

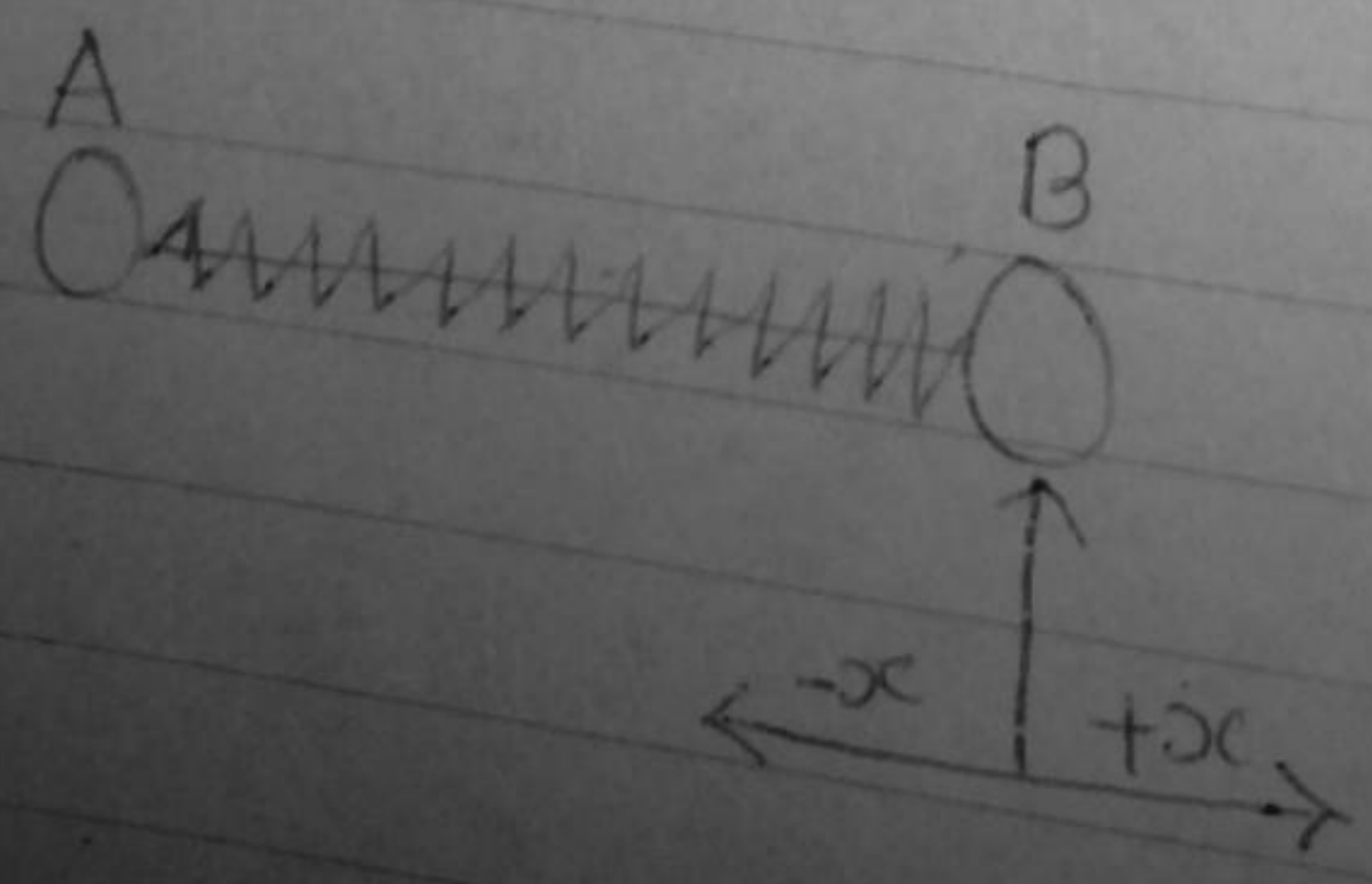
or.  
Vibrational Spectra

Due to elasticity of the bond, atoms in a molecule vibrate about the mean position. A molecule can absorb I.R radiation and increase its vibrational energy. This vibrational energy is quantised. The vibrational energy levels of a molecule is related to the stiffness ( $\overline{m\omega^2}$ ) of the bond. When I.R radiation is absorbed rotational energy may also change along with vibrational energy. Rotational energy change is avoided by using the sample in pure liquid state or in solution.

Spectral Range  $\Rightarrow$

$$\bar{\nu} = 10^2 \text{ to } 10^4 \text{ cm}^{-1}$$

Simple Harmonic Oscillator  $\Rightarrow$



In a diatomic molecule 'AB' the bond behaves as a spring and atoms are displaced from equilibrium positions due to interaction between atomic nuclei and electrons. If only atom 'A' is displaced by an amount  $x$ , a restoring force 'f' acts in opposite direction on 'A' tends to bring 'B' to the equilibrium position. For a small displacement, the motion of 'A' is 'simple harmonic' ~~motion~~ and restoring force acts in opposite direction. So that we have Hooke's law

$$f = -kx$$

where  $k$  is force constant of bond.

If  $x = 1$ , Then

$$k = -f$$

Thus,  $k$  is the restoring force per unit displacement and measures stiffness of the bond.

As the motion of B is periodic simple harmonic

$$x = A \cos 2\pi \nu_0 t$$

where,  $A$  = amplitude of vibration

$\nu_0$  = frequency of vibration

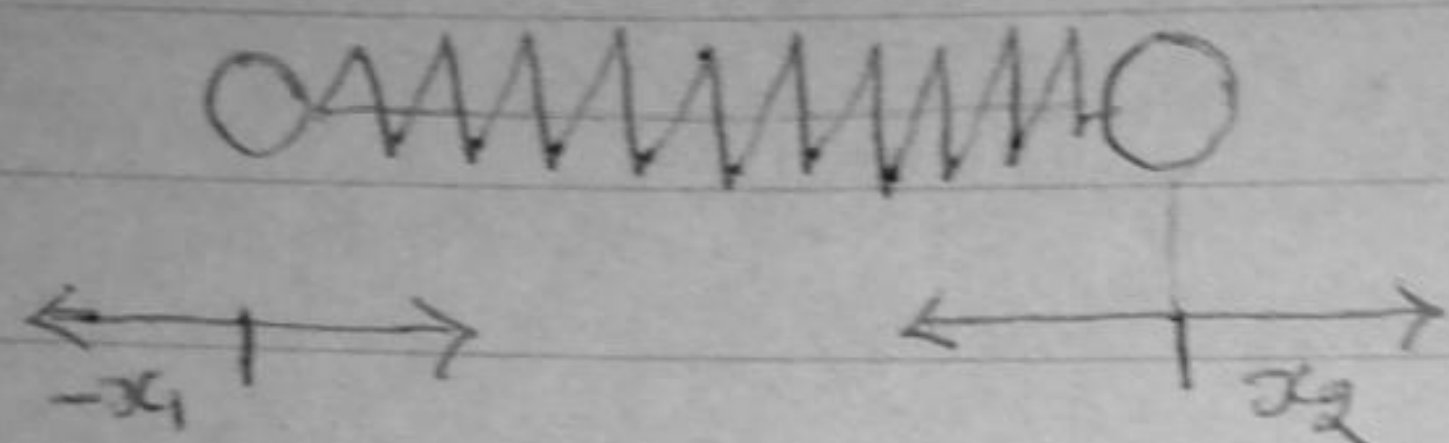
per second

Where,

$$\nu_0 = \frac{1}{2\pi} \sqrt{K/m}$$

where,  $\nu_0$  = fundamental frequency

for the displacement of both atoms is



$$f = -K(x_2 - x_1)$$

and

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

where,  $\mu$  = reduced

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$\nu_0$  = fundamental frequency of a simple harmonic oscillator.

The vibrational energy of molecular systems is quantised and allowed energy values as solved by Schrödinger equation are

$$E_v = \left(v + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{K/\mu}$$

$$= h\left(v + \frac{1}{2}\right) \left(\frac{1}{2\pi} \sqrt{K/\mu}\right)$$

$$= h\nu_0 \left( v + \frac{1}{2} \right)$$

in Spectroscopic unit

$$\bar{\nu} = E/hc = \frac{h\nu_0 \left( v + \frac{1}{2} \right)}{hc}$$

$$= \frac{\nu_0}{c} \left( v + \frac{1}{2} \right)$$

$$= \bar{\nu}_0 \left( v + \frac{1}{2} \right) \text{ cm}^{-1}$$

$$\bar{\nu} = \cancel{hc} \bar{\nu}_0 \left( v + \frac{1}{2} \right)$$

Vibrational energy levels  $\rightarrow$

The allowed vibrational energy levels and their frequencies are as -

$$n \quad (n + \frac{1}{2}) h c \bar{\nu}_0 \quad (n + \frac{1}{2}) \bar{\nu}_0$$

4	$4\frac{1}{2} h c \bar{\nu}_0$	$4\frac{1}{2} \bar{\nu}_0$	
3	$3\frac{1}{2} h c \bar{\nu}_0$	$3\frac{1}{2} \bar{\nu}_0$	$\bar{\nu}_0$
2	$2\frac{1}{2} h c \bar{\nu}_0$	$2\frac{1}{2} \bar{\nu}_0$	$\bar{\nu}_0$
1	$1\frac{1}{2} h c \bar{\nu}_0$	$1\frac{1}{2} \bar{\nu}_0$	$\bar{\nu}_0$
0	$\frac{1}{2} h c \bar{\nu}_0$	$\frac{1}{2} \bar{\nu}_0$	$\bar{\nu}_0$
$\nu$	E	$\bar{\nu}$	$\Delta \bar{\nu}$

Spectrum

## Energy level spacing $\Rightarrow$

As,

$$E_n = (n + \frac{1}{2}) h c \bar{\nu}_0$$

$$E_{n+1} = (n + 1 + \frac{1}{2}) h c \bar{\nu}_0$$

for the transition,

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

$$\Delta E = h c \bar{\nu}_0$$

and,

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

that is energy levels are equally spaced.

## Selection Rule $\Rightarrow$

Selection rule for vibrational quantum number is —

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

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

## Morse Curve $\rightarrow$

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.

