

Classically it can be shown that the oscillation frequency is:

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

$\mu \rightarrow$ reduced mass of the system.

To convert this frequency to wavenumbers, the unit usually used in vibrational spectroscopy, divide by the ~~velocity~~ velocity of light, c , expressed in ~~cm/s~~ cm^{-1}

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

Vibrational energies \rightarrow like all other molecular energies, are quantized, and the allowed vibrational energies for any particular system may be calculated from the Schrödinger eqⁿ. for simple harmonic oscillator:

$$E_v = \left(v + \frac{1}{2}\right) h \omega_{osc} \text{ Joules} \quad (v = 0, 1, 2, \dots) \quad \text{--- (5)}$$

$v \rightarrow$ vibrational quantum number

Converting to spectroscopic units, cm^{-1} , we have

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

As the only energies allowed to a simple harmonic vibrator.

The lowest vibrational energy, obtained by putting

$v=0$ in eqⁿ (5) & (6)

$$E_0 = \frac{1}{2} h \omega_{osc} \text{ Joules}$$

or $\epsilon_0 = \frac{1}{2} \bar{\omega}_{osc} \text{ cm}^{-1}$ — (7)

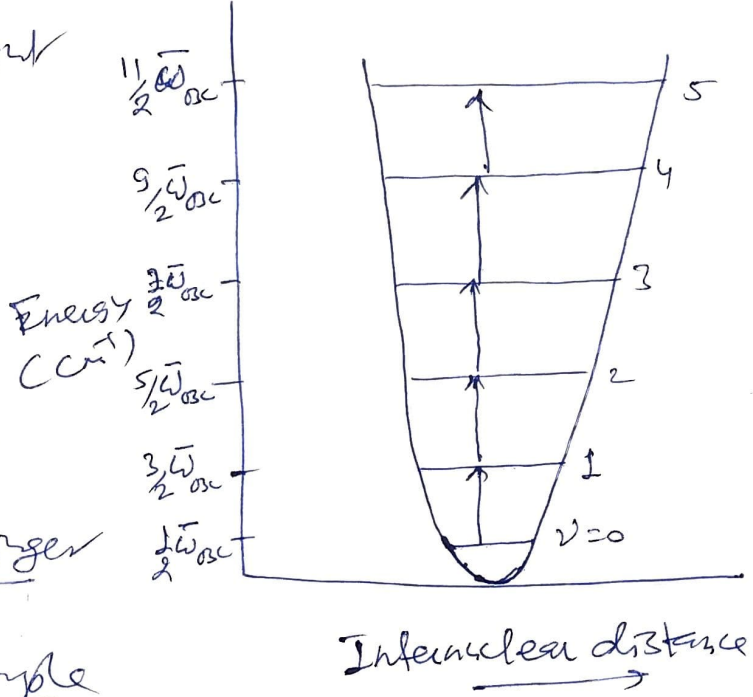
⇒ The diatomic molecule (or any molecule) can never have zero vibrational energy; The atoms can never be at rest relative to each other.

$\frac{1}{2} h \omega_{osc}$ Joules or $\frac{1}{2} \bar{\omega}_{osc} \text{ cm}^{-1}$ is → zero point energy

→ It depends only on the classical vibration frequency and hence on the strength of the chemical bond and the atomic masses.

The prediction of zero-point energy is the basic difference between the wave mechanical and classical approaches to molecular vibrations.

~~The~~ Use of ~~the~~ Schrodinger



eqⁿ leads to the simple selection rule for harmonic oscillator undergoing vibrational changes

$\Delta v = \pm 1$ — (8)

To this we must add the condition that vibrational energy changes will only give rise to an observable spectrum if the vibrator can interact with radiation, i.e., if the vibrator involves a change in the dipole moment of the molecule. → Vibrational spectra will be observable only in heteronuclear diatomic

molecules since → homonuclear molecules have no dipole moment.

Applying the selection rules

$$\begin{aligned} \Sigma_{\nu+1 \rightarrow \nu} &= (\nu+1 + \frac{1}{2}) \bar{\omega}_{osc} - (\nu + \frac{1}{2}) \bar{\omega}_{osc} \\ &= \bar{\omega}_{osc} \text{ cm}^{-1} \quad \text{--- (99)} \end{aligned}$$

for emission and

$$\Sigma_{\nu \rightarrow \nu+1} = \bar{\omega}_{osc} \text{ cm}^{-1} \quad \text{--- (96)}$$

for absorption, whatever the initial value ν .

Since the vibrational levels are equally spaced, transitions between any two neighbouring states will give rise to the same energy change. Since the difference between energy levels expressed in cm^{-1} gives directly the wavenumber of the spectral line absorbed or emitted

$$\bar{\nu}_{\text{spectroscopy}} = \Sigma = \bar{\omega}_{osc} \text{ cm}^{-1} \quad \text{--- (10)}$$

This is again obvious in classical terms, if we consider the mechanism of absorption or emission.

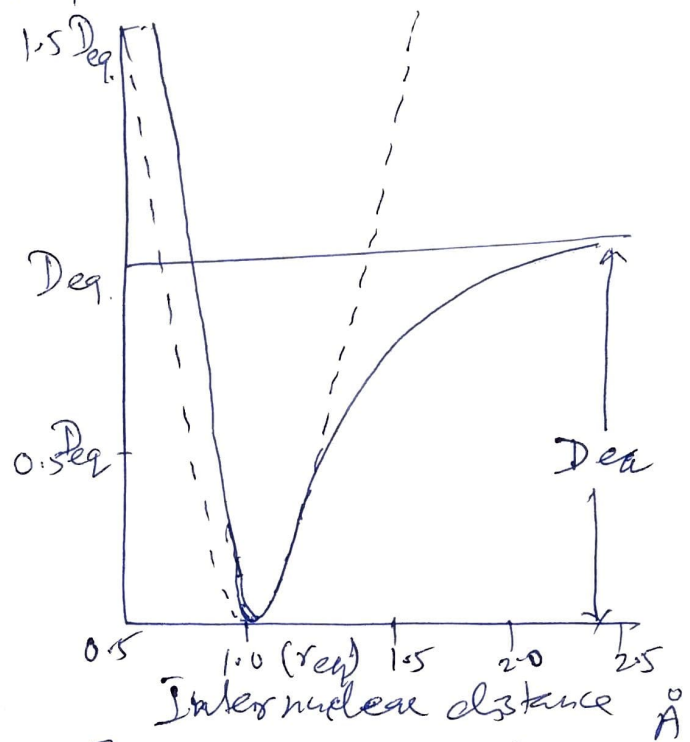
In absorption, for instance, the vibrating molecule will absorb energy only from radiation with which it can coherently interact and this must be radiation of its own oscillation frequency.

The Anharmonic Oscillator: 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. For small compressions and extensions the bond may be taken as perfectly elastic, for larger amplitudes say greater than 10%.

As the bond length \rightarrow a much more complicated behaviour must be assumed.

Shape of the energy curve for a typical diatomic molecule, together with (dashed) the ideal, simple harmonic parabola.



The purely empirical expression which fits this curve to a good approximation was derived by P. M. Morse

The Morse Curve: the energy of diatomic molecule undergoing anharmonic extensions and compressions

and is called the Morse function:

$$E = D_{eq} \left[1 - \exp\left\{ a (r_{eq} - r) \right\} \right]^2 \quad (11)$$

$a \rightarrow$ constant for a particular molecule

$D_{eq} \rightarrow$ dissociation energy.

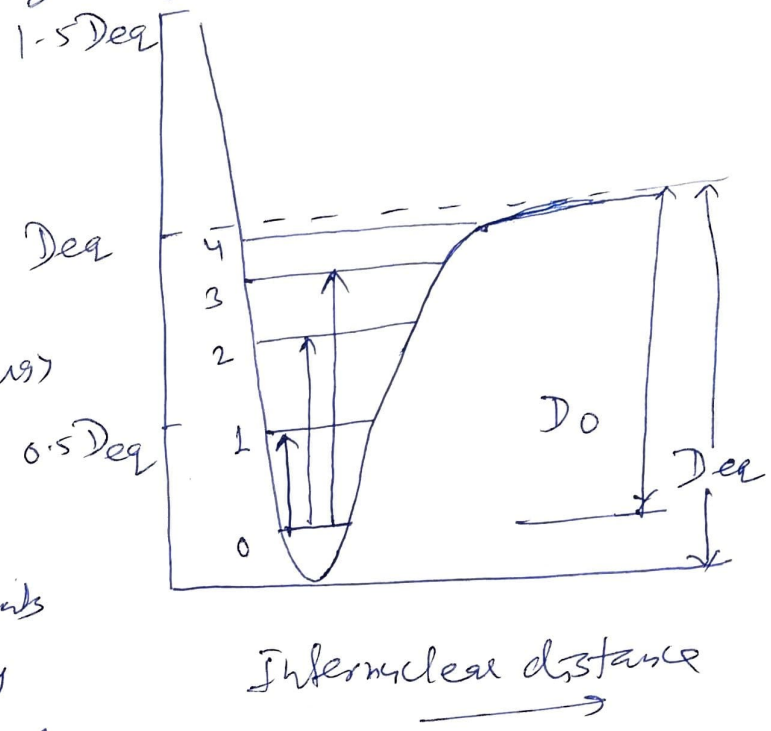
When eqⁿ(11) is used instead of eqⁿ(2) in Schrödinger eqⁿ, the pattern of allowed vibrational energy levels is found to be

$$E_v = (v + \frac{1}{2}) \bar{\omega}_e - (v + \frac{1}{2})^2 \bar{\omega}_e x_e \text{ cm}^{-1} \quad (12)$$

(v = 0, 1, 2, ...)

Where $\bar{\omega}_e \rightarrow$ an oscillator frequency (in wave numbers)
 $x_e \rightarrow$ corresponding anharmonicity constant
 \rightarrow for bond stretching vibrations, is always small and positive ($\approx +0.01$), so that vibrational levels crowd more closely together with increasing v .

Eqⁿ (12) is an approximate only;
 more precise expressions for energy levels require cubic, quartic etc. terms in $(v + \frac{1}{2})$ with anharmonicity constants y_e, z_e , etc. rapidly diminishing in magnitude.



If we rewrite eqⁿ (12) for the anharmonic oscillator as;

$$E_v = \bar{\omega}_e \left\{ 1 - x_e \left(v + \frac{1}{2} \right) \right\} \left(v + \frac{1}{2} \right) \quad \text{--- (13)}$$

and compare with the energy levels of the harmonic oscillator (eqⁿ (6)), we see that we can write

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

Thus \rightarrow the anharmonic oscillator behaves like the harmonic oscillator but with an oscillator frequency which decreases steadily with increasing v .