P.G. Sem. IIIrd. Core course X

Unit II

Infra red Spectroscopy
or
vibrational Spectroscopy →

Due to elastisity of bond the bond atoms in a molecule vibrate about the mean position. A molecule can absorbed I R. radiation and increase its vibrationa energy. This vibrational energy is quantise The vibrational energy levels of a molecule is related to the stiffness (कड़ापन) of the bond. When I R. radiation is absorbed rotational energy may also change along with vibrational energy. Rotational energy change is avoided b using the sample in pure liquid state or in solution.

Spectral Range →

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

$$\lambda = 10^{-2} \text{ to } 10^{-4} \text{ cm.}$$

$$\nu = c\bar{\nu} = 3\times10^{12} \text{ to } 3\times10^{14} \text{ sec}^{-1}$$

Simple Harmonic Oscillator

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

$$f = -kx$$

where k = force constant of the bond

If, $x = 1$, Thus

$$K = -f$$

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

As, the motion of B is periodic and simple harmonic

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

Where, A = Amplitude of vibration
ν_0 = frequency of vibration per second.

Whence,

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

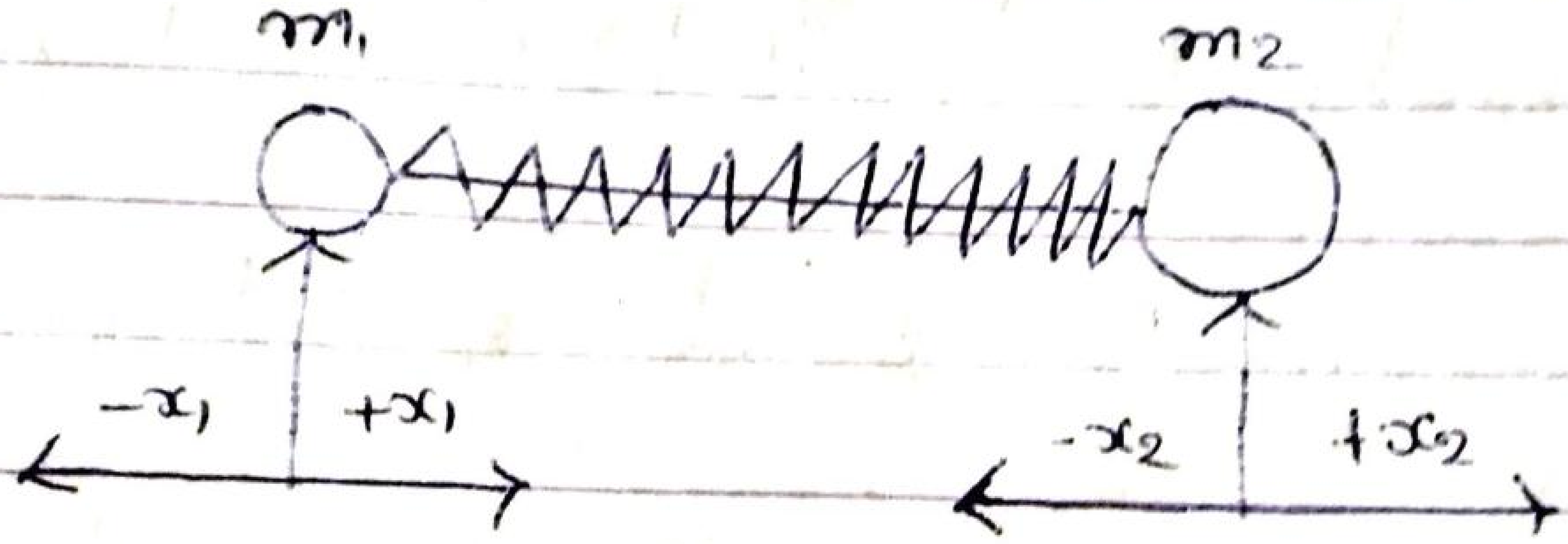
Where, ν_0 = fundamental frequency and
m = mass of the atom [illegible]

or

$$\bar{\nu}_0 = \frac{1}{2\pi c}\sqrt{K/m}$$

where, K = force constant
μ = reduced mass
$= m_1 m_2 / m_1 + m_2$
c = velocity of radiation in cm sec^{-1}.

For the displacement of both Atoms



Restoring force (f) is given by Hooke's law

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

and fundamental vibrational frequency

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

where, $\mu = \frac{m_1 m_2}{m_1 + m_2}$ = reduced mass

ν_0 = fundamental vib. frequency of a simple harmonic oscillator.

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The vibrational energy of a molecular system is quantized and allowed energy values of solved by schrodinger equation are —

$$E_{vib.} = (v+1/2)\frac{h}{2\pi}\sqrt{K/\mu}$$

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

$$= h\nu_0 (v+1/2) \text{ Joules.}$$

$\boxed{\nu_0 = c\bar{\nu}_0}$

$$= hc\bar{\nu}_0 (v+1/2) \text{ Joules.}$$

where v = vibrational quantum no

$v = 0, 1, 2, 3, \ldots$

In spectroscopic unit —

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

$\boxed{\bar{\nu} = \frac{\nu}{c}}$

$$= \nu_0 (v+1/2) \text{ sec}^{-1}.$$

$E = hc\bar{\nu}$

$$\bar{\nu} = \frac{E}{hc} = \frac{h\bar{\nu}_0 c(v+1/2)}{hc} \text{ cm}^{-1}$$

Vibrational Energy levels

n	$(n+1/2)hc\bar{\nu}_0$	$(n+1/2)\bar{\nu}_0$	
3	$7/2\, hc\bar{\nu}_0$	$7/2\, \bar{\nu}_0$	
			$\bar{\nu}_0$
2	$5/2\, hc\bar{\nu}_0$	$5/2\, \bar{\nu}_0$	
			$\bar{\nu}_0$
1	$3/2\, hc\bar{\nu}_0$	$3/2\, \bar{\nu}_0$	
			$\bar{\nu}_0$
$v=0$	$1/2\, hc\bar{\nu}_0$	$\frac{1}{2}\bar{\nu}_0$	
	E_{vib}	$\bar{\nu}$	$\Delta\bar{\nu}$

Spectrum