

### Vibration motion

For the study of vibrational we consider where compression and extension of the bond may be likened to the behaviour of a spring, obeying Hooke's Law. Then, we may write:

$$F = -k(r-r_{eq}) \quad (29)$$

where  $k$  is the force constant,  $F$  is the restoring force,  $r$  the internuclear distance and  $r_{eq}$  where the internuclear distance is a minimum of energy of the bond. In this case, the energy curve is a parabolic and has the form:

$$E = \frac{1}{2}k(r-r_{eq})^2 \quad (30)$$

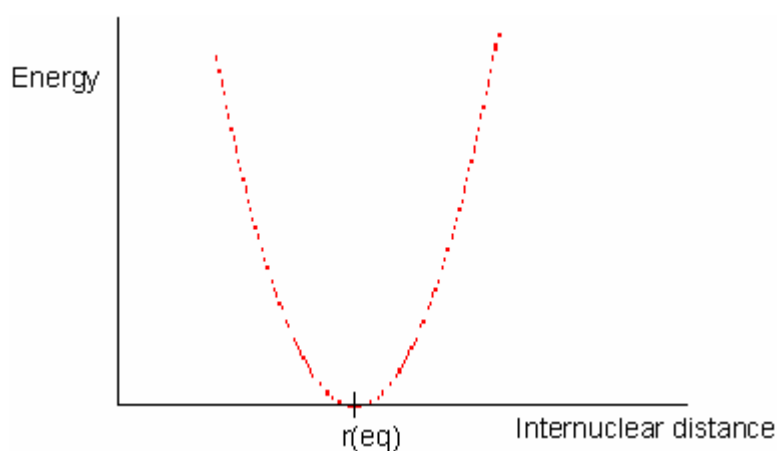


Fig 8.

This model of vibrating diatomic molecule is called simple harmonic oscillator model. If the energy of the molecule increases, the oscillation will be more vigorous, i.e. the degree of compression and extension will be greater, but the vibrational frequency will not change. A bond, like a spring, has an intrinsic vibrational frequency, dependent of the mass of the system and the force constant, but is independent of the amount of distortion. Classically:

$$\bar{\omega} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \quad (31)$$

Vibrational energies are quantized, and using the Schrodinger equation:

$$-\frac{\hbar^2}{2m} \times \frac{d^2\Psi}{dx^2} + \frac{1}{2}kx^2 = E\Psi$$

we may calculate them for any particular system:

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega \text{ Joules } v = 0,1,2,\dots \quad (32)$$

$\omega$  is the angular frequency,  $\nu$  is the quantum number for the vibrational motion.

$$\epsilon_{\nu} = \frac{E_{\nu}}{hc} = \left( \nu + \frac{1}{2} \right) \bar{\omega} \text{ cm}^{-1} \quad \nu = 0, 1, 2, \dots \quad (33)$$

$\bar{\omega} = \frac{\omega}{c}$  giving the energies allowed for a simple harmonic vibrator

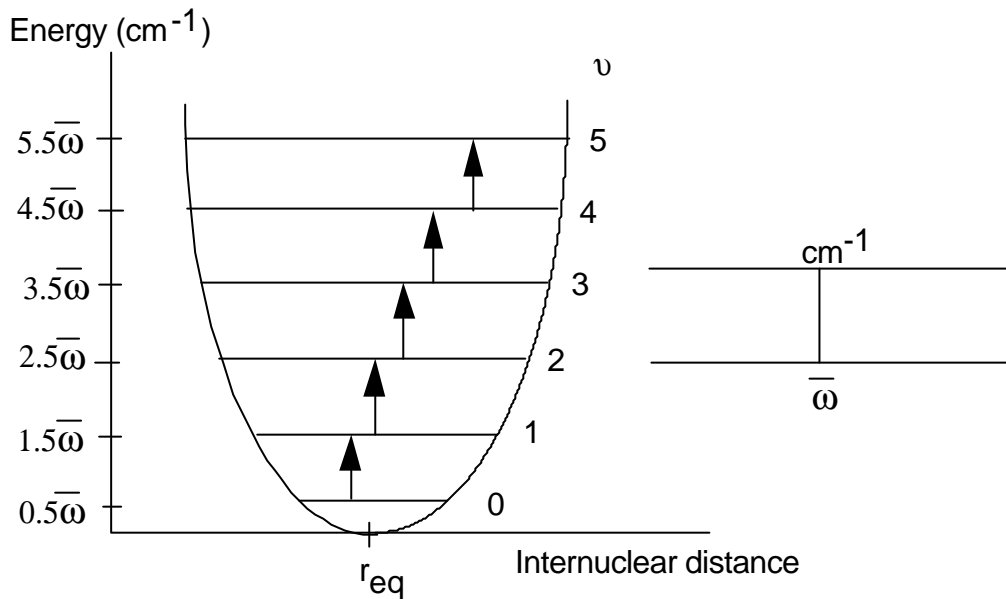


Fig 9. The vibrational energy levels and allowed transitions between them for a diatomic molecule undergoing simple harmonic motion.

As we can see, the zero-point energy does not corresponds with zero vibrational energy:  $0.5\bar{\omega}$  in  $\text{cm}^{-1}$  for  $\nu = 0$ , which is the minimum vibrational quantum number, and depends only on the classical vibration frequency, and hence on the strength of the chemical bond and the atomic masses.

Further use of the Schrodinger equation leads to the selection rule for the harmonic oscillator undergoing vibrational changes:

$$\Delta\nu = \pm 1 \quad (34)$$

Moreover, we must bear in mind that the observable spectrum is produced with the condition of that the molecule must be heteronuclear diatomic since the vibration involves a change in the dipole moment and homonuclear molecules do not have one.

Applying the selection rule, we have:

$$\Delta\epsilon = \epsilon_{v+1 \leftarrow v} = \epsilon_{v+1} - \epsilon_v = \hbar \bar{\omega} \quad \text{cm}^{-1} \quad (35)$$

for absorption and

$$\Delta\epsilon = \epsilon_{v+1 \rightarrow v} = \epsilon_{v+1} - \epsilon_v = \hbar \bar{\omega} \quad \text{cm}^{-1} \quad (36)$$

for emission. Therefore, the vibrational levels are equally spaced and hence the transitions between any two neighbouring states will have the same energy change, and we can obtain the wavenumber of the spectral line absorbed or emitted through of that difference between energy levels expressed in  $\text{cm}^{-1}$ .

$$\bar{\nu}_{\text{spectroscopic}} = \epsilon = \bar{\omega} \quad \text{cm}^{-1} \quad (37)$$

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

But real molecules do not obey exactly the laws of simple harmonic motion. If the bond between atoms is stretched, for example, there will be a point at which it will break. an empirical expression, which fits this curve to a good approximation, is the Morse function:

$$E = D_{\text{eq}} [1 - \exp\{a(r_{\text{eq}} - r)\}]^2 \quad (38)$$

Where "a" is a constant for a particular molecule and  $D_{\text{eq}}$  is the dissociation energy.

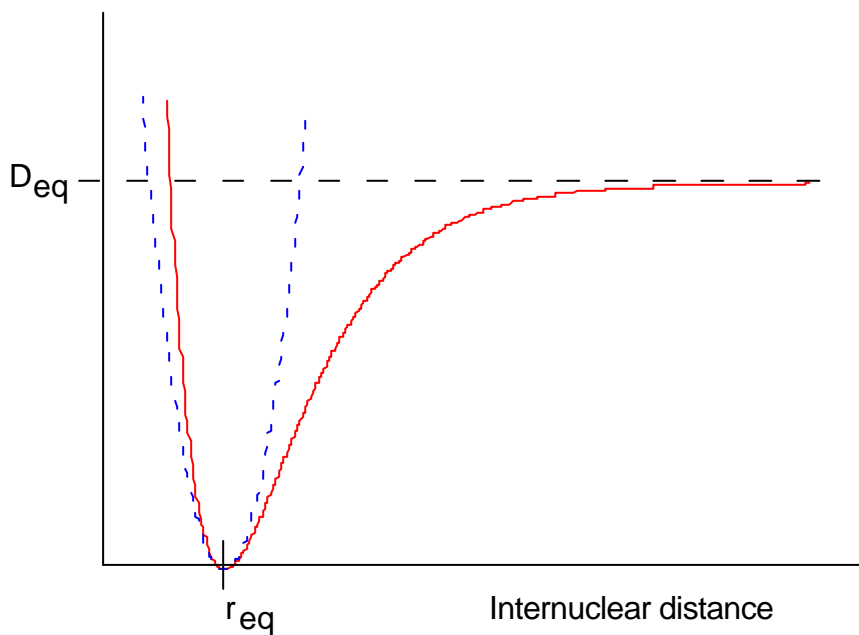


Fig 10. The Morse curve: the energy of a diatomic molecule undergoing anharmonic extensions and compressions.

The dashed curve is the ideal simple harmonic vibration parabola.

Using the Morse equation in the Schrodinger equation, the pattern of allowed vibrational energy levels is given by:

$$\epsilon_v = \left( v + \frac{1}{2} \right) \bar{\omega}_e - \left( v + \frac{1}{2} \right)^2 \bar{\omega}_e x_e \text{ cm}^{-1} \quad v = 0, 1, 2, \dots \quad (39)$$

Where  $x_e$  is the corresponding anharmonicity constant, which, for bond stretching vibrations is always small and positive ( $\approx +0.01$ ), so that the vibrational levels crowd more closely together with increasing  $v$ .

Note that this equation is only an approximation, because more precise expressions require cubic, quartic, etc., ... terms in  $\left( v + \frac{1}{2} \right)$  with anharmonic constants  $y_e$ ,  $z_e$ , etc., but this terms are important only at large values of  $v$ .

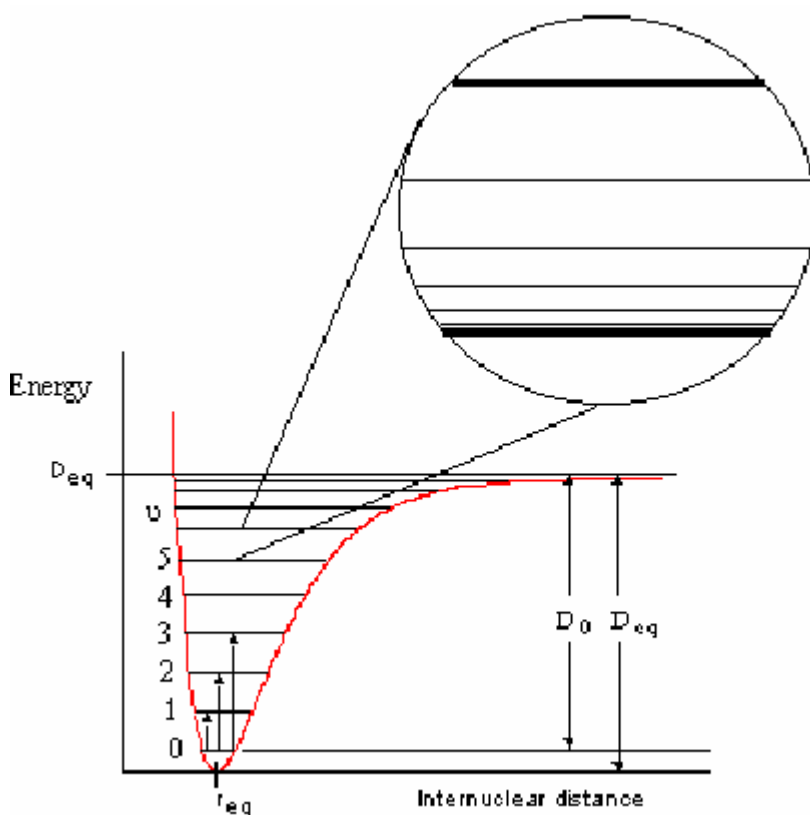


Fig 11. The picture shows vibrational levels and rotational fine structure superimposed on the Morse potential.  $D_0$  is the dissociation energy from the ground vibrational level.

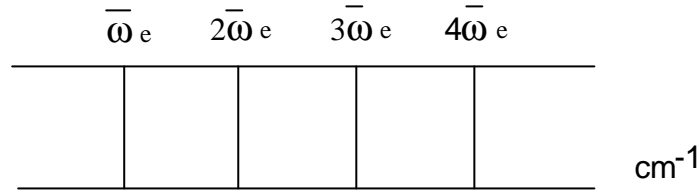


Fig 12. The vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.

To define  $\bar{\omega}_e$ , oscillation frequency, we rewrite the equation for  $\epsilon_v$  for the anharmonic oscillator, as

$$\epsilon_v = \bar{\omega} \left\{ 1 - x_e \left( v + \frac{1}{2} \right) \right\} \left( v + \frac{1}{2} \right) \quad (40)$$

and we compare it with the energy levels of the harmonic oscillator, then:

$$\bar{\omega}_a = \bar{\omega}_e \left\{ 1 - x_e \left( v + \frac{1}{2} \right) \right\} \quad (41)$$

$\bar{\omega}_a$  is the oscillation frequency for the anharmonicity and is smaller than that for the harmonic case.

We can see that the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency, which decreases steadily with increasing  $v$ . If we replace  $v$  by

$$v = - \frac{1}{2} \quad (42)$$

(an hypothetical state), then  $\epsilon = 0$ , so the molecule would be at the equilibrium point with zero vibrational energy. Its oscillation frequency ( in  $\text{cm}^{-1}$ ) would be:

$$\bar{\omega}_a = \bar{\omega}_e \quad (43)$$

Then,  $\bar{\omega}_e$  may be defined as the ( hypothetical) equilibrium oscillation frequency of the anharmonic system, i.e., the frequency for infinitely small vibrations about the equilibrium point.

For any real state specified by a positive integral  $v$ , the oscillation frequency will be given by (1), then for  $v=0$  we have:

$$\bar{\omega}_0 = \bar{\omega}_e \left( 1 - \frac{1}{2} x_e \right) \text{ cm}^{-1} \quad (44)$$

and

$$\epsilon_0 = \frac{1}{2} \bar{\omega}_e \left( 1 - \frac{1}{2} x_e \right) \text{ cm}^{-1} \quad (45)$$

therefore the zero-point energy differs slightly from that for the harmonic oscillator. The selection rules for the anharmonic oscillator are found to be:

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots \quad (46)$$

but only the lines  $\Delta v = \pm 1, \pm 2$  and  $\pm 3$  have observable intensity, and this is predicted by theory and observed in practice.

An important consideration is that a diatomic molecule can execute rotations and vibrations, independently of the electronic state, using the Born-Oppenheimer approximation. Then, we assume that the combined rotational-vibrational energy is simply the sum of the separate energies:

$$\epsilon_{\text{total}} = \epsilon_{\text{rot}} + \epsilon_{\text{vib}} \quad (47)$$

Then, taking the separate expressions for  $\epsilon_{\text{rot}}$  and  $\epsilon_{\text{vib}}$ , we have:

$$\epsilon_{J,v} = \epsilon_J + \epsilon_v \quad (48)$$

So:

$$\epsilon_{J,v} = BJ(J+1) - DJ^2(J+1)^2 + \left( v + \frac{1}{2} \right) \bar{\omega}_e - x_e \left( v + \frac{1}{2} \right)^2 \bar{\omega}_e \quad \text{in cm}^{-1}. \quad (49)$$

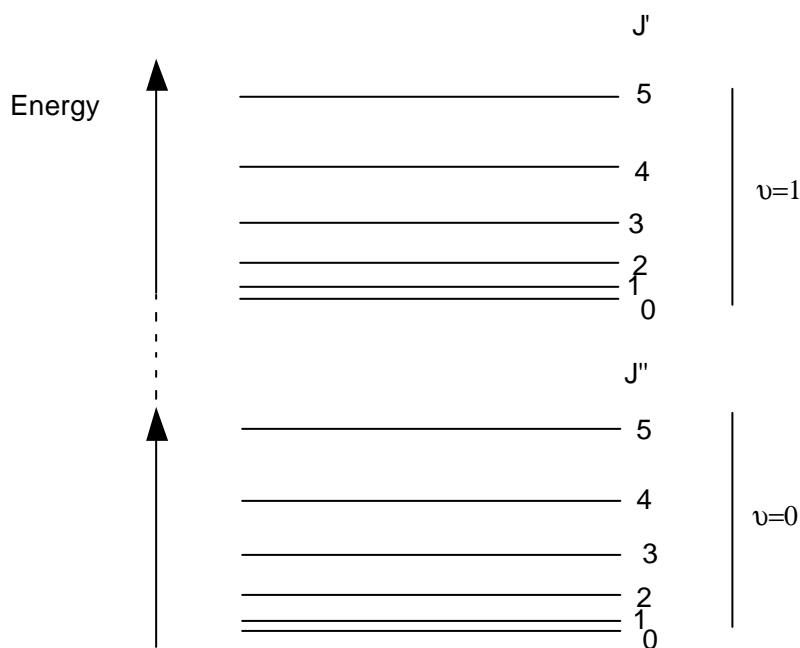


Fig 13. The electronics levels are more widely spaced than vibrational and rotational levels. They are bands, consisting of a series of vibrational (and rotational) transitions within the electronic transition. A series of vibrational transitions from one initial vibrational state (in the lower electronic state) to a number of different final vibrational states (within the final electronic state) is called a Franck-Condon progression, and the intensity distribution within this progression is determined by the difference in equilibrium bond length of the molecule in the two electronic states.