

The Simple Harmonic Oscillator OR Vibrating diatomic Molecule :-

When two atoms combine to form a stable covalent molecule (e.g. HCl gas) as a result of some internal electronic rearrangements. There is a repulsion between the positively charged nuclei of both atoms and between the negative electron clouds on the other hand there is an ^{attraction} repulsion between the nucleus of one atom and the electrons of the other and vice versa. The two atoms settle at a mean internuclear distance such that these forces are just balanced and the energy of the whole system is at a minimum.

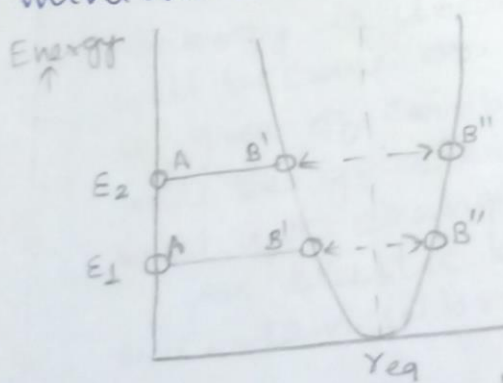


Fig. 1 - Parabolic Curve of energy vs extension or compression of a spring obeying Hooke's law

Attempt to squeeze the atoms more closely together will rise repulsive force rapidly, whereas attempt to pull them further apart will be resisted by the attractive force. Hence in either case an attempt to distort the bond requires an input of energy.

At the minimum the internuclear distance is referred to as the equilibrium distance r_{eq} or bond length.

In such case an oscillator, then the restoring force on the atom of the molecule is given by

$$f = -k(r - r_{eq}) \quad \text{--- (1)}$$

In this case the energy curve ~~is~~ is parabolic and has the form

$$E = \frac{1}{2}k(r - r_{eq})^2 \quad \text{--- (2)}$$

In fig. 1, we have plotted the energy according to eq. (2). The zero of the curve is found at $r = r_{eq}$. If one atom A is considered to be stationary on the $r=0$ axis and the other will oscillate between B' and B''. Extension or compression of the bond leads to increase in energy e.g. E_1 . If the energy is increased to E_2 the oscillation will become more vigorous i.e. the degree of compression or extension will be greater but the vibrational freq will not change.

An elastic bond, like a spring has a certain vibration freq. which is given by

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} \quad \text{--- (3)}$$

μ - reduced mass of the system

$$\bar{\omega}_{osc} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \quad \text{--- (4)}$$

Vibrational energies are quantised and the allowed vibration energies can be calculated from the Schrodinger eq.

S.H.O. (Contd.)

③

The energy values for the energy of a S.H.O. are of the following type:

$$E_v = (v + \frac{1}{2}) h\nu_{osc} \text{ joules } (v=0,1,2,\dots)$$

⑤

v - vibrational quantum no.

$$E_v = \frac{E_v}{hc} = (v + \frac{1}{2}) \bar{\nu}_{osc} \text{ cm}^{-1} - \text{⑥}$$

Lowest Vibrational Energy -

$$\text{Put } v=0 \Rightarrow E_0 = \frac{1}{2} h\nu_{osc} \text{ joules} - \text{⑦}$$

Hence the diatomic molecule can never have zero vibrational energy, the atoms can never be completely at rest relative to each other. E_0 is known as zero point energy, it depends only on the classical vibration frequency and hence on the strength of the chemical bond and the atomic masses. Even at absolute zero, when the translational and rotational motion cease, vibrational motion still exists.

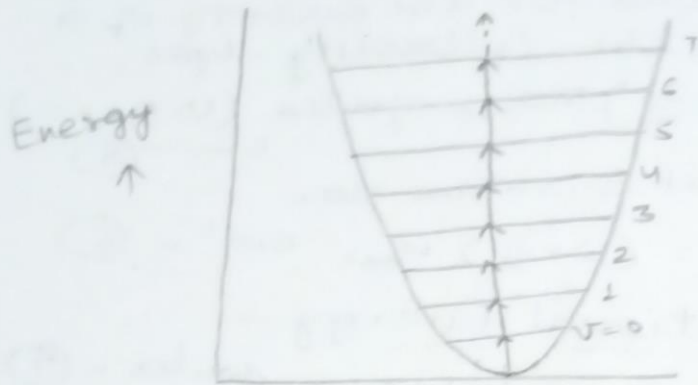
Further use of the Schrodinger eq. leads to the simple selection rule for the H.O. undergoing vibrational changes:

$$\Delta v = \pm 1 - \text{⑧}$$

with the condition that vibrational energy changes will only give rise to an observable spectrum if vibration induces a change in the dipole moment of the molecule. Hence only in heteronuclear diatomic molecules since homonuclear molecules have no dipole moment.

Applying the selection rules, for emission

$$E_{v+1 \rightarrow v} = (v+1 + \frac{1}{2}) \bar{\nu}_{osc} - (v + \frac{1}{2}) \bar{\nu}_{osc} \\ = \bar{\nu}_{osc} \text{ cm}^{-1} - \text{⑨a}$$



→ Internuclear
→ cm distance

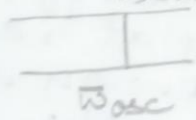


Fig 2 - Allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing S.H. motion

for absorption-

$$E_{v \rightarrow v+1} = \bar{\omega}_{osc} \text{ cm}^{-1}$$

(9b)

Fig. 2 shows equally spaced vibrational levels, transitions between any two neighbouring states will give rise to same energy change.

selection rule $\Delta v = \pm 1$ and hence each mode of vibration yields one band only.

The plus sign applies to the absorption spectra and minus sign to emission spectra.

Discussions → We observe following imp pts-

- ① Considering a diatomic molecule as H.O., ~~the~~ describes lowest vibrational states, but fails for higher vibrational states. Therefore this requires correction.
- ② Experimental observations show that vibrational energy levels are less and less separated as v increases whereas Harmonic oscillator results in even spacing.
- ③ Overtones and Combination terms are also observed in vibrational spectra. But the H.O. does not explain this.

The Anharmonic Oscillator ①

Real Molecules do not obey exactly the laws of simple Harmonic motion; Real bonds although elastic, are not so homogeneous as to obey Hooke's law. If the bond between atoms is stretched, there comes a point at which it will break - the molecule dissociates into atoms

For small compressions and extensions the bond may be taken as perfectly elastic, for ~~for~~ larger amplitudes (greater than 10% of the bond length), a much more complicated behaviour appears. Fig. 1 shows the energy curve for a typical diatomic molecule - undergoing anharmonic extensions & compression together with the ~~ideal~~ dotted parabola due to an ideal diatomic molecule obeying simple Harmonic motion.

In order to explain the energy curve due to a real molecule, P.M. Morse invented a purely empirical expression known as Morse function:

$$E = D_{eq} \left[1 - \exp\left\{a(r_{eq} - r)\right\}\right]^2 \quad (2)$$

a - Const. for a particular molecule
 D_{eq} - Dissociation energy.

Following eq. (2) instead of $E = \frac{1}{2}k(r - r_{eq})^2$ and using Schrodinger eq., the pattern of the allowed vibrational energy levels is found to be:

$$E_v = \left(v + \frac{1}{2}\right) \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e \text{ cm}^{-1} \quad (3)$$

$(v = 0, 1, 2, \dots)$

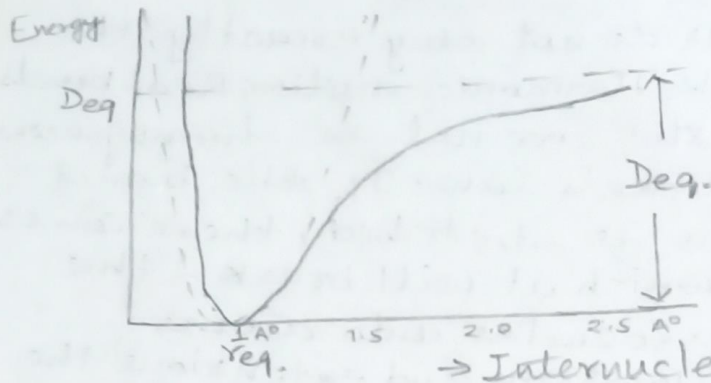


Fig. 1 Morse Curve - the energy of a diatomic molecule undergoing anharmonic extensions and compressions.

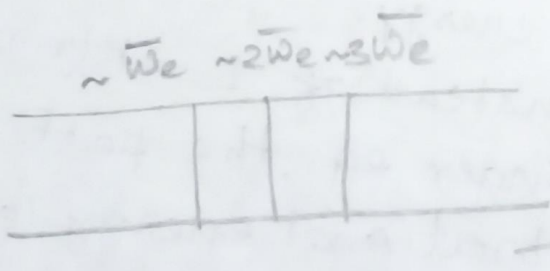
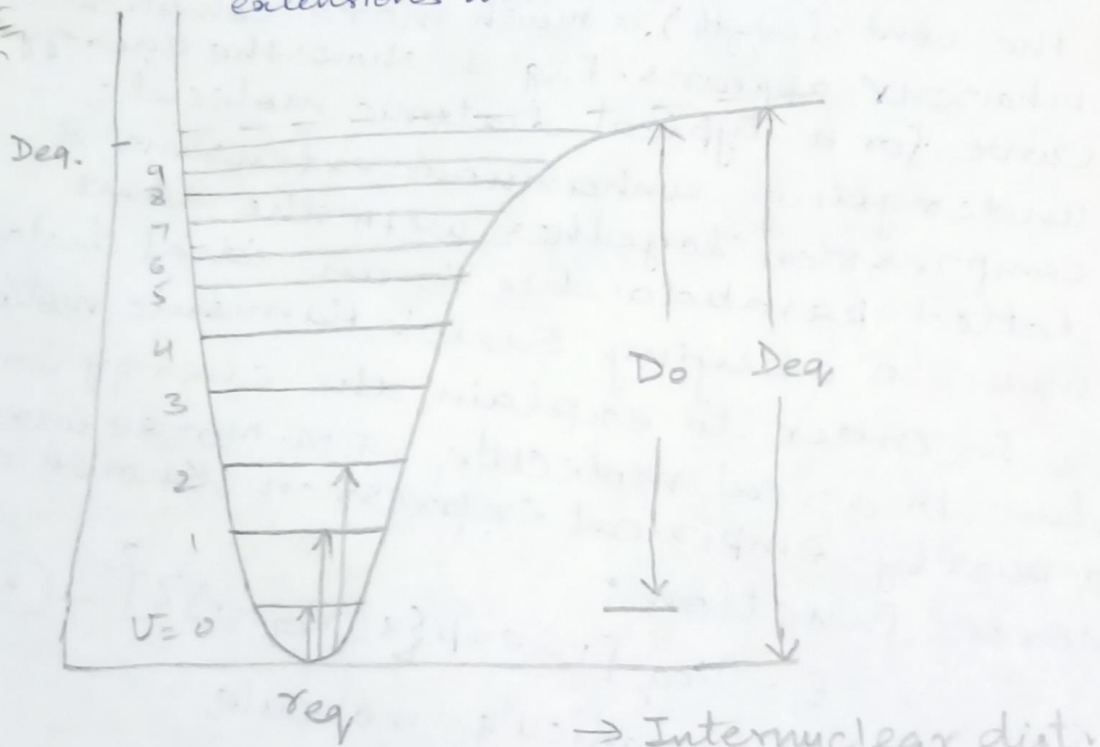


Fig. 2 Allowed vibrational energy levels and some transitions between them for a diatomic mol. undergoing anharmonic oscillations.

ω_e - oscillation freq., x_e - corresponding anharmonicity constant ($x_e \approx \pm 0.01$) leads to vibrational levels crowd more closely together with increasing v . Some of these levels are sketched in fig (2)

On rewriting eq. (3) for the anharmonic oscillator, as

$$E_v = \bar{\omega}_e \left\{ 1 - x_e \left(v + \frac{1}{2} \right) \right\} \left(v + \frac{1}{2} \right) \quad (4)$$

Comparing eq. (4) with the energy levels of the harmonic oscillator i.e.

$$E_v = \left(v + \frac{1}{2} \right) \bar{\omega}_{osc}$$

We can write

$$\bar{\omega}_{osc} = \bar{\omega}_e \left\{ 1 - x_e \left(v + \frac{1}{2} \right) \right\} \quad (5)$$

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation freq. which decreases steadily with increasing v .

If we put $v = -\frac{1}{2}$ (an hypothetical energy state with $E=0$, zero vibrational energy), oscillation freq. would be

$$\bar{\omega}_{osc} = \bar{\omega}_e$$

Thus $\bar{\omega}_e$ may be defined as the hypothetical equilibrium oscillation freq. of the anharmonic system - the frequency for infinitely small vibration about the equilibrium point.

In the ground state ($v=0$)

$$\bar{\omega}_0 = \bar{\omega}_e \left(1 - \frac{1}{2} x_e \right) \text{ cm}^{-1}$$

$$\& \quad E_0 = \frac{1}{2} \bar{\omega}_e \left(1 - \frac{1}{2} x_e \right) \text{ cm}^{-1}$$

i.e. zero point energy differs slightly from that for the harmonic oscillator.

The selection rules for the anharmonic oscillator are found to be

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

(P.T.O.)

These rules indicate the additional possibility of larger jumps.

Consider these transitions:-

1) $v=0 \rightarrow v=1$, $\Delta v = +1$ with considerable intensity

$$\Delta E = E_{v=1} - E_{v=0} = \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

2) $v=0 \rightarrow v=2$, $\Delta v = +2$ with small intensity

$$\Delta E = 2\bar{\omega}_e (1 - 3x_e) \text{ cm}^{-1}$$

3) $v=0 \rightarrow v=3$, $\Delta v = +3$, with normally negligible intensities

$$\Delta E = 3\bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1}$$

Since $x_e \approx 0.01$, the three spectral lines lie very close to $\bar{\omega}_e$, $2\bar{\omega}_e$, $3\bar{\omega}_e$. The line near $\bar{\omega}_e$ is called the fundamental absorption while those near $2\bar{\omega}_e$, $3\bar{\omega}_e$ are called the first and second overtones respectively.