

3.1.3 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. If the bond between atoms is stretched, for instance, there comes a point at which it will break—the molecule dissociates into atoms. Thus although for small compressions and extensions the bond may be taken as perfectly elastic, for larger amplitudes—say greater than 10 per cent of the bond length—a much more complicated behaviour must be assumed. Figure 3.3 shows, diagrammatically, the shape of the energy curve for a typical diatomic molecule, together with (dashed) the ideal, simple harmonic parabola.

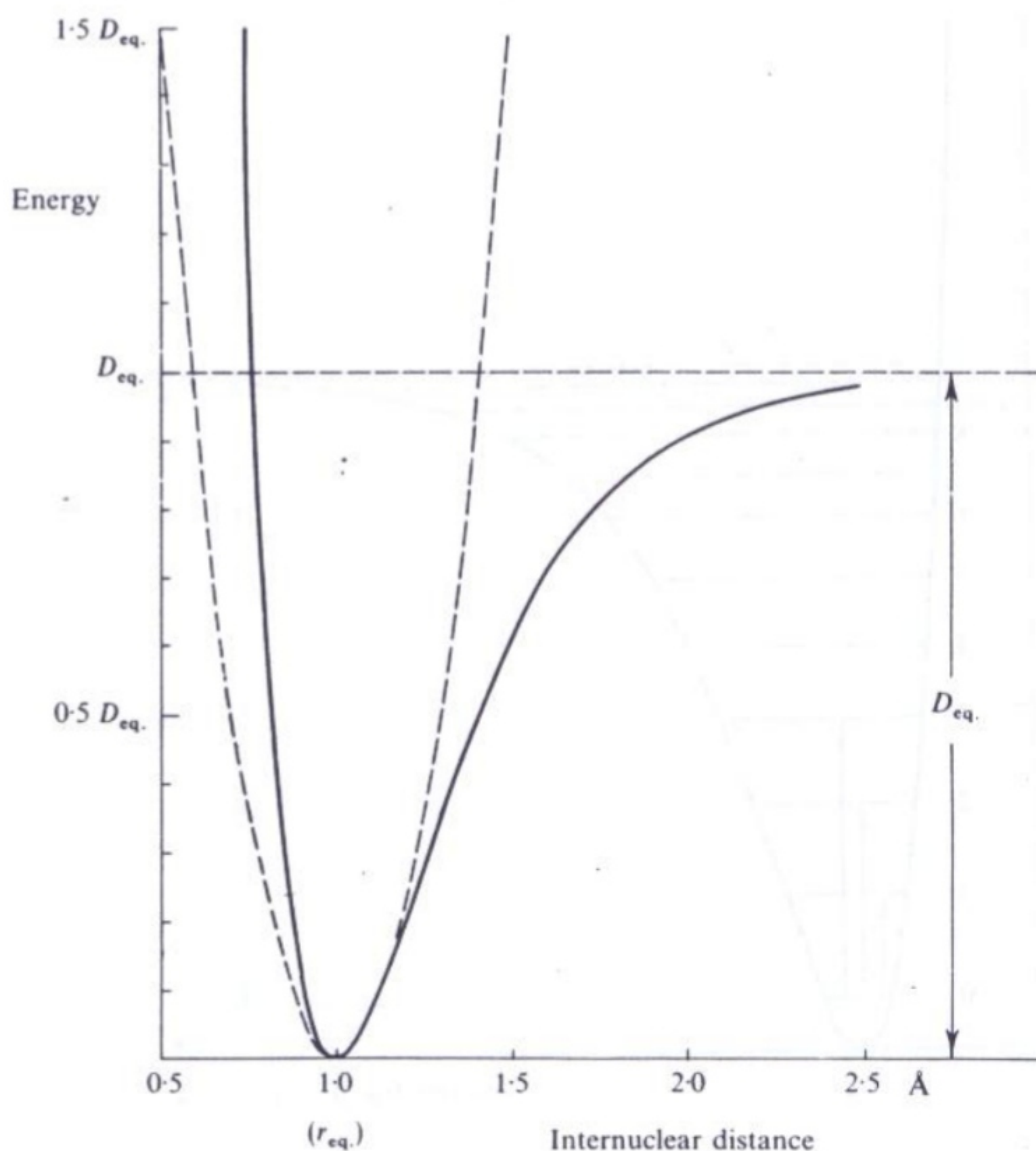


Figure 3.3 The Morse curve: the energy of a diatomic molecule undergoing anharmonic extensions and compressions.

A purely empirical expression which fits this curve to a good approximation was derived by P. M. Morse, and is called the Morse function:

$$E = D_{\text{eq.}} [1 - \exp \{a(r_{\text{eq.}} - r)\}]^2 \quad (3.11)$$

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

When Eq. (3.11) is used instead of Eq. (3.2) in the Schrödinger equation, the pattern of the allowed vibrational energy levels is found to be:

$$\epsilon_v = (v + \frac{1}{2})\bar{\omega}_e - (v + \frac{1}{2})^2\bar{\omega}_e x_e \quad \text{cm}^{-1} \quad (v = 0, 1, 2, \dots) \quad (3.12)$$

where $\bar{\omega}_e$ is an oscillation frequency (expressed in wavenumbers) which we shall define more closely below, and x_e is the corresponding anharmonicity constant which, for bond stretching vibrations, is always small and positive

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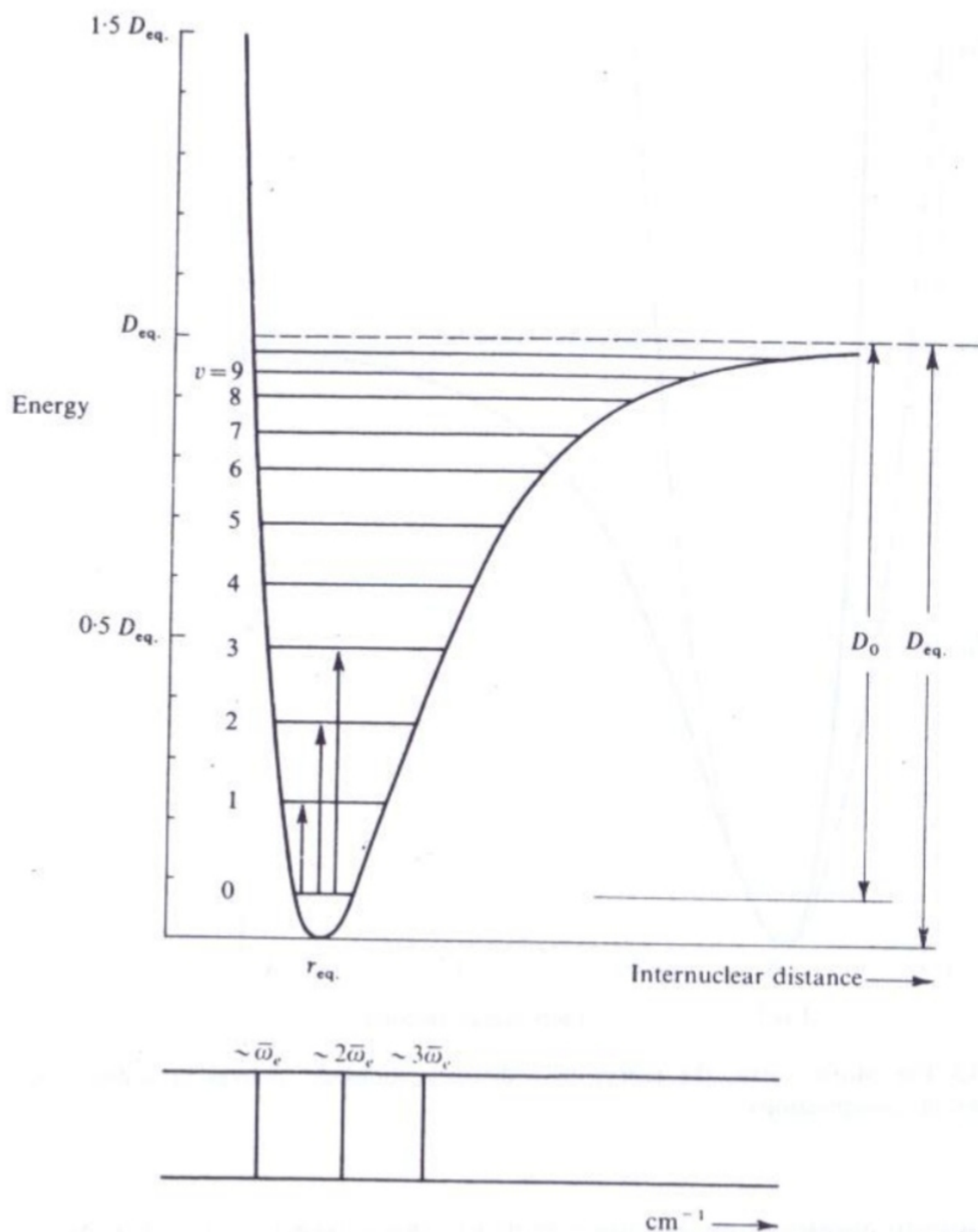


Figure 3.4 The allowed vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.

($\approx +0.01$), so that the vibrational levels crowd more closely together with increasing v . Some of these levels are sketched in Fig. 3.4.

It should be mentioned that Eq. (3.12), like (3.11), is an approximation only; more precise expressions for the energy levels require cubic, quartic, etc., terms in $(v + \frac{1}{2})$ with anharmonicity constants y_e , z_e , etc., rapidly

diminishing in magnitude. These terms are important only at large values of v , and we shall ignore them.

If we rewrite Eq. (3.12), for the anharmonic oscillator, as:

$$\varepsilon_v = \bar{\omega}_e \left\{ 1 - x_e \left(v + \frac{1}{2} \right) \right\} \left(v + \frac{1}{2} \right) \quad (3.13)$$

and compare with the energy levels of the *harmonic* oscillator (Eq. (3.6)), we see that we can write:

$$\bar{\omega}_{\text{osc.}} = \bar{\omega}_e \left\{ 1 - x_e \left(v + \frac{1}{2} \right) \right\} \quad (3.14)$$

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing v . If we now consider the hypothetical energy state obtained by putting $v = -\frac{1}{2}$ (at which, according to Eq. (3.13), $\varepsilon = 0$) the molecule would be at the equilibrium point with zero vibrational energy. Its oscillation frequency (in cm^{-1}) would be:

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

Thus we see that $\bar{\omega}_e$ may be defined as the (hypothetical) *equilibrium oscillation frequency* of the anharmonic system—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 Eq. (3.14). Thus in the ground state ($v = 0$) we would have:

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

and

$$\varepsilon_0 = \frac{1}{2} \bar{\omega}_e \left(1 - \frac{1}{2} x_e \right) \quad \text{cm}^{-1}$$

and we see that the zero point energy differs slightly from that for the harmonic oscillator (Eq. (3.7)).

The selection rules for the anharmonic oscillator are found to be:

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

Thus they are the same as for the harmonic oscillator, with the additional possibility of larger jumps. These, however, are predicted by theory and observed in practice to be of rapidly diminishing probability and normally only the lines of $\Delta v = \pm 1, \pm 2$, and ± 3 , at the most, have observable intensity. Further, the spacing between the vibrational levels is, as we shall shortly see, of order 10^3 cm^{-1} and, at room temperature, we may use the Boltzmann distribution (Eq. (1.12)) to show

$$\begin{aligned} \frac{N_{v=1}}{N_{v=0}} &= \exp \left\{ - \frac{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 10^3}{1.38 \times 10^{-23} \times 300} \right\} \\ &\approx \exp(-4.8) \approx 0.008. \end{aligned}$$

In other words, the population of the $v = 1$ state is nearly 0.01 or some one per cent of the ground state population. Thus, to a very good approximation, we may ignore all transitions originating at $v = 1$ or more and

restrict ourselves to the three transitions:

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

$$\begin{aligned}\Delta\varepsilon &= \varepsilon_{v=1} - \varepsilon_{v=0} \\ &= (1 + \frac{1}{2})\bar{\omega}_e - x_e(1 + \frac{1}{2})^2\bar{\omega}_e - \{\frac{1}{2}\bar{\omega}_e - (\frac{1}{2})^2x_e\bar{\omega}_e\} \\ &= \bar{\omega}_e(1 - 2x_e) \text{ cm}^{-1}\end{aligned}\tag{3.15a}$$

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

$$\begin{aligned}\Delta\varepsilon &= (2 + \frac{1}{2})\bar{\omega}_e - x_e(2 + \frac{1}{2})^2\bar{\omega}_e - \{\frac{1}{2}\bar{\omega}_e - (\frac{1}{2})^2x_e\bar{\omega}_e\} \\ &= 2\bar{\omega}_e(1 - 3x_e) \text{ cm}^{-1}\end{aligned}\tag{3.15b}$$

3. $v = 0 \rightarrow v = 3$, $\Delta v = +3$, with normally negligible intensity.

$$\begin{aligned}\Delta\varepsilon &= (3 + \frac{1}{2})\bar{\omega}_e - \{\frac{1}{2}\bar{\omega}_e - (\frac{1}{2})^2x_e\bar{\omega}_e\} \\ &= 3\bar{\omega}_e(1 - 4x_e) \text{ cm}^{-1}\end{aligned}\tag{3.15c}$$

These three transitions are shown in Fig. 3.4. To a good approximation, since $x_e \approx 0.01$, the three spectral lines lie very close to $\bar{\omega}_e$, $2\bar{\omega}_e$, and $3\bar{\omega}_e$. The line near $\bar{\omega}_e$ is called the *fundamental absorption*, while those near $2\bar{\omega}_e$ and $3\bar{\omega}_e$ are called the *first* and *second overtones*, respectively. The spectrum of HCl, for instance, shows a very intense absorption at 2886 cm^{-1} , a weaker one at 5668 cm^{-1} , and a very weak one at 8347 cm^{-1} . If we wish to find the equilibrium frequency of the molecule from these data, we must solve any two of the three equations (cf. Eqs. (3.15)):

$$\bar{\omega}_e(1 - 2x_e) = 2886$$

$$2\bar{\omega}_e(1 - 3x_e) = 5668$$

$$3\bar{\omega}_e(1 - 4x_e) = 8347 \text{ cm}^{-1}$$

and we find $\bar{\omega}_e = 2990 \text{ cm}^{-1}$, $x_e = 0.0174$. Thus we see that, whereas for the ideal harmonic oscillator the spectral absorption occurred *exactly* at the classical vibration frequency, for real, anharmonic molecules the observed fundamental absorption frequency and the equilibrium frequency may differ considerably.

The force constant of the bond in HCl may be calculated directly from Eq. (2.22) by inserting the value of $\bar{\omega}_e$:

$$\begin{aligned}k &= 4\pi^2\bar{\omega}_e^2c^2\mu \text{ N m}^{-1} \\ &= 516 \text{ N m}^{-1}\end{aligned}$$

when the fundamental constants and the reduced mass are inserted. These data, together with that for a few of the very many other diatomic molecules studied by infra-red techniques, are collected in Table 3.1.

Table 3.1 Some molecular data for diatomic molecules determined by infra-red spectroscopy

Molecule	Vibration (cm^{-1})	Anharmonicity constant, x_e	Force constant (N m^{-1})	Internuclear distance r_{eq} (nm)
HF	4138.5	0.0218	966	0.0927
HCl†	2990.6	0.0174	516	0.1274
HBr	2649.7	0.0171	412	0.1414
HI	2309.5	0.0172	314	0.1609
CO	2169.7	0.0061	1902	0.1131
NO	1904.0	0.0073	1595	0.1151
ICl†	384.2	0.0038	238	0.2321

† Data refers to the ^{35}Cl isotope.

Although we have ignored transitions from $v = 1$ to higher states, we should note that, if the temperature is raised or if the vibration has a particularly low frequency, the population of the $v = 1$ state may become appreciable. Thus at, say, 600 K (i.e., about 300°C) $N_{v=1}/N_{v=0}$ becomes $\exp(-2.4)$ or about 0.09, and transitions from $v = 1$ to $v = 2$ will be some 10 per cent the intensity of those from $v = 0$ to $v = 1$. A similar increase in the excited state population would arise if the vibrational frequency were 500 cm^{-1} instead of 1000 cm^{-1} . We may calculate the wavenumber of this transition as:

4. $v = 1 \rightarrow v = 2$, $\Delta v = +1$, normally very weak,

$$\begin{aligned} \Delta\varepsilon &= 2\frac{1}{2}\bar{\omega}_e - 6\frac{1}{4}x_e\bar{\omega}_e - \{1\frac{1}{2}\bar{\omega}_e - 2\frac{1}{4}x_e\bar{\omega}_e\} \\ &= \bar{\omega}_e(1 - 4x_e) \text{ cm}^{-1} \end{aligned} \quad (3.15d)$$

Thus, should this weak absorption arise, it will be found close to and at slightly *lower* wavenumber than the fundamental (since x_e is small and positive). Such weak absorptions are usually called *hot bands* since a high temperature is one condition for their occurrence. Their nature may be confirmed by raising the temperature of the sample when a true hot band will increase in intensity.

We turn now to consider a diatomic molecule undergoing simultaneous vibration and rotation.