P. G. Sem. IIIrd ; core course X

Unit II

Energy level Spacing

For the transition.

$$v_{n+1} \leftarrow v_n$$

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

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

$$\Delta E_{vib} = hc\bar{\nu}_0 (\cancel{n}+1+\cancel{1/2}-\cancel{n}-\cancel{1/2})$$

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

Frequency difference of the vib. levels.

$$\bar{\nu} = \bar{\nu}_0 (v+1/2)$$

for the transition

$$v_{n+1} \leftarrow v_n$$

$$\bar{\nu}_{n+1} = \bar{\nu}_0 (n+1+1/2)$$

$$\bar{\nu}_n = \bar{\nu}_0 (n+1/2)$$

$$\Delta\bar{\nu} = \bar{\nu}_0 (\cancel{n}+1+\cancel{1/2}-\cancel{n}-\cancel{1/2})$$

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

That is the major limitation of the vibrational spectrum of the classic oscillation.

Selection Rule →

~~Selection~~ Selection rule for the harmonic oscillator undergoing vibrational changes are:

(i) $\Delta v = \pm 1$

(ii) The vibration must involve a change in dipole moment of the molecule. Thus, vibrational spectra observed only in heteronuclear diatomic molecules since homonuclear diatomic molecules have no permanent dipole moment.

Morse Curve →

Simple harmonic vibration of a diatomic molecules and the allowed vib. energy levels along with the transitions between them is explained by the

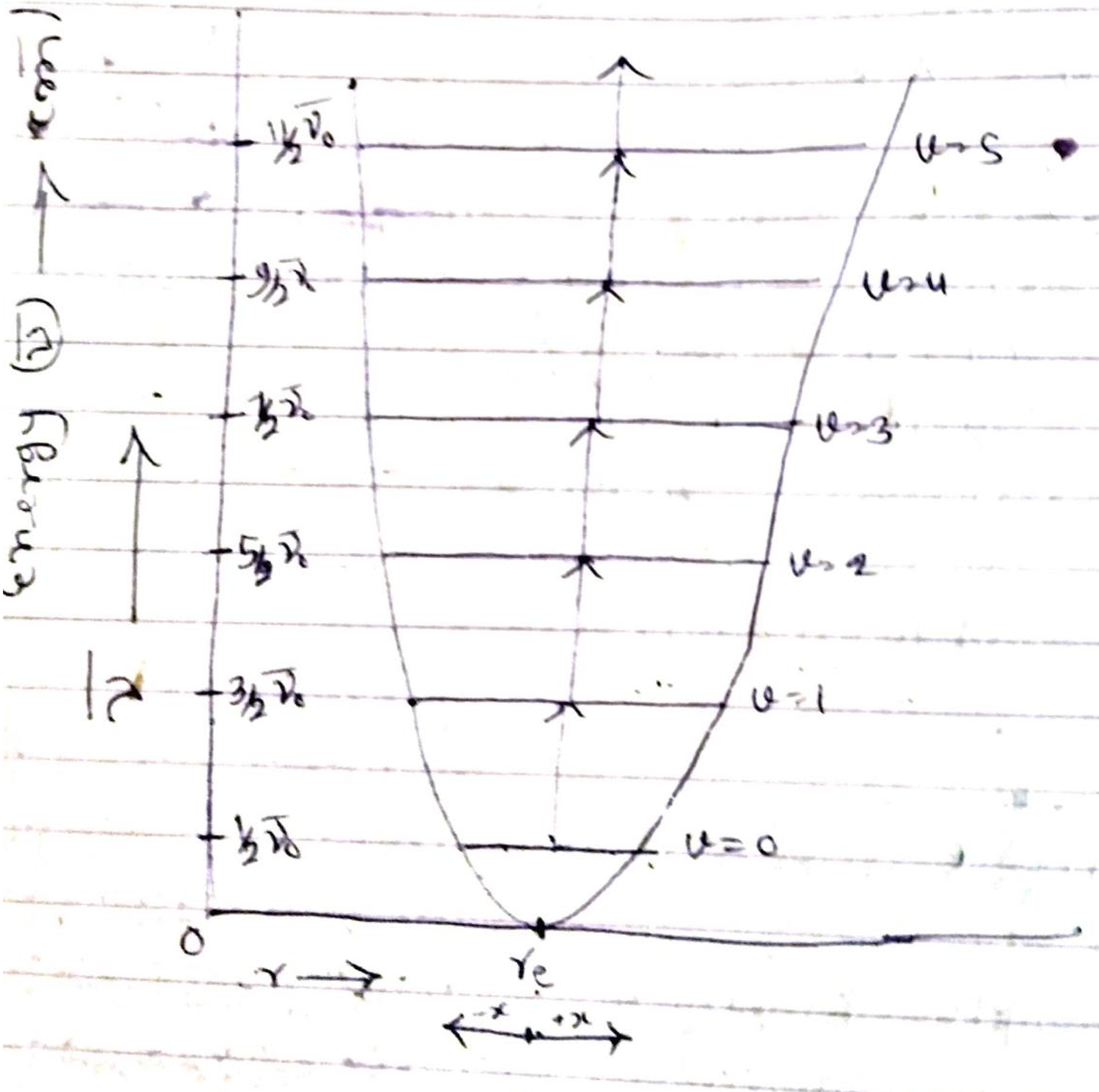
Scanned by TapScanner

following potential energy curve known as Morse curve.

As,

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

The potential energy curve is parabolic.



Internuclear distance (r) →.

I. R. Spectrum :→.

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

Spectrum cm^{-1} →

$\bar{\nu}_0$ cm^{-1} (i.e oscillation frequency)

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

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

$$\text{or} \quad \bar{\nu} = \bar{\nu}_0$$

Thus, for ideal harmonic oscillator the spectral absorption occurs at the fundamental vibrational frequency. ($\bar{\nu}_0$).