \tag{3.26}$$

where v is the vibrational quantum number in the initial state. Thus,

(i) For fundamental band, v=1 to v=0

$$\bar{v}_1 = (1 - 2x)\bar{w}_e \tag{3.27}$$

(ii) For first overtone band, v=2 to v=0

$$\bar{v}_2 = (1 - 3x)2\bar{w}_e \tag{3.28}$$

(iii) For second overtone band, v=3 to v=0

$$\bar{v}_3 = (1 - 4x)3\bar{w}_e \tag{3.29}$$

Where $\bar{v}_1$, $\bar{v}_2$ and $\bar{v}_3$ are the frequencies of the origins or centres of fundamental, first and second overtone respectively. As the frequencies of the first and second overtone bands are 2 to 3 times the frequency of the fundamental, they appear in the regions of shorter wavelength as compared to the fundamental band. These have been shown in Fig. 3.4.

Diatomic Vibrating Rotator. In the earlier discussion it was assumed that a diatomic molecule behaves as harmonic or anharmonic oscillator. But it seems natural to assume that the rotation and vibration must take place simultaneously and in fact the observed fine structure of rotation bands reveals that a simultaneous rotation and vibration do occur in such molecules. For this reason, a diatomic molecule will be considered which can execute rotations and vibrations simultaneously. Such a system is termed as a *rotating vibrator or a rotating oscillator*.

of vibration and rotation, the total energy of the vibrating rotator would