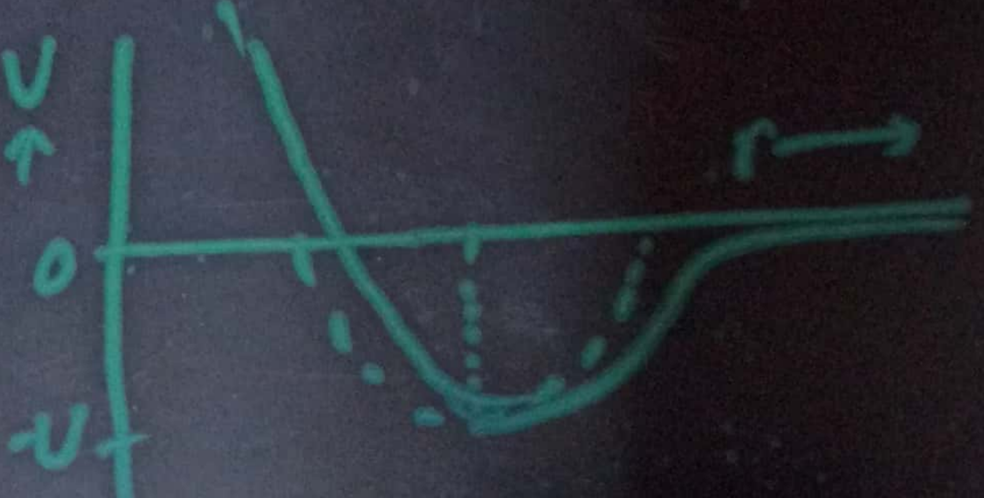
Quantisation of Vibrational Energies; Pure Vibrational spectra

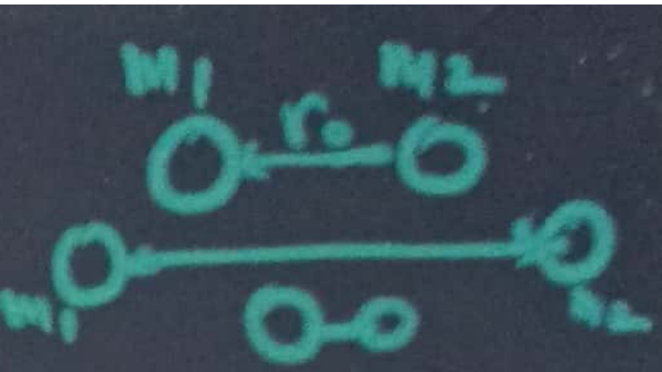
→ A diatomic Molecule may be considered as a Harmonic oscillator.

→ An excited Molecule, start vibrating abt its mean position along the axis joining two atoms.

→ Change PE with change in position is represented by fig:



let the reduced Mass of Molecule be:



$$\mu = \frac{m_1 m_2}{m_1+m_2}$$, then eqn of motion for vibration

$$\frac{d^2r}{dt^2}+\frac{k}{\mu}(r-r_0)=0; \quad \mu\frac{d^2r}{dt^2}=-k(r-r_0)$$

or,
$$\frac{d^2r}{dt^2}+\omega^2(r-r_0)=0$$

$$\omega^2=\sqrt{\frac{k}{\mu}}$$

then;
$$\nu_0=\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

& $$E_n=\left(n+\frac{1}{2}\right)h\nu_0 ; \quad n=0,1,2..$$

n — vib. quantum no.

<u>Now</u>; If at equilibrium, the PE is $-U_0$ then total Energy of vibrating mole-

$$E = -U_0 + E_n$$

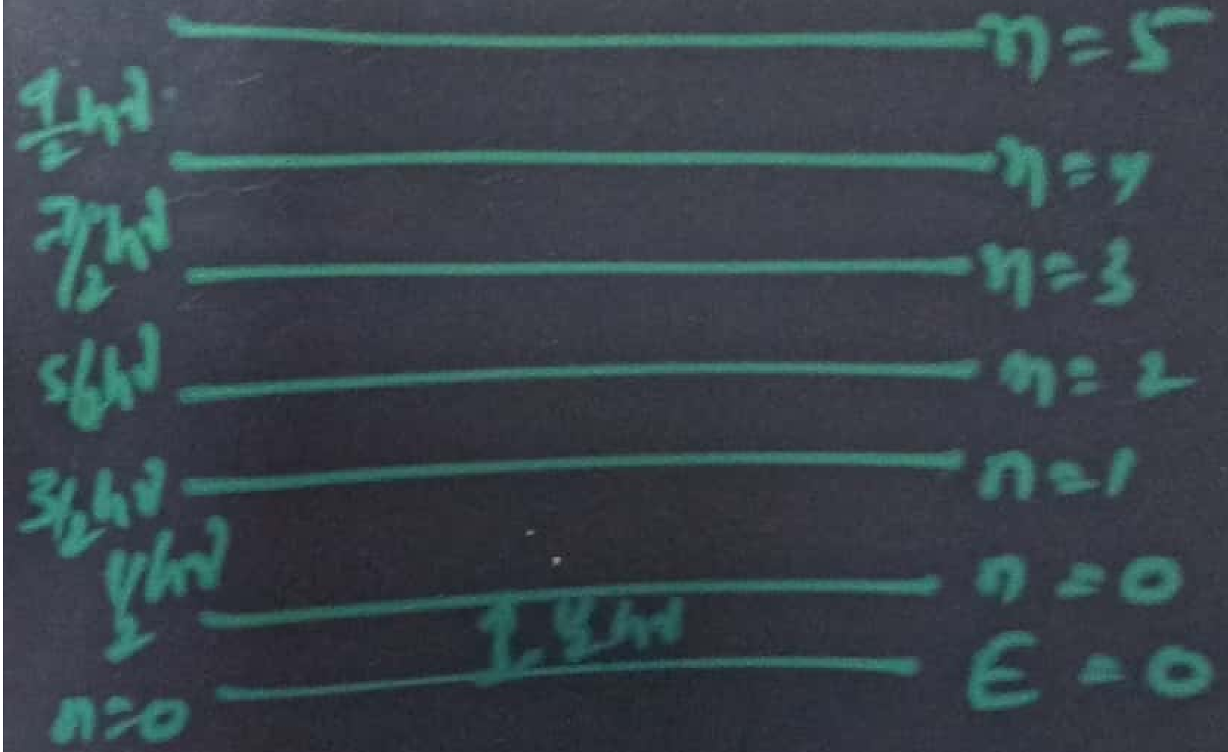
$$E = -U_0 + \left(n + \frac{1}{2}\right) h\nu_0$$

$$\Delta E = E_{n+1} - E_n = h\nu_0$$

So, if Energy at equilibria be considered $= 0$

then, $E_n = E_0 = \frac{1}{2} h\nu_0$ is called <u>Zero point Energy</u>.

for HCl $\Delta E \simeq 0.36\,eV$



Equispaced & quantized vibrational energy state.

Transition Rule for Pure Vib Spectra

Among diff energy states of a molecule, only allowed transitions are for

$$\Delta n = \pm 1 \text{ ; ie}$$

the transitions for which change in Vib Q No is either +1 or -1 is allowed.

Hence;
freq of line due to absorption or emission from (n+1) to (n) state is :

$$h\nu = E_{n+1} - E_n = h\nu_0$$

⇒ freq of spectral line;

$$\nu = \nu_0 = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

or wave No;

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

Hence; Equispace energy states and transition rule $\Delta n = \pm 1$ results in a spectral line of a specific freq ν_0, which is chrachteristic of that molecule of reduced mass μ.