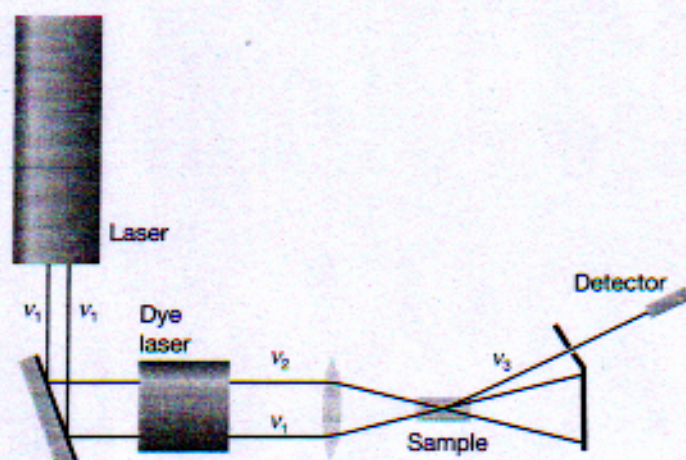


16.52 The resonance Raman spectra of a protein complex that is responsible for some of the initial electron transfer events in plant photosynthesis. (a) Laser excitation of the sample at 407 nm shows Raman bands due to both chlorophyll *a* and β -carotene bound to the protein because both pigments absorb light at this wavelength. (b) Laser excitation at 488 nm shows Raman bands from β -carotene only because chlorophyll *a* does not absorb light very strongly at this wavelength. (Adapted from D.F. Ghanotakis et al., *Biochim. Biophys. Acta* 974, 44 (1989).)



16.53 The experimental arrangement for the CARS experiment.

have electronic transitions at the laser wavelengths used in the experiment, so their conventional Raman spectra are weak compared to the enhanced spectra of the pigments. Comparison of the spectra in Figs 16.52a and 16.52b also shows that, with proper choice of excitation wavelength, it is possible to examine individual classes of pigments bound to the same protein: excitation at 488 nm, where β -carotene absorbs strongly, shows vibrational bands from β -carotene only, whereas excitation at 407 nm, where chlorophyll *a* and β -carotene absorb to similar extents, reveals features from both types of pigments.

(c) Coherent anti-Stokes Raman spectroscopy

The intensity of Raman transitions may be enhanced by **coherent anti-Stokes Raman spectroscopy (CARS, Fig. 16.53)**. The technique relies on the fact that, if two laser beams of frequencies ν_1 and ν_2 pass through a sample, then they may mix together and give rise to coherent radiation of several different frequencies, one of which is

$$\nu_3 = 2\nu_1 - \nu_2 \quad (16.75)$$

Suppose that ν_2 is varied until it matches any Stokes line from the sample, such as the one with frequency $\nu_1 - \Delta\nu$; then the coherent emission will have frequency

$$\nu_3 = 2\nu_1 - (\nu_1 - \Delta\nu) = \nu_1 + \Delta\nu \quad (16.76)$$

which is the frequency of the corresponding anti-Stokes line. This coherent radiation forms a narrow beam of high intensity.

An advantage of CARS is that it can be used to study Raman transitions in the presence of competing incoherent background radiation, and so can be used to observe the Raman spectra of species in flames. One example is the vibration-rotation CARS spectrum of N_2 gas in a methane-air flame shown in Fig. 16.54.

16.17 Symmetry aspects of molecular vibrations

One of the most powerful ways of dealing with normal modes, especially of complex molecules, is to classify them according to their symmetries. Each normal mode must belong to one of the symmetry species of the molecular point group, as discussed in Chapter 15.

$$\frac{\text{Number of ways of achieving odd } J}{\text{Number of ways of achieving even } J} = \begin{cases} (I+1)/I & \text{for half-integral spin nuclei} \\ I/(I+1) & \text{for integral spin nuclei} \end{cases} \quad (16.50)$$

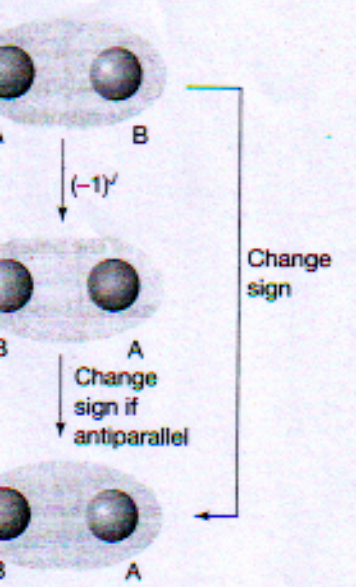
For hydrogen, $I = \frac{1}{2}$, and the ratio is 3:1. For N_2 , with $I = 1$, the ratio is 1:2.

Justification 16.6

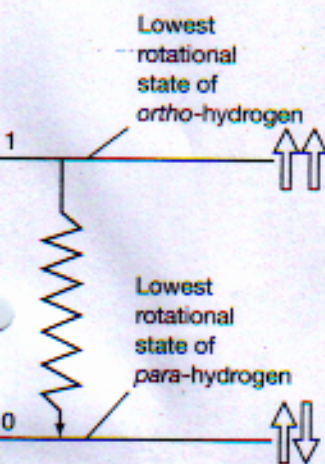
Hydrogen nuclei are fermions, so the Pauli principle requires the overall wavefunction to change sign under particle interchange. However, the rotation of an H_2 molecule through 180° has a more complicated effect than merely relabelling the nuclei, because it interchanges their spin states too if the nuclear spins are paired ($\uparrow\downarrow$) but not if they are parallel ($\uparrow\uparrow$).

For the overall wavefunction of the molecule to change sign when the spins are parallel, the rotational wavefunction must change sign. Hence, only odd values of J are allowed. In contrast, if the nuclear spins are paired, their wavefunction is $\alpha(A)\beta(B) - \alpha(B)\beta(A)$, which changes sign when α and β are exchanged in order to bring about a simple $A \leftrightarrow B$ interchange overall (Fig. 16.31). Therefore, for the overall wavefunction to change sign in this case requires the rotational wavefunction not to change sign. Hence, only even values of J are allowed if the nuclear spins are paired.

As there are three nuclear spin states with parallel spins (just like the triplet state of two parallel electrons, as in Fig. 13.26), but only one state with paired spins (the analogue of the singlet state of two electrons, see Fig. 13.20), it follows that the populations of the odd J and even J states should be in the ratio of 3:1, and hence the intensities of transitions originating in these levels will be in the same ratio.



The interchange of two identical nuclei results in the change in sign of the overall wavefunction. The relabelling can be thought of as occurring in two steps: the rotation of the molecule; the second is the change of unlike spins (represented by different colours of the nuclei). The overall wavefunction changes sign in the second step if the nuclei have antiparallel spins.



When hydrogen is cooled, the molecules with parallel nuclear spins accumulate in their lowest available rotational state, the one with $J = 1$. They can enter the lowest rotational state only if the spins change their relative orientation and become antiparallel. This is a slow process under normal circumstances, so the energy is slowly released.

Different relative nuclear spin orientations change into one another only very slowly, so an H_2 molecule with parallel nuclear spins remains distinct from one with paired nuclear spins for long periods. The two forms of hydrogen can be separated by physical techniques, and stored. The form with parallel nuclear spins is called ortho-hydrogen and the form with paired nuclear spins is called para-hydrogen. Because ortho-hydrogen cannot exist in a state with $J = 0$, it continues to rotate at very low temperatures and has an effective rotational zero-point energy (Fig. 16.32). This energy is of some concern to manufacturers of liquid hydrogen, for the slow conversion of ortho-hydrogen into para-hydrogen (which can exist with $J = 0$) as nuclear spins slowly realign releases rotational energy, which vaporizes the liquid. Techniques are used to accelerate the conversion of ortho-hydrogen to para-hydrogen to avoid this problem. One such technique is to pass hydrogen over a metal surface: the molecules adsorb on the surface as atoms, which then recombine in the lower energy para-hydrogen form.

The vibrations of diatomic molecules

In this section, we adopt the same strategy of finding expressions for the energy levels, establishing the selection rules, and then discussing the form of the spectrum. We shall also see how the simultaneous excitation of rotation modifies the appearance of a vibrational spectrum.

Inc Note

16.9 Molecular vibrations

We base our discussion on Fig. 16.33, which shows a typical potential energy curve (as in Fig. 14.1) of a diatomic molecule. In regions close to R_0 (at the minimum of the curve) the potential energy can be approximated by a parabola, so we can write

$$V = \frac{1}{2} kx^2 \quad x = R - R_0 \quad (16.51)$$

where k is the force constant of the bond. The steeper the walls of the potential (the stiffer the bond), the greater the force constant.

To see the connection between the shape of the molecular potential energy curve and the value of k , note that we can expand the potential energy around its minimum by using a Taylor series:

$$V(x) = V(0) + \left(\frac{dV}{dx}\right)_0 x + \frac{1}{2} \left(\frac{d^2V}{dx^2}\right)_0 x^2 + \dots \quad (16.52)$$

The term $V(0)$ can be set arbitrarily to zero. The first derivative of V is 0 at the minimum. Therefore, the first surviving term is proportional to the square of the displacement. For small displacements we can ignore all the higher terms, and so write

$$V(x) = \frac{1}{2} \left(\frac{d^2V}{dx^2}\right)_0 x^2 \quad (16.53)$$

Therefore, the first approximation to a molecular potential energy curve is a parabolic potential, and we can identify the force constant as

$$k = \left(\frac{d^2V}{dx^2}\right)_0 \quad (16.54)$$

We see that, if the potential energy curve is sharply curved close to its minimum, then k will be large. Conversely, if the potential energy curve is wide and shallow, then k will be small (Fig. 16.34).

The Schrödinger equation for the relative motion of two atoms of masses m_1 and m_2 with a parabolic potential energy is

$$-\frac{\hbar^2}{2m_{\text{eff}}} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi = E\psi \quad (16.55)$$

where m_{eff} is the effective mass:

$$m_{\text{eff}} = \frac{m_1 m_2}{m_1 + m_2} \quad (16.56)$$

These equations are derived in the same way as in Justification 13.1, but here the separation of variables procedure is used to separate the relative motion of the atoms from the motion of the molecule as a whole.⁹

The Schrödinger equation in eqn 55 is the same as eqn 12.31 for a particle of mass m undergoing harmonic motion. Therefore, we can use the results of Section 12.4 to write down the permitted vibrational energy levels:

$$E_v = \left(v + \frac{1}{2}\right) \hbar \omega \quad \omega = \left(\frac{k}{m_{\text{eff}}}\right)^{1/2} \quad v = 0, 1, 2, \dots \quad (16.57)$$

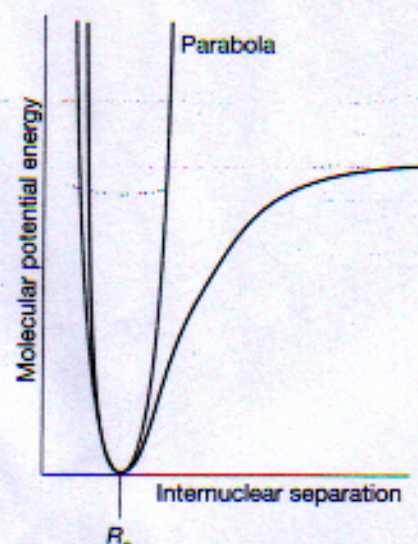
The vibrational terms of a molecule, the energies of its vibrational states expressed in wavenumbers, are denoted $G(v)$, with $E_v = hcG(v)$, so

9. In that context, the effective mass is called the 'reduced mass', and the name is widely used in this context too.

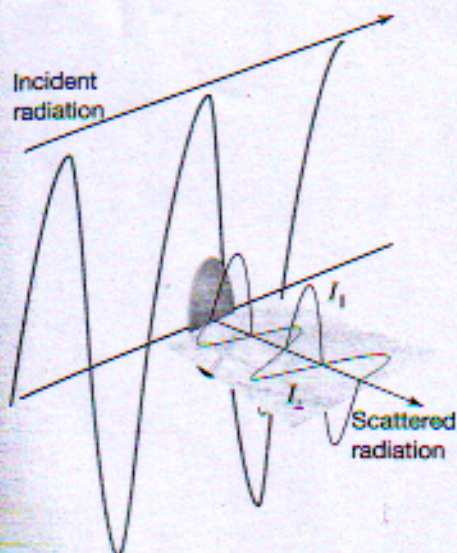
It is often useful to express a function $f(x)$ in the vicinity of $x = a$ as an infinite Taylor series of the form:

$$\begin{aligned} f(x) &= f(a) + \left(\frac{df}{dx}\right)_a (x-a) \\ &+ \frac{1}{2!} \left(\frac{d^2f}{dx^2}\right)_a (x-a)^2 + \dots \\ &= \sum_n \frac{1}{n!} \left(\frac{d^n f}{dx^n}\right)_a (x-a)^n \end{aligned}$$

where $n = 0, 1, 2, \dots$



16.33 A molecular potential energy curve can be approximated by a parabola near the bottom of the well. The parabolic potential leads to harmonic oscillations. At high excitation energies the parabolic approximation is poor (the true potential is less confining), and is totally wrong near the dissociation limit.



16.50 The definition of the planes used for the specification of the depolarization ratio, ρ , in Raman scattering.

(a) Depolarization

The assignment of Raman lines to particular vibrational modes is aided by noting the state of polarization of the scattered light. The **depolarization ratio**, ρ , of a line is the ratio of the intensities, I , of the scattered light with polarizations perpendicular and parallel to the plane of polarization of the incident radiation:

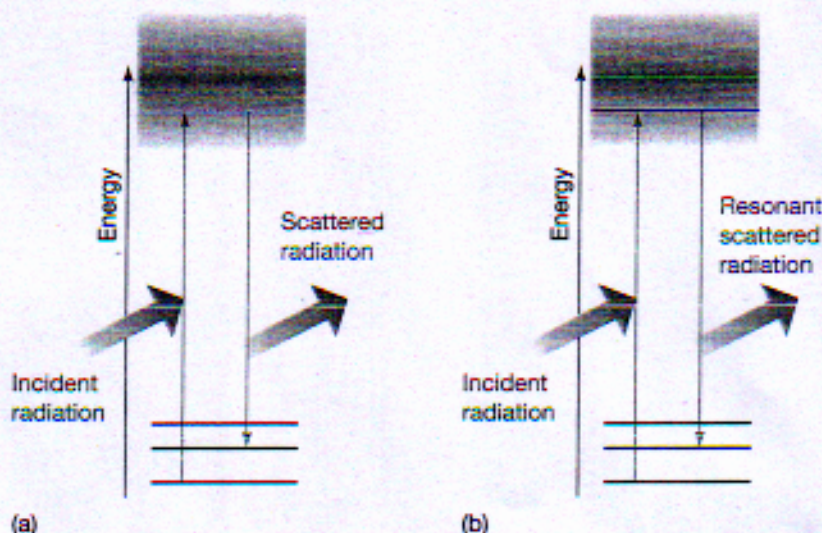
$$\rho = \frac{I_{\perp}}{I_{\parallel}} \quad [16.74]$$

To measure ρ , the intensity of a Raman line is measured with a polarizing filter (a 'half-wave plate') first parallel and then perpendicular to the polarization of the incident beam. If the emergent light is not polarized, then both intensities are the same and ρ is close to 1; if the light retains its initial polarization, then $I_{\perp} = 0$, so $\rho = 0$ (Fig. 16.50). A line is classified as **depolarized** if it has ρ close to or greater than 0.75 and as **polarized** if $\rho < 0.75$. Only totally symmetrical vibrations give rise to polarized lines in which the incident polarization is largely preserved. Vibrations that are not totally symmetrical give rise to depolarized lines because the incident radiation can give rise to radiation in the perpendicular direction too.

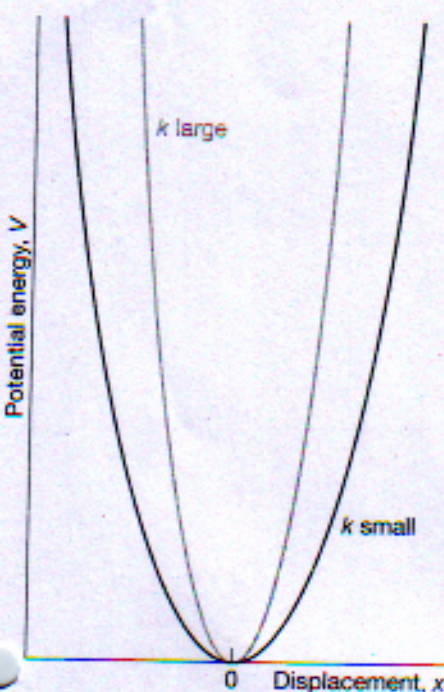
(b) Resonance Raman spectra

A modification of the basic Raman effect involves using incident radiation that nearly coincides with the frequency of an electronic transition of the sample (Fig. 16.51). The technique is then called **resonance Raman spectroscopy**. It is characterized by a much greater intensity in the scattered radiation. Furthermore, because it is often the case that only a few vibrational modes contribute to the more intense scattering, the spectrum is greatly simplified.

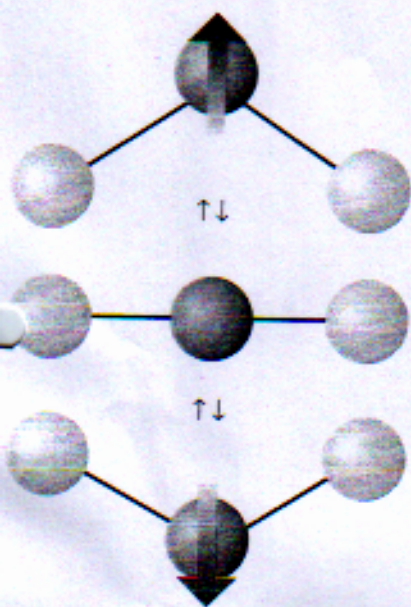
Resonance Raman spectroscopy is used to study biological molecules that absorb strongly in the ultraviolet and visible regions of the spectrum. Examples include the pigments β -carotene and chlorophyll, which capture solar energy during plant photosynthesis (see Box 26.2). The resonance Raman spectra of Fig. 16.52 show vibrational transitions from only the few pigment molecules that are bound to very large proteins dissolved in an aqueous buffer solution. This selectivity arises from the fact that water (the solvent), amino acid residues, and the peptide group do not



16.51 (a) In conventional Raman spectroscopy, the incident radiation does not match an absorption frequency of the molecule, and there is only a 'virtual' transition to an excited state. (b) However, in the resonance Raman effect, the incident radiation has a frequency that coincides with a molecular transition.



16.34 The force constant is a measure of the curvature of the potential energy close to the equilibrium extension of the bond. A strongly confining well (one with steep sides, a stiff bond) corresponds to high values of k .



16.35 The oscillation of a molecule, even if it is nonpolar, may result in an oscillating dipole that can interact with the electromagnetic field.

$$G(v) = (v + \frac{1}{2})\tilde{\nu} \quad \tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k}{m_{\text{eff}}} \right)^{1/2} \quad (16.58)$$

The vibrational wavefunctions are the same as those discussed in Section 12.5.

It is important to note that the vibrational terms depend on the effective mass of the molecule, not directly on its total mass. This dependence is physically reasonable for, if atom 1 were as heavy as a brick wall, then we would find $m_{\text{eff}} = m_2$, the mass of the lighter atom. The vibration would then be that of a light atom relative to that of a stationary wall (this is approximately the case in HI, for example, where the I atom barely moves and $m_{\text{eff}} = m_{\text{H}}$). For a homonuclear diatomic molecule $m_1 = m_2$, and the effective mass is half the total mass: $m_{\text{eff}} = \frac{1}{2}m$.

Illustration 16.4

An HCl molecule has a force constant of 516 N m^{-1} , a reasonably typical value. The effective mass of $^1\text{H}^{35}\text{Cl}$ is $1.63 \times 10^{-27} \text{ kg}$ (note that this mass is very close to the mass of the hydrogen atom, $1.67 \times 10^{-27} \text{ kg}$, so the Cl atom is acting like a brick wall). These values imply $\omega = 5.63 \times 10^{14} \text{ s}^{-1}$, $\nu = 89.5 \text{ THz}$ ($1 \text{ THz} = 10^{12} \text{ Hz}$), $\tilde{\nu} = 2990 \text{ cm}^{-1}$, $\lambda = 3.35 \text{ mm}$. These characteristics correspond to electromagnetic radiation in the infrared region.

16.10 Selection rules

The gross selection rule for absorption of radiation by a molecular vibration is that the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. Such vibrations are said to be **infrared active**. The classical basis of this rule is that the molecule can shake the electromagnetic field into oscillation if its dipole changes as it vibrates, and vice versa (Fig. 16.35); its formal basis is given in the following Justification. Note that the molecule need not have a permanent dipole: the rule requires only a change in dipole moment, possibly from zero. Some vibrations do not affect the molecule's dipole moment (for example, the stretching motion of a homonuclear diatomic molecule), so they neither absorb nor generate radiation: such vibrations are said to be **infrared inactive**. Homonuclear diatomic molecules are infrared inactive because their dipole moments remain zero however long the bond; heteronuclear diatomic molecules are infrared active.

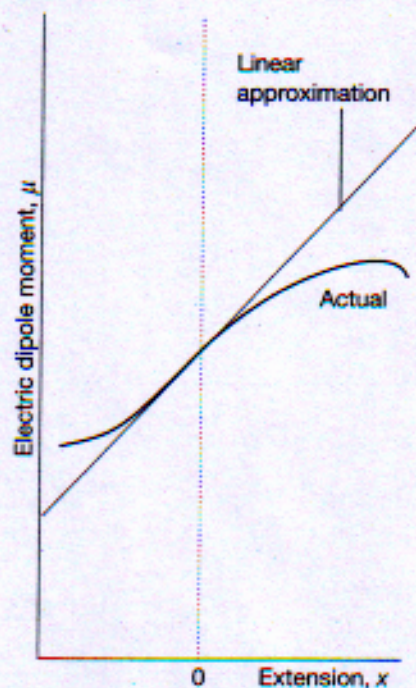
Justification 16.7

The gross selection rule is based on an analysis of the transition dipole moment $\langle v_f | \mu | v_i \rangle$. For simplicity, we shall consider a one-dimensional oscillator (like a diatomic molecule). The electric dipole moment operator depends on the location of all the electrons and all the nuclei in the molecule, so it varies as the internuclear separation changes (Fig. 16.36). If we think of the dipole moment as arising from two partial charges $\pm \delta q$ separated by a distance $R = R_0 + x$, we can write its variation with displacement from the equilibrium separation, x , as

$$\mu = R\delta q = R_0\delta q + x\delta q = \mu_0 + x\delta q$$

where μ_0 is the electric dipole moment operator when the nuclei have their equilibrium separation. It then follows that, with $f \neq i$,

$$\langle v_f | \mu | v_i \rangle = \mu_0 \langle v_f | v_i \rangle + \delta q \langle v_f | x | v_i \rangle$$



16.36 The electric dipole moment of a heteronuclear diatomic molecule varies as shown by the blue curve. For small displacements the change in dipole moment is proportional to the displacement.

An important integral involving Hermite polynomials is

$$\int_{-\infty}^{\infty} H_{v'} H_v e^{-y^2} dy = \begin{cases} 0 & \text{if } v' \neq v \\ \pi^{1/2} 2^v v! & \text{if } v' = v \end{cases}$$

The term proportional to μ_0 is zero because the states with different values of v are orthogonal. It follows that the transition dipole moment is

$$\langle v_f | \mu | v_i \rangle = \langle v_f | x | v_i \rangle \delta q$$

Because

$$\delta q = \frac{d\mu}{dx}$$

we can write the transition dipole moment more generally as

$$\langle v_f | \mu | v_i \rangle = \langle v_f | x | v_i \rangle \left(\frac{d\mu}{dx} \right)$$

and we see that the right-hand side is zero unless the dipole moment varies with displacement. This is the gross selection rule for vibrational spectroscopy.

The specific selection rule is determined by considering the value of $\langle v_f | x | v_i \rangle$. We need to write out the wavefunctions in terms of the Hermite polynomials given in Section 12.5 and then to use their properties (Example 12.3 should be reviewed, for it gives further details of the calculation). We note that $x = \alpha y$ with $\alpha = (\hbar^2/m_{\text{eff}}k)^{1/4}$ (eqn 12.35), and write

$$\langle v_f | x | v_i \rangle = N_{v_f} N_{v_i} \int_{-\infty}^{\infty} H_{v_f} x H_{v_i} e^{-y^2} dx = \alpha^2 N_{v_f} N_{v_i} \int_{-\infty}^{\infty} H_{v_f} y H_{v_i} e^{-y^2} dy$$

To evaluate the integral we use the recursion relation

$$yH_v = vH_{v-1} + \frac{1}{2}H_{v+1}$$

which turns the matrix element into

$$\langle v_f | x | v_i \rangle = \alpha^2 N_{v_f} N_{v_i} \left\{ v_i \int_{-\infty}^{\infty} H_{v_f} H_{v_i-1} e^{-y^2} dy + \frac{1}{2} \int_{-\infty}^{\infty} H_{v_f} H_{v_i+1} e^{-y^2} dy \right\}$$

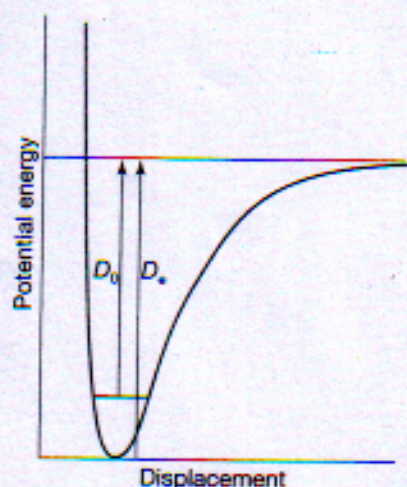
The first integral is zero unless $v_f = v_i - 1$ and the second is zero unless $v_f = v_i + 1$. It follows that the transition dipole moment is zero unless $\Delta v = \pm 1$.

Illustration 16.5

Of the molecules N_2 , CO_2 , OCS , H_2O , $CH_2=CH_2$, and C_6H_6 , all except N_2 possess at least one vibrational mode that results in a change of dipole moment, so all except N_2 can show a vibrational absorption spectrum. Not all the modes of complex molecules are vibrationally active. For example, the symmetric stretch of CO_2 , in which the O—C—O bonds stretch and contract symmetrically is inactive because it leaves the dipole moment unchanged (at zero).

Self-test 16.6 Which of the molecules H_2 , NO , N_2O , and CH_4 have infrared active vibrations? [NO, N_2O , CH_4]

The specific vibrational selection rule, which is obtained from an analysis of the expression for the transition moment and the properties of integrals over harmonic oscillator wavefunctions (as shown in Justification 16.7), is



16.37 The dissociation energy of a molecule, D_e , differs from the depth of the potential well, D_0 , on account of the zero-point energy of the vibrations of the bond.

$$\Delta v = \pm 1 \quad (16.59)$$

Transitions for which $\Delta v = +1$ correspond to absorption and those with $\Delta v = -1$ correspond to emission.

It follows from the specific selection rules that the wavenumbers of allowed vibrational transitions, which are denoted $\Delta G_{v+1/2}$ for the transition $v+1 \leftarrow v$, are

$$\Delta G_{v+1/2} = G(v+1) - G(v) = \tilde{\nu} \quad (16.60)$$

As we have seen, $\tilde{\nu}$ lies in the infrared region of the electromagnetic spectrum, so vibrational transitions absorb and generate infrared radiation.

At room temperature $kT/hc = 200 \text{ cm}^{-1}$, and most vibrational wavenumbers are significantly greater than 200 cm^{-1} . It follows from the Boltzmann distribution that almost all the molecules will be in their vibrational ground states initially. Hence, the dominant spectral transition will be the **fundamental transition**, $1 \leftarrow 0$. As a result, the spectrum is expected to consist of a single absorption line. If the molecules are formed in a vibrationally excited state, such as when vibrationally excited HF molecules are formed in the reaction $\text{H}_2 + \text{F}_2 \rightarrow 2 \text{HF}^*$, the transitions $5 \rightarrow 4, 4 \rightarrow 3, \dots$ may also appear (in emission). In the harmonic approximation, all these lines lie at the same frequency, and the spectrum is also a single line. However, as we shall now show, the breakdown of the harmonic approximation causes the transitions to lie at slightly different frequencies, so several lines are observed.

16.11 Anharmonicity

The vibrational terms in eqn 60 are only approximate because they are based on a parabolic approximation to the actual potential energy curve. A parabola cannot be correct at all extensions because it does not allow a bond to dissociate. At high vibrational excitations the swing of the atoms (more precisely, the spread of the vibrational wavefunction) allows the molecule to explore regions of the potential energy curve where the parabolic approximation is poor and additional terms in the Taylor expansion of V (eqn 52) must be retained. The motion then becomes **anharmonic**, in the sense that the restoring force is no longer proportional to the displacement. Because the actual curve is less confining than a parabola, we can anticipate that the energy levels become less widely spaced at high excitations.

(a) The convergence of energy levels

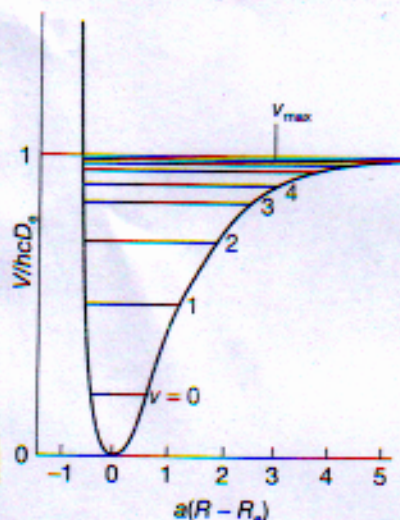
One approach to the calculation of the energy levels in the presence of anharmonicity is to use a function that resembles the true potential energy more closely. The **Morse potential energy** is

$$V = hcD_e(1 - e^{-a(R-R_e)})^2 \quad a = \left(\frac{m_{\text{eff}}\omega^2}{2hcD_e} \right)^{1/2} \quad (16.61)$$

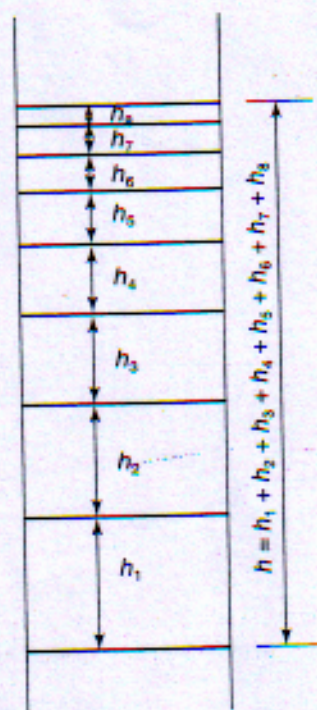
where D_e is the depth of the potential minimum (Fig. 16.37). Near the well minimum the variation of V with displacement resembles a parabola (as can be checked by expanding the exponential as far as the first term), but unlike a parabola, eqn 61 allows for dissociation at large displacements. The Schrödinger equation can be solved for the Morse potential and the permitted energy levels are

$$G(v) = (v + \frac{1}{2})\tilde{\nu} - (v + \frac{1}{2})^2 x_e \tilde{\nu} \quad x_e = \frac{a^2 \hbar}{2m_{\text{eff}}\omega} = \frac{\tilde{\nu}}{4D_e} \quad (16.62)$$

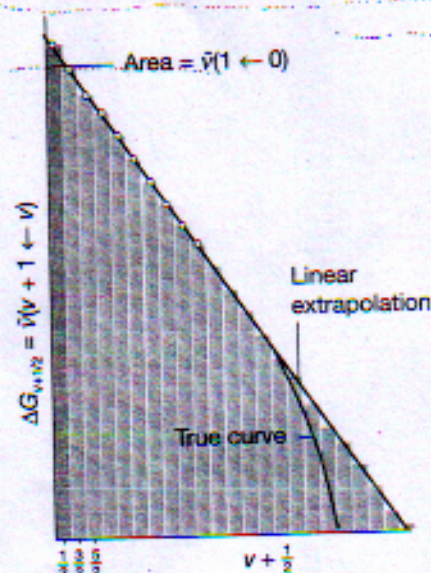
The parameter x_e is called the **anharmonicity constant**. The number of vibrational levels of a Morse oscillator is finite, and $v = 0, 1, 2, \dots, v_{\text{max}}$, as shown in Fig. 16.38



16.38 The Morse potential energy curve reproduces the general shape of a molecular potential energy curve. The corresponding Schrödinger equation can be solved, and the values of the energies obtained. The number of bound levels is finite.



16.39 The dissociation energy is the sum of the separations of the vibrational energy levels up to the dissociation limit just as the length of a ladder is the sum of the separations of its rungs.



16.40 The area under a plot of transition wavenumber against vibrational quantum number is equal to the dissociation energy of the molecule. The assumption that the differences approach zero linearly is the basis of the Birge-Sponer extrapolation.

(see also Problem 16.28). The second term in the expression for G subtracts from the first with increasing effect as v increases, and hence gives rise to the convergence of the levels at high quantum numbers.

Although the Morse oscillator is quite useful theoretically, in practice the more general expression

$$G(v) = (v + \frac{1}{2})\tilde{\nu} - (v + \frac{1}{2})^2 x_e \tilde{\nu} + (v + \frac{1}{2})^3 y_e \tilde{\nu} + \dots \quad (16.63)$$

where x_e, y_e, \dots are empirical constants characteristic of the molecule, is used to fit the experimental data and to find the dissociation energy of the molecule. When anharmonicities are present, the wavenumbers of transitions with $\Delta v = +1$ are

$$\Delta G_{v+1/2} = \tilde{\nu} - 2(v+1)x_e \tilde{\nu} + \dots \quad (16.64)$$

Equation 64 shows that, when $x_e \neq 0$, the transitions move to lower wavenumbers as v increases.

Anharmonicity also accounts for the appearance of additional weak absorption lines corresponding to the transitions $2 \leftarrow 0, 3 \leftarrow 0, \dots$, even though these first, second, ... overtones are forbidden by the selection rule $\Delta v = \pm 1$. The first overtone, for example, gives rise to an absorption at

$$G(v+2) - G(v) = 2\tilde{\nu} - 2(2v+3)x_e \tilde{\nu} + \dots \quad (16.65)$$

The reason for the appearance of overtones is that the selection rule is derived from the properties of harmonic oscillator wavefunctions, which are only approximately valid when anharmonicity is present. Therefore, the selection rule is also only an approximation. For an anharmonic oscillator, all values of Δv are allowed, but transitions with $\Delta v > 1$ are allowed only weakly if the anharmonicity is slight.

(b) The Birge-Sponer plot

When several vibrational transitions are detectable, a graphical technique called a Birge-Sponer plot may be used to determine the dissociation energy, D_0 , of the bond. The basis of the Birge-Sponer plot is that the sum of successive intervals $\Delta G_{v+1/2}$ from the zero-point level to the dissociation limit is the dissociation energy:

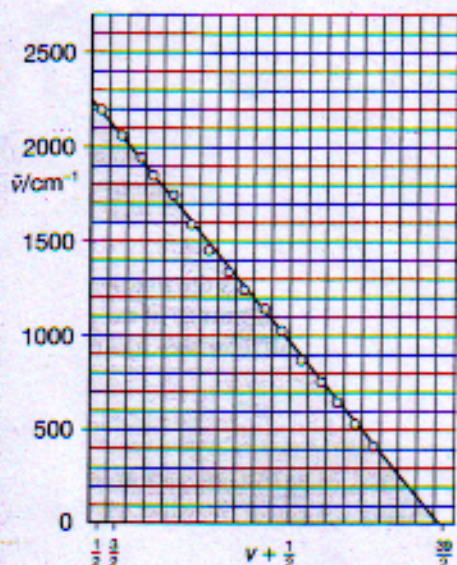
$$D_0 = \Delta G_{1/2} + \Delta G_{3/2} + \dots = \sum_v \Delta G_{v+1/2} \quad (16.66)$$

just as the height of the ladder is the sum of the separations of its rungs (Fig. 16.39). The construction in Fig. 16.40 shows that the area under the plot of $\Delta G_{v+1/2}$ against $v + \frac{1}{2}$ is equal to the sum, and therefore to D_0 . The successive terms decrease linearly when only the x_e anharmonicity constant is taken into account and the inaccessible part of the spectrum can be estimated by linear extrapolation. Most actual plots differ from the linear plot as shown in Fig. 16.39, so the value of D_0 obtained in this way is usually an overestimate of the true value.

Example 16.5 Using a Birge-Sponer plot

The observed vibrational intervals of H_2^+ lie at the following values for $1 \leftarrow 0, 2 \leftarrow 1, \dots$ respectively (in cm^{-1}): 2191, 2064, 1941, 1821, 1705, 1591, 1479, 1368, 1257, 1145, 1033, 918, 800, 677, 548, 411. Determine the dissociation energy of the molecule.

Method Plot the separations against $v + \frac{1}{2}$, extrapolate linearly to the point cutting the horizontal axis, and then measure the area under the curve.



16.41 The Birge-Sponer plot used in Example 16.5. The area is obtained simply by counting the squares beneath the line or using the formula for the area of a right triangle.

Answer The points are plotted in Fig. 16.41, and a linear extrapolation is shown as a dotted line. The area under the curve (use the formula for the area of a triangle or count the squares) is 214. Each square corresponds to 100 cm^{-1} (refer to the scale of the vertical axis); hence the dissociation energy is $21\,400 \text{ cm}^{-1}$ (corresponding to 256 kJ mol^{-1}).

Self-test 16.7 The vibrational levels of HgH converge rapidly, and successive intervals are 1203.7 , 965.6 , 632.4 , and 172 cm^{-1} . Estimate the dissociation energy. [35.6 kJ mol^{-1}]

16.12 Vibration-rotation spectra

Each line of the high-resolution vibrational spectrum of a gas-phase heteronuclear diatomic molecule is found to consist of a large number of closely spaced components (Fig. 16.42). Hence, molecular spectra are often called **band spectra**. The separation between the components is of the order of 10 cm^{-1} , which suggests that the structure is due to rotational transitions accompanying the vibrational transition. A rotational change should be expected because classically we can think of the transition as leading to a sudden increase or decrease in the instantaneous bond length. Just as ice-skaters rotate more rapidly when they bring their arms in, and more slowly when they throw them out, so the molecular rotation is either accelerated or retarded by a vibrational transition.

(a) Spectral branches

A detailed analysis of the quantum mechanics of simultaneous vibrational and rotational changes shows that the rotational quantum number J changes by ± 1 during the vibrational transition of a diatomic molecule. If the molecule also possesses angular momentum about its axis, as in the case of the electronic orbital angular momentum of the paramagnetic molecule NO , then the selection rules also allow $\Delta J = 0$.

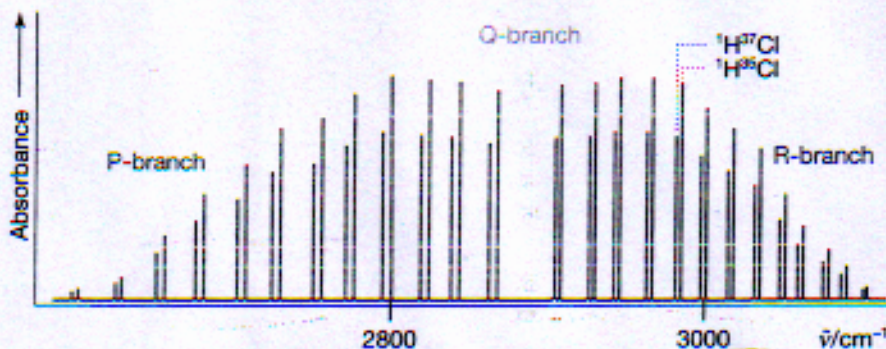
The appearance of the vibration-rotation spectrum of a diatomic molecule can be discussed in terms of the combined vibration-rotation terms, S :

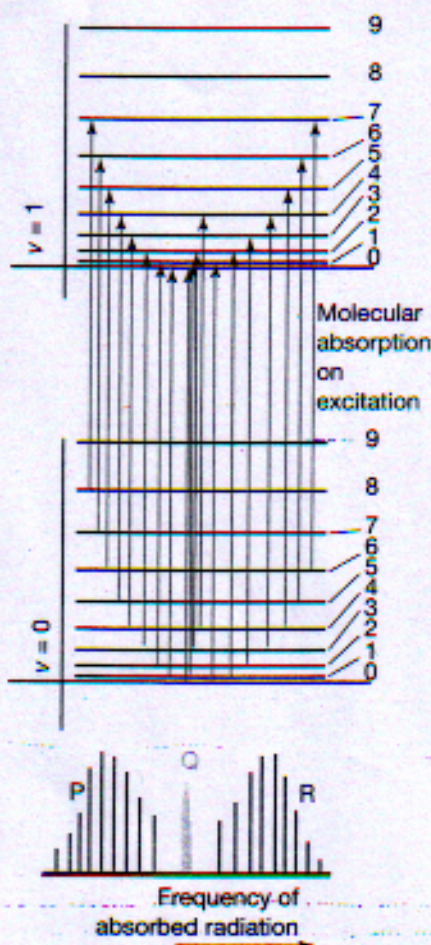
$$S(v, J) = G(v) + F(J) \quad (16.67)$$

If we ignore anharmonicity and centrifugal distortion,

$$S(v, J) = (v + \frac{1}{2})\tilde{\nu} + B_J(J + 1) \quad (16.68)$$

16.42 A high-resolution vibration-rotation spectrum of HCl . The lines appear in pairs because $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ both contribute (their abundance ratio is 3:1). There is no Q branch, because $\Delta J = 0$ is forbidden for this molecule.





16.43 The formation of P, Q, and R branches in a vibration-rotation spectrum. The intensities reflect the populations of the initial rotational levels.



16.44 The method of combination differences makes use of the fact that some transitions share a common level.

In a more detailed treatment, B is allowed to depend on the vibrational state because as v increases the molecule swells slightly and the moment of inertia changes. We shall continue with the simple expression initially.

When the vibrational transition $v + 1 \leftarrow v$ occurs, J changes by ± 1 and in some cases by 0 (when $\Delta J = 0$ is allowed). The absorptions then fall into three groups called **branches of the spectrum**. The **P branch** consists of all transitions with $\Delta J = -1$:

$$\tilde{\nu}_P(J) = S(v + 1, J - 1) - S(v, J) = \tilde{\nu} - 2BJ \quad (16.69a)$$

This branch consists of lines at $\tilde{\nu} - 2B, \tilde{\nu} - 4B, \dots$ with an intensity distribution reflecting both the populations of the rotational levels and the magnitude of the $J - 1 \leftarrow J$ transition moment (Fig. 16.43). The **Q branch** consists of all lines with $\Delta J = 0$, and its wavenumbers are all

$$\tilde{\nu}_Q(J) = S(v + 1, J) - S(v, J) = \tilde{\nu} \quad (16.69b)$$

for all values of J . This branch, when it is allowed (as in NO), appears at the vibrational transition wavenumber. In Fig. 16.43 there is a gap at the expected location of the Q branch because it is forbidden in HCl. The **R branch** consists of lines with $\Delta J = +1$:

$$\tilde{\nu}_R(J) = S(v + 1, J + 1) - S(v, J) = \tilde{\nu} + 2B(J + 1) \quad (16.69c)$$

This branch consists of lines displaced from $\tilde{\nu}$ to high wavenumber by $2B, 4B, \dots$

The separation between the lines in the P and R branches of a vibrational transition gives the value of B . Therefore, the bond length can be deduced without needing to take a pure rotational microwave spectrum. However, the latter is more precise.

(b) Combination differences

The rotational constant of the vibrationally excited state, B_1 (in general, B_v), is in fact slightly smaller than that of the ground vibrational state, B_0 , because the anharmonicity of the vibration results in a slightly extended bond in the upper state. As a result, the Q branch (if it exists) consists of a series of closely spaced lines. The lines of the R branch converge slightly as J increases; and those of the P branch diverge:

$$\begin{aligned} \tilde{\nu}_R(J) &= \tilde{\nu} - (B_1 + B_0)J + (B_1 - B_0)J^2 \\ \tilde{\nu}_Q(J) &= \tilde{\nu} + (B_1 - B_0)J(J + 1) \end{aligned} \quad (16.70)$$

$$\tilde{\nu}_P(J) = \tilde{\nu} + (B_1 + B_0)(J + 1) + (B_1 - B_0)(J + 1)^2$$

To determine the two rotational constants individually, we use the method of **combination differences**. This procedure is used widely in spectroscopy to extract information about a particular state. It involves setting up expressions for the difference in the wavenumbers of transitions to a common state; the resulting expression then depends solely on properties of the other state.

As can be seen from Fig. 16.44, the transitions $\tilde{\nu}_R(J - 1)$ and $\tilde{\nu}_P(J + 1)$ have a common upper state, and hence can be anticipated to depend on B_0 . Indeed, it is easy to show from eqn 70 that

$$\tilde{\nu}_R(J - 1) - \tilde{\nu}_P(J + 1) = 4B_0(J + \frac{1}{2}) \quad (16.71a)$$

Therefore, a plot of the combination difference against $J + \frac{1}{2}$ should be a straight line of slope $4B_0$, so the rotational constant of the molecule in the state $v = 0$ can be determined. (Any deviation from a straight line is a consequence of centrifugal distortion, so that effect can be investigated too.) Similarly, $\tilde{\nu}_R(J)$ and $\tilde{\nu}_P(J)$ have a common lower state, and hence their combination difference gives information about the upper state:

$$\tilde{\nu}_R(J) - \tilde{\nu}_P(J) = 4B_1(J + \frac{1}{2}) \quad (16.71b)$$

The two rotational constants of $^1\text{H}^{35}\text{Cl}$ found in this way are $B_0 = 10.440 \text{ cm}^{-1}$ and $B_1 = 10.136 \text{ cm}^{-1}$.

16.13 Vibrational Raman spectra of diatomic molecules

The gross selection rule for vibrational Raman transitions is that the polarizability should change as the molecule vibrates. As homonuclear and heteronuclear diatomic molecules swell and contract during a vibration, the control of the nuclei over the electrons varies, and hence the molecular polarizability changes. Both types of diatomic molecule are therefore vibrationally Raman active. The specific selection rule for vibrational Raman transitions in the harmonic approximation is $\Delta v = \pm 1$. The formal basis for the gross and specific selection rules is given in the following justification.

Justification 16.8

The gross selection rule is based on an analysis of the transition dipole moment $\langle \nu_f | \mu | \nu_i \rangle$, where, as in Justification 16.4, we use the Born-Oppenheimer approximation, and neglect the effect of rotation and electron spin. For simplicity, we consider a one-dimensional harmonic oscillator (like a diatomic molecule).

First, we use eqn 47 to write the transition dipole moment as

$$\mu_{fi} = \langle \nu_f | \mu | \nu_i \rangle = \langle \nu_f | \alpha | \nu_i \rangle \mathcal{E} = \langle \nu_f | \alpha(x) | \nu_i \rangle \mathcal{E}$$

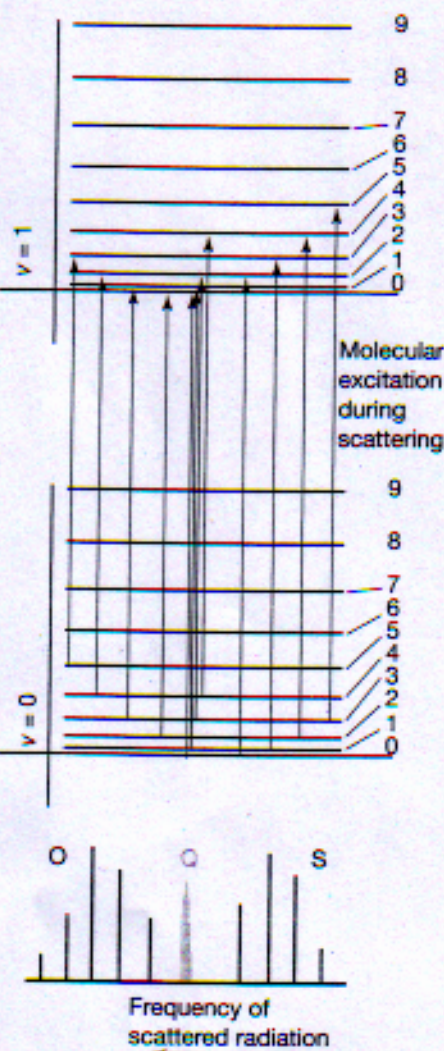
where $\alpha(x) = (\epsilon | \alpha | \epsilon)$ is the polarizability of the molecule, which we expect to be a function of small displacements x from the equilibrium bond length of the molecule. Next, we expand $\alpha(x)$ as a Taylor series, so the transition dipole moment becomes

$$\mu_{fi} = \left\langle \nu_f \left| \alpha(0) + \left(\frac{d\alpha}{dx} \right)_0 x + \dots \right| \nu_i \right\rangle \mathcal{E} = \langle \nu_f | \nu_i \rangle \alpha(0) \mathcal{E} + \left(\frac{d\alpha}{dx} \right)_0 \langle \nu_f | x | \nu_i \rangle \mathcal{E} + \dots$$

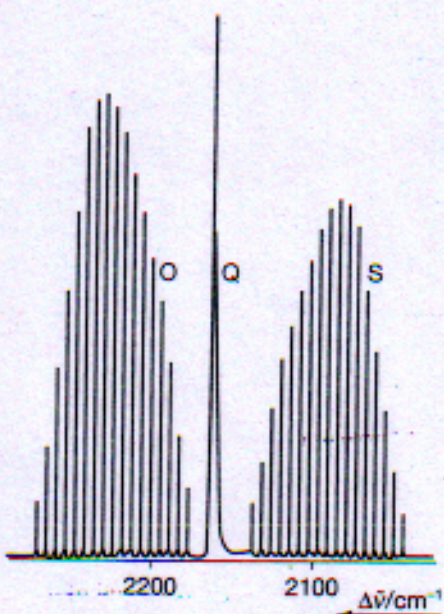
The term containing $\langle \nu_f | \nu_i \rangle$ vanishes for $f \neq i$ because the harmonic oscillator wavefunctions are orthogonal. Therefore, the vibration is Raman active if $(d\alpha/dx)_0 \neq 0$ and $\langle \nu_f | x | \nu_i \rangle \neq 0$. Therefore, the polarizability of the molecule must change during the vibration; this is the gross selection rule of Raman spectroscopy. Also, we know from Justification 16.7 that $\langle \nu_f | x | \nu_i \rangle \neq 0$ if $\nu_f - \nu_i = \pm 1$; this is the specific selection rule of Raman spectroscopy.

The lines to high frequency of the incident radiation, the anti-Stokes lines, are those for which $\Delta v = -1$. The lines to low frequency, the Stokes lines, correspond to $\Delta v = +1$. The intensities of the anti-Stokes and Stokes lines are governed largely by the Boltzmann populations of the vibrational states involved in the transition. It follows that anti-Stokes lines are usually weak because very few molecules are in an excited vibrational state initially.

In gas-phase spectra, the Stokes and anti-Stokes lines have a branch structure arising from the simultaneous rotational transitions that accompany the vibrational excitation (Fig. 16.45). The selection rules are $\Delta J = 0, \pm 2$ (as in pure rotational Raman



16.45 The formation of O, Q, and S branches in a vibration-rotation Raman spectrum of a linear rotor. Note that the frequency scale runs in the opposite direction to that in Fig. 16.43, because the higher energy transitions (on the right) extract more energy from the incident beam and leave it at lower frequency.



16.46 The structure of a vibrational line in the vibrational Raman spectrum of carbon monoxide, showing the O, Q, and S branches.

Table 16.2* Properties of diatomic molecules

	$\tilde{\nu}/\text{cm}^{-1}$	B/cm^{-1}	$k/(\text{N m}^{-1})$
$^1\text{H}_2$	4400	60.86	575
$^1\text{H}^{35}\text{Cl}$	2991	10.59	516
$^1\text{H}^{127}\text{I}$	2309	6.61	313
$^{35}\text{Cl}_2$	560	0.244	323

* More values are given in the Data section. See Tables 14.2 and 14.3 for related information (on D_e and R_e).

spectroscopy), and give rise to the O branch ($\Delta J = -2$), the Q branch ($\Delta J = 0$), and the S branch ($\Delta J = +2$):

$$\begin{aligned}\tilde{\nu}_O(J) &= \tilde{\nu}_1 - \tilde{\nu} - 2B + 4BJ \\ \tilde{\nu}_Q(J) &= \tilde{\nu}_1 - \tilde{\nu} \\ \tilde{\nu}_S(J) &= \tilde{\nu}_1 - \tilde{\nu} + 6B + 4BJ\end{aligned}\quad (16.72)$$

Note that, unlike in infrared spectroscopy, a Q branch is obtained for all linear molecules. The spectrum of CO, for instance, is shown in Fig. 16.46: the structure of the Q branch arises from the differences in rotational constants of the upper and lower vibrational states.

The information available from vibrational Raman spectra adds to that from infrared spectroscopy because homonuclear diatomics can also be studied. The spectra can be interpreted in terms of the force constants, dissociation energies, and bond lengths, and some of the information obtained is included in Table 16.2.

The vibrations of polyatomic molecules

There is only one mode of vibration for a diatomic molecule, the bond stretch. In polyatomic molecules there are several modes of vibration because all the bond lengths and angles may change and the vibrational spectra are very complex. Nonetheless, we shall see that infrared and Raman spectroscopy can be used to obtain information about the structure of systems as large as animal and plant tissues (Box 16.2).

16.14 Normal modes

We begin by calculating the total number of vibrational modes of a polyatomic molecule. We then see that we can choose combinations of these atomic displacements that give the simplest description of the vibrations.

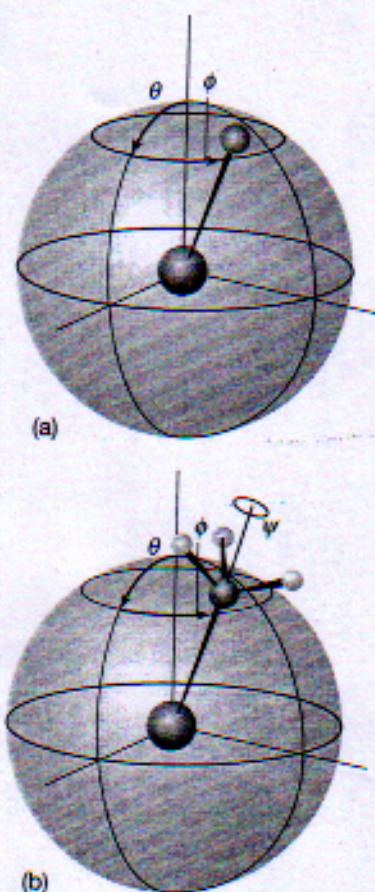
(a) The number of vibrational modes

As shown in the justification below, for a nonlinear molecule that consists of N atoms, there are $3N - 6$ independent modes of vibration. If the molecule is linear, there are $3N - 5$ independent vibrational modes.

Box 16.2 Vibrational spectroscopy of biological cells

Optical microscopes can now be combined with infrared and Raman spectrometers and the vibrational spectra of specimens as small as single biological cells obtained. The techniques of vibrational microscopy provide details of cellular events that cannot be observed with traditional light or electron microscopy.

Although infrared and Raman microscopes are complex devices, the principles behind their operation are simple: radiation illuminates a small area of the sample, and the transmitted, reflected, or scattered light is first collected by a microscope and then analysed by a spectrometer. The sample is then moved by very small increments along a



16.47 (a) The orientation of a linear molecule requires the specification of two angles.
 (b) The orientation of a nonlinear molecule requires the specification of three angles.

Justification 16.9

The total number of coordinates needed to specify the locations of N atoms is $3N$. Each atom may change its location by varying one of its three coordinates (x , y , and z), so the total number of displacements available is $3N$. These displacements can be grouped together in a physically sensible way. For example, three coordinates are needed to specify the location of the centre of mass of the molecule, so three of the $3N$ displacements correspond to the translational motion of the molecule as a whole. The remaining $3N - 3$ are non-translational 'internal' modes of the molecule.

Two angles are needed to specify the orientation of a linear molecule in space: in effect, we need to give only the latitude and longitude of the direction in which the molecular axis is pointing (Fig. 16.47a). However, three angles are needed for a nonlinear molecule because we also need to specify the orientation of the molecule around the direction defined by the latitude and longitude (Fig. 16.47b). Therefore two (linear) or three (nonlinear) of the $3N - 3$ internal displacements are rotational. This leaves $3N - 5$ (linear) or $3N - 6$ (nonlinear) displacements of the atoms relative to one another: these are the vibrational modes. It follows that the number of modes of vibration N_{vb} is $3N - 5$ for linear molecules and $3N - 6$ for nonlinear molecules.

Illustration 16.6

Water, H_2O , is a nonlinear triatomic molecule, and has three modes of vibration (and three modes of rotation); CO_2 is a linear triatomic molecule, and has four modes of vibration (and only two modes of rotation). Even a middle-sized molecule such as naphthalene (C_{10}H_8) has 48 distinct modes of vibration.

(b) Combinations of displacements

The next step is to find the best description of the modes. One choice for the four modes of CO_2 , for example, might be the ones in Fig. 16.48a and c. This illustration shows the stretching of one bond (the mode ν_1), the stretching of the other (ν_2), and the two perpendicular bending modes (ν_3). The description, while permissible, has a disadvantage: when one CO bond vibration is excited, the motion of the C atom sets the other CO bond in motion, so energy flows backwards and forwards between ν_1 and ν_2 . Moreover, the position of the centre of mass of the molecule varies in the course of either vibration.

The description of the vibrational motion is much simpler if linear combinations of ν_1 and ν_2 are taken. For example, one combination is ν_1 in Fig. 16.48b: this mode is the **symmetric stretch**. In this mode, the C atom is buffeted simultaneously from each side and the motion continues indefinitely. Another mode is ν_3 , the **antisymmetric stretch**, in which the two O atoms always move in the same direction and opposite to that of the C atom. Both modes are independent in the sense that, if one is excited, then it does not excite the other. They are two of the 'normal modes' of the molecule, its independent, collective vibrational displacements. The two other normal modes are the bending modes ν_2 . In general, a **normal mode** is an independent, synchronous motion of atoms or groups of atoms that may be excited without leading to the excitation of any other normal mode.

The four normal modes of CO_2 , and the N_{vb} normal modes of polyatomics in general, are the key to the description of molecular vibrations. Each normal

Table 16.3* Typical vibrational wavenumbers, $\tilde{\nu}/\text{cm}^{-1}$

C—H stretch	2850–2960
C—H bend	1340–1465
C—C stretch	700–1250
C=C stretch	1620–1680

* More values are given in the Data section.

The web site contains links to sites with free software for quantum mechanical calculations of frequencies and atomic displacements of normal modes of simple molecules.

The web site contains links to databases of infrared spectra.

perpendicular to the principal axis, so transitions involving them lead to a **perpendicular band** in the spectrum. The latter bands eliminate the linearity of the molecule, and as a result a Q branch is observed; a parallel band does not have a Q branch.

The active modes are subject to the specific selection rule $\Delta v_i = \pm 1$ in the harmonic approximation, so the wavenumber of the fundamental transition (the 'first harmonic') of each active mode is $\tilde{\nu}_i$. From the analysis of the spectrum, a picture may be constructed of the stiffness of various parts of the molecule: that is, we can establish its **force field**, the set of force constants corresponding to all the displacements of the atoms. The force field may also be estimated by using the semi-empirical and *ab initio* computational techniques described in Section 14.9. Superimposed on the simple force field scheme are the complications arising from anharmonicities and the effects of molecular rotation. Very often the sample is a liquid or a solid, and the molecules are unable to rotate freely. In a liquid, for example, a molecule may be able to rotate through only a few degrees before it is struck by another, so it changes its rotational state frequently. This random changing of orientation is called **tumbling**.

The lifetimes of rotational states in liquids are very short, so in most cases the rotational energies are ill-defined. Collisions occur at a rate of about 10^{13} s^{-1} and even allowing for only a 10 per cent success rate in knocking the molecule into another rotational state, a lifetime broadening (eqn 26) of more than 1 cm^{-1} can easily result. The rotational structure of the vibrational spectrum is blurred by this effect, so the infrared spectra of molecules in condensed phases usually consist of broad lines spanning the entire range of the resolved gas-phase spectrum, and showing no branch structure.

One very important application of infrared spectroscopy to condensed phase samples, and for which the blurring of the rotational structure by random collision is a welcome simplification, is chemical analysis. The vibrational spectra of different groups in a molecule give rise to absorptions at characteristic frequencies. Their intensities are also transferable between molecules. Consequently, the molecules in a sample can often be identified by examining its infrared spectrum and referring to a table of characteristic frequencies and intensities (Table 16.3).

16.16 Vibrational Raman spectra of polyatomic molecules

The normal modes of vibration of molecules are Raman active if they are accompanied by a changing polarizability. It is sometimes quite difficult to judge by inspection when this is so. The symmetric stretch of CO_2 , for example, alternately swells and contracts the molecule: this motion changes the polarizability of the molecule, so the mode is Raman active. The other modes of CO_2 leave the polarizability unchanged, so they are Raman inactive.

A more exact treatment of infrared and Raman activity of normal modes leads to the **exclusion rule**:

If the molecule has a centre of symmetry, then no modes can be both infrared and Raman active.

(A mode may be inactive in both.) Because it is often possible to judge intuitively if a mode changes the molecular dipole moment, we can use this rule to identify modes that are not Raman active. The rule applies to CO_2 but to neither H_2O nor CH_4 because they have no centre of symmetry. In general, it is necessary to use group theory to predict whether a mode is infrared or Raman active (Section 16.17).