

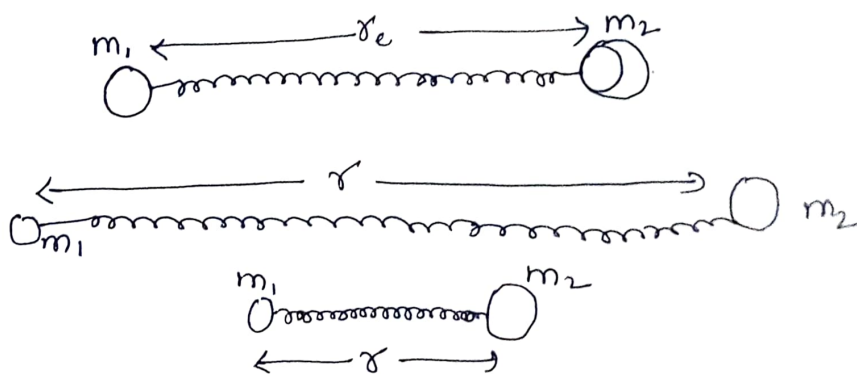
Vibrational (InfraRed) Spectra of Diatomic molecules

A diatomic molecule with atomic masses m_1 and m_2 joined by a chemical bond vibrates as a one-dimensional simple harmonic oscillator (S.H.O)

Classically, the vibrational frequency of a mass point m connected by a spring of force constant k is given by

$$\nu = \frac{1}{2\pi} \left(\frac{k}{m} \right)^{1/2} \quad \text{--- (1)}$$

In case of diatomic molecule, the masses m_1 and m_2 vibrate back and forth relative to their centre of masses in opposite direction.



Vibration of diatomic molecule

The two masses reach the extreme of their respective motion at the same time. The vibrational frequency of the molecule is given by a relation analogous to that of eq (1) and μ is used instead of m .

$\mu \rightarrow$ refers to reduced mass.

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \text{ s}^{-1} \quad \text{--- (2)}$$

To convert frequency into cm^{-1} the eqn (2) is divided by c

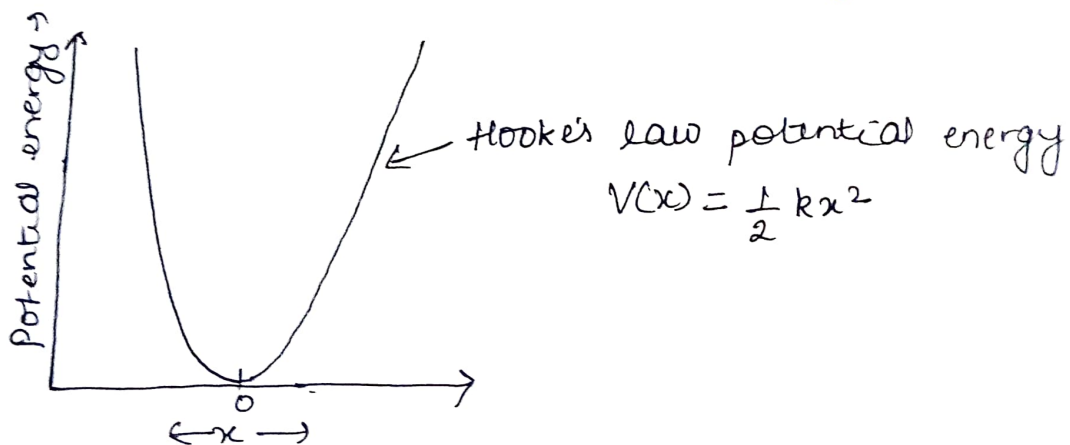
$$\bar{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \text{ cm}^{-1} \quad \text{--- (3)}$$

→ The unit of force constant is Nm^{-1} .

The potential energy of SHO as a function of displacement from the equilibrium configuration is given by the parabolic Hooke's Law:-

$$V(x) = \frac{1}{2} k (r - r_e)^2 = \frac{1}{2} k x^2 \quad \text{--- (4)}$$

$x = (r - r_e) \rightarrow$ displacement
and $r_e \rightarrow$ equilibrium bond length



The solution of the Schrodinger equation for a single harmonic oscillator gives the quantized vibrational energy levels.

$$E_v = \left(v + \frac{1}{2} \right) h\nu \quad \text{--- (5)}$$

where $v = 0, 1, 2, 3, \dots$ vibrational quantum number,

$\nu \rightarrow$ vibrational frequency.

At $v = 0$

$$E_0 = \left(0 + \frac{1}{2} \right) h\nu = \frac{1}{2} h\nu. \quad \text{--- (6)}$$

\Rightarrow Even at the lowest vibrational level the energy of the oscillator is not zero but equal to $\frac{1}{2} h\nu$. This is called zero point energy (ZPE). The energy level of SHO are equally spaced, the spacing being equal to $h\nu$.

To convert the energy from joules to cm^{-1} we divide it by hc ,

$$G(v) = E_v / hc = \left(v + \frac{1}{2} \right) \nu / c = \left(v + \frac{1}{2} \right) \omega_e \quad \text{--- (7)}$$

$G(v) \rightarrow$ vibrational term.

The selection rule for a vibrational transition in the SHO is

$$\Delta v = \pm 1 \quad \text{--- (8)}$$

Hence, the operating part of the selection rule for the absorption spectrum is $\Delta v = \pm 1$ i.e. the vibrational quantum number changes by unity. Using the selection the frequency of vibrational transition is given as :-

$$\begin{aligned}\bar{\nu} &= G(v \rightarrow v+1) \\ &= \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right) \omega_e \\ &= \frac{1}{2} \left(v + 1 + \frac{1}{2} - \frac{1}{2} - v\right) \omega_e \\ \bar{\nu} &= \omega_e \quad \text{--- (9)}\end{aligned}$$

At room temperature, most of the molecules are in ground vibrational state ($v=0$) so that the only transition of interest is that which takes place from $v=0$ to $v=1$.

For transition from $v_0 \rightarrow v_1$, the frequency that corresponds is called Fundamental frequency of ~~transition~~ vibration.

- Diatomic molecules have only one vibrational frequency. The frequency is stretching vibrational frequency.
- Diatomic molecules do not have bending vibrational frequency.
- vibrational spectra are obtained in Infrared (IR) region.

The most important factor a molecule to be IR active is that the dipole moment of molecule must change during the vibration.

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