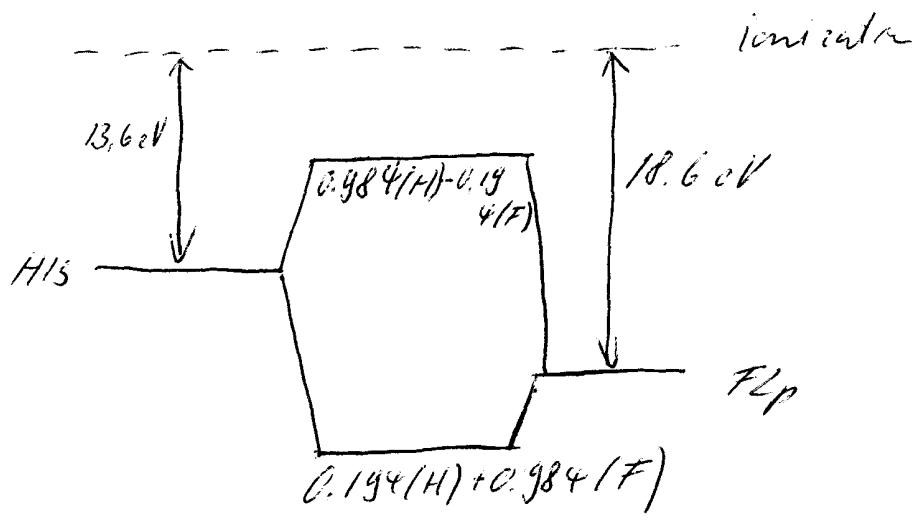


# Heteronuclear diatomic molecules

polar bonds: covalent bond, in which the electron pair is shared *unequally* by the 2 atoms  
 ⇒ partial negative charge δ-  
 " positive charge δ+

HF:  $\psi = c_H \psi_H + c_F \psi_F$



in general:  $\psi = c_A A + c_B B$

due to variation principle problem of energy minimization!

$$(\alpha_A - E)c_A + (\beta - ES)c_B = 0$$

$$(\beta - ES)c_A + (\alpha_B - E)c_B = 0$$

- S: overlap integral
- $\alpha_i$ : Coulomb integrals
- $\beta$ : resonance integral

Ethene:

$\pi$  orbitals as LCAO of C2p

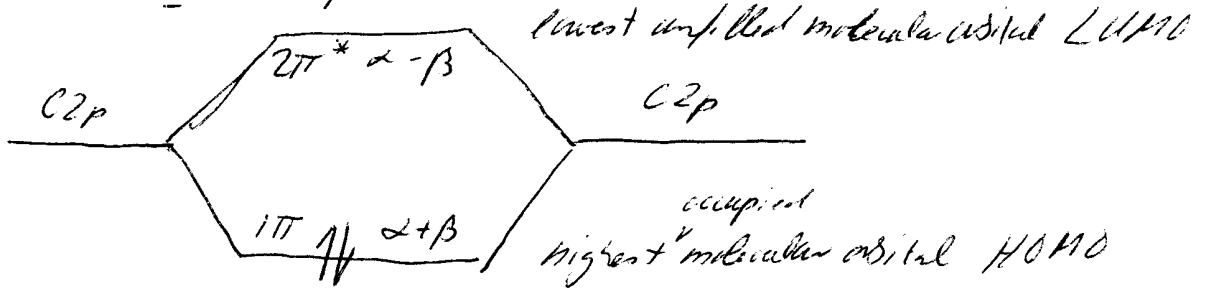
$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$

Hückel approximation:

- 1.  $S = 0$
- 2.  $\beta = 0$  for non-neighbors
- 3. all remaining resonance integrals =  $\beta$

$$\Rightarrow \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0$$

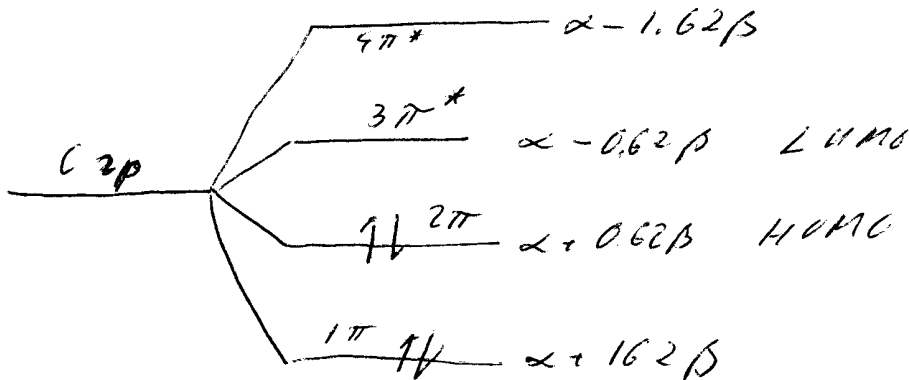
$$\Rightarrow E_{\pm} = \alpha \pm \beta$$



Butadiene:

four LCAO-MOs:

$$E = \alpha \pm 1.62\beta, \alpha \pm 0.62\beta$$



## $\pi$ - electron binding energy

(3)

ethene:  $E_{\pi} = 2(\alpha + \beta) = 2\alpha + 2\beta$   $2e^{-}$

butadiene:  $E_{\pi} = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) =$   
 $= 4\alpha + 4.48\beta$   $4e^{-}$

$\Rightarrow 0.48\beta$  delocalization energy

## Molecular Symmetry

- symmetry of molecules
- symmetry ~~the~~ transformations of orbitals  
identify overlap integrals that vanish
- consider symmetry for LCAOS
- group ~~symmetry~~ theory

Symmetry elements:

- identity
- n-fold rotation
- reflection
- inversion
- n-fold improper rotation (rotation + reflection)

⇒ symmetry classification of molecules  
 notation: Schoenflies system

immediate consequences:

- only molecules belonging to the groups  $C_n$ ,  $C_{nv}$  and  $C_s$  may have a permanent electric dipole moment = polar molecules
- a molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation  $S_n$

Vanishing integrals and orbital overlap

Symmetry characteristics of orbitals that belong to atoms in a molecule

⇒ character table

$$S = \int \psi_1 \psi_2 d\tau$$

$\psi_1$ : atomic orbital A

$\psi_2$ : atomic orbital B

S: overlap integral S

The value of S is ~~the~~ independent of the orientation of the molecule.

⇒ S is invariant under any symmetry operation of the molecule

⇒ The integral is nonzero only if the integrand itself the product  $\psi_1 \psi_2$  is unchanged by any symmetry operation

⇒ only orbitals of the same symmetry species may ~~not~~ have nonzero overlap!

⇒ considers this in construction of LCAOs ⇒ symmetry-adapted linear combinations (SALCs)

same applies to selection rules:

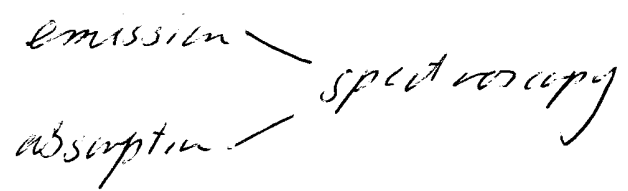
$$\mu_{z,fi} = -e \int \psi_f^* z \psi_i dz$$
  
unchanged by any symmetry operation

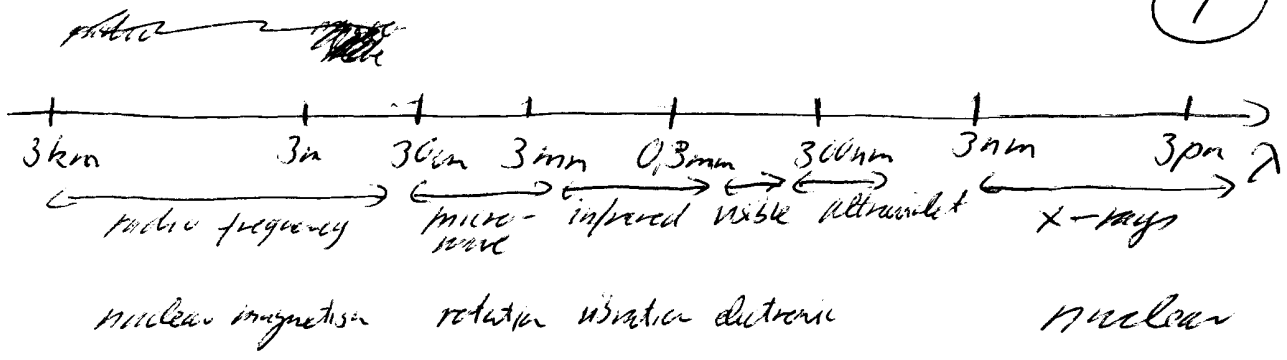
# Spectroscopy

spectral lines: absorption, emission, or scattering of photons when the energy of a molecule changes

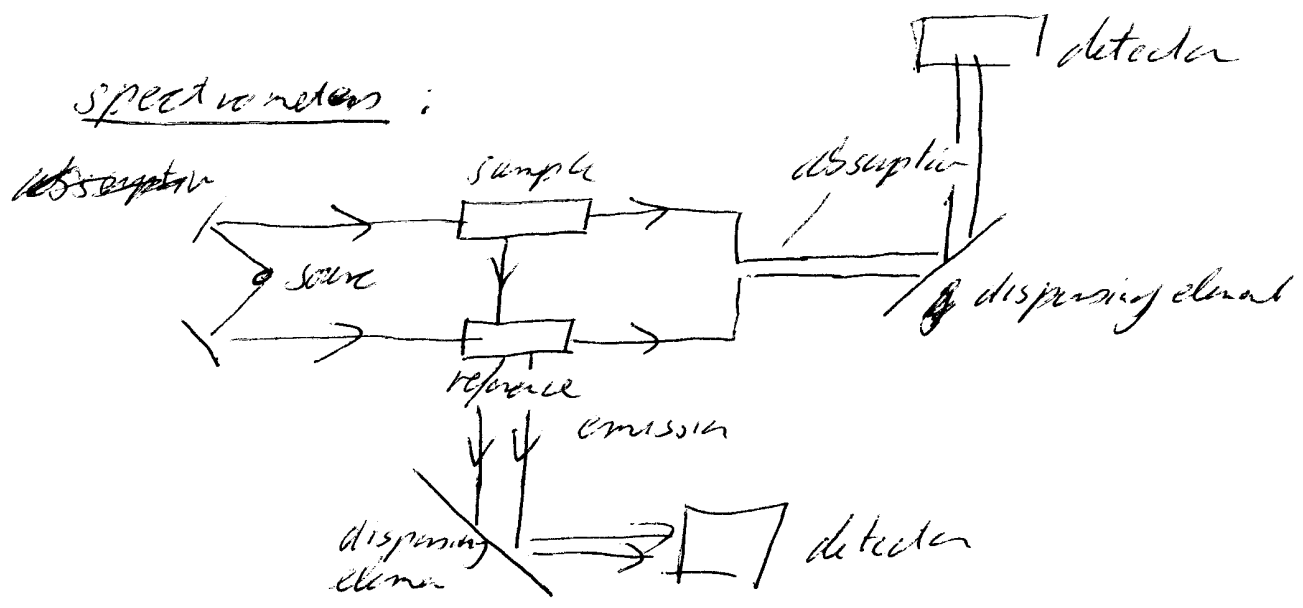
frequency  $\nu$ , wavelength  $\lambda$ , wavenumber  $\tilde{\nu}$

$$\lambda = \frac{c}{\nu} \quad \tilde{\nu} = \frac{\nu}{c}$$





Speedometers:



Source:

- lamps: tungsten, quartz-tungsten-halogen
- gas discharge lamps: Xenon, Mercury, Deuterium
- lasers: + OPOs, tapered fibers, Ti:Sapphire-lasers

dispersive element:

separates radiation into different frequencies

8

# diffraction grating

$$n\lambda = d(\sin\theta - \sin\phi)$$

↑ spacing of grating  
↑ angle of incidence  
↑ angle of emergence  
↑ order

+ slit  $\Rightarrow$  monochromator

or Fourier transformation:

use Michelson interferometer with path difference  $p$

$$J(p, \tilde{\nu}) d\tilde{\nu} = \int_{\text{from simple}} J(\tilde{\nu}) (1 + \cos 2\pi \tilde{\nu} p) d\tilde{\nu}$$

$$\Rightarrow J(p) = \int_0^{\infty} J(p, \tilde{\nu}) d\tilde{\nu} = \int_0^{\infty} J(\tilde{\nu}) (1 + \cos 2\pi \tilde{\nu} p) d\tilde{\nu}$$

$$\Rightarrow \boxed{J(\tilde{\nu}) = 4 \int_0^{\infty} \left\{ \frac{1}{2} J(p) - \frac{1}{2} J(0) \right\} \cos 2\pi \tilde{\nu} p dp}$$

## Detectors:

- photomultiplier (PMT): tube or photo diode
- charge-coupled device (CCD)
- mercury-cadmium-telluride (MCT) - detector



# Raman Spectroscopy

9

molecular energy levels are explored by examining the frequencies present in the radiation scattered by molecules

Stokes radiation: laser

1 in  $10^7$  of the incident photons collide with molecules, give up some of their energy, and emerge with a lower energy

Anti-Stokes radiation:

incident photons collect energy from molecules  $\Rightarrow$  higher frequency radiation

Raleigh radiation:

radiation without change of frequency  
notch filter absorbs this radiation

### Intensities of spectral lines

$$T = \frac{J}{J_0}$$

transmitted  
incident

### Beer - Lambert law:

$$J = J_0 10^{-\epsilon c l}$$

- $\epsilon$ : molar absorption coefficient
- $l$ : length of sample
- $c$ : molar concentration

### Absorption intensities: (- Einstein)

stimulated absorption  $w = B \rho$

$w$ : rate of change of probability of the molecule being forced in the upper state

$B$ : Einstein coefficient

$\rho d\nu$ : energy density of radiation in the frequency range  $\nu$  to  $\nu + d\nu$

stimulated emission:  $w' = B' \rho$  Einstein coeff. of stimulated emission

+ spontaneous emission:

total rate of transition from the upper to the lower state:

$$w' = A + B' \rho$$

$$B = B'$$

Einstein coeff. of spontaneous emission

$$A = \left( \frac{8\pi h \nu^3}{c^3} \right) B$$

$$\vec{\mu}_{fi} = \langle f | \vec{\mu} | i \rangle = \int \psi_f^* \vec{\mu} \psi_i d\tau$$

electric dipole moment operator

for the molecule to be able to interact with the EM-field and absorb or create a photon of frequency  $\omega$ , it must possess, at least transiently, a dipole oscillating at that frequency.

$$B = \frac{1/\epsilon_0 \hbar^2}$$

**Justification 16.3**

We know from the Boltzmann distribution (Section 2.1) that the probability that a gas molecule of mass  $m$  and speed  $s$  in a sample with temperature  $T$  has kinetic energy  $E_K = \frac{1}{2}ms^2$  is proportional to  $e^{-ms^2/2kT}$ . The observed frequencies,  $\nu_{\text{obs}}$ , emitted or absorbed by the molecule are related to its speed by eqn 23:

$$\nu_{\text{obs}} = \nu \left( \frac{1}{1 \pm s/c} \right)$$

where  $\nu$  is the unshifted frequency. When  $s \ll c$ , the Doppler shift in the frequency is

$$\nu_{\text{obs}} - \nu \approx \pm \nu s/c$$

which implies a symmetrical distribution of observed frequencies with respect to molecular speeds. More specifically, the intensity  $I$  of a transition at  $\nu_{\text{obs}}$  is proportional to the probability of finding the molecule that emits or absorbs at  $\nu_{\text{obs}}$ , so it follows from the Boltzmann distribution and the expression for the Doppler shift that

$$I(\nu_{\text{obs}}) \propto e^{-m c^2 (\nu_{\text{obs}} - \nu)^2 / 2 \nu^2 k T}$$

which has the form of a Gaussian function. The width at half-height can be calculated directly from the exponent (see the Maths commentary) to give eqn 24.

**(b) Lifetime broadening**

It is found that spectroscopic lines from gas-phase samples are not infinitely sharp even when Doppler broadening has been largely eliminated by working at low temperatures. The same is true of the spectra of samples in condensed phases and solution. This residual broadening is due to quantum mechanical effects. Specifically, 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  $\tau$  (tau), the **lifetime** of the state, then its energy levels are blurred to an extent of order  $\delta E$ , where

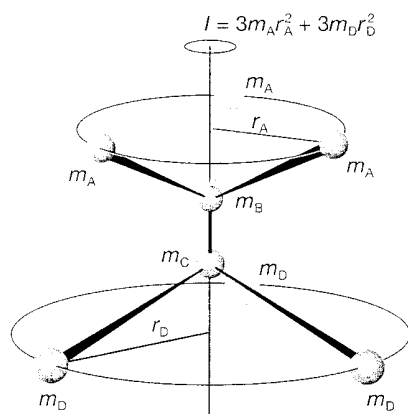
$$\delta E \approx \frac{\hbar}{\tau} \quad (16.25)$$

This expression is reminiscent of the Heisenberg uncertainty principle (eqn 11.46), and consequently this **lifetime broadening** is often called 'uncertainty broadening'. When the energy spread is expressed as a wavenumber through  $\delta E = hc\delta\tilde{\nu}$ , and the values of the fundamental constants introduced, this relation becomes

$$\delta\tilde{\nu} \approx \frac{5.3 \text{ cm}^{-1}}{\tau/\text{ps}} \quad (16.26)$$

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 corresponding spectral lines.

Two processes are responsible for the finite lifetimes of excited states. The dominant one for low-frequency transitions is **collisional deactivation**, which arises from collisions between molecules or with the walls of the container. If the **collisional lifetime**, the mean time between collisions, is  $\tau_{\text{col}}$ , the resulting collisional



**16.15** The definition of moment of inertia. In this molecule there are three identical atoms attached to the B atom and three different but mutually identical atoms attached to the C atom. In this example, the centre of mass lies on an axis passing through the B and C atom, and the perpendicular distances are measured from this axis.

linewidth is  $\delta F_{\text{col}} \approx \hbar/\tau_{\text{col}}$ . Because  $\tau_{\text{col}} = 1/z$ , where  $z$  is the collision frequency, and from the kinetic model of gases (Section 24.1) we know that  $z$  is proportional to the pressure, we see that the collisional linewidth is proportional to the pressure. The collisional linewidth can therefore be 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 the coefficient of spontaneous emission  $A$  and therefore as  $\nu^3$ ), 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, 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 ns), corresponding to a natural width of about  $5 \times 10^{-4} \text{ cm}^{-1}$  (15 MHz). A typical rotational state natural lifetime is about  $10^3$  s, corresponding to a natural linewidth of only  $5 \times 10^{-15} \text{ cm}^{-1}$  (of the order of  $10^{-4}$  Hz).

## Pure rotation spectra

The general strategy we 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 transition moments and the populations of the states. In this section we illustrate the strategy by considering the rotational states of molecules.

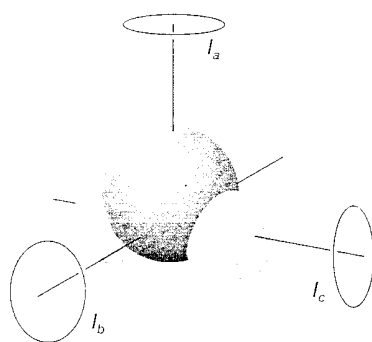
### 16.4 Moments of inertia

The key molecular parameter we shall need is the **moment of inertia**,  $I$ , of the molecule (Section 12.6). The moment of inertia of a molecule is defined as the mass of each atom multiplied by the square of its distance from the rotational axis through the centre of mass of the molecule (Fig. 16.15):

$$I = \sum_i m_i r_i^2 \quad [16.27]$$

where  $r_i$  is the perpendicular distance of the atom  $i$  from the axis of rotation. 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.

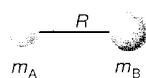
In general, the rotational properties of any molecule can be expressed in terms of the moments of inertia about three perpendicular axes set in the molecule (Fig. 16.16). The convention is to label the moments of inertia  $I_a$ ,  $I_b$ , and  $I_c$ , with the axes chosen so that  $I_c \geq I_b \geq I_a$ . For linear molecules, the moment of inertia around the internuclear axis is zero. The explicit expressions for the moments of inertia of some symmetrical molecules are given in Table 16.1.



**16.16** An asymmetric rotor has three different moments of inertia; all three rotation axes coincide at the centre of mass of the molecule.

**Table 16.1** Moments of inertia†

1. Diatomics



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

2. Linear rotors

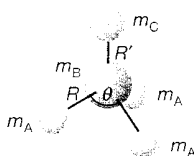


$$I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$$



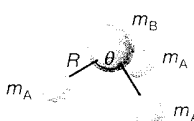
$$I = 2m_A R^2$$

3. Symmetric rotors



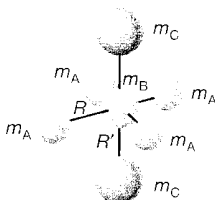
$$I_{\parallel} = 2m_A R^2 (1 - \cos \theta)$$

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



$$I_{\parallel} = 2m_A R^2 (1 - \cos \theta)$$

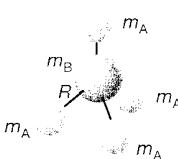
$$I_{\perp} = m_A R^2 (1 - \cos \theta) + \frac{m_A m_B}{m} R^2 (1 + 2 \cos \theta)$$



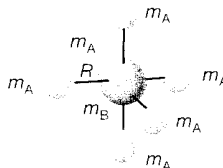
$$I_{\parallel} = 4m_A R^2$$

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

4. Spherical rotors

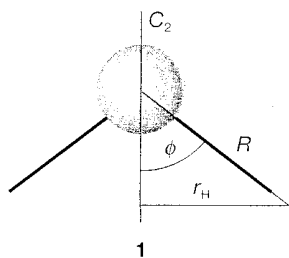


$$I = \frac{8}{3} m_A R^2$$



$$I = 4m_A R^2$$

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



**Example 16.1** Calculating the moment of inertia of a molecule

Calculate the moment of inertia of an H<sub>2</sub>O molecule around the axis defined by the bisector of the HOH angle (1). The HOH bond angle is 104.5° and the bond length is 95.7 pm.

**Method** According to eqn 27, the moment of inertia is the sum of the masses multiplied by the squares of their distances from the axis of rotation. The latter can be expressed by using trigonometry and the bond angle and bond length.

**Answer** From eqn 27,

$$I = \sum_i m_i r_i^2 = m_H r_H^2 + 0 + m_H r_H^2 = 2m_H r_H^2$$

If the bond angle of the molecule is denoted  $2\phi$  and the bond length is  $R$ , trigonometry gives  $r_H = R \sin \phi$ . It follows that

$$I = 2m_H R^2 \sin^2 \phi$$

Substitution of the data gives

$$I = 2 \times (1.67 \times 10^{-27} \text{ kg}) \times (9.57 \times 10^{-11} \text{ m})^2 \times \sin^2 52.3^\circ = 1.91 \times 10^{-47} \text{ kg m}^2$$

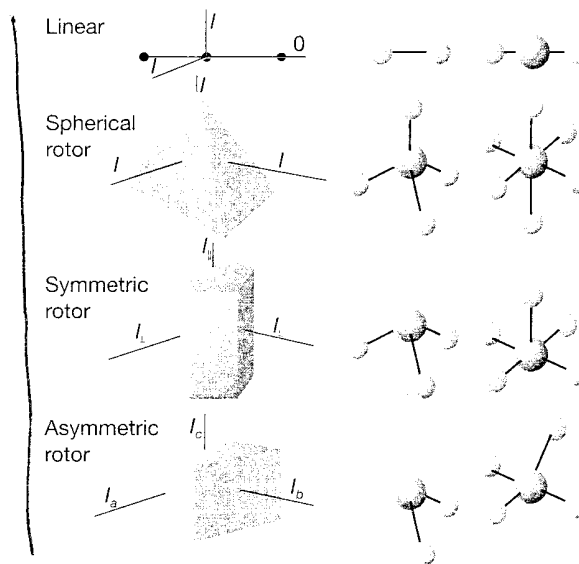
**Comment** The mass of the O atom makes no contribution to the moment of inertia for this mode of rotation as the atom is immobile while the H atoms circulate around it.

**Self-test 16.1** Calculate the moment of inertia of a  $\text{CH}^{35}\text{Cl}_3$  molecule around a rotational axis that contains the C—H bond. The C—Cl bond length is 177 pm and the HCCl angle is  $107^\circ$ ;  $m(^{35}\text{Cl}) = 34.97 \text{ u}$ .  $[4.99 \times 10^{-45} \text{ kg m}^2]$

We shall suppose initially that molecules are **rigid rotors**, bodies that do not distort under the stress of rotation. Rigid rotors can be classified into four types (Fig. 16.17):

**Spherical rotors** have three equal moments of inertia (examples:  $\text{CH}_4$ ,  $\text{SiH}_4$ , and  $\text{SF}_6$ ).

**Symmetric rotors** have two equal moments of inertia (examples:  $\text{NH}_3$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CH}_3\text{CN}$ ).



**16.17** A schematic illustration of the classification of rigid rotors.

**Linear rotors** have one moment of inertia (the one about the molecular axis) equal to zero (examples:  $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{OCS}$ , and  $\text{HC}\equiv\text{CH}$ ).

**Asymmetric rotors** have three different moments of inertia (examples:  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}$ , and  $\text{CH}_3\text{OH}$ ).

## 16.5 The rotational energy levels

The rotational energy levels of a rigid rotor may be obtained by solving the appropriate Schrödinger equation. Fortunately, however, there is a much less onerous short cut to the exact expressions that 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 classical expression for the energy of a body rotating about an axis  $a$  is

$$E_a = \frac{1}{2}I_a\omega_a^2 \quad (16.28)$$

where  $\omega_a$  is the angular velocity (in radians per second,  $\text{rad s}^{-1}$ ) about that axis and  $I_a$  is the corresponding moment of inertia. A body free to rotate about three axes has an energy

$$E = \frac{1}{2}I_a\omega_a^2 + \frac{1}{2}I_b\omega_b^2 + \frac{1}{2}I_c\omega_c^2$$

Because the classical angular momentum about the axis  $a$  is  $J_a = I_a\omega_a$ , with similar expressions for the other axes, it follows that

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} \quad (16.29)$$

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

### (a) Spherical rotors

When all three moments of inertia are equal to some value  $I$ , as in  $\text{CH}_4$  and  $\text{SF}_6$ , the classical expression for the energy is

$$E = \frac{J_a^2 + J_b^2 + J_c^2}{2I} = \frac{J^2}{2I}$$

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

$$J^2 \rightarrow J(J+1)\hbar^2 \quad J = 0, 1, 2, \dots$$

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

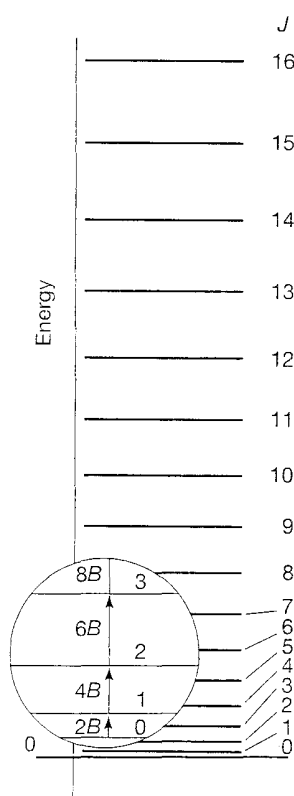
$$E_J = J(J+1)\frac{\hbar^2}{2I} \quad J = 0, 1, 2, \dots \quad (16.30)$$

The resulting ladder of energy levels is illustrated in Fig. 16.18. The energy is normally expressed in terms of the **rotational constant**,  $B$ , of the molecule, where

$$hcB = \frac{\hbar^2}{2I} \quad \text{so} \quad B = \frac{\hbar}{4\pi cl} \quad (16.31)$$

The expression for the energy is then

$$E_J = hcB J(J+1) \quad J = 0, 1, 2, \dots \quad (16.32)$$



**16.18** The rotational energy levels of a linear or spherical rotor. Note that the energy separation between neighbouring levels increases as  $J$  increases.



The rotational constant as defined by eqn 31 is a wavenumber.<sup>5</sup> The energy of a rotational state is normally reported as the **rotational term**,  $F(J)$ , a wavenumber, by division by  $hc$ :

$$F(J) = B J(J + 1) \quad (16.33)$$

The separation of adjacent levels is

$$F(J) - F(J - 1) = 2BJ \quad (16.34)$$

Because the rotational constant 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  $\text{CCl}_4$ : from the bond lengths and masses of the atoms we find  $I = 4.85 \times 10^{-45} \text{ kg m}^2$ , and hence  $B = 0.0577 \text{ cm}^{-1}$ .

### (b) Symmetric rotors

In symmetric rotors, two moments of inertia are equal but different from the third (as in  $\text{CH}_3\text{Cl}$ ,  $\text{NH}_3$ , and  $\text{C}_6\text{H}_6$ ); the unique axis of the molecule is its **principal axis** (or **figure axis**). We shall write the unique moment of inertia (that about the principal axis) as  $I_{\parallel}$  and the other two as  $I_{\perp}$ . If  $I_{\parallel} > I_{\perp}$ , the rotor is classified as **oblate** (like a pancake, and  $\text{C}_6\text{H}_6$ ); if  $I_{\parallel} < I_{\perp}$  it is classified as **prolate** (like a cigar, and  $\text{CH}_3\text{Cl}$ ). The classical expression for the energy, eqn 29, becomes

$$E = \frac{J_b^2 + J_c^2}{2I_{\perp}} + \frac{J_a^2}{2I_{\parallel}}$$

This expression can be written in terms of  $J^2 = J_a^2 + J_b^2 + J_c^2$ :

$$E = \frac{J^2 - J_a^2}{2I_{\perp}} + \frac{J_a^2}{2I_{\parallel}} = \frac{J^2}{2I_{\perp}} + \left( \frac{1}{2I_{\parallel}} - \frac{1}{2I_{\perp}} \right) J_a^2 \quad (16.35)$$

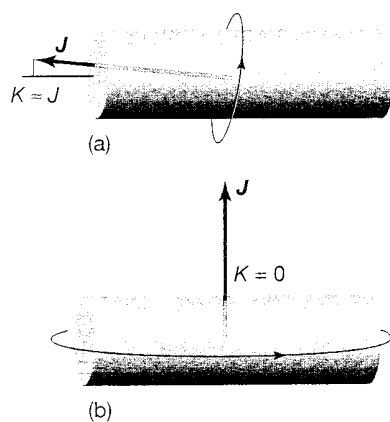
Now we generate the quantum expression by replacing  $J^2$  by  $J(J + 1)\hbar^2$ , where  $J$  is the angular momentum quantum number. We also know from the quantum theory of angular momentum (Section 12.7b) that the component of **angular momentum** about any axis is restricted to the values  $K\hbar$ , with  $K = 0, \pm 1, \dots, \pm J$ . ( $K$  is the quantum number used to signify a component on the principal axis;  $M_J$  is reserved for a component on an externally defined axis.) Therefore, we also replace  $J_a^2$  by  $K^2\hbar^2$ . It follows that the rotational terms are

$$F(J, K) = B J(J + 1) + (A - B)K^2 \quad J = 0, 1, 2, \dots \quad K = 0, \pm 1, \dots, \pm J \quad (16.36)$$

with

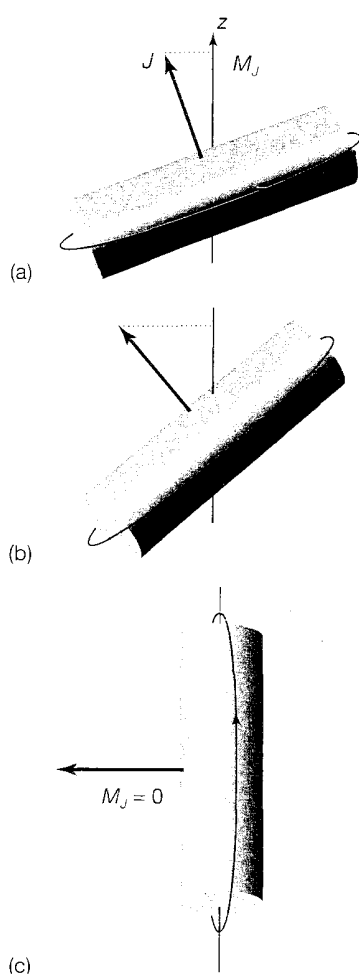
$$A = \frac{\hbar^2}{4\pi c I_{\parallel}} \quad B = \frac{\hbar^2}{4\pi c I_{\perp}} \quad (16.37)$$

Equation 36 matches what we should expect for the dependence of the energy levels on the two distinct moments of inertia of the molecule. When  $K = 0$ , there is no component of angular momentum about the principal axis, and the energy levels depend only on  $I_{\perp}$  (Fig. 16.19). When  $K = \pm J$ , almost all the angular momentum arises from rotation around the principal 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.



**16.19** 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 principal axis: it is undergoing end-over-end rotation.

5. 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. Then  $B = \hbar/4\pi I$  and the energy is  $E = \hbar B J(J + 1)$ .



**16.20** The significance of the quantum number  $M_J$ . (a) When  $M_J$  is close to its maximum value,  $J$ , most of the molecular rotation is around the laboratory  $z$ -axis. (b) an intermediate value of  $M_J$ . (c) When  $M_J = 0$  the molecule has no angular momentum about the  $z$ -axis. All three diagrams correspond to a state with  $K = 0$ ; there are corresponding diagrams for different values of  $K$ , in which the angular momentum makes a different angle to the molecule's principal axis.

### Example 16.2 Calculating the rotational energy levels of a molecule

A  $^{14}\text{NH}_3$  molecule is a symmetric rotor with bond length 101.2 pm and HNH bond angle  $106.7^\circ$ . Calculate its rotational terms.

**Method** Begin by calculating the rotational constants  $A$  and  $B$  by using the expressions for moments of inertia given in Table 16.1. Then use eqn 36 to find the rotational terms.

**Answer** Substitution of  $m_A = 1.0078$  u,  $m_B = 14.0031$  u,  $R = 101.2$  pm, and  $\theta = 106.7^\circ$  into the second of the symmetric rotor expressions in Table 16.1 gives  $I_{\parallel} = 4.4128 \times 10^{-47}$  kg m $^2$  and  $I_{\perp} = 2.8059 \times 10^{-47}$  kg m $^2$ . Hence,  $A = 6.344$  cm $^{-1}$  and  $B = 9.977$  cm $^{-1}$ . It follows from eqn 36 that

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

Upon multiplication by  $c$ ,  $F(J, K)$  acquires units of frequency:

$$F(J, K)/\text{GHz} = 299.1J(J+1) - 108.9K^2$$

**Comment** For  $J = 1$ , the energy needed for the molecule to rotate mainly about its figure axis ( $K = \pm J$ ) is equivalent to  $16.32$  cm $^{-1}$  (489.3 GHz), but end-over-end rotation ( $K = 0$ ) corresponds to  $19.95$  cm $^{-1}$  (598.1 GHz).

**Self-test 16.2** A  $\text{CH}_3^{35}\text{Cl}$  molecule has a C—Cl bond length of 178 pm, a C—H bond length of 111 pm, and an HCH angle of  $110.5^\circ$ . Calculate its rotational energy terms.

$$[F(J, K)]/\text{cm}^{-1} = 0.444J(J+1) + 4.58K^2; \\ \text{also } F(J, K)/\text{GHz} = 13.3J(J+1) + 137K^2$$

### (c) Linear rotors

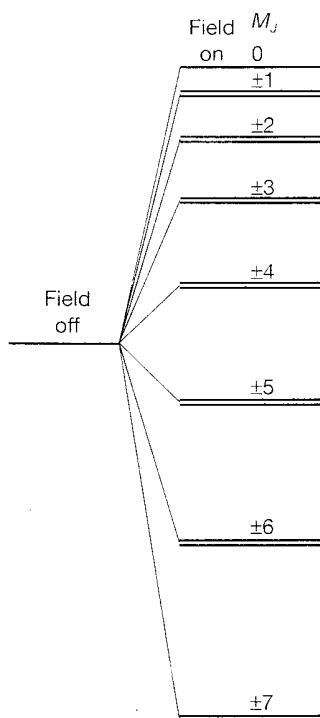
For a linear rotor (such as  $\text{CO}_2$ ,  $\text{HCl}$ , and  $\text{C}_2\text{H}_2$ ), in which the nuclei are regarded as mass points, the rotation occurs only about an axis perpendicular to the line of atoms and there is zero angular momentum around the line. Therefore, the component of angular momentum around the figure axis of a linear rotor is identically zero, and  $K = 0$  in eqn 36. The rotational terms of a linear molecule are therefore

$$F(J) = BJ(J+1) \quad J = 0, 1, 2, \dots \quad (16.38)$$

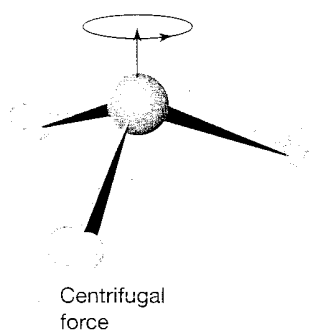
This expression is the same as eqn 33 but we have arrived at it in a significantly different way: here  $K = 0$ , but for a spherical rotor  $A = B$ .

### (d) Degeneracies and the Stark effect

The energy of a symmetric rotor depends on  $J$  and  $K$ , and each level except those with  $K = 0$  is doubly degenerate: the states with  $K$  and  $-K$  have the same energy. However, we must not forget that the angular momentum of the molecule has a component on an external, laboratory-fixed axis. This component is quantized, and its permitted values are  $M_J\hbar$ , with  $M_J = 0, \pm 1, \dots, \pm J$ , giving  $2J + 1$  values in all (Fig. 16.20). The quantum number  $M_J$  does not appear in the expression for the energy, but it is necessary for a complete specification of the state of the rotor. Consequently, all  $2J + 1$  orientations of the rotating molecule have the same energy. It follows that a symmetric rotor level is  $2(2J + 1)$ -fold degenerate for  $K \neq 0$  and



**16.21** The effect of an electric field on the energy levels of a polar linear rotor. All levels are doubly degenerate except that with  $M_J = 0$ .



**16.22** The effect of rotation on a molecule. The centrifugal force arising from rotation distorts the molecule, opening out bond angles and stretching bonds slightly. The effect is to increase the moment of inertia of the molecule and hence to decrease its rotational constant.

$(2J + 1)$ -fold degenerate for  $K = 0$ . A linear rotor has  $K$  fixed at 0, but the angular momentum may still have  $2J + 1$  components on the laboratory axis, so its degeneracy is  $2J + 1$ .

A spherical rotor can be regarded as a version of a symmetric rotor in which  $A$  is equal to  $B$ : The quantum number  $K$  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 its orientation in space, the rotor also has a  $(2J + 1)$ -fold degeneracy arising from its orientation with respect to an arbitrary axis in the molecule. The overall degeneracy of a symmetric rotor with quantum number  $J$  is therefore  $(2J + 1)^2$ . This degeneracy increases very rapidly: when  $J = 10$ , for instance, there are 441 states of the same energy.

The degeneracy associated with the quantum number  $M_J$  (the orientation of the rotation in space) is partly removed when an electric field is applied to a polar molecule (for example,  $\text{HCl}$  or  $\text{NH}_3$ ), as illustrated in Fig. 16.21. 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 of the state  $|J, M_J\rangle$  is given by

$$E(J, M_J) = hcB_f(J + 1) + a(J, M_J)\mu^2\mathcal{E}^2 \quad (16.39a)$$

where<sup>6</sup>

$$a(J, M_J) = \frac{J(J + 1) - 3M_J^2}{2hcB_f(J + 1)(2J - 1)(2J + 3)} \quad (16.39b)$$

Note that the energy of a state with quantum number  $M_J$  depends on the square of the permanent electric dipole moment,  $\mu$ . The observation of the Stark effect can therefore be used to measure this property, but the technique is limited to molecules that are sufficiently volatile to be studied by microwave spectroscopy. However, as spectra can be recorded for samples at pressures of only about 1 Pa, even some quite non-volatile substances may be studied. Sodium chloride, for example, can be studied as diatomic  $\text{NaCl}$  molecules at high temperatures.

### (e) Centrifugal distortion

We have treated molecules as rigid rotors. However, the atoms of rotating molecules are subject to centrifugal forces that tend to distort the molecular geometry and change the moments of inertia (Fig. 16.22). The effect of centrifugal distortion on a diatomic molecule is to stretch the bond and hence to increase the moment of inertia. As a result, centrifugal distortion reduces the rotational constant and consequently the energy levels are slightly closer than the rigid-rotor expressions predict. The effect is usually taken into account largely empirically by subtracting a term from the energy and writing

$$F(J) = B_f J(J + 1) - D_J J^2(J + 1)^2 \quad (16.40)$$

The parameter  $D_J$  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), through the approximate relation (see Problem 16.23)

$$D_J \approx \frac{4B_f^3}{\tilde{\nu}^2} \quad (16.41)$$

6. For a derivation of this expression, see *Further reading*.