16

Rotational and vibrational spectra

Check-list of key ideas

1. The classification of spectra as *emission*, *absorption*, and *Raman* and the experimental techniques used for their study (Section 16.1).

2. The general principles of *Fourier transform spectroscopy* (Section 16.1).

3. The *Einstein transition probabilities*, and the coefficients of *stimulated absorption and emission* and of *spontaneous emission* (Section 16.2).

4. The *transition dipole moment* (eqn 10), the *gross selection rule*, and the *specific selection rules* of transitions (Section 16.2).

5. The contributions to spectral *linewidths* (Section 16.3), particularly *Doppler broadening* (eqn 11) and *lifetime broadening* (eqn 12).

6. The principles of *Lamb-dip spectroscopy* (Section 16.3).

7. The *rotational energy levels* of *rigid rotors* (Section 16.4) in terms of the *moments of inertia* of molecules and their *rotational constants* (eqns 14 to 16).

8. The *Stark effect* on the rotational energies of polar molecules in electric fields (eqn 17).

9. The effect of *centrifugal distortion* on the rotational energy levels of molecules (eqn 18).

10. The *selection rules* and transition moments of pure rotational transitions and the contribution of state populations to the intensities of spectral lines (Section 16.5).

11. The *electric polarizabilities* of molecules and their contribution to the detection of rotational Raman transitions (Section 16.6).

12. The *Stokes* and *anti-Stokes lines* in a Raman spectrum (eqn 21).

13. The *harmonic approximation* for the description of the vibrations of molecules (Section 16.7) and the *vibrational terms* of a diatomic molecule (eqn 22).

14. The *anharmonicity* of molecular vibrations, its description in terms of the *Morse potential* (eqn 23), and its effect on the vibrational spectrum (Section 16.7).

15. The *selection rules* for vibrational transitions and the appearance of vibrational spectra (Section 16.8).

16. The use of the *Birge–Sponer extrapolation* to determine dissociation energies (Section 16.8 and Example 16.9).

17. The formation of *P, Q, and R branches* in *vibration–rotation spectra* (Section 16.9).

18. The *vibrational Raman spectra* of diatomic molecules (Section 16.10).

19. The number of vibrations of polyatomic molecules (eqn 28) and their description in terms of *normal modes* (Section 16.11).

20. The *symmetry analysis* of normal modes and their *infrared and Raman activities* (Section 16.11 and Examples 16.10 to 16.12).

21. The appearance and analysis of the infrared spectra of polyatomic molecules (Section 16.12).

22. The *exclusion rule* for centrosymmetric molecules (Section 16.13) and information from the *depolarization ratios* of Raman transitions about the symmetries of normal modes (Section 16.13).

The origin of spectral lines in molecular spectroscopy is the emission or absorption of a photon when the energy of a molecule changes. The difference from atomic spectroscopy is that the energy of a molecule can change not only as a result of electronic transitions but also because it can undergo transitions between its rotational and vibrational states. Molecular spectra are therefore more complex than atomic spectra. However, they also contain information relating to more properties, and their analysis leads to values of bond strengths, lengths, and angles. They also provide a way of measuring a variety of molecular properties, particularly electric dipole moments.

A pure rotational spectrum (one in which only the rotational state of the molecule changes) can be observed, but vibrational spectra of gaseous samples show features that arise from simultaneous rotational transitions. Similarly, electronic spectra (Chapter 17) show features arising from simultaneous vibrational and rotational transitions. The simplest way of dealing with these complexities is to tackle each type of transition in turn, and then to see how simultaneous changes affect the appearance of the spectrum.

General features of spectroscopy

All types of spectra have some features in common, and we examine these first.

16.1 Experimental techniques

In **emission spectroscopy**, a molecule undergoes a transition from a state of high energy E_1 to a state of lower energy E_2 and emits the excess energy as a photon. In **absorption spectroscopy**, the net absorption[1] of nearly

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[1] We say *net* absorption, since it will become clear that when a sample is irradiated, both absorption and emission at a given frequency are stimulated, and the detector measures the difference, the net absorption.

monochromatic incident radiation is monitored as it is swept over a range of frequencies. The energy $h\nu$ of the photon emitted or absorbed, and therefore the frequency ν of the radiation emitted or absorbed, is given by the same Bohr frequency condition as we met for atoms:

$$h\nu = E_1 - E_2 \tag{1}$$

This relation is often expressed in terms of the **vacuum wavelength** λ (usually in nanometers)

$$\lambda = \frac{c}{\nu} \tag{2a}$$

or the **vacuum wavenumber** $\tilde{\nu}$

$$\tilde{\nu} = \frac{\nu}{c} \tag{2b}$$

The units of the latter are almost always chosen as cm^{-1}. Figure 16.1 summarizes the frequencies, wavelengths, and wavenumbers of the various regions of the electromagnetic spectrum.

Emission and absorption spectroscopy give the same information about energy level separations, but practical considerations generally determine which technique is employed. In practice, emission spectroscopy, if it is used at all, is used only for optical and ultraviolet spectroscopy; absorption spectroscopy is much more widely used, and we shall concentrate on it.

All absorption spectrometers consist of a source of radiation, a sample cell, usually a dispersing element, and a detector, and the characteristics of each component depend on the region of the electromagnetic spectrum being considered. Most spectrometers also include a monochromator.

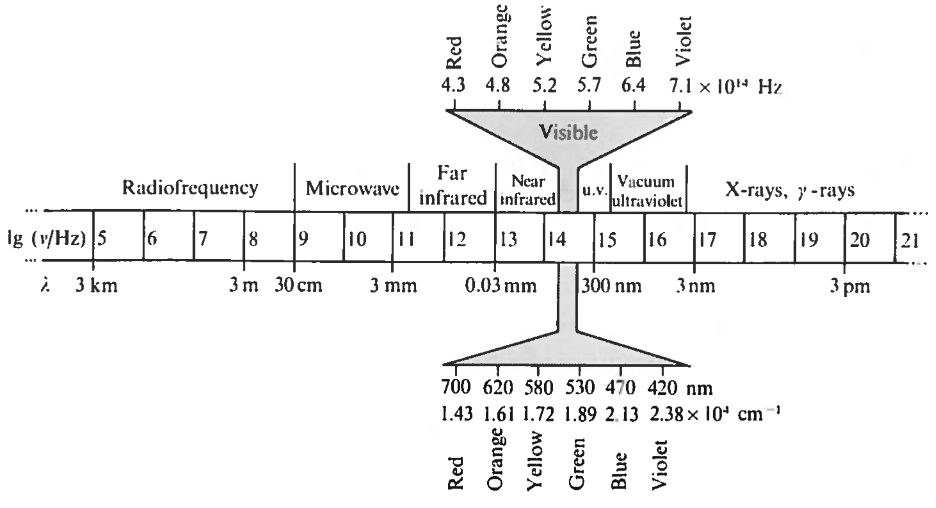


Fig. 16.1 The electromagnetic spectrum and the classification of the spectral regions.

Sources of radiation

The source generally produces radiation spanning a range of frequencies, but in a few cases it generates monochromatic—single frequency—radiation. One such case is the **klystron**, an electronic device used to generate microwaves. Lasers—which we discuss in more detail in the next chapter—give monochromatic radiation that can often be tuned over a range of frequencies. For the far infrared, the source is a mercury arc inside a quartz envelope, most of the radiation being generated by the hot quartz. A **Nernst filament** is used to generate radiation in the near infrared. This consists of a heated ceramic filament containing rare-earth oxides, which emits radiation closely resembling that of a true black body. For the visible region of the spectrum, a tungsten/iodine lamp is used, which gives out intense white light. A discharge through deuterium gas or xenon in quartz is still widely used for the near ultraviolet.

For certain applications, **synchrotron radiation** from a **synchrotron storage ring** is appropriate. A synchrotron ring consists of an electron beam (actually a series of closely spaced packets) travelling in a circle of several metres in diameter. Since accelerated charges emit radiation, and electrons travelling in a circle are being constantly accelerated by the forces that constrain them to their path, the beam emits radiation. The emitted radiation spans a wide range of frequencies, up to and including the far ultraviolet, and in all except the microwave region is much more intense than can be obtained by most conventional sources. The disadvantage of the source is that it is so large and costly that it is essentially a national facility, and not a laboratory commonplace.

The dispersing element and Fourier spectroscopy

In all but specialized techniques using monochromatic microwave radiation, spectrometers include a component for separating the frequencies of the radiation so that the variation of the absorption with frequency can be monitored. In conventional spectrometers, this component is a **dispersing element** that separates different frequencies into different spatial directions.

The simplest dispersing element is a glass or quartz prism (Fig. 16.2), which utilizes the variation of refractive index with frequency of the incident radiation. High-frequency radiation generally (but not always) results in a higher refractive index than low-frequency radiation, and therefore undergoes a greater deflection when passing through the prism. Problems of absorption by the prism can be avoided by replacing it by a **diffraction grating**. A diffraction grating consists of a glass or ceramic plate into which fine grooves have been cut about 1000 nm apart (comparable to the wavelength of visible light) and covered with a reflective aluminium coating. The grating causes interference between waves reflected from its surface, and constructive interference occurs at specific angles that depend on the frequency of the radiation being used. By shaping the grooves appropriately, the process called **blazing** (Fig. 16.3), the intensity of the interference pattern can be enhanced.

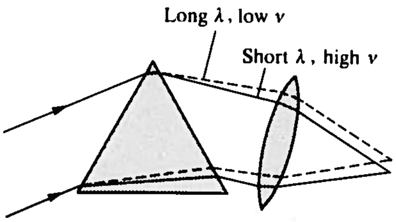


Fig. 16.2 One simple dispersing element is a prism, which separates frequencies spatially by making use of the higher refractive index of high-frequency radiation. The shortest wavelengths for which a glass prism can be used is about 400 nm, but quartz can be used down to 180 nm.

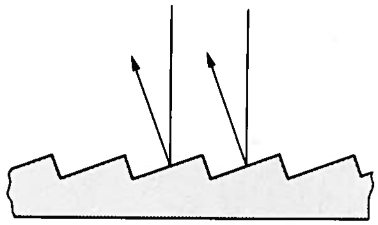


Fig. 16.3 A diffraction grating is 'blazed' as shown here in order to enhance the intensity of the diffracted radiation in each direction.

Fourier transform techniques

Modern spectrometers, particularly those operating in the infrared, now almost always use **Fourier transform techniques** of spectral detection and analysis. The heart of a Fourier transform spectrometer is a **Michelson interferometer**, which is a device for analyzing the frequencies present in a composite signal. The total signal from a sample is the analogue of a chord played on a piano, and the Fourier transformation of the signal is equivalent to the separation of the chord into its individual notes, the spectrum. The advantage of this procedure is the greater sensitivity that stems from the fact that the detector monitors the entire spectrum simultaneously rather than one frequency at a time.

The Michelson interferometer works by splitting the beam from the sample into two (Fig. 16.4) and introducing a varying path difference p into one of them. When the two components recombine, there is a phase difference between them, and they interfere either constructively or destructively depending on the extra path that one has taken. The detected signal oscillates as the two components alternately come into and out of phase as p is changed (Fig. 16.5), and if the radiation has wavenumber $\tilde{\nu}$, the detected signal varies with p as

$$I(p) = I(\tilde{\nu}) \cos 2\pi\tilde{\nu}p$$

Hence, the interferometer converts the presence of a particular component in the signal into a variation in intensity of the radiation reaching the detector. An actual signal consists of radiation spanning a large number of wavenumbers, and the total intensity at the detector is the sum of all their oscillating intensities:

$$I(p) = \int_0^{\infty} I(\tilde{\nu}) \cos 2\pi\tilde{\nu}p \, d\tilde{\nu}$$

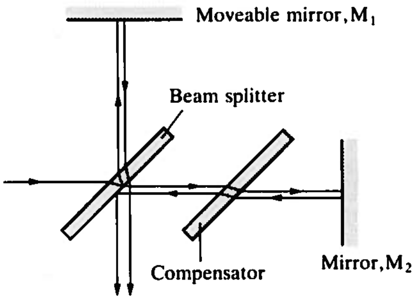


Fig. 16.4 A Michelson interferometer. The beam-splitting element divides the incident beam into two beams with a path difference that depends on the location of the mirror M_1. The compensator ensures that both beams pass through the same thickness of material.

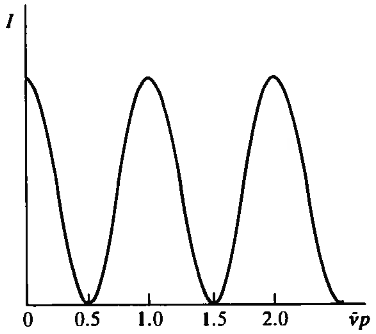


Fig. 16.5 An interferogram produced as the path length p is changed in the interferometer shown in Fig. 16.4 and radiation of wavelength λ is present.

Example 16.1: *Calculating a Fourier transform spectrum*

Draw the total signal that would be expected for a signal consisting of three wavenumbers, one of 1000 cm^{-1} of intensity I, another of wavenumber 1100 cm^{-1} of intensity $2I$, and a third of wavenumber 1150 cm^{-1} of intensity $\frac{1}{2}I$.

Answer. The only contributions to the integral defining $I(p)$ are at the three specified wavenumbers, so the integral consists of the three terms

$$I(p) = I\cos 2\pi \times \frac{1000p}{\text{cm}} + 2I\cos 2\pi \times \frac{1100p}{\text{cm}} + \tfrac{1}{2}I\cos 2\pi \times \frac{1150p}{\text{cm}}$$

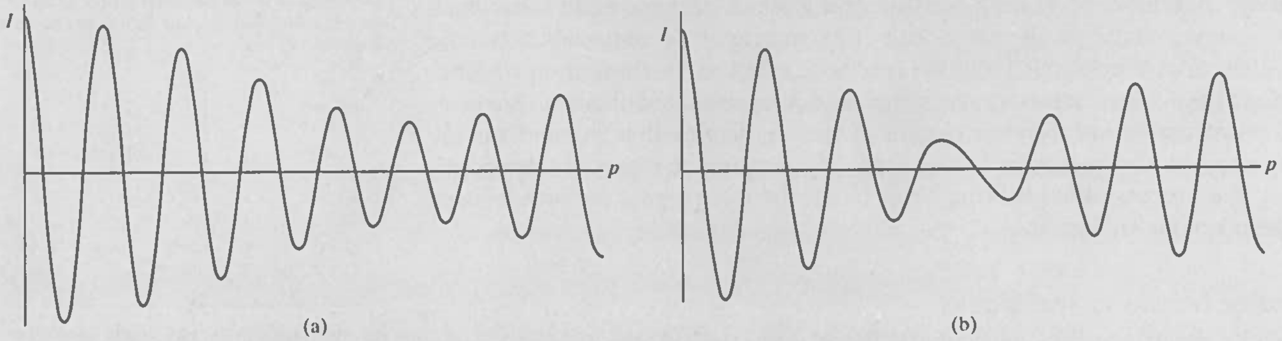


Fig. 16.6 (a) The interferogram obtained under the circumstances described in Example 16.1 when three components are present in the radiation and (b) the interferogram when five components are present.

The plot of $I(p)/I$ against p in the range $p = 0$ to 0.1 cm is shown in Fig. 16.6a, and shows the signal that would be detected.

Comment. It is very easy to program calculations like these for a computer, and to explore how the signal changes as different components are included in the spectrum.

Exercise. Include two further components in the spectrum, one at 950 cm^{-1} of intensity $2I$ and another at 975 cm^{-1} of intensity $0.75I$. [Fig. 16.6b]

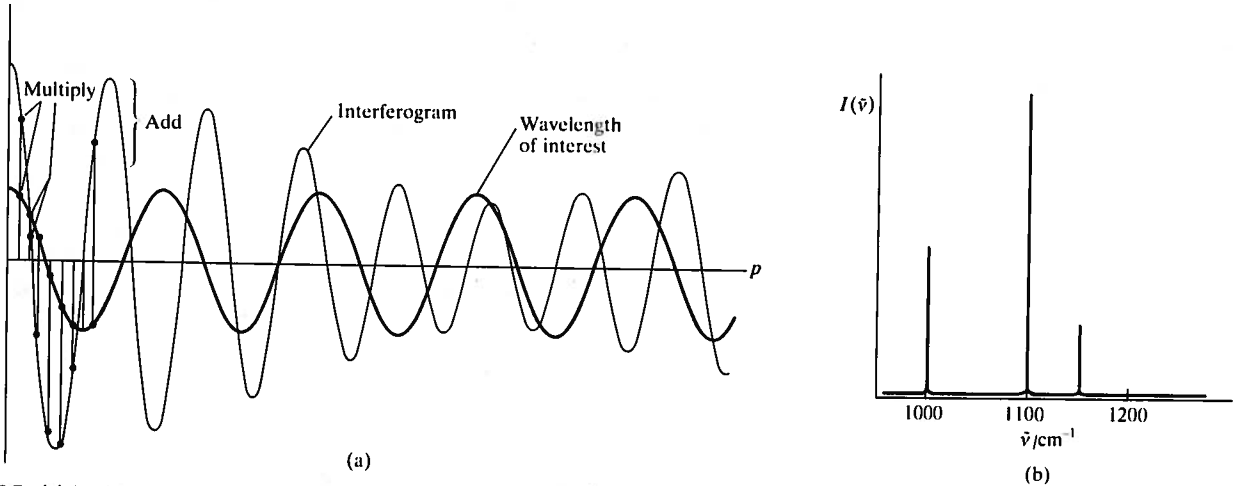
The problem is to find $I(\tilde{\nu})$, the variation of intensity with wavenumber, which is the spectrum we require. This step is a standard technique of mathematics, and is the 'Fourier transformation' step from which this form of spectroscopy takes its name. Specifically:

$$I(\tilde{\nu}) = \int_0^{\infty} I(p) \cos 2\pi\tilde{\nu}p \, \mathrm{d}p$$

Thus, as we illustrate schematically in Fig. 16.7, we take the signal $I(p)$ for each path difference, multiply the intensity at each value of p by the value of $\cos 2\pi\tilde{\nu}p$, and add all the products together. When the result is plotted against wavenumber, we get the absorption spectrum (Fig. 16.7b). In practice, the Fourier analysis step is carried out in a computer built into the spectrometer.

Detectors

The third component of a spectrometer is the **detector**, the device that converts incident radiation into an electric current for the appropriate signal processing or plotting. Radiation-sensitive semiconductor devices are increasingly dominating this role in the spectrometer. However, in the optical and ultraviolet region, photographic recording or a **photomultiplier** are widely used. In the latter device, an incident photon ejects an electron from a photosensitive surface, the electron is accelerated by a potential difference, and ejects a shower of electrons where it strikes a screen. These



(a)

(b)

Fig. 16.7 (a) A schematic diagram illustrating the principle of the extraction of a Fourier transform of an interferogram. At each value of p the observed spectrum is multiplied by the amplitude of the cosine function at the wavelength of interest. The sum of the products (the integration) is zero if the harmonic is not present in the signal but is non-zero if it is present. (b) When the procedure is repeated for all wavelengths, the function obtained is the absorption spectrum of the sample.

electrons are accelerated, and each one releases a further shower on impact with another screen. Thus the impact of the initial photon is converted into a cascade of electrons, which is converted into a current in an external circuit.

Although semiconductor detectors are increasingly being used in the infrared, thermocouples are still widely used. A thermocouple detector consists typically of a blackened gold foil to which are attached thermoelectric alloys. A **thermistor bolometer** is essentially a resistance thermometer, and is typically formed from a mixture of oxides deposited on quartz. In each case the radiation is chopped by a shutter that rotates in the beam so that an alternating signal is obtained from the detector (which is easier to amplify than a steady signal). A microwave detector is typically a **crystal diode** consisting of a tungsten tip in contact with a semiconductor, such as germanium, silicon, or gallium arsenide.

The sample

The highest resolution is obtained when the sample is gaseous and of such low pressure that collisions between the molecules are infrequent. Gaseous samples are essential for rotational (microwave) spectroscopy, for only then can molecules rotate freely. To achieve sufficient absorption, the path lengths of gaseous samples must be very long, of the order of metres; long path lengths are achieved by multiple passage of the beam between two parallel mirrors at each end of the sample cavity.

For infrared spectroscopy, the sample is typically a liquid held between windows of sodium chloride (which is transparent down to $700\,\mathrm{cm^{-1}}$) or potassium bromide (down to $400\,\mathrm{cm^{-1}}$). Other ways of preparing the sample include grinding into a paste with 'Nujol', a hydrocarbon oil, or pressing it into a solid disk, perhaps with powdered potassium bromide.

Raman spectroscopy

In **Raman spectroscopy** the energy levels of molecules are explored by examining the frequencies present in the radiation scattered by molecules. In a typical experiment, a monochromatic incident beam—typically in the visible region of the spectrum—is passed through the sample and the radiation scattered perpendicular to the beam is monitored. Some of the incident photons collide with the molecules, give up some of their energy, and emerge with a lower energy. These scattered photons constitute the lower-frequency **Stokes radiation** from the sample. Other incident photons may collect energy from the molecules (if they are already excited), and emerge as higher-frequency **anti-Stokes radiation**. The shifts in frequency of the scattered radiation from the incident radiation are quite small, and the latter must be very monochromatic if the shifts are to be observed. Moreover, the intensity of scattered radiation is low, and so very intense incident beams are needed. Lasers are ideal in both respects, and have entirely displaced the mercury arcs used originally. Detection is usually with a photomultiplier.

16.2 The intensities of spectral lines

A glance at the spectra (whether emission, absorption, or Raman) illustrated in this chapter and the next shows that their lines occur with a variety of intensities. We shall also see that some lines that might be expected to occur do not appear at all. To account for these features, we must see how the intensities of spectral lines depend on the numbers of molecules in various states and how strongly individual transitions are able to interact with the electromagnetic field and generate or absorb photons.

The Einstein transition probabilities

Einstein considered the question of the rates of transitions between two levels in the presence of an electromagnetic field, and wrote the **transition rate**[2] w from the lower to the upper state as

$$w = B\rho \qquad (3)$$

B is the **Einstein coefficient of stimulated absorption** and ρ is the energy density of radiation at the frequency of the transition. If the molecule is exposed to black-body radiation from a source of temperature T, ρ is given by the Planck distribution (eqn 12 of Section 11.2 expressed in terms of frequency[3]):

$$\rho = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1} \qquad (4)$$

The coefficient B depends only on the wavefunctions of the states involved in the transition, and we describe it in more detail later. For the time being we can treat B as an empirical parameter that characterizes the transition. The total **rate of absorption** W, the number of molecules undergoing excitation, is the transition rate of a single molecule multiplied by the number of molecules N in the lower state:

$$W = Nw \qquad (5)$$

Einstein considered that the radiation was also able to induce the molecule in the upper state to undergo a transition to the lower state, and hence to generate a photon of frequency ν. Thus, he wrote the rate of this **stimulated emission** as

$$w' = B'\rho \qquad (6)$$

where B' is the **Einstein coefficient of stimulated emission**. However, he

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[2] Specifically, w is the rate of change of probability of the molecule being found in the upper state:

$$w = \frac{dP}{dt}$$

[3] The energy density is expressed in terms of frequency by writing

$$d\mathcal{U} = \rho(\nu)\,d\nu$$

in place of

$$d\mathcal{U} = \rho(\lambda)\,d\lambda$$

The relation between the ρ used here, which is $\rho(\nu)$, and $\rho(\lambda)$ in eqn 12 of Section 12.2 is then obtained using

$$d\nu = \frac{-c\,d\lambda}{\lambda^2}$$

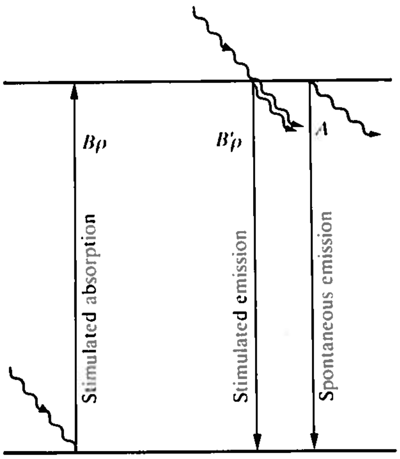


Fig. 16.8 The processes that account for absorption and emission of radiation and the attainment of thermal equilibrium. The excited state can return to the lower state spontaneously as well as by a process stimulated by radiation already present at the transition frequency.

realized that this was not the only means by which the excited state could generate radiation and return to the lower state. If it were, the total rate of return would be $N'w'$, and at thermal equilibrium, when the rate of absorption is equal to the rate of emission, we would be able to write

$$NB\rho = N'B'\rho$$

which rearranges to

$$\frac{N'}{N} = \frac{B}{B'}$$

However, it is known from very general grounds (which will be derived in Chapter 19), that the populations of the two states are given by the Boltzmann distribution:

$$\frac{N'}{N} = e^{-h\nu/kT} \qquad h\nu = E' - E$$

The ratio of populations should therefore be temperature-dependent, but the ratio of the Einstein coefficients is independent of the temperature.

To resolve this inconsistency, Einstein proposed that the upper state was able to discard energy by **spontaneous emission** at a rate that is independent of the intensity of radiation already present (Fig. 16.8). He therefore wrote the total rate of transition to a lower state as

$$w' = A + B'\rho \tag{7}$$

A is the **Einstein coefficient of spontaneous emission**. The overall rate of emission is

$$W' = N'(A + B'\rho) \tag{8}$$

At thermal equilibrium, the rates of emission and absorption are equal, and so

$$NB\rho = N'(A + B'\rho)$$

Since the radiation intensity no longer cancels, and is temperature dependent, the ratio of populations is no longer inconsistent with the Boltzmann distribution. More specifically, we can arrange the last expression into

$$\begin{aligned}\rho &= \frac{N'A}{NB - N'B'} = \frac{A}{B}\,\frac{1}{\dfrac{N}{N'} - \dfrac{B'}{B}} \\ &= \frac{A}{B}\,\frac{1}{e^{h\nu/kT} - \dfrac{B'}{B}}\end{aligned}$$

We have used the Boltzmann expression in the last line. This result is encouraging, since it has the same form as the Planck distribution (eqn 4), which is known to describe the radiation density at thermal equilibrium. Indeed, when we compare the two expressions for ρ, we can conclude that

$$B' = B \tag{9a}$$

$$A = \frac{8\pi h\nu^3}{c^3} \times B \tag{9b}$$

That is, the coefficients of stimulated absorption and emission are equal, and the relative importance of spontaneous emission grows as the cube of the frequency of the transition. The strong growth of the relative importance of spontaneous emission with increasing frequency is a very important conclusion, as we shall see when we consider the operation of lasers in the next chapter. The equality of B and B' implies that if two states happen to have equal populations, then the rate of stimulated emission is exactly equal to the rate of stimulated absorption, and there is then no net absorption.

The population of states

At low frequencies, such as those involved in rotational and vibrational transitions considered in this chapter, spontaneous emission can be largely ignored and the intensities of the transition discussed in terms of the coefficients of stimulated emission and absorption. Then the net rate of absorption is given by

$$W_{\text{net}} = NB\rho - N'B'\rho = (N - N')B\rho$$

and is proportional to the population difference of the two states involved in the transition. If the sample is at thermal equilibrium at a temperature T we may use the Boltzmann distribution to write the population difference as

$$\begin{aligned} N - N' &= N\left(1 - \frac{N'}{N}\right) \\ &= N(1 - \mathrm{e}^{-h\nu/kT}) \end{aligned}$$

Therefore, the intensity of net absorption is proportional to the population N of the lower state as well as to the difference in population of the upper and lower states.

Example 16.2: *Estimating relative transition intensities*

Estimate the relative intensities at 25°C of absorptions originating in the ground state and the first excited state when the energy levels involved are separated by (a) 10 000 cm^{-1}, (b) 1000 cm^{-1}, and (c) 1 cm^{-1}.

Answer. At 25°C, $kT/hc = 207\ \text{cm}^{-1}$, so the population differences between adjacent states is determined by the factor

$$1 - \mathrm{e}^{-h\tilde{\nu}c/kT} = \begin{cases} \text{(a)}\ 1 - \mathrm{e}^{-48} = 1.000 \\ \text{(b)}\ 1 - \mathrm{e}^{-4.8} = 0.992 \\ \text{(c)}\ 1 - \mathrm{e}^{-0.0048} = 0.0048 \end{cases}$$

We draw two conclusions. The first is that the population of the upper state is negligible in (a) and (b), the only significant absorption is from the lower state. The second is that in these two cases, the stimulated emission from the upper state is also negligible, and we need consider only stimulated absorption when assessing the intensity of a transition. However, for (c) we can draw neither conclusion. Since in this case adjacent states are almost equally populated, transitions can originate with significant intensity from many states, and stimulated emission from upper states makes a significant contribution to the net absorption intensity.

Exercise. Repeat the analysis for a temperature of 1500 K.

[(a) As before, upper-state populations significant for (b) and (c)]

It follows from the last equation that the relative intensities of two lines corresponding to transitions originating from two different states should be proportional to the relative populations of the two initial states. Since the first electronically excited state of a molecule is usually of the order of $10^4\,\mathrm{cm}^{-1}$ above the ground state, it is not populated at room temperature (see Example 16.2). Therefore, an electronic absorption spectrum is normally due entirely to transitions originating from the ground electronic state. Vibrational energy levels are separated by around 10^2 to $10^3\,\mathrm{cm}^{-1}$, and so the principal transitions are also normally those from the ground vibrational state, and stimulated emission makes a negligible contribution to the net absorption. In contrast, rotational energy levels are separated by only 1 to $10^2\,\mathrm{cm}^{-1}$, and many states are occupied even at room temperature; consequently, rotational transitions occur from a wide range of initial states, not only the lowest, and stimulated emission from the occupied higher states is important.

Molecules are often prepared in short-lived excited states as a result of chemical reaction, electric discharge, or photolysis. In these cases the populations may be quite different from those at thermal equilibrium, and the spectra—if they can be taken quickly enough—then arise from transitions from all the populated levels.

Selection rules and transition moments

We met the concept of a 'selection rule' in Section 13.3 as a rule that determines whether a transition is forbidden or allowed. Selection rules also apply to molecular spectra, and the form they take depends on the type of transition. The underlying classical idea is that, for the molecule to be able to interact with the electromagnetic field and absorb or create a photon of frequency ν, it must possess, at least transiently, a dipole oscillating at that frequency. For emission and absorption spectra (we treat Raman spectra later) this transient dipole is expressed quantum mechanically in terms of the **transition dipole moment**, and for a transition between states with wavefunctions ψ_i and ψ_f is defined as

$$\boldsymbol{\mu}_{fi} = -e\int \psi_f^* \boldsymbol{r}\psi_i\,d\tau \qquad (10a)$$

where $\boldsymbol{r}$ is the location of the electron. The coefficient of stimulated absorption (and emission), and therefore the intensity of the transition, is proportional to the square of the transition dipole moment, and a detailed analysis gives

$$B = \frac{|\mu_{fi}|^2}{6\varepsilon_0\hbar^2} \qquad (10b)$$

and so only if the transition moment is non-zero does the transition contribute to the spectrum. We see that, to identify the selection rules, we must establish the conditions for which $\mu_{fi} \neq 0$.

A **gross selection rule** specifies the general features a molecule must have if it is to have a spectrum of a given kind. For rotational transitions, the transition moment is zero unless the molecule has a permanent electric dipole. That is, the molecule must be polar. The classical basis of this rule is that a polar molecule appears to possess a fluctuating dipole when rotating (Fig. 16.9) but a nonpolar molecule does not. The permanent dipole can be regarded as a handle with which the molecule stirs the electromagnetic field into oscillation (and vice versa for absorption).

The transition moment is zero in a vibrational transition unless the electric dipole moment of the molecule changes during the vibration. The classical basis of this rule is that the molecule can shake the electromagnetic field into oscillation if its dipole changes as it vibrates (Fig. 16.10). 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 (e.g. the stretching motion of a homonuclear diatomic molecule), and so they neither absorb nor generate radiation: such vibrations are said to be **inactive** in the infrared.

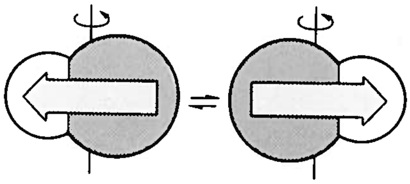


Fig. 16.9 To a stationary observer, a rotating polar molecule looks like an oscillating dipole which can stir the electromagnetic field into oscillation. This picture is the classical origin of the gross selection rule for rotational transitions.

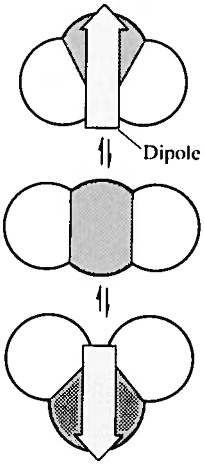


Fig. 16.10 The oscillation of a molecule, even if it is nonpolar, may result in an oscillating dipole that can interact with the electromagnetic field.

Example 16.3: *Using the gross selection rules*

State which of the following molecules have (a) rotational absorption spectra, (b) vibrational absorption spectra: N_2, CO_2, OCS, H_2O, $CH_2{=}CH_2$, C_6H_6.

Answer. (a) Molecules that give rise to rotational spectra have a permanent dipole moment; therefore, select the polar molecules. Only OCS and H_2O are polar, and so only these two give rise to a rotational absorption spectrum. (b) Molecules that give rise to vibrational spectra have dipole moments that change during the course of a vibration. Therefore, judge whether a distortion of the molecule can change its dipole moment (including changing it from zero). All the molecules except N_2 possess at least one vibrational mode that results in a change of a dipole moment, and so all except N_2 can show a vibrational absorption spectrum.

Comment. 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),

Exercise. Repeat the question for H_2, NO, N_2O, CH_4.

[(a) NO, N_2O; (b) NO, N_2O, CH_4]

A more detailed study of the transition moment leads to the **specific selection rules** that express the allowed transitions in terms of the changes in quantum numbers (as in the rule $\Delta l = \pm 1$ for atoms). Specific selection rules can often be interpreted in terms of the changes of angular momentum when a photon (with its intrinsic spin angular momentum $s = 1$) enters or leaves a molecule, and we shall discuss them once we have set up the quantum numbers needed to describe rotation and vibration.

16.3 Linewidths

Spectral lines are not infinitely narrow, and in condensed media may spread over several thousand cm^{-1}.

Doppler broadening

One important broadening process in gaseous samples is the **Doppler effect**, in which radiation is shifted in frequency when the source is moving towards or away from the observer. When a source emitting radiation of frequency ν

recedes with a speed v, the observer detects radiation of frequency

$$\nu' = \frac{\nu}{1 + v/c}$$

where c is the speed of the radiation (the speed of light for electromagnetic radiation, the speed of sound for sound waves). A source approaching the observer appears to be emitting radiation of frequency

$$\nu' = \frac{\nu}{1 - v/c}$$

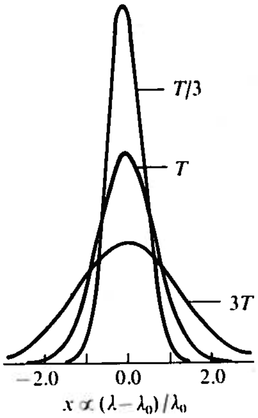


Fig. 16.11 The shape of a Doppler-broadened spectral line reflects the Maxwell distribution of speeds in the sample at the temperature of the experiment. Notice that the line broadens as the temperature is increased. The width at half height, $\delta\lambda$, is given by eqn 11.

Molecules reach high speeds in all directions in a gas, and a static observer detects the corresponding Doppler shifted range of frequencies. Some molecules approach the observer, some move away; some move quickly, others slowly. The detected spectral 'line' is the absorption or emission profile arising from all the resulting Doppler shifts. The profile reflects the Maxwell distribution of molecular speeds parallel to the line of sight (see Section 24.2), which is a bell-shaped Gaussian curve (of the form e^{-x^2}). The Doppler line shape is therefore also a Gaussian curve (Fig. 16.11), and calculation shows that when the temperature is T and the mass of the molecule is m, the width of the line at half-height is

$$\delta\nu = \frac{2\nu}{c} \times \left(\frac{2kT}{m}\ln 2\right)^{1/2} \tag{11a}$$

In terms of the wavelength,

$$\delta\lambda = \frac{2\lambda}{c} \times \left(\frac{2kT}{m}\ln 2\right)^{1/2} \tag{11b}$$

Example 16.4: *Using the linewidth to measure a temperature*

The sun emits a spectral line at 677.4 nm which has been identified as arising from a transition in highly ionized ^{57}Fe. Its width at half-height is 5.3 pm. What is the temperature of the sun's surface?

Answer. Equation 11b rearranges to

$$T = \left(\frac{mc^2}{8k\ln 2}\right)\left(\frac{\delta\lambda}{\lambda}\right)^2 = 1.949 \times 10^{12}\,\mathrm{K} \times M/(\mathrm{g\,mol^{-1}}) \times \left(\frac{\delta\lambda}{\lambda}\right)^2$$

where M is the molar mass of the emitter. Since $M = 57\,\mathrm{g\,mol^{-1}}$, and $\delta\lambda/\lambda = 7.82 \times 10^{-6}$, we find $T = 6.8 \times 10^3$ K.

Comment. Temperatures may also be judged using Wien's Law (eqn 8 of Section 11.2) and looking for the maximum in the intensity of output of the sun (or star) regarded as a black body. Fitting the entire Planck distribution (eqn 4) to the observed intensity profile is another approach.

Exercise. What is the Doppler linewidth of the spectrum of an interstellar NH_3 molecule close to 240 GHz at 10 K? [50 Hz]

Doppler broadening increases with temperature because the molecules acquire a wider range of speeds. Therefore, to obtain spectra of maximum sharpness, it is best to work with cold samples.

Lamb-dip spectroscopy

A novel approach to the elimination of Doppler broadening has become available with the advent of lasers and their extremely high monochromaticity and of radiofrequency techniques with precise frequency control. The precise location of absorption frequencies in this way is called **Lamb-dip spectroscopy**, which is named after its discoverer.

When an intense, monochromatic beam with a frequency slightly higher than that of the absorption maximum passes through a gaseous sample, only the molecules that happen to be moving away from the source at some precise speed absorb radiation. If the beam is then reflected back through the sample (Fig. 16.12), more radiation is absorbed, but this time by the molecules that happen to be moving at the same precise speed but away from the mirror. The detector therefore observes a double dose of absorption. However, when the incident radiation is at the absorption peak, only those molecules moving perpendicular to the line of the beam (and therefore having no Doppler shift) absorb on the reflected path. Because some of those molecules were excited on the first passage, fewer are available to absorb the light on its second passage, and so a less intense absorption is observed. This appears as a dip, the **Lamb dip**, in the absorption curve, and its position gives a very precise location of the transition frequency.

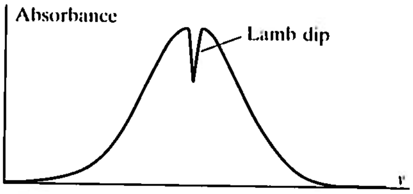


Fig. 16.12 A Lamb dip. The origin is explained in the text: Lamb-dip spectroscopy enables the positions of the centres of absorption lines to be pinpointed very precisely even if there is Doppler broadening.

Lifetime broadening

It is found that spectral lines are still not infinitely sharp even when Doppler broadening has been largely eliminated, either by working at low temperatures or by Lamb-dip spectroscopy.

When the Schrödinger equation is solved for a system that is changing with time, it is found that it is impossible to specify the energy levels exactly. If on average a system survives in a state for a time τ, the **lifetime** of the state, its energy levels are blurred to an extent of order δE, where

$$\delta E \approx \frac{\hbar}{\tau} \qquad (12a)$$

Equation 12a is reminiscent of the Heisenberg uncertainty principle (eqn 33 of Section 11.6), and although the connection is tenuous, lifetime broadening is often called 'uncertainty broadening'. Expressing the energy spread in wavenumbers through $\delta E = hc\delta\tilde{\nu}$ and using the values of the fundamental constants gives the practical form of the relation as

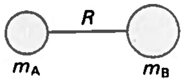
$$\delta\tilde{\nu} \approx \frac{5.3\,\mathrm{cm}^{-1}}{\tau/\mathrm{ps}} \qquad (12b)$$

No excited state has an infinite lifetime; therefore, all states are subject to some lifetime broadening, and the shorter the lifetimes of the states involved in a transition, the broader the spectral lines.

Three processes are principally responsible for the finite lifetimes of excited states. The dominant one is **collisional deactivation**, which arises from collisions between molecules or with the walls of the container. If the collisional lifetime is τ_{col}, the resulting collisional linewidth is $\delta E_{\mathrm{col}} \approx \hbar/\tau_{\mathrm{col}}$.

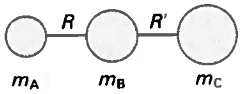
Table 16.1. Moments of inertia†

1. *Diatomics*

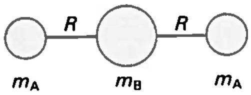


$$I = \frac{m_A m_B}{m} R^2 = \mu R^2$$

2. *Linear rotors*

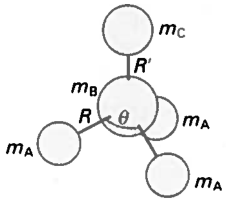


$$I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$$

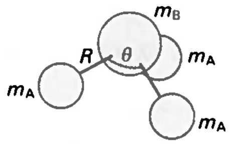


$$I = 2m_A R^2$$

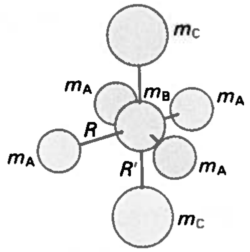
3. *Symmetric rotors*



$$I_{\parallel} = 2m_A R^2(1 - \cos\theta)$$
$$I_{\perp} = m_A R^2(1 - \cos\theta) + \frac{m_A}{m}(m_B + m_C)R^2(1 + 2\cos\theta) + \frac{m_C R'}{m}\{(3m_A + m_B)R' + 6m_A R[\tfrac{1}{3}(1 + 2\cos\theta)]^{1/2}\}$$

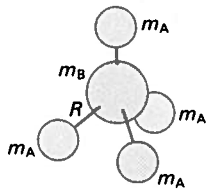


$$I_{\parallel} = 2m_A R^2(1 - \cos\theta)$$
$$I_{\perp} = m_A R^2(1 - \cos\theta) + \frac{m_A m_B}{m} R^2(1 + 2\cos\theta)$$

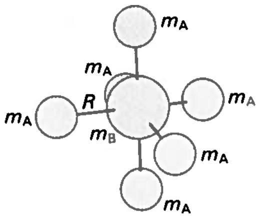


$$I_{\parallel} = 4m_A R^2$$
$$I_{\perp} = 2m_A R^2 + 2m_C R'^2$$

4. *Spherical rotors*



$$I = \tfrac{8}{3} m_A R^2$$



$$I = 4m_A R^2$$

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† In each case m is the total mass of the molecule.

The collisional lifetime can be lengthened, and the broadening minimized, by working at low pressures.

The rate of spontaneous emission cannot be changed. Hence it is a natural limit to the lifetime of an excited state, and the resulting lifetime broadening is the **natural linewidth** of the transition. The natural linewidth is an intrinsic property of the transition, and cannot be changed by modifying the conditions.

Natural linewidths depend strongly on the transition frequency (they increase with A and therefore as ν^3), and so low-frequency transitions (such as the microwave transitions of rotational spectroscopy) have very small natural linewidths, and collisional and Doppler line-broadening processes are dominant. The natural lifetimes of electronic transitions are very much shorter than for vibrational and rotational transitions, and so the natural linewidths of electronic transitions are much greater than those of vibrational and rotational transitions. For example, a typical electronic excited state natural lifetime is about 10^{-8} s (10^4 ps), corresponding to a natural width of about 5×10^{-4} cm^{-1} (15 MHz). A typical rotational natural lifetime is about 10^3 s, corresponding to a natural linewidth of only 5×10^{-15} cm^{-1} (10^{-4} Hz).

Pure rotational spectra

The general strategy that we shall adopt for discussing molecular spectra and the information they contain is to find expressions for the energy levels of molecules and then to calculate the transition frequencies by applying the selection rules. We then predict the appearance of the spectrum by taking into account the populations of the states. In this section we illustrate the strategy by considering the rotational energy levels and selection rules for molecules.

The key molecular parameter we shall need is the **moment of inertia** I of the molecule about various axes. The moment of inertia is defined as the mass of each atom multiplied by the square of its distance from the rotational axis (Fig. 16.13):

$$I = \sum_i m_i x_i^2$$

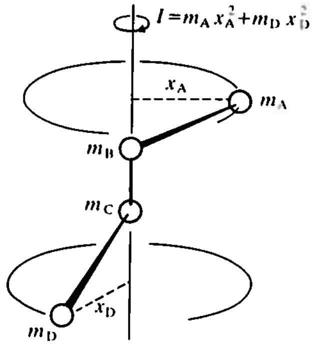

Fig. 16.13 The definition of the moment of inertia, the sum of each mass multiplied by the square of its perpendicular distance from the axis of rotation. Neither B nor C contributes to the moment about the axis shown.

The moment of inertia depends on the masses of the atoms present and the molecular geometry, so we can suspect (and later shall see explicitly) that rotational spectroscopy will give information about bond lengths and bond angles. The explicit expressions for the moments of inertia of some symmetrical molecules are given in Table 16.1. The convention is to label the moments of inertia I_A, I_B, and I_C, with $I_C \geq I_B \geq I_A$.

Example 16.5: *Calculating the moment of inertia of a molecule*

Calculate the moment of inertia of an H_2O molecule around its two-fold axis (the bisector of the HOH angle.

Answer. The moment of inertia is the sum of the masses multiplied by the squares of their distances from the axis of rotation:

$$\begin{aligned} I &= \sum_i m_i x_i^2 = m_H x^2 + 0 + m_H x^2 \\ &= 2m_H x^2 \end{aligned}$$

If the bond angle of the molecule is denoted 2ϕ and the bond length is R, trigonometry gives

$$x = R \sin \phi$$

and therefore

$$I = 2m_{\mathrm{H}}R^2 \sin^2 \phi$$

For H_2O, with bond angle 104.5° and bond length 95.7 pm, we obtain

$$\begin{aligned} I &= 2 \times 1.67 \times 10^{-27}\,\mathrm{kg} \times (9.57 \times 10^{-11}\,\mathrm{m})^2 \times \sin^2 52.3^\circ \\ &= 1.91 \times 10^{-47}\,\mathrm{kg\,m^2} \end{aligned}$$

Comment. The mass of the O atom makes no contribution to the moment of inertia for this mode of rotation as it is immobile while the H atoms rotate around it.

Exercise. Calculate the moment of inertia of a $CHCl_3$ molecule around its threefold axis. The C—Cl bond length is 177 pm and the HCCl angle is 142°.
[$2.1 \times 10^{-45}\,\mathrm{kg\,m^2}$]

We shall suppose initially that molecules are **rigid rotors** that do not distort under the stress of rotation. **Spherical rotors** are molecules with all three moments of inertia equal (such as CH_4); **symmetric rotors** have two equal moments of inertia (such as NH_3). **Linear rotors** have one moment of inertia (the one about the axis) equal to zero (such as CO_2 and HCl). In group theoretical language, a spherical rotor is a molecule belonging to a cubic point group and a symmetric rotor is one with at least a threefold axis of symmetry. All diatomic molecules are linear rotors. The energy levels of **asymmetric rotors**, which have three different moments of inertia (e.g. H_2O) are complicated and we shall not consider them.

16.4 The rotational energy levels

The rotational energy levels of a molecule may be obtained by solving the Schrödinger equation. Fortunately there is a much less onerous short-cut which depends on noting the classical expression for the energy of a rotating body, expressing it in terms of the angular momentum, and then importing the quantum mechanical properties of angular momentum into the equations.

The energy of a body rotating about some axis x is

$$E = \tfrac{1}{2}I_x\omega_x^2$$

where ω_x is the angular velocity (in rad s^{-1}) about the axis and I_x is the moment of inertia about the axis. A body free to rotate about three axes has an energy

$$E = \tfrac{1}{2}I_x\omega_x^2 + \tfrac{1}{2}I_y\omega_y^2 + \tfrac{1}{2}I_z\omega_z^2$$

Since the classical angular momentum about x is

$$J_x = I_x\omega_x$$

with similar expressions for the other directions, it follows that

$$E = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z} \qquad (13)$$

This is the key equation. We described the quantum-mechanical properties of angular momentum in Section 12.7 (see Box 12.1), and we can now make use of them in conjunction with this equation to obtain the rotational energy levels.

Spherical rotors

When all three moments of inertia are equal to some value I, as in CH_4 and SF_6, the classical expression for the energy is

$$E = \frac{1}{2I}(J_x^2 + J_y^2 + J_z^2) = \frac{J^2}{2I}$$

where J is the magnitude of the angular momentum. We can immediately find the quantum expression by making the replacement

$$J^2 \rightarrow J(J+1)\hbar^2 \quad \text{with} \quad J = 0, 1, 2, \ldots$$

Therefore, the energy of a spherical rotor is confined to the values

$$E_J = J(J+1)\frac{\hbar^2}{2I} \quad \text{with} \quad J = 0, 1, 2, \ldots$$

The energy is normally expressed in terms of the **rotational constant** B of the molecule, where

$$hcB = \frac{\hbar^2}{2I}$$

The rotational constant as defined by this equation has the dimensions of a wavenumber[4] and is normally expressed in cm^{-1}. The energy of a rotational state is normally reported as the **rotational term** $F(J)$, its value expressed as a wavenumber, by division by hc:

$$F(J) = BJ(J+1) \qquad B = \frac{\hbar}{4\pi c I} \tag{14}$$

The separation of adjacent terms is

$$F(J+1) - F(J) = 2BJ$$

Since the separation decreases as I increases, we see that large molecules have closely spaced rotational energy levels. We can estimate the magnitude of the separation by considering CCl_4: from the bond lengths and masses of the atoms we find $I = 4.85 \times 10^{-45}\ \mathrm{kg\ m^2}$, and hence $B = 5.24\ \mathrm{cm^{-1}}$.

Symmetric rotors

In symmetric rotors $I_x = I_y \neq I_z$ (as in CH_3Cl, NH_3, and C_6H_6) and z is the **figure axis** (the principal axis) of the molecule. We shall write $I_z = I_\parallel$ and $I_x = I_y = I_\perp$. If $I_\parallel > I_\perp$ the rotor is **oblate** (like a pancake, such as C_6H_6); if

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[4] The definition of B as a wavenumber is convenient when we come to vibration-rotation spectra. However, for pure rotational spectroscopy it is more common to define B as a frequency and to report it in MHz or GHz. The appropriate definition is then

$$B = \frac{\hbar}{4\pi I}$$

$I_\parallel < I_\perp$ it is **prolate** (like a cigar, such as PCl_5). The classical expression for the energy becomes

$$E = \frac{J_x^2 + J_y^2}{2I_\perp} + \frac{J_z^2}{2I_\parallel}$$

We can rewrite this in terms of $J^2 = J_x^2 + J_y^2 + J_z^2$ by adding and subtracting $J_z^2/2I_\perp$:

$$E = \frac{J_x^2 + J_y^2 + J_z^2}{2I_\perp} + \frac{J_z^2}{2I_\parallel} - \frac{J_z^2}{2I_\perp}$$

$$= \frac{J^2}{2I_\perp} + \left(\frac{1}{2I_\parallel} - \frac{1}{2I_\perp}\right)J_z^2$$

Now we generate the quantum expression by replacing J^2 by $J(J+1)\hbar^2$, where J is the angular momentum quantum number. We also know from the quantum theory of angular momentum (Box 12.1) that the component of angular momentum about any axis is restricted to the values

$$J_z = K\hbar \qquad K = 0, \pm1, \dots, \pm J$$

(K is the quantum number used to signify a component on the figure axis; M is reserved for a component on a laboratory axis.) Consequently we also replace J_z^2 by $K^2\hbar^2$. The rotational terms are therefore

$$F(J, K) = BJ(J+1) + (A - B)K^2 \qquad (15a)$$

$$J = 0, 1, 2, \dots; \qquad K = 0, \pm1, \dots, \pm J$$

$$A = \frac{\hbar}{4\pi c I_\parallel} \qquad B = \frac{\hbar}{4\pi c I_\perp} \qquad (15b)$$

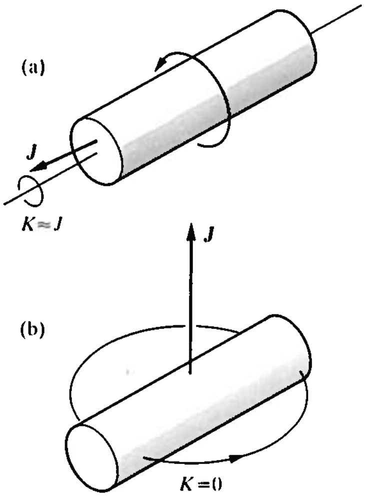

Fig. 16.14 The significance of the quantum number K. (a) When $|K|$ is close to its maximum value, J, most of the molecular rotation is around the figure axis. (b) When $K = 0$ the molecule has no angular momentum about its figure axis: it is undergoing end-over-end rotation.

Equation 15a matches what we should expect for the dependence of the energy levels on the two moments of inertia of the molecule. When $K = 0$, there is no component of angular momentum about the figure axis (Fig. 16.14) and the energy levels depend only on $I_\perp$. When $K = \pm J$, almost all the angular momentum arises from rotation around the figure axis, and the energy levels are determined largely by $I_\parallel$. The sign of K does not affect the energy because opposite values of K correspond to opposite senses of rotation, and the energy does not depend on the sense of rotation.

Example 16.6: *Calculating the rotational energy levels of a molecule*

The $^{14}NH_3$ molecule is a symmetric rotor with bond length 101.2 pm and HNH bond angle 106.7°. Calculate its rotational terms.

Answer. We need to calculate the rotational constants A and B using the expressions for moments of inertia given in Table 16.1. Substitution of $m_A = 1.0078\,\mathrm{u}$, $m_B = 14.0031\,\mathrm{u}$, $R = 101.2\,\mathrm{pm}$, and $\theta = 106.7°$ into the second of the symmetric rotor expressions in Table 16.1 gives

$$I_\parallel = 4.4128 \times 10^{-47}\,\mathrm{kg\,m^2} \qquad I_\perp = 2.8059 \times 10^{-47}\,\mathrm{kg\,m^2}$$

Hence, $A = 6.344\,\mathrm{cm^{-1}}$ and $B = 9.977\,\mathrm{cm^{-1}}$. It follows from eqn 15a that

$$F(J, K)/\mathrm{cm^{-1}} = 9.977J(J+1) - 3.633K^2$$

Comment. For $J = 1$, the energy needed for the molecule to rotate mainly about its figure axis ($K = J$) is equivalent to $16.32\,\text{cm}^{-1}$, but end-over-end rotation ($K = 0$) corresponds to $19.95\,\text{cm}^{-1}$.

Exercise. The $CH_3^{35}Cl$ molecule has a C—Cl bond length of 178 pm, a C—H bond length of 111 pm, and an HCH angle of 110.5°. Calculate its rotational energy levels. $[F(J, K)/\text{cm}^{-1} = 0.444J(J+1) + 4.58K^2]$

Linear rotors

For a linear rotor (such as CO_2, HCl, and C_2H_2) in which the atoms are regarded as mass points, the rotation occurs only about an axis perpendicular to the line of atoms and there is zero angular momentum around the line. Therefore we can use eqn 15a with $K = 0$. The rotational terms are therefore

$$F(J) = BJ(J+1) \qquad J = 0, 1, 2, \ldots \tag{16}$$

Degeneracies and the Stark effect

The symmetric rotor has an energy that depends on J and K, and each level except those with $K = 0$ is doubly degenerate (the K, $-K$ degeneracy). However, we must not forget that an angular momentum has a component on a laboratory axis. This component is quantized, and its permitted values are $M_J\hbar$ with $M_J = 0, \pm1, \ldots, \pm J$ for $2J + 1$ values in all. The quantum number M_J does not appear in the expression for the energy, but it is still necessary for a complete specification of the state of the rotor. Therefore, a symmetric rotor level is $2(2J + 1)$-fold degenerate for $K \neq 0$ and $(2J + 1)$-fold degenerate if $K = 0$:

$$g(J, K) = 2(2J+1) \qquad g(J, 0) = 2J + 1$$

where g denotes the degeneracy. A linear rotor has K fixed at 0, but the angular momentum may still have $2J + 1$ components on the laboratory axis; hence,

$$g(J) = 2J + 1$$

A spherical rotor is the limit of a symmetric rotor with A vanishingly different from B: K may still take any one of $2J + 1$ values, but the energy is independent of which value it takes. Therefore, as well as having a $(2J + 1)$-fold degeneracy arising from the orientation in space, it also has a $(2J + 1)$-fold degeneracy arising from the orientation with respect to an axis selected in the molecule. The overall degeneracy of a symmetric rotor with quantum number J is therefore

$$g(J) = (2J+1)^2$$

This degeneracy increases very rapidly: when $J = 10$, for instance, there are 441 states of the same energy.

The M_J-degeneracy is removed when an electric field is applied to a polar molecule (e.g. HCl or NH_3) because now the energy of the molecule depends on its orientation in space. The splitting of states by an electric field is called the **Stark effect**. For a linear rotor in an electric field $\mathcal{E}$ the energy is given by

$$E_{J,M_J} = hcBJ(J+1) + \frac{\mu^2\mathscr{E}^2\{J(J+1) - 3M_J^2\}}{2hcBJ(J+1)(2J-1)(2J+3)} \tag{17}$$

Note that the energy depends on the square of the permanent electric dipole moment μ, and so the measurement of the Stark effect is a way of measuring this property.

Centrifugal distortion

The atoms of rotating molecules are subject to centrifugal forces that tend to distort the molecular geometry and change the moments of inertia. For a diatomic molecule, the centrifugal distortion stretches the bond, and therefore increases the moment of inertia; as a result, the energy levels are less far apart than the rigid-rotor expressions predict. The effect is usually taken into account by subtracting a term from the energy and writing

$$F(J) = BJ(J+1) - D_J J^2(J+1)^2 \tag{18a}$$

D_J is the **centrifugal distortion constant**: it is large when the bond is easily stretched. The centrifugal distortion constant of a diatomic molecule is related to the vibrational wavenumber of the bond $\tilde{\nu}$ (which, as we shall see later, is a measure of its stiffness):

$$D_J = \frac{4B^3}{\tilde{\nu}^2} \tag{18b}$$

Hence the observation of the convergence of the rotational levels as J increases can be interpreted in terms of the rigidity (specifically, the force constant) of the bond.

16.5 Rotational transitions

Typical values of B for small molecules are in the region of 1 to $10\,\mathrm{cm^{-1}}$ (e.g. $0.356\,\mathrm{cm^{-1}}$ for NF_3 and $10.59\,\mathrm{cm^{-1}}$ for HCl), and so the transitions lie in the microwave region of the spectrum. The transitions are detected by monitoring the net absorption of microwave radiation generated either by a klystron or, in modern instruments, by a 'backward wave oscillator', which is tunable over a wide range of frequencies. For technical reasons related to the detection system, it is desirable to modulate the energy levels (that is, vary them in an oscillatory manner) so that the absorption intensity, and therefore the detected signal, oscillates: it is easier to amplify an alternating signal than a steady one. The oscillation is achieved by **Stark modulation**, in which an alternating electric field (of strength of the order of $10^2\,\mathrm{V\,cm^{-1}}$ and frequency between 50 and 100 kHz) is applied to the sample to modulate the energies of the rotational states.

If a *constant* electric field is applied to the sample, the levels shift to an extent determined by the magnitude of the molecular dipole moment (eqn 17), and so the modification in the spectrum brought about by a known field can be used to measure the dipole moment. Since microwave frequencies can be measured with very high precision, rotational spectroscopy is one of the most precise spectroscopic techniques.

Rotational selection rules

We have already seen (Section 16.2) that the gross selection rule for the observation of a pure rotational spectrum is that it must have a permanent electric dipole moment. Consequently, homonuclear diatomic molecules and symmetrical ($D_{\infty h}$) linear molecules such as CO_2 are rotationally inactive. Spherical rotors cannot have electric dipole moments unless they become distorted by rotation, and so they are also inactive except in special cases. An example of a spherical rotor that does become sufficiently distorted for it to acquire a dipole moment is SiH_4, which has a dipole moment of about 8.3 μD by virtue of its rotation (for comparison, HCl has a dipole moment of 1.1 D). The pure rotational spectrum of SiH_4 has been detected by using long path lengths (10 m) through high pressure (4 atm) samples.

The specific selection rules are found by evaluating the transition dipole moment between the states. For a linear molecule, the transition moment vanishes unless the following conditions are fulfilled:

$$\Delta J = \pm 1 \qquad \Delta M_J = 0, \pm 1$$

The change in J matches what we already know about the role of the conservation of angular momentum when a photon is emitted or absorbed. When these conditions are fulfilled, the total $J+1 \leftarrow J$ transition intensity (the intensity summed over all the values of M_J that contribute to the line) is proportional to

$$|\mu_{J+1,J}|^2 = \frac{\mu^2(J+1)}{2J+1} \rightarrow \tfrac{1}{2}\mu^2 \text{ for } J \gg 1$$

where μ is the permanent electric dipole moment of the molecule.

The only extension needed for the discussion of symmetric rotors is a selection rule for K. If a symmetric rotor has a dipole it must lie parallel to the figure axis, as in NF_3. Such a molecule cannot be accelerated into different states of rotation around the figure axis by the absorption of radiation, so $\Delta K = 0$.

When these selection rules are applied to the expressions for the energy levels, it follows that the wavenumbers of the allowed $J+1 \leftarrow J$ absorptions are

$$\tilde{\nu} = 2B(J+1) \qquad J = 0, 1, 2, \ldots \tag{19}$$

Example 16.7: *Predicting the appearance of a rotational spectrum*

Predict the form of the rotational spectrum of NH_3.

Answer. We calculated the energy levels in Example 16.6. The NH_3 molecule is a polar symmetric rotor, and so the selection rules $\Delta J = \pm 1$ and $\Delta K = 0$ apply. For absorption, $\Delta J = +1$ and we can use eqn 19. Intrinsic intensities are proportional to $|\mu_{J+1,J}|^2$ (we take populations into account later). Since $B = 9.977\ \text{cm}^{-1}$, we can draw up the following table for the $J+1 \rightarrow J$ transitions.

$J =$	0	1	2	3	...
ν/cm^{-1}	19.95	39.91	59.86	79.82	
$\|\mu_{J+1,J}\|^2/\mu^2$	1	0.67	0.60	0.57	

The line spacing is 19.95 cm^{-1}.

Comment. The intensities are the intrinsic intensities of the lines; that is, they do not take into account the different populations of the initial rotational levels. A complication that we have ignored is the modification of the numbers of possible rotational states by the Pauli principle, which allows only some of the states to be occupied.

Exercise. Repeat the problem for $CH_3^{35}Cl$ (see Example 16.6 for details).
[Lines of separation 0.888 cm^{-1}]

The appearance of rotational spectra

The form of the spectrum predicted by eqn 19 is shown in Fig. 16.15. The most significant feature is that it consists of a series of lines with wavenumbers $2B, 4B, 6B, \ldots$ and separation $2B$. The intensities increase with increasing J and pass through a maximum before tailing off as J becomes large. It should be recalled from Section 16.2 that the observed absorption is the *net* outcome of the stimulated absorption less the

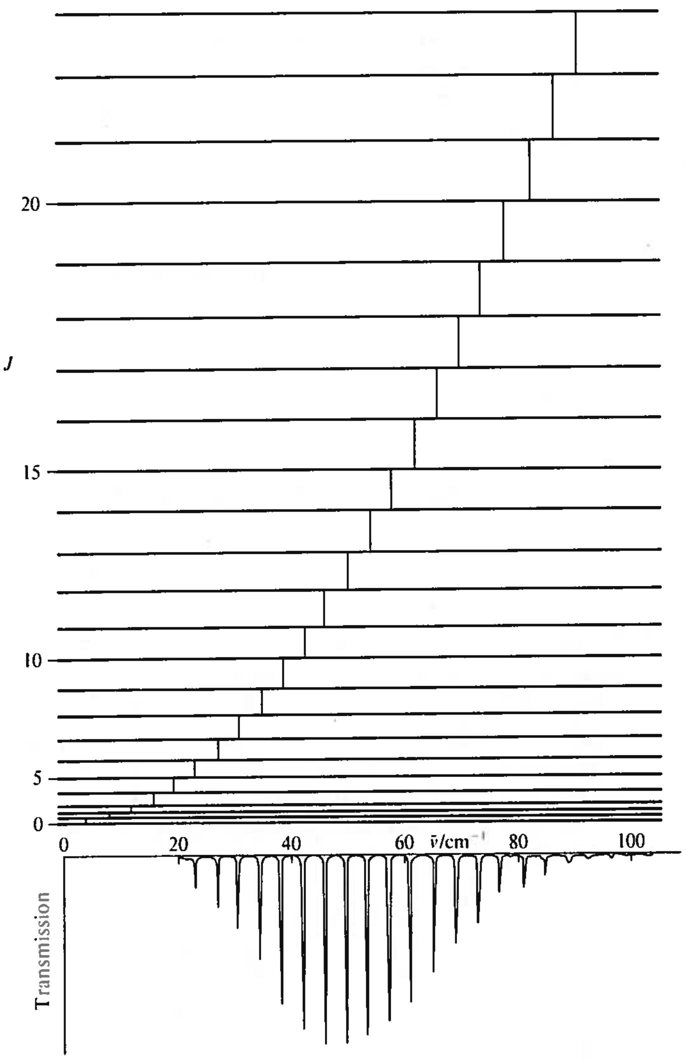

Fig. 16.15 The rotational energy levels of a linear rotor, the transitions allowed by the selection rule $\Delta J = \pm 1$, and a typical pure rotational absorption spectrum. The intensities reflect the populations of the initial level in each case and the strengths of the transition dipole moments.

stimulated emission, and that the intensity of each transition depends on the value of J. Hence the value of J corresponding to the most intense line is not quite the same as the value of J for the most highly populated level.

The measurement of the line spacing gives B, and hence the moment of inertia perpendicular to the figure axis. Since the masses of the atoms are known, it is a simple matter to deduce the bond length of a diatomic molecule. However, in the case of a polyatomic molecule such as OCS or NH_3, the analysis gives only a single quantity $I_\perp$ and we cannot deduce both bond lengths (in OCS) or the bond length and bond angle (in NH_3). This difficulty can be overcome by using isotopically substituted molecules, such as ABC and A′BC; then, by assuming that $R(\text{A—B}) = R(\text{A}'\text{—B})$, both A—B and B—C bond lengths can be extracted from the two moments of inertia. A famous example of this procedure is the study of OCS, and the actual calculation is worked through in Problem 16.9.

16.6 Rotational Raman spectra

The gross selection rule for rotational Raman transitions is that the molecule must be anisotropically polarizable. We shall begin by explaining what this means.

The distortion of a molecule in an electric field is determined by its **polarizability** α (we deal with polarizabilities in detail in Chapter 22). More precisely, if the strength of the field is $\mathscr{E}$, the molecule acquires a dipole moment

$$\mu = \alpha\mathscr{E} \tag{20}$$

in addition to any dipole moment it may have in the absence of the field. We see that the greater the polarizability, the greater the dipole induced by a given field. A Xe atom, for example, has a greater polarizability than a He atom because its outer electrons are less tightly under the control of the more distant central nucleus and are more easily displaced by an externally applied field.

An atom is isotropically polarizable. That is, the same distortion is induced whatever the direction of the applied field. The polarizability of a spherical rotor is also isotropic. However, nonspherical rotors have polarizabilities that do depend on the direction of the field and hence are anisotropically polarizable (Fig. 16.16). The electron distribution in H_2, for example, is more distorted when the field is applied parallel to the bond than when it is applied perpendicular to it, and we write $\alpha_\parallel > \alpha_\perp$.

All linear molecules and diatomics (whether homonuclear or heteronuclear) have anisotropic polarizabilities and so are rotationally Raman active. This is one reason for the importance of rotational Raman spectroscopy: it enables us to examine many of the molecules that are inaccessible to pure rotational microwave spectroscopy. CH_4 and SF_6, however, being spherical rotors, are rotationally Raman inactive as well as rotationally inactive.

The specific rotational Raman selection rules are

$$\Delta J = \begin{cases} 0, \pm 2 & \text{linear rotor} \\ 0, \pm 1, \pm 2 \quad \Delta K = 0 & \text{symmetric rotor} \end{cases}$$

The $\Delta J = 0$ transitions do not lead to a shift of the scattered photon's

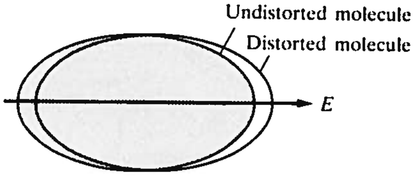

Fig. 16.16 The electric polarizability of a molecule is a measure of its ability to distort in response to an applied field. For most molecules the polarizability is anisotropic.

frequency in pure rotational Raman spectroscopy, and contribute to the unshifted **Rayleigh scattered** light.[5]

We can predict the form of the Raman spectrum of a linear rotor (Fig. 16.18) by applying the selection rule $\Delta J = \pm 2$ to the rotational energy levels. When the molecule makes a transition with $\Delta J = +2$, the scattered radiation leaves it in a higher rotational state, and so the wavenumber of the incident radiation, initially $\tilde{\nu}_i$, is decreased. These transitions account for the **Stokes lines** in the spectrum:

$$\begin{aligned}\tilde{\nu}(J+2 \leftarrow J) &= \tilde{\nu}_i - \{F(J+2) - F(J)\}\\ &= \tilde{\nu}_i - 2B(2J+3) \qquad (21a)\end{aligned}$$

The Stokes lines appear to low frequency of the incident light and at displacements $6B, 10B, 14B, \ldots$ from $\tilde{\nu}_i$ for $J = 0, 1, 2, \ldots$ When the molecule makes a transition with $\Delta J = -2$, the scattered photon emerges with increased energy. These transitions account for the **anti-Stokes lines** of the spectrum:

$$\begin{aligned}\tilde{\nu}(J \rightarrow J-2) &= \tilde{\nu}_i + \{F(J) - F(J-2)\}\\ &= \tilde{\nu}_i + 2B(2J-1) \qquad (21b)\end{aligned}$$

The anti-Stokes lines occur at displacements of $6B, 10B, 14B, \ldots$ (for $J = 2, 3, \ldots$; $J = 2$ is the lowest state that can contribute under the selection rule $\Delta J = -2$) to high frequency of the incident radiation. The separation of the lines in both the Stokes and the anti-Stokes regions is $4B$, and so from its measurement $I_\perp$ can be determined and then used to find the bond lengths exactly as in the case of microwave spectroscopy.

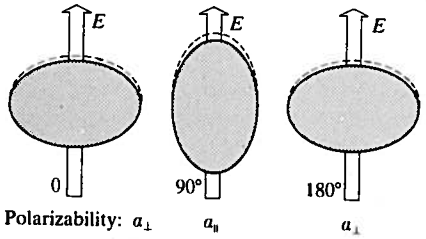

Fig. 16.17 The distortion induced in a molecule by an applied electric field returns to its initial value after a rotation of only 180° (i.e. twice a revolution). This is the origin of the $\Delta J = \pm 2$ selection rule in rotational Raman spectroscopy.

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[5] The classical origin of the 2 in the selection rule is as follows. In an electric field $\mathscr{E}$, a molecule acquires a dipole moment of magnitude $\alpha\mathscr{E}$, where α is the polarizability. If the electric field is that of a light wave of frequency ω_i, the induced dipole moment is time dependent and has the form

$$\mu = \alpha\mathscr{E} = \alpha\mathscr{E}_i \cos \omega_i t$$

If the molecule is rotating, its polarizability in the direction of the field is also time dependent (if it is anisotropic), and we can write

$$\alpha = \alpha_0 + \Delta\alpha \cos 2\omega_R t$$

the 2 appearing because the polarizability returns to its initial value twice each revolution (Fig. 16.17). Substituting this expression into the expression for the induced dipole moment gives

$$\begin{aligned}\mu &= (\alpha_0 + \Delta\alpha \cos 2\omega_R t) \times (\mathscr{E}_i \cos \omega_i t)\\ &= \alpha_0\mathscr{E}_i \cos \omega_i t + \mathscr{E}_i\,\Delta\alpha \cos 2\omega_R t \cos \omega_i t\\ &= \alpha_0\mathscr{E}_i \cos \omega_i t + \tfrac{1}{2}\mathscr{E}_i\,\Delta\alpha\{\cos(\omega_i + 2\omega_R)t + \cos(\omega_i - 2\omega_R t)\}\end{aligned}$$

This shows that the induced dipole has a component oscillating at the incident light frequency (so that it radiates Rayleigh radiation), and that it also has two components at $\omega_i \pm 2\omega_R$ which give rise to the shifted Raman lines. Note that these lines appear only if $\Delta\alpha \neq 0$, hence the need for anisotropy in the polarizability.

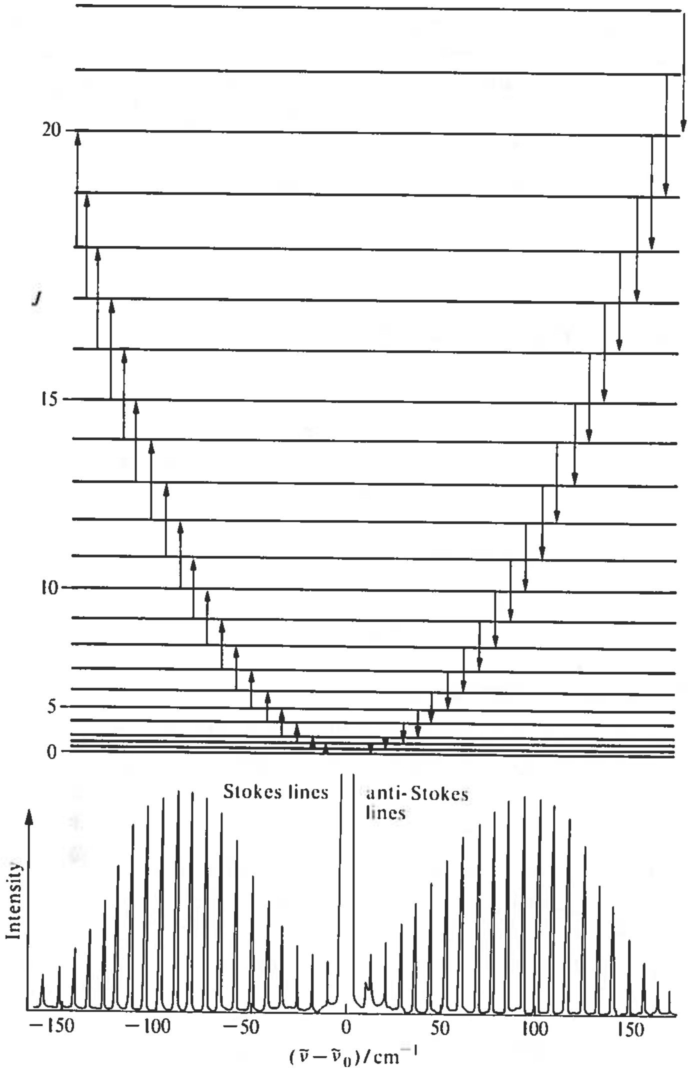

Fig. 16.18 The rotational energy levels of a linear rotor and the transitions allowed by the $\Delta J = \pm 2$ Raman selection rules. The form of a typical rotational Raman spectrum is also shown.

Example 16.8: *Predicting the form of a Raman spectrum*

Predict the form of the rotational Raman spectrum of $^{14}N_2$, for which $B = 1.99\ \mathrm{cm}^{-1}$ when it is irradiated with monochromatic 336.732 nm laser light.

Comment. The molecule is rotationally Raman active because end-over-end rotation modulates its polarizability as viewed by a stationary observer. The Stokes and anti-Stokes lines are given by the expressions above. Since $\lambda_i = 336.732$ nm corresponds to $\tilde{\nu}_i = 29\,697.2\ \mathrm{cm}^{-1}$, eqns 21a and 21b give the following line positions:

$J =$	0	1	2	3
Stokes:				
$\tilde{\nu}/\mathrm{cm}^{-1}$	29 685.3	29 677.3	29 669.3	29 661.4
λ/nm	336.868	336.958	337.048	337.139
Anti-Stokes:				
$\tilde{\nu}/\mathrm{cm}^{-1}$			29 709.1	29 717.1
λ/nm			336.597	336.507

Comment. There will be a strong central line at 336.732 nm accompanied on either side by lines of increasing and then decreasing intensity (as a result of transition moment and population effects). The spread of the entire spectrum is very small (about 300 cm^{-1} at room temperature), and so the incident light must be highly monochromatic.

Exercise. Repeat the calculation for the rotational Raman spectrum of NH_3 ($B = 9.977\ \mathrm{cm}^{-1}$).

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 the spectrum.

16.7 Molecular vibrations.

We shall base our discussion on Fig. 16.19, which shows a typical potential energy curve (Section 14.1) of a diatomic molecule.

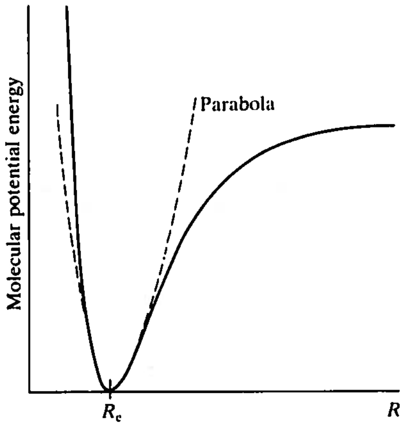

Fig. 16.19 The molecular potential energy curve can be approximated by a parabola near the bottom of the well. The parabolic potential leads to harmonic oscillations. At high excitation energies the parabolic approximation is poor (the true potential is less confining), and is totally wrong near the dissociation limit.

The harmonic approximation

In regions close to R_e (at the minimum of the curve) the potential energy can be approximated by a parabola, and we can write

$$V = \tfrac{1}{2}k(R - R_e)^2$$

where k is the **force constant** of the bond. The steeper the walls of the potential, the greater the force constant. This is another way of saying the stiffer the bond, the higher the force constant. The Schrödinger equation for the motion of the two atoms of masses m_1 and m_2 with this potential energy is

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

where μ is the **reduced mass**:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

This equation is derived in the same way as in the *Further information* section of Chapter 14, where the separation of variables procedure was used to separate the relative motion of the atoms from the motion of the molecule as a whole.

The Schrödinger equation we have obtained is that for a particle of mass μ undergoing harmonic motion. Therefore, we can use the results of Section 12.4 directly, and immediately write down the permitted vibrational energy levels:

$$E_v = (v + \tfrac{1}{2})\hbar\omega \qquad \omega = \left(\frac{k}{\mu}\right)^{1/2} \qquad v = 0, 1, 2, \ldots$$

The **vibrational terms** of a molecule, the energies of its vibrational states expressed in wavenumbers, are denoted by G, and so

$$G(v) = (v + \tfrac{1}{2})\tilde{\nu} \qquad \tilde{\nu} = \frac{\omega}{2\pi c} \tag{22}$$

The vibrational wavefunctions are the same as in Section 12.5.

It is important to note that the vibrational terms depend on the *reduced* mass of the molecule, not its total mass, which is physically reasonable. If atom 1 were as heavy as a brick wall, we would find $\mu \approx m_2$, the mass of the lighter atom, and the vibration would 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 $\mu \approx m_{\mathrm{H}}$). In the case of a homonuclear diatomic molecule, for which $m_1 = m_2$, the reduced mass is half the total mass: $\mu = \tfrac{1}{2}m$.

Anharmonicity

The vibrational terms in eqn 22 are only approximate because they are based on the parabolic approximation to the actual potential energy curve. 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 curve where the parabolic approximation is poor. The motion then becomes **anharmonic** since the force is no longer proportional to the displacement. In particular, because the actual curve is less confining than a parabola (Fig. 16.19) we can anticipate that the energy levels become less widely spaced at high excitations.

One approach to the calculation of the energy levels over a wider range is to use a function that resembles the true potential energy more closely. The **Morse potential energy** is

$$V = D_e\{1 - e^{-a(R-R_e)}\}^2 \tag{23a}$$

where D_e is the depth of the potential minimum and

$$a = \left(\frac{\mu}{2D_e}\right)^{1/2}\omega \tag{23b}$$

Equation 23a is plotted in Fig. 16.20. Near the well minimum it resembles a parabola (as can be checked by expanding the exponential as far as the first term), but unlike a parabola it allows for dissociation at high energies. The Schrödinger equation can be solved for this potential and the permitted energy levels are

$$G(v) = (v + \tfrac{1}{2})\tilde{\nu} - (v + \tfrac{1}{2})^2 x_e\tilde{\nu} \qquad x_e = \frac{a^2\hbar}{2\mu\omega} \tag{24}$$

x_e is called the **anharmonicity constant**. The number of vibrational levels of a Morse oscillator is finite, and $v = 1, 2, \ldots, v_{\max}$, as shown in Fig. 16.20. The second term in eqn 24 subtracts from the first, and gives rise to the convergence of the levels at high quantum numbers.

Although the Morse oscillator is quite useful theoretically, in practice the

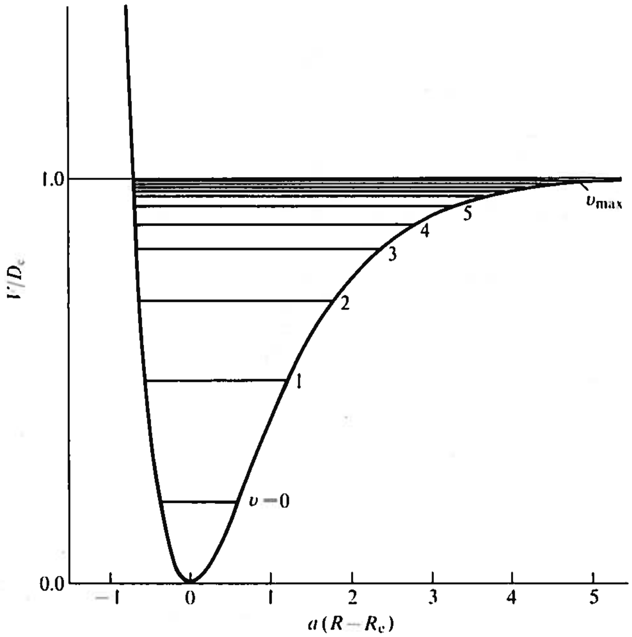

Fig. 16.20 The Morse potential energy curve reproduces the general shape of a molecular potential energy. The corresponding Schrödinger equation can be solved, and the values of the energies obtained. The number of bound levels is finite.

more general expression

$$G(v) = (v + \tfrac{1}{2})\tilde{\nu} - (v + \tfrac{1}{2})^2 x_e\tilde{\nu} + (v + \tfrac{1}{2})^3 y_e\tilde{\nu} + \ldots$$

where x_e and y_e are empirical constants, is used to fit the experimental data and to find the dissociation energy of the molecule.

16.8 The vibrational spectra of diatomic molecules

We have seen that the gross selection rule for vibrational transitions is that the electric dipole moment of the molecule must change in the course of a vibration. Homonuclear diatomic molecules are therefore inactive, because their dipole moments remain zero however long the bond, but heteronuclear diatomic molecules are infrared active.

The spectra of heteronuclear diatomic molecules

The specific selection rule is obtained from an analysis of the expression for the transition moment (and the properties of integrals over Hermite polynomials, Table 12.1), and is

$$\Delta v = \pm 1$$

It follows that the difference between terms of the allowed transitions, which is denoted $\Delta G_{v+1/2}$ for the transition $v + 1 \leftarrow v$, is

$$\Delta G_{v+1/2} = G(v + 1) - G(v) = \tilde{\nu} \qquad (25a)$$

in the harmonic approximation, and

$$\Delta G_{v+1/2} = \tilde{\nu} - 2(v + 1)x_e\tilde{\nu} + \ldots \qquad (25b)$$

if anharmonicity is taken into account. The latter equation shows that the lines converge as v increases. In the harmonic approximation all lines lie at the same wavenumber $\tilde{\nu}$.

HCl has a force constant of $516\,\mathrm{N\,m^{-1}}$, a reasonably typical value. The reduced mass of $^{1}H^{35}Cl$ is 1.63×10^{-27} kg (note that this is very close to the mass of the hydrogen atom, 1.67×10^{-27} kg, and so the Cl atom is like a brick wall). These values imply

$$\omega = 5.63\times10^{14}\,\mathrm{s^{-1}} \qquad \nu = 8.95\times10^{13}\,\mathrm{Hz}$$
$$\tilde{\nu} = 2990\,\mathrm{cm^{-1}} \qquad \lambda = 3.35\,\mu\mathrm{m}$$

The radiation lies in the infrared region of the spectrum, and so vibrational spectroscopy is an infrared technique.

At room temperature $kT/hc \approx 200\,\mathrm{cm^{-1}}$, and the Boltzmann distribution implies that almost all the molecules will be in their vibrational ground states initially. Hence, the dominant spectral transition will be $1 \leftarrow 0$. As a result, the spectrum is expected to consist of a single absorption line. If the sample molecules are formed in a vibrationally excited state, such as when vibrationally 'hot' HF is formed in the reaction $H_2 + F_2 \rightarrow 2HF^*$, the transitions $5 \rightarrow 4$, $4 \rightarrow 3$, etc. may also appear (in emission). In the harmonic approximation, all these lines lie at the same frequency, and the spectrum is a single line. However, the presence of anharmonicity causes the transition to lie at slightly different frequencies, and so several lines are observed.

Anharmonicity also accounts for the appearance of additional weak absorption lines corresponding to the transitions $2 \leftarrow 0$, $3 \leftarrow 0, \ldots$, even though these second, third, ... **harmonics** are forbidden by the selection rule $\Delta v = \pm 1$. The reason is that the selection rule is derived using harmonic oscillator wavefunctions, and these 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 $\Delta v > 1$ is allowed only weakly if the anharmonicity is slight. The second harmonic, for example, gives rise to an absorption at

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

The Birge–Sponer extrapolation

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

$$D_0 = \Delta G_{1/2} + \Delta G_{1+1/2} \ldots = \sum_{v} \Delta G_{v+1/2} \qquad (26)$$

just as the height of the ladder is the sum of the separation of its rungs. The construction in Fig. 16.21 shows that the area under the plot of $\Delta G_{v+1/2}$ against v 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 the illustration, so the value of D_0 obtained in this way is usually an overestimate of the true value. The depth of the potential well, D_e, differs from D_0 by the

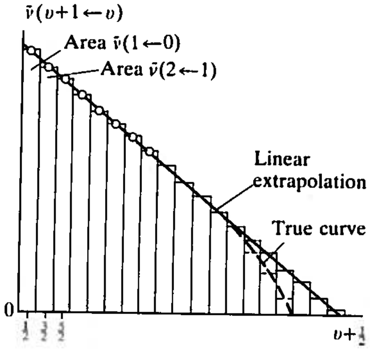

Fig. 16.21 The area under a plot of energy difference against vibrational quantum number is equal to the dissociation energy of the molecule. The assumption that the differences approach zero linearly is the basis of the Birge–Sponer extrapolation.

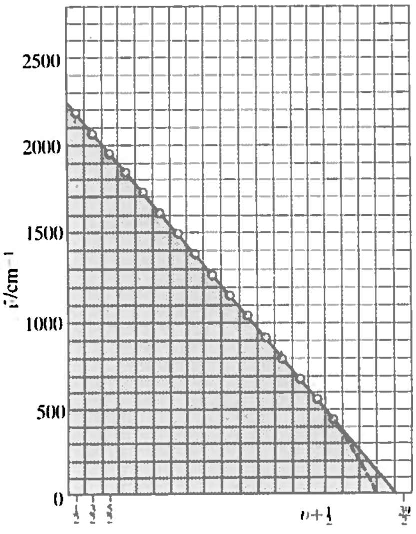

Fig. 16.22 The Birge–Sponor plot used in Example 16.9. The area is obtained simply by counting the squares beneath the line.

zero-point energy:

$$D_e = D_0 + \tfrac{1}{2}(1 - \tfrac{1}{2}x_e)\tilde{\nu}$$

Example 16.9: *Using a Birge–Sponer extrapolation*

The observed vibrational energy level separations of H_2^+ lie at the following values for $1 \leftarrow 0$, $2 \leftarrow 1$, . . . 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.

Answer. We need to plot the separations against v, extrapolate linearly to the point cutting the v axis, and then measure the area under the curve. The points are plotted in Fig. 16.22; the full line is the Birge–Sponer linear extrapolation. The area under the curve (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 cm^{-1} (corresponding to 256 kJ mol^{-1}).

Exercise. The vibrational levels of HgH converge rapidly, and successive separations are 1203.7, 965.6, 632.4, and 172 cm^{-1}. Estimate the dissociation energy. [40 kJ mol^{-1}]

16.9 Vibration–rotation spectra

At high resolution, each line of the vibrational spectrum of a gas-phase heteronuclear diatomic molecule is found to consist of a large number of closely spaced components (Fig. 16.23). For this reason, molecular spectra are often called **band spectra**. The separation between the components is of the order of 1 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. A detailed analysis of the quantum mechanics of the process shows that the rotational quantum number J changes by ±1 during a vibrational transition. If the molecule possesses angular momentum about its axis, as in the case of the electronic orbital angular momentum of the $^2\Pi$ molecule NO, the selection rules also allow $\Delta J = 0$.

The appearance of the vibration–rotation spectrum of a diatomic mole-

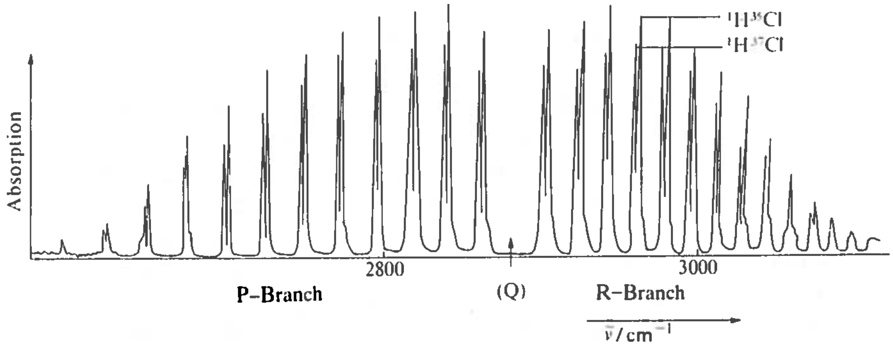

Fig. 16.23 A high-resolution vibration–rotation spectrum of HCl. The lines appear in pairs because $H^{35}Cl$ and $H^{37}Cl$ both contribute (their abundance ratio is 3 : 1). There is no Q branch, because $\Delta J = 0$ is forbidden for this molecule.

cule can be discussed in terms of the combined vibration–rotation terms S:

$$S(v, J) = G(v) + F(J)$$

If we ignore anharmonicity and centrifugal distortion,

$$S(v, J) = (v + \tfrac{1}{2})\tilde{\nu} + BJ(J + 1)$$

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. However, these features lengthen the algebra without introducing anything new, and so we shall continue with the simple expression.

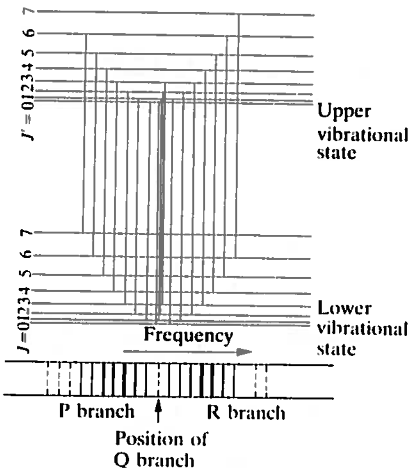

Fig. 16.24 The formation of P, Q, and R branches in a vibration–rotation spectrum. The intensities reflect the populations of the initial rotational levels.

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 groups called the **P**, **Q**, and **R branches** of the spectrum. The P branch consists of all transitions with $\Delta J = -1$:

$$\tilde{\nu}_P(J) = \tilde{\nu} - 2BJ \qquad (27a)$$

This branch (Figs. 16.23 and 16.24), consists of lines at $\tilde{\nu} - 2B$, $\tilde{\nu} - 4B, \ldots$ with an intensity distribution reflecting both the populations of the rotational levels and the $J - 1 \leftarrow J$ transition moment.

The Q branch consists of all lines with $\Delta J = 0$, and its wavenumbers are all

$$\tilde{\nu}_Q(J) = \tilde{\nu} \qquad (27b)$$

for all values of J. This branch, when it is allowed, forms a single line at the vibrational transition wavenumber. In practice, since the rotational constants of the two vibrational levels are slightly different, the Q branch appears as a cluster of closely spaced lines. In Fig. 16.23 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 $\Delta J = +1$:

$$\tilde{\nu}_R(J) = \tilde{\nu} + 2B(J + 1) \qquad (27c)$$

This branch consists of lines displaced from $\tilde{\nu}$ to high wavenumber by $2B, 4B, \ldots$ (Fig. 16.24).

The separation between the lines in the P and R branches of a vibrational transition gives the value of B, and so the bond length can be deduced without needing to record a pure rotation microwave spectrum (although the latter is more accurate).

16.10 Vibrational Raman spectra of diatomic molecules

The gross selection rule for vibrational Raman transitions is that the polarizability should change as the molecule vibrates. Both homonuclear and heteronuclear diatomic molecules swell and contract during a vibration, and the control of the nuclei over the electrons, and hence the molecular polarizability, changes too. Both types of diatomic molecule are therefore vibrationally Raman active.

The specific selection rule is $\Delta v = \pm 1$. The lines to high frequency of the incident light, the anti-Stokes lines, are those for which $\Delta v = -1$. They are

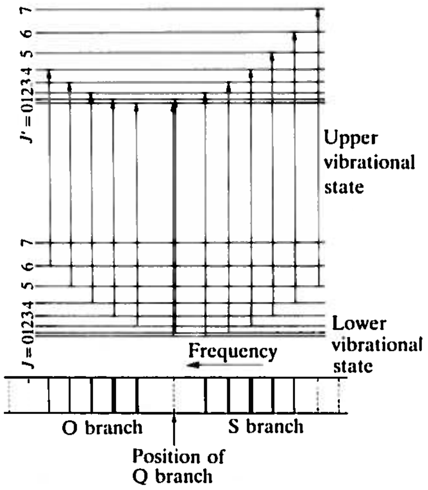

Fig. 16.25 The formation of O, Q, and S branches in a vibration–rotation Raman spectrum of a linear rotor. Note that the frequency scale runs in the opposite direction to that in Fig. 16.24, because the higher-energy transitions (on the right) extract more energy from the incident beam and leave it at lower frequency.

usually weak because very few molecules are in an excited vibrational state initially. The lines to low frequency, the Stokes lines, correspond to $\Delta v = +1$. Superimposed on these is a branch structure arising from the simultaneous rotational transitions that accompany the vibrational excitation (Fig. 16.25). The selection rules are $\Delta J = 0, \pm 2$ (as in pure rotational Raman spectroscopy), and give rise to the **O branch** ($\Delta J = -2$), the **Q branch** ($\Delta J = 0$), and the **S branch** ($\Delta J = +2$).

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.

Table 16.2. Properties of diatomic molecules.

	$\tilde{\nu}/\mathrm{cm}^{-1}$	B/cm^{-1}	$k/(\mathrm{N\,m}^{-1})$
$^1H_2$	4400	60.86	575
$^1H^{35}Cl$	2991	10.59	516
$^1H^{127}I$	2308	6.61	314
$^{35}Cl_2$	560	0.244	323

The vibrations of polyatomic molecules

In a diatomic molecule there is only one mode of vibration, the bond stretch. In a polyatomic molecule there are several modes because bonds may stretch and angles may bend.

16.11 Normal modes

We begin by calculating the total number of vibrational modes of a polyatomic molecule consisting of N atoms. We then see that we can choose combinations of atomic motion that gives the simplest description of the vibrations of the molecule.

The number of vibrational modes

The total number of coordinates needed to specify the locations of all N atoms is $3N$. Each atom may change its location by varying one of its coordinates, and so the total number of displacements available is $3N$. We can group these displacements together in a physically sensible way. For example, three coordinates are needed to specify the location of the centre of mass of the molecule, and so three of the 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. 16.26a). However,

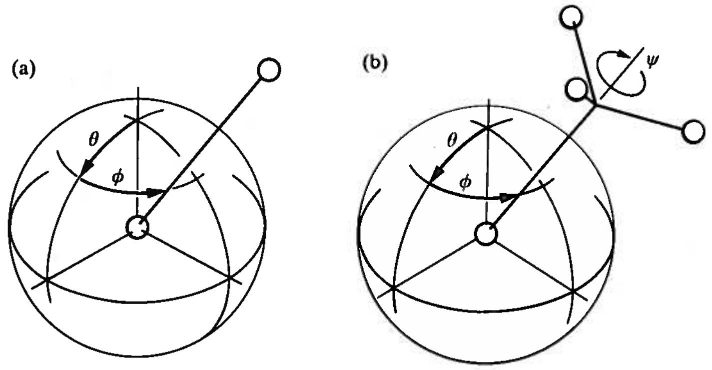

Fig. 16.26 The specification of the centre of mass of a molecule uses up three degrees of freedom. (a) The orientation of a linear molecule requires the specification of two angles. (b) The orientation of a non-linear molecule requires the specification of three angles.

three angles are needed for a non-linear molecule because we also need to specify the orientation of the molecule around the direction defined by the latitude and longitude (Fig. 16.26b). Therefore 2 (linear) or 3 (non-linear) of the $3N-3$ internal displacements are rotational. This leaves $3N-5$ (linear) or $3N-6$ (non-linear) displacements of the atoms relative to each other: these are the vibrational modes. It follows that the number of modes of vibration N_{vib} is

$$N_{\mathrm{vib}} = \begin{cases} 3N-5 \text{ for linear molecules} \\ 3N-6 \text{ for non-linear molecules} \end{cases} \qquad (28)$$

For example, H_2O is a 3-atom non-linear molecule, and has three modes of vibration (and three modes of rotation); CO_2 is a 3-atom linear 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.

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. 16.27a. This illustration shows the stretching of one bond (the mode ν_L), the stretching of the other (ν_R), and the two perpendicular bending modes (ν_2). The description, while permissible, has a disadvantage: when one C—O vibration is excited, the motion of the C atom sets the other C—O in motion, and so energy flows backwards and forwards between ν_L and ν_R.

The description of the vibrational motion is much simpler if linear combinations of ν_L and ν_R are taken. For example, one combination is ν_1 in Fig. 16.27b: this is the **symmetric stretch**, and in it 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 out of phase (in opposite directions). 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_{vib} normal modes of polyatomics in general, are the key to the description of molecular vibrations. Each normal mode behaves like an independent harmonic oscillator (if anharmonicities are neglected), and so each has a series of terms

$$G_Q(v) = (v + \tfrac{1}{2})\tilde{\nu}_Q$$

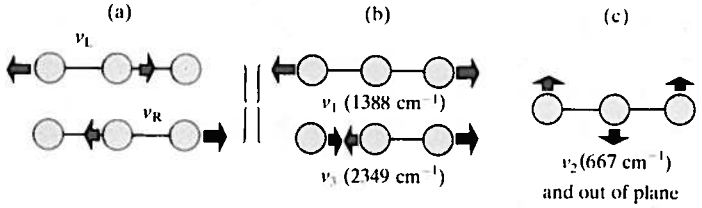

Fig. 16.27 Alternative descriptions of the vibrations of CO_2. (a) The stretching modes are not independent, and if one C–O is excited the other begins to vibrate. (b) The symmetric and antisymmetric stretches are independent, and one can be excited without affecting the other: they are normal modes. (c) The two perpendicular bending motions are normal modes.

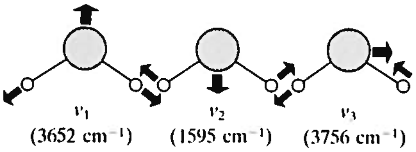

Fig. 16.28 The normal modes of H_2O. The mode ν_2 is predominantly bending, and occurs at lower wavenumber than the other two.

$\tilde{\nu}_Q$ is the wavenumber of mode Q and depends on the force constant k_Q for the mode and on the reduced mass μ_Q of the mode, with

$$\tilde{\nu}_Q = \frac{\omega}{2\pi c} \quad \text{and} \quad \omega_Q = \left(\frac{k_Q}{\mu_Q}\right)^{1/2}$$

The reduced mass of the mode is a measure of the mass that is swung about by the vibration. For example, in the symmetric stretch of CO_2 the C atom is stationary, and the reduced mass depends on the masses of only the O atoms. In the antisymmetric stretch and in the bends, all three atoms move, and so all contribute to the reduced mass. The three normal modes of H_2O are shown in Fig. 16.28: note that the predominantly bending mode (ν_2) has a lower frequency than the others, which are predominantly stretching modes. One point that must be appreciated is that only in special cases (such as the CO_2 molecule) are the normal modes purely stretches or purely bends. In general a normal mode is a composite motion of simultaneous stretching and bending of bonds.

The symmetry species of normal modes

One of the most powerful ways of dealing with normal modes, especially of complex molecules, is to classify them according to their symmetries.

The procedure begins by deciding on the symmetry species of the irreducible representations spanned by all the $3N$ displacements of the atoms, using the characters of the molecular point group. We find these characters (as explained in Example 15.4) by counting 1 if the displacement is unchanged under a symmetry operation, -1 if it changes sign, and 0 if it is changed into some other displacement. Next, we subtract the symmetry species of the translations. These span the same symmetry species as x, y, and z, so they can be obtained from the right-hand columns of the character table. Finally, we subtract the symmetry species of the rotations, which are also given in the character table.

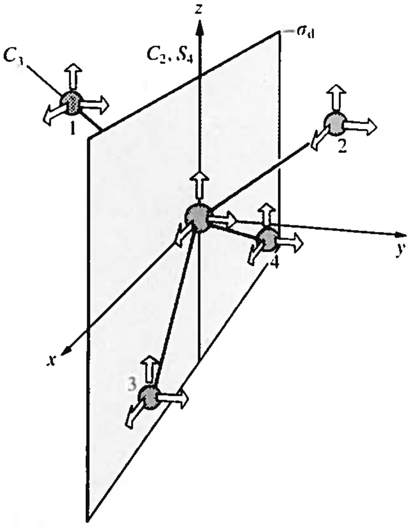

Fig. 16.29 The atomic displacements of CH_4 and the symmetry elements used to calculate the characters. Since all operations of the same class have the same character, there is no need to consider more than one element of each class.

Example 16.10: *Identifying the symmetry species of a normal mode*

Establish the symmetry species of the normal mode vibrations of CH_4.

Answer. There are $3 \times 5 = 15$ modes of motion, of which $3 \times 5 - 6 = 9$ are vibrations. Refer to Fig. 16.29. Under E, no displacement coordinates are changed, and so the character is 15. Under C_3, no displacements are left unchanged, and so the character is 0. Under a C_2 rotation the z-displacement of the central atom is left unchanged, while its x- and y-components both change sign. Therefore $\chi(C_2) = 1 - 1 - 1 + 0 + 0 + \ldots = -1$. Under S_4, the z-displacement of the central atom is reversed, and so $\chi(S_4) = -1$. Under σ_d, the z-displacement of C, H_3, and H_4 are left unchanged, three of the H displacements are left unchanged and three are reversed; hence $\chi(\sigma_d) = 3 + 3 - 3 = 3$. The characters are therefore 15 0 -1 -1 3, corresponding to $A_1 + E + T_1 + 3T_2$. The translations span T_2; the rotations span T_1. Hence the vibrations span $A_1 + E + 2T_2$.

Comment. We shall soon see that symmetry analysis gives a quick way of deciding which modes are active.

Exercise. Establish the symmetry species of the normal modes of H_2O.

[$2A_1 + B_2$]

16.12 The vibrational spectra of polyatomic molecules

The gross selection rule for infrared activity is that the motion corresponding to a normal mode should be accompanied by a change of dipole moment. Deciding whether this is so can sometimes be done by inspection. For example, the symmetric stretch of CO_2 leaves the dipole moment unchanged (at zero), and so this mode is infrared inactive. The antisymmetric stretch, however, changes the dipole moment because the molecule becomes unsymmetrical as it vibrates, and so this mode is infrared active. Since in this case the dipole moment change is parallel to the figure axis, the transitions arising from this mode are classified as **parallel bands** in the spectrum. Both bending modes are infrared active: they are accompanied by a changing dipole perpendicular to the figure axis, and so transitions involving them lead to a **perpendicular band** in the spectrum.

Symmetry and normal mode activity

It is best to use group theory to judge the activities of more complex modes of vibration. This is easily done by checking the character table of the molecular point group for the symmetry species of the irreducible representations spanned by x, y, and z, for these are also the symmetry species of the components of the electric dipole moment. Then the rule to apply is as follows:

If the symmetry species of a normal mode is the same as any of the symmetry species of x, y, or z, the mode is infrared active.

Example 16.11: *Identifying infrared active modes*

Which modes of CH_4 are infrared active?

Answer. Refer to the T_d character table to establish the symmetry species of x, y, and z; it is T_2. We found in Example 16.10 that the symmetry species of the normal modes are $A_1 + E + 2T_2$. Therefore, only the T_2 modes are infrared active.

Comment. The distortions accompanying the T_2 modes lead to a changing dipole moment. The A_1 mode, which is inactive, is the symmetrical 'breathing' mode of the molecule.

Exercise. Which of the normal modes of H_2O are infrared active?

[All three]

The appearance of the spectrum

The active modes are subject to the specific selection rule $\Delta v_Q = \pm 1$, and so the wavenumber of the **fundamental transition** (the first harmonic) of each active mode is $\tilde{\nu}_Q$. 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.

Superimposed on this simple 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, and so it changes its rotational state frequently. This random changing of orientation is called **tumbling**.

Since the lifetimes of rotational states in liquids are very short, 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 12) of more than $1\,cm^{-1}$ can easily result. The rotational structure of the vibrational spectrum is blurred by this effect, and so the infrared spectrum 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 collisions is a welcome simplification, is to chemical analysis. The vibrational spectra of different groups in a molecule give rise to absorptions at characteristic frequencies. Their intensities are also approximately transferable between molecules. Consequently, the molecules in a sample can often be identified by examining its infrared spectrum and accounting for all the bands by referring to a table of characteristic frequencies and intensities (Table 16.3 and Fig. 16.30).

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

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

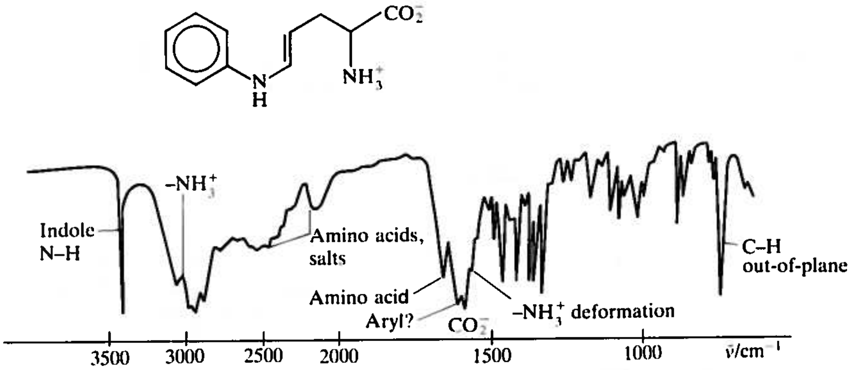

Fig. 16.30 The infrared absorption spectrum of an amino acid and a partial assignment.

16.13 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 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 its polarizability, and so the mode is Raman active. The other modes of CO_2 leave the polarizability unchanged, and so they are Raman inactive.

Symmetry aspects of Raman transitions

Group theory provides an explicit recipe for judging the Raman activity of a normal mode. In this case, the symmetry species of the quadratic forms (x^2, xy, etc) listed in the character table are noted (they transform in the same way as the polarizability), and then we use the following rule:

> If the symmetry species of a normal mode is the same as the symmetry species of a quadratic form, the mode is Raman active.

Example 16.12: *Identifying Raman-active normal modes*

Which of the vibrations of CH_4 are Raman active?

Answer. Refer to the T_d character table. We found in Example 16.10 that the symmetry species of the normal modes are $A_1 + E + 2T_2$. Since the quadratic forms span $E + T_2$, the E and T_2 normal modes are Raman active.

Answer. Notice that the A_1 breathing mode is neither infrared nor Raman active.

Exercise. Which of the vibrational modes of H_2O are Raman active?

[All three]

The **exclusion rule** also helps us to decide which modes are active:

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

(A mode may be inactive in both.) Since we can often judge intuitively when 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.

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 of the scattered light with a polarization parallel and perpendicular to the plane of polarization of the incident radiation (Fig. 16.31):

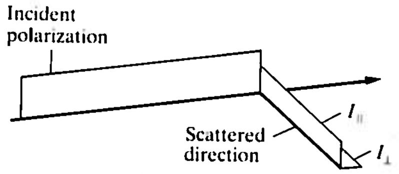

Fig. 16.31 The definition of the planes used for the specification of the depolarization ratio ρ in Raman scattering.

$$\rho = \frac{I_{\perp}}{I_{\parallel}}$$

If the emergent light is not polarized, both intensities are the same and $\rho = 1$; if the light retains its initial polarization, $I_{\perp} = 0$ and so $\rho = 0$. We classify a line as **depolarized** if it has ρ close to 1 and as **polarized** if it has ρ close to zero. A general rule is that totally symmetrical vibrations give rise to polarized Raman lines in which the incident polarization is largely preserved. Vibrations that are not totally symmetrical give rise to depolarized lines since the incident radiation can give rise to radiation in the perpendicular direction too. This means that if we observe the Raman spectrum with a polarizing filter (a 'half-wave plate') first parallel and then perpendicular to the polarization of the incident beam, the intensity of the polarized lines will appear significantly reduced and hence these lines can be ascribed to symmetrical vibrations.

Applications

One application of vibrational Raman spectroscopy is to the determination of the structures of symmetrical molecules such as XeF_4 and SF_6. Another application makes use of the fact that the intensity characteristics of Raman transitions, which depend on molecular polarizabilities, are more readily transferred from molecule to molecule than the intensities of infrared spectra, which depend on dipole moments and are more sensitive to the

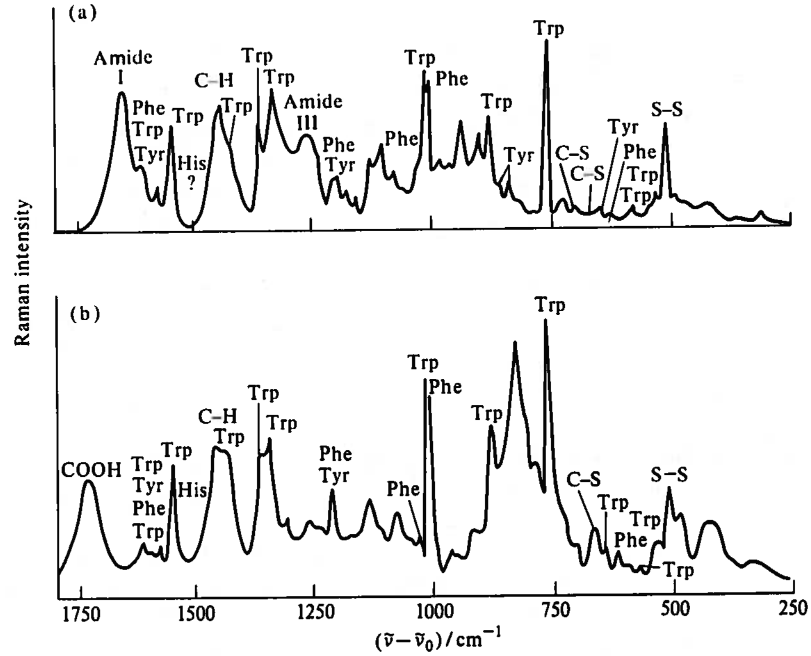

Fig. 16.32 The vibrational Raman spectrum of lysozyme in water and the superposition of the Raman spectra of the constituent amino acids. (From *Raman spectroscopy*, D. A. Long. Copyright 1977, McGraw-Hill Inc. Used with the permission of the McGraw-Hill Book Company.)

other groups present in a molecule and to the solvent. Hence, Raman spectra are useful in the identification of organic and inorganic species in solution. An example of the technique is shown in Fig. 16.32, which shows the vibrational Raman spectrum of an aqueous solution of lysozyme and, for comparison, a superposition of the Raman spectra of the constituent amino acids. The differences are indications of the effects of conformation, environment, and specific interactions (such as S–S linking) in the enzyme molecule.

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Exercises

16.1 Calculate the reduced masses of (a) $^{1}H^{35}Cl$, (b) $^{2}H^{35}Cl$, and $^{1}H^{37}Cl$ and identify the atom that makes the greater contribution.

16.2 The bond length of $^{79}Br^{81}Br$ is 228 pm; calculate the moment of inertia of the molecule.

16.3 The rotational constant of $^{127}I^{35}Cl$ is $0.1142\ cm^{-1}$. Calculate the bond length of the molecule.

16.4 The wavenumber of the incident radiation in a Raman spectrometer is $20\,487\ cm^{-1}$. What is the wavenumber of the scattered Stokes radiation for the $J = 2 \leftarrow 0$ transition of $^{14}N^{14}N$?

16.5 Infrared absorption by $^{1}H^{81}Br$ gives rise to an R branch from $v = 0$. What is the wavenumber of the line originating from the rotational state with $J = 2$?

16.6 Calculate the percentage difference in the fundamental vibration wavenumber of $^{23}Na^{35}Cl$ and $^{23}Na^{37}Cl$ on the assumption that their force constants are the same.

16.7 The wavenumber of the fundamental vibrational transition of $^{35}Cl_2$ is $564.9\ cm^{-1}$. Calculate the force constant of the bond.

16.8 For $^{127}I^{35}Cl$, $\tilde{\nu} = 384.3\ cm^{-1}$ and $x_e\tilde{\nu} = 1.5\ cm^{-1}$. Calculate the wavenumber of the pure fundamental ($\Delta v = 1$) vibrational transition with the highest wavenumber and that of the next highest.

16.9 The bond dissociation energy of $^{127}I^{35}Cl$ is 2.153 eV. Use the information in Exercise 16.8 to calculate the depth of the molecular potential energy curve of this molecule.

16.10 The molecule CH_2Cl_2 belongs to the point group C_{2v}. The displacements of the atoms span $5A_1 + 2A_2 + 4B_1 + 4B_2$. What are the symmetries of the normal modes of vibration?

16.11 Which of the following molecules may show a pure rotational microwave absorption spectrum: (a) H_2, (b) HCl, (c) CH_4, (d) CH_3Cl, (e) CH_2Cl_2, (f) H_2O, (g) H_2O_2, (h) NH_3?

16.12 Which of the following molecules may show infrared absorption spectra: (a) H_2, (b) HCl, (c) CO_2, (d) H_2O, (e) CH_3CH_3, (f) CH_4, (g) CH_3Cl, (h) N_2?

16.13 Which of the following molecules may show a pure rotational Raman spectrum: (a) H_2, (b) HCl, (c) CH_4, (d) CH_3Cl, (e) CH_2Cl_2, (f) CH_3CH_3, (g) SF_6?

16.14 What is the Doppler-shifted wavelength of a red (660 nm) traffic light approached at 50 m.p.h.? At what speed would it appear green (520 nm)?

16.15 A spectral line of $^{48}Ti^{8+}$ in a distant star was found to be shifted from 654.2 nm to 706.5 nm and to be broadened to 61.8 pm. What is the speed of recession and the surface temperature of the star?

16.16 Estimate the lifetime of a state that gives rise to a line of width (a) $0.1\ cm^{-1}$, (b) $1\ cm^{-1}$, (c) 100 MHz.

16.17 A molecule in a liquid undergoes about 1×10^{13} collisions in each second. Suppose that (a) every collision is effective in deactivating the molecule vibrationally and (b) that one collision in 100 is effective. Calculate the width (in cm^{-1}) of vibrational transitions in the molecule.

16.18 Calculate the relative numbers of Cl_2 molecules ($\tilde{\nu} = 559.7\,cm^{-1}$) in the ground and first excited vibrational states at (a) 298 K, (b) 500 K.

16.19 The pure rotational spectrum of $^1H^{131}I$ consists of a series of lines separated by $13.10\,cm^{-1}$. Calculate the bond length of the molecule.

16.20 The hydrogen halides have the following fundamental vibrational wavenumbers:

	HF	$H^{35}Cl$	$H^{81}Br$	$H^{127}I$
$\tilde{\nu}/cm^{-1}$	4143.3	2988.9	2649.7	2309.5

Calculate the force constants of the hydrogen–halogen bonds.

16.21 From the data in Exercise 16.20, predict the fundamental vibrational wavenumbers of the deuterium halides.

16.22 The first five vibrational energy levels of HCl are at 1481.86, 4367.50, 7149.04, 9826.48, and $12\,399.8\,cm^{-1}$. Calculate the dissociation energy of the molecule in cm^{-1} and eV.

16.23 The vibrational Raman spectrum of $^{35}Cl_2$ shows a series of Stokes lines separated by $0.9752\,cm^{-1}$ and a similar series of anti-Stokes lines. Calculate the bond length of the molecule.

16.24 Which of the three vibrations of an AB_2 molecule are infrared or Raman active when it is (a) non-linear, (b) linear?

16.25 Consider the vibrational mode that corresponds to the uniform expansion of the benzene ring. Is it (a) Raman, (b) infrared active?

Problems

Numerical problems

16.1 Calculate the Doppler width (as a fraction of the transition wavelength) for any kind of transition in (a) HCl, (b) ICl at 25°C. What would be the widths of the rotational and vibrational transitions in these molecules (in MHz and cm^{-1} respectively), given $B(\mathrm{ICl}) = 0.1142\,cm^{-1}$, $\tilde{\nu}(\mathrm{ICl}) = 384\,cm^{-1}$, and the information in Table 16.2.

16.2 The number of collisions that a molecule undergoes per unit time in a gas of pressure p is

$$z = 4\sigma\left(\frac{kT}{\pi m}\right)^{1/2} \times \frac{p}{kT}$$

where σ is the collision cross-section. Find an expression for the collision-limited lifetime of an excited state assuming that every collision is effective. Estimate the width of a rotational transition in HCl ($\sigma = 0.30\,nm^2$) at 25°C and 1.0 atm. To what value must the pressure of the gas be reduced in order to ensure that collision broadening is less important than Doppler broadening?

16.3 The rotational constant of NH_3 is equivalent to 298 GHz. Compute the separation of the pure rotational spectrum lines in GHz and cm^{-1}, and show that the value of B is consistent with an N—H bond length of 101.4 pm and a bond angle of 106° 47′.

16.4 The vibrational energy levels of NaI lie at wavenumbers 142.81, 427.31, 710.31, and $991.81\,cm^{-1}$. Show that they fit the expression $(v+\frac{1}{2})\tilde{\nu} - (v+\frac{1}{2})^2 x_e\tilde{\nu}$ and deduce the force constant, zero-point energy, and dissociation energy of the molecule.

16.5 A space probe was designed to look for CO in the atmosphere of Saturn, and it was decided to use a microwave technique from an orbiting satellite. Given the bond length of the molecule as 112.82 pm, at what frequencies will the first four transitions of $^{12}C^{16}O$ lie? What precision is needed in order to distinguish the 1–0 transition in the spectra of $^{12}C^{16}O$ and $^{13}C^{16}O$ in order to determine the relative abundances of the two carbon isotopes?

16.6 Rotational absorption lines from $^1H^{35}Cl$ gas were found at the following wavenumbers (R. L. Hausler and R. A. Oetjen, *J. chem. Phys.*, **21**, 1340 (1953)): 83.32, 104.13, 124.73, 145.37, 165.89, 186.23, 206.60, $226.86\,cm^{-1}$. Calculate the moment of inertia and the bond length of the molecule. Predict the positions of the corresponding lines in $^2H^{35}Cl$.

16.7 Is the bond length in HCl the same as that in DCl? The data (in cm^{-1}) from the rotational structure of the infrared spectrum of the two molecules are as follows (I. M. Mills, H. W. Thompson, and R. L. Williams, *Proc. R. Soc.*, **A218,** 29 (1953); J. Pickworth and H. W. Thompson, *Proc. R. Soc.*, **A218,** 37 (1953)):

J	0	1	2	3	4	5	6
$^1H^{35}Cl$(R branch)	2906.25	2925.92	2944.99	2963.35	2981.05	2998.05	3014.50
$^1H^{35}Cl$(P branch)		2865.14	2843.63	2821.59	2799.00	2775.77	2752.01
$^2H^{35}Cl$(R branch)	2101.60	2111.94	2122.05	2131.91	2141.53	2150.93	2160.06
$^2H^{35}Cl$(P branch)		2080.26	2069.24	2058.02	2046.58	2034.95	2023.12

16.8 Thermodynamic considerations suggest that the copper monohalides CuX should exist mainly as polymers in the gas phase, and indeed it proved difficult to obtain the monomers in sufficient abundance to detect spectroscopically. This difficulty was overcome by flowing the halogen gas over copper heated to 1100 K (E. L. Manson, F. C. de Lucia, and W. Gordy, *J. chem. Phys.*, **63,** 2724 (1975)). For CuBr the

$J = 13$–14, 14–15, and 15–16 transitions occurred at 84 421.34, 90 449.25, and 96 476.72 MHz respectively. Calculate the rotational constant and bond length of CuBr.

16.9 The microwave spectrum of $^{16}O^{12}CS$ (C. H. Townes, A. N. Holden, and F. R. Merritt, *Phys. Rev.*, **74**, 1113 (1948)) gave absorption lines (in GHz) as follows:

J	1	2	3	4
^{32}S	24.325 92	36.488 82	48.651 64	60.814 08
^{34}S	23.732 33		47.462 40	

Use the expressions for moments of inertia in Table 16.1 and assume that the bond lengths are unchanged by substitution, calculate the CO and CS bond lengths in OCS.

16.10 The HCl molecule is quite well described by the Morse potential with $D_e = 5.33\,\text{eV}$, $\tilde{\nu} = 2989.7\,\text{cm}^{-1}$, and $x_e\tilde{\nu} = 52.05\,\text{cm}^{-1}$. Assuming that the potential is unchanged on deuteration, predict the dissociation energies (D_0) of (a) HCl, (b) DCl.

16.11 The Morse potential (eqn 23) is very useful as a simple representation of the actual molecular potential energy. When RbH was studied it was found that $\tilde{\nu} = 936.8\,\text{cm}^{-1}$ and $x_e\tilde{\nu} = 14.15\,\text{cm}^{-1}$. Plot the potential energy curve from 50 pm to 800 pm around $R_e = 236.7\,\text{pm}$. Then go on to explore how the rotation of a molecule may weaken its bond by allowing for the kinetic energy of rotation of a molecule and plotting

$$V^* = V + hcBJ(J+1) \qquad B = \frac{\hbar}{4\pi c\mu R^2}$$

Plot these curves on the same diagram for $J = 40$, 80, and 100, and observe how the dissociation energy is affected by the rotation. (Taking $B = 3.020\,\text{cm}^{-1}$ at the equilibrium bond length will greatly simplify the calculation.)

Theoretical problems

16.12 Show that the moment of inertia of a diatomic molecule composed of atoms of masses m_A and m_B and bond length R is equal to μR^2, where μ is the reduced mass of the molecule.

16.13 Derive an expression for the value of J corresponding to the most highly populated rotational energy level of a diatomic rotor at a temperature T remembering that the degeneracy of each level is $2J+1$. Evaluate the expression for ICl (for which $B = 0.1142\,\text{cm}^{-1}$) at 25°C. Repeat the problem for the most highly populated level of a spherical rotor, taking note of the fact that each level is $(2J+1)^2$-fold degenerate. Evaluate the expression for CH_4 (for which $B = 5.24\,\text{cm}^{-1}$) at 25°C.

16.14 Derive expressions for the P, Q, and R branches of a diatomic rotor without making the assumption that the rotational constants are the same in the lower and upper vibrational states. Lines in the P branch of $^1H^{35}Cl$ were observed at 2865.1, 2843.6, and 2821.6 cm^{-1} for $J = 1$, 2, and 3, and in the R branch at 2906.2, 2925.9, 2945.0, and 2963.3 cm^{-1} for $J = 0$, 1, 2, 3 (I. M. Mills, H. W. Thompson, and R. L. Williams, *Proc. R. Soc.*, **A218**, 29 (1953)). Calculate the force constant of the bond and the bond lengths of the upper and lower vibrational states.

16.15 The set of relations known as 'Kraitchman's equations' relate the change in rotational constant (or moments of inertia) to the positions at which isotopic substitution is made. Show that when an isotope is substituted at a distance z along the axis from the original centre of mass of a symmetric rotor, then the change in rotational constant B is given by

$$(z/\text{pm})^2 = 1.685\,90 \times 10^5 \frac{\Delta B/\text{cm}^{-1}}{(B/\text{cm}^{-1})(B'/\text{cm}^{-1})(\Delta M/\text{g mol}^{-1})}$$

where B is the rotational constant before substitution, B' that after substitution, and

$$\Delta M = \frac{M(M'-M)}{M'}$$

where M and M' are the initial and final molar masses of the molecule. The microwave spectra of various isotopic species of $ClTeF_5$ show rigid symmetric rotor behaviour (A. C. Legon, *J. chem. Soc. Faraday Trans.*, II, **29** (1973)). Four of the F atoms lie in a square, the Te atom lies just above the plane of the square they form, the fifth F atom lies beneath this plane and the Cl atom lies above it. Use Kraitchman's equation to deduce the Te–Cl bond length on the assumption that all the Te–F bond lengths are identical. The relevant data are that the 11–10 transition occurs at 30 711.18 MHz in $^{35}Cl^{126}TeF_5$, at 30 713.24 MHz in $^{35}Cl^{125}TeF_5$, and at 29 990.54 MHz in $^{37}Cl^{126}TeF_5$. Use $M(^{126}Te) = 125.0331\,\text{g mol}^{-1}$ and $M(^{125}Te) = 124.0443\,\text{g mol}^{-1}$.

16.16 The moments of inertia of the linear mercury(II) halides are very large, and so the O and S branches of their vibrational Raman spectra show little rotational structure. Nevertheless, the peaks of both branches can be identified and have been used to measure the rotational constants of the molecules (R. J. H. Clark and D. M. Rippon, *J. chem. Soc. Faraday Trans.*, II, **69**, 1496 (1973)). Show, from a knowledge of the value of J corresponding to the intensity maximum, that the separation of the peaks of the O and S branches is given by the 'Placzek–Teller relation'

$$\delta\tilde{\nu} = \left(\frac{32BkT}{hc}\right)^{1/2}$$

The following widths were obtained at the temperatures stated:

	$HgCl_2$	$HgBr_2$	HgI_2
$\theta/°\text{C}$	282	292	292
$\delta\tilde{\nu}/\text{cm}^{-1}$	23.8	15.2	11.4

Calculate the bond lengths in the three molecules.

17

Electronic transitions

Check-list of key ideas

1. The *Beer–Lambert law* for the reduction in intensity of light passing through an absorbing medium and the definition of the *molar absorption coefficient* (eqn 1).

2. The intensity of absorption in terms of the *oscillator strength* (eqn 3a) and its relation to the transition dipole moment (eqn 3b).

3. The use of the *Franck–Condon principle* to account for the vibrational structure of electronic transitions and the concept of a *vertical transition* (Section 17.2).

4. The *Laporte selection rule* and the *vibronic character* of *d–d transitions* in complexes (Section 17.3).

5. *Charge-transfer transitions* and π^*,π and π^*,n transitions (Section 17.3).

6. The mechanisms of *fluorescence* and *phosphorescence* and the characteristics of a *fluorescence spectrum* (Section 17.4).

7. The mechanisms of *intersystem crossing* (Section 17.4) and *internal conversion* leading to *predissociation* (Section 17.5).

8. The principles of *laser action*, including *population inversion*, *pumping*, and the difference between *three-level* and *four-level* lasers (Section 17.6).

9. The characteristics of laser radiation and the formation of pulses by *Q-switching* and *mode locking* (Section 17.6).

10. Examples of practical lasers, including *solid-state lasers*, *gas lasers*, *ion lasers*, *chemical lasers*, *excimer lasers*, *dye lasers*, and *semiconductor lasers* (Section 17.7).

11. The applications of lasers in chemistry, particularly to *multiphoton spectroscopy*, *laser Raman spectroscopy*, and to precision *state-selection* and *fast reactions* (Section 17.8).

12. The techniques of *ultraviolet photoelectron spectroscopy* and *X-ray photoelectron spectroscopy* (Section 17.9 to 17.11).

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