T.D.C. Part IIIrd

Chemistry paper Vth ; Physical chemistry

Energy level spacing :→

As,

$$E_n = (n + 1/2)\, hc\bar{\nu}_0$$

$$E_{n+1} = (n + 1 + 1/2)\, hc\bar{\nu}_0$$

for the transition.

$$v = n+1 \leftarrow n$$

$$\Delta E = hc\bar{\nu}_0$$

and,

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

that is energy levels are equally spaced.

Selection Rule :→

Selection rule for vibrational quantum number is —

(I) $\Delta v = \pm 1$.

(II) The vibration must involved a change in dipole moment of the molecule. Thus vibrational spectra observed only in heteronuclear diatomic molecule. Since homonuclear diatomic molecules have no dipole moment.

Morse Curve :→

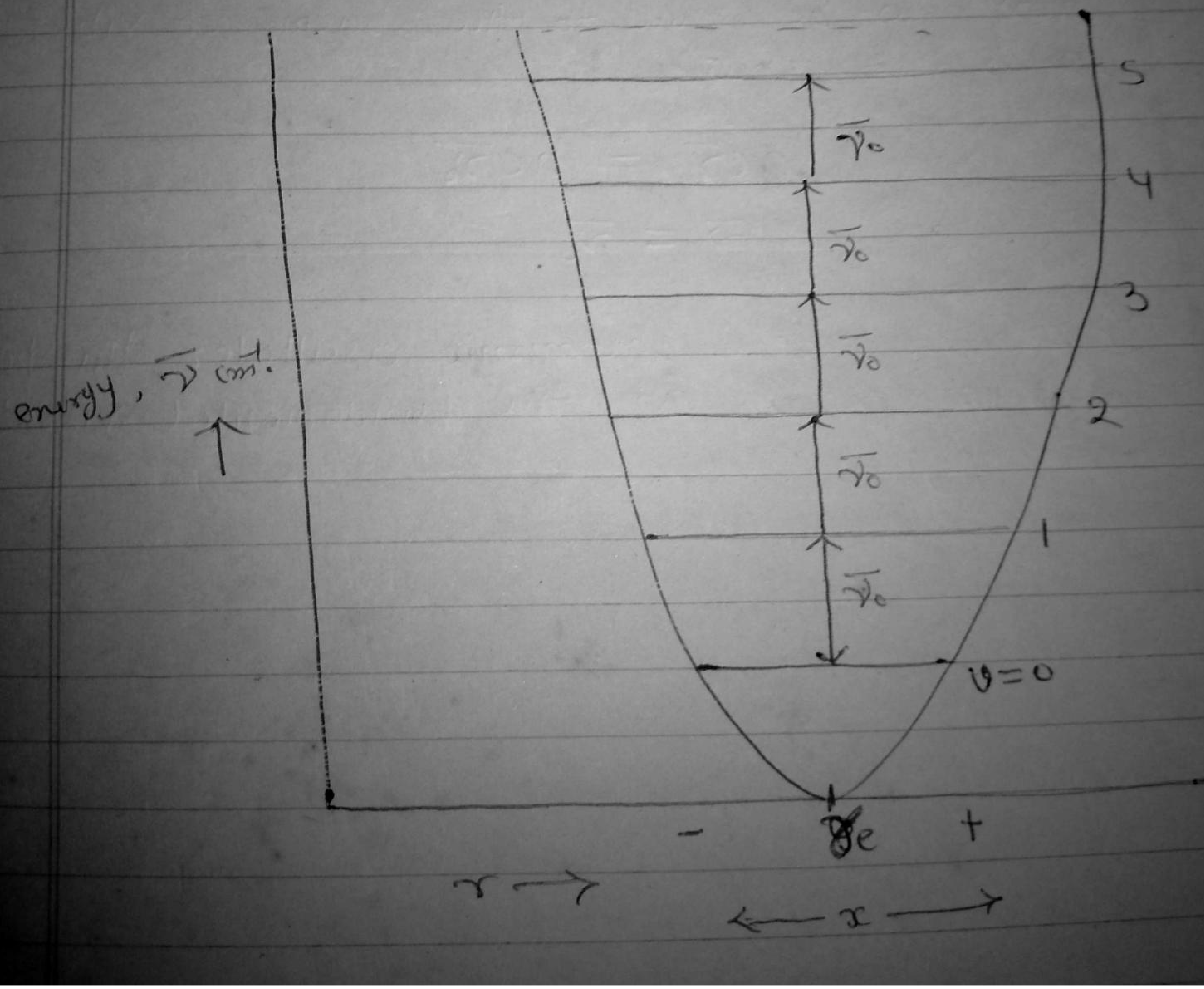
Simple harmonic vibrations of a diatomic molecule and the allowed vibrational energy levels along with the transitions between them is explained by the following potential energy curve known as Morse curve.

As,

$$E = \frac{1}{2} K (r - r_e)^2$$

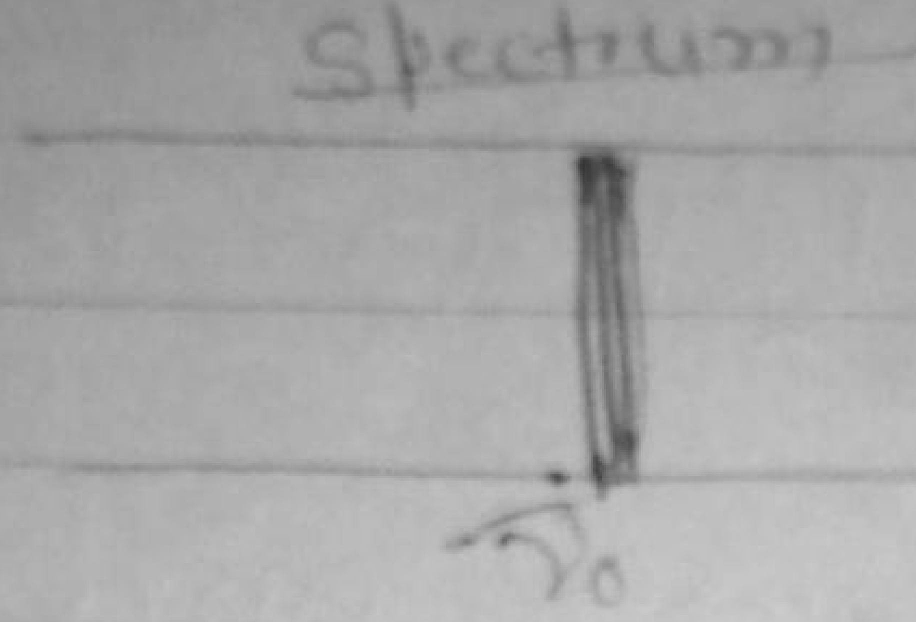
∴

The potential energy curve is parabolic.



I.R Spectra :→

As frequency separation between vib. energy levels in a transition is always equal to $\bar{\nu}_0$, all lines in the spectrum fall at the same place.



For ~~the~~ interaction the energy of absorbed radiation $hc\bar{\nu}$ must be equal to the spacing of vib. energy levels, so that,

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

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

Thus for ideal harmonic oscillator the spectral absorption occurs at the fundamental vibrational frequency.

Pobulation of vibrational Energy levels :→

If

n_1 = No. of molecules in vibrational level $v=1$
and n_0 = " " " " " " $v=0$

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

As. $\Delta E >> KT$

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

i.e. At ordinary tempe 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 absorved

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

Transition involved is

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

since frequency fundamental frequency

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

and as.

$$\bar{\nu}_0 = \bar{\nu} = \frac{1}{2\pi c}\sqrt{k/\mu}$$

or,

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

or,

$$\underset{\text{force constant}}{k} = 4\pi^2 c^2 \bar{\nu}^2 \cdot \mu$$

CO > NO > HF > HI

k k k k