

# 16 Spectroscopy 1: rotational and vibrational spectroscopy

## Solutions to exercises

### Discussion questions

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- E16.1(b)**
- (1) *Doppler broadening.* This contribution to the linewidth is due to the Doppler effect which shifts the frequency of the radiation emitted or absorbed when the atoms or molecules involved are moving towards or away from the detecting device. Molecules have a wide range of speeds in all directions in a gas and the detected spectral line is the absorption or emission profile arising from all the resulting Doppler shifts. As shown in *Justification 16.3*, the profile reflects the distribution of molecular velocities parallel to the line of sight which is a bell-shaped Gaussian curve.
  - (2) *Lifetime broadening.* The Doppler broadening is significant in gas phase samples, but lifetime broadening occurs in all states of matter. This kind of broadening is a quantum mechanical effect related to the uncertainty principle in the form of eqn 16.25 and is due to the finite lifetimes of the states involved in the transition. When  $\tau$  is finite, the energy of the states is smeared out and hence the transition frequency is broadened as shown in eqn 16.26.
  - (3) *Pressure broadening or collisional broadening.* The actual mechanism affecting the lifetime of energy states depends on various processes one of which is collisional deactivation and another is spontaneous emission. The first of these contributions can be reduced by lowering the pressure, the second cannot be changed and results in a natural linewidth.
- E16.2(b)**
- (1) *Rotational Raman spectroscopy.* The gross selection rule is that the molecule must be anisotropically polarizable, which is to say that its polarizability,  $\alpha$ , depends upon the direction of the electric field relative to the molecule. Non-spherical rotors satisfy this condition. Therefore, linear and symmetric rotors are rotationally Raman active.
  - (2) *Vibrational Raman spectroscopy.* The gross selection rule is that the polarizability of the molecule must change as the molecule vibrates. All diatomic molecules satisfy this condition as the molecules swell and contract during a vibration, the control of the nuclei over the electrons varies, and the molecular polarizability changes. Hence both homonuclear and heteronuclear diatomics are vibrationally Raman active. In polyatomic molecules it is usually quite difficult to judge by inspection whether or not the molecule is anisotropically polarizable; hence group theoretical methods are relied on for judging the Raman activity of the various normal modes of vibration. The procedure is discussed in Section 16.17(b) and demonstrated in *Illustration 16.7*.
- E16.3(b)** The exclusion rule applies to the benzene molecule because it has a center of symmetry. Consequently, none of the normal modes of vibration of benzene can be both infrared and Raman active. If we wish to characterize all the normal modes we must obtain both kinds of spectra. See the solutions to Exercises 16.29(a) and 16.29(b) for specified illustrations of which modes are IR active and which are Raman active.

### Numerical exercises

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- E16.4(b)** The ratio of coefficients  $A/B$  is

$$(a) \quad \frac{A}{B} = \frac{8\pi h\nu^3}{c^3} = \frac{8\pi(6.626 \times 10^{-34} \text{ J s}) \times (500 \times 10^6 \text{ s}^{-1})^3}{(2.998 \times 10^8 \text{ m s}^{-1})^3} = \boxed{7.73 \times 10^{-32} \text{ J m}^{-3} \text{ s}}$$

(b) The frequency is

$$\nu = \frac{c}{\lambda} \quad \text{so} \quad \frac{A}{B} = \frac{8\pi h}{\lambda^3} = \frac{8\pi(6.626 \times 10^{-34} \text{ J s})}{(3.0 \times 10^{-2} \text{ m})^3} = \boxed{6.2 \times 10^{-28} \text{ J m}^{-3} \text{ s}}$$

**E16.5(b)** A source approaching an observer appears to be emitting light of frequency

$$\nu_{\text{approaching}} = \frac{\nu}{1 - \frac{s}{c}} \quad [16.22, \text{Section 16.3}]$$

$$\text{Since } \nu \propto \frac{1}{\lambda}, \quad \lambda_{\text{obs}} = \left(1 - \frac{s}{c}\right) \lambda$$

For the light to appear green the speed would have to be

$$s = \left(1 - \frac{\lambda_{\text{obs}}}{\lambda}\right) c = (2.998 \times 10^8 \text{ m s}^{-1}) \times \left(1 - \frac{520 \text{ nm}}{660 \text{ nm}}\right) = \boxed{6.36 \times 10^7 \text{ m s}^{-1}}$$

or about  $1.4 \times 10^8$  m.p.h.

(Since  $s \approx c$ , the relativistic expression

$$\nu_{\text{obs}} = \left(\frac{1 + \frac{s}{c}}{1 - \frac{s}{c}}\right)^{1/2} \nu$$

should really be used. It gives  $s = 7.02 \times 10^7 \text{ m s}^{-1}$ .)

**E16.6(b)** The linewidth is related to the lifetime  $\tau$  by

$$\delta\tilde{\nu} = \frac{5.31 \text{ cm}^{-1}}{\tau/\text{ps}} \quad [16.26] \quad \text{so} \quad \tau = \frac{5.31 \text{ cm}^{-1}}{\delta\tilde{\nu}} \text{ ps}$$

(a) We are given a frequency rather than a wavenumber

$$\tilde{\nu} = \nu/c \quad \text{so} \quad \tau = \frac{(5.31 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})}{100 \times 10^6 \text{ s}^{-1}} \text{ ps} = 1.59 \times 10^3 \text{ ps}$$

or  $\boxed{1.59 \text{ ns}}$

$$(b) \quad \tau = \frac{5.31 \text{ cm}^{-1}}{2.14 \text{ cm}^{-1}} \text{ ps} = \boxed{2.48 \text{ ps}}$$

**E16.7(b)** The linewidth is related to the lifetime  $\tau$  by

$$\delta\tilde{\nu} = \frac{5.31 \text{ cm}^{-1}}{\tau/\text{ps}} \quad \text{so} \quad \delta\nu = \frac{(5.31 \text{ cm}^{-1})c}{\tau/\text{ps}}$$

(a) If every collision is effective, then the lifetime is  $1/(1.0 \times 10^9 \text{ s}^{-1}) = 1.0 \times 10^{-9} \text{ s} = 1.0 \times 10^3 \text{ ps}$

$$\delta\tilde{\nu} = \frac{(5.31 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})}{1.0 \times 10^3} = 1.6 \times 10^8 \text{ s}^{-1} = \boxed{160 \text{ MHz}}$$

(b) If only one collision in 10 is effective, then the lifetime is a factor of 10 greater,  $1.0 \times 10^4 \text{ ps}$

$$\delta\tilde{\nu} = \frac{(5.31 \text{ cm}^{-1}) \times (2.998 \times 10^{10} \text{ cm s}^{-1})}{1.0 \times 10^4} = 1.6 \times 10^7 \text{ s}^{-1} = \boxed{16 \text{ MHz}}$$

**E16.8(b)** The frequency of the transition is related to the rotational constant by

$$h\nu = \Delta E = hc\Delta F = hcB[J(J+1) - (J-1)J] = 2hcBJ$$

where  $J$  refers to the upper state ( $J = 3$ ). The rotational constant is related to molecular structure by

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi m_{\text{eff}}R^2}$$

where  $I$  is moment of inertia,  $m_{\text{eff}}$  is effective mass, and  $R$  is the bond length. Putting these expressions together yields

$$\nu = 2cBJ = \frac{\hbar J}{2\pi m_{\text{eff}}R^2}$$

The reciprocal of the effective mass is

$$m_{\text{eff}}^{-1} = m_{\text{C}}^{-1} + m_{\text{O}}^{-1} = \frac{(12\text{ u})^{-1} + (15.9949\text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 8.78348 \times 10^{25} \text{ kg}^{-1}$$

$$\text{So } \nu = \frac{(8.78348 \times 10^{25} \text{ kg}^{-1}) \times (1.0546 \times 10^{-34} \text{ J s}) \times (3)}{2\pi(112.81 \times 10^{-12} \text{ m})^2} = \boxed{3.4754 \times 10^{11} \text{ s}^{-1}}$$

**E16.9(b)** (a) The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta F = hcB[J(J+1) - (J-1)J] = 2hcBJ$$

where  $J$  refers to the upper state ( $J = 1$ ). The rotational constant is related to molecular structure by

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

where  $I$  is moment of inertia. Putting these expressions together yields

$$\tilde{\nu} = 2BJ = \frac{\hbar J}{2\pi cI} \quad \text{so} \quad I = \frac{\hbar J}{c\tilde{\nu}} = \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (1)}{2\pi(2.998 \times 10^{10} \text{ cm s}^{-1}) \times (16.93 \text{ cm}^{-1})}$$

$$I = \boxed{3.307 \times 10^{-47} \text{ kg m}^2}$$

(b) The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2 \quad \text{so} \quad R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{H}}^{-1} + m_{\text{Br}}^{-1} = \frac{(1.0078\text{ u})^{-1} + (80.9163\text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 6.0494 \times 10^{26} \text{ kg}^{-1}$$

$$\text{and } R = \left\{ (6.0494 \times 10^{26} \text{ kg}^{-1}) \times (3.307 \times 10^{-47} \text{ kg m}^2) \right\}^{1/2} \\ = 1.414 \times 10^{-10} \text{ m} = \boxed{141.4 \text{ pm}}$$

**E16.10(b)** The wavenumber of the transition is related to the rotational constant by

$$hc\tilde{\nu} = \Delta E = hc\Delta F = hcB[J(J+1) - (J-1)J] = 2hcBJ$$

where  $J$  refers to the upper state. So wavenumbers of adjacent transitions (transitions whose upper states differ by 1) differ by

$$\Delta\tilde{\nu} = 2B = \frac{\hbar}{2\pi cI} \quad \text{so} \quad I = \frac{\hbar}{2\pi c\Delta\tilde{\nu}}$$

where  $I$  is moment of inertia,  $m_{\text{eff}}$  is effective mass, and  $R$  is the bond length.

$$\text{So } I = \frac{(1.0546 \times 10^{-34} \text{ J s})}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1}) \times (1.033 \text{ cm}^{-1})} = \boxed{5.420 \times 10^{-46} \text{ kg m}^2}$$

The moment of inertia is related to the bond length by

$$I = m_{\text{eff}}R^2 \quad \text{so} \quad R = \left(\frac{I}{m_{\text{eff}}}\right)^{1/2}$$

$$m_{\text{eff}}^{-1} = m_{\text{F}}^{-1} + m_{\text{Cl}}^{-1} = \frac{(18.9984 \text{ u})^{-1} + (34.9688 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 4.89196 \times 10^{25} \text{ kg}^{-1}$$

$$\begin{aligned} \text{and } R &= \left\{ (4.89196 \times 10^{25} \text{ kg}^{-1}) \times (5.420 \times 10^{-46} \text{ kg m}^2) \right\}^{1/2} \\ &= 1.628 \times 10^{-10} \text{ m} = \boxed{162.8 \text{ pm}} \end{aligned}$$

**E16.11(b)** The rotational constant is

$$B = \frac{\hbar}{4\pi cI} = \frac{\hbar}{4\pi c(2m_{\text{O}}R^2)} \quad \text{so} \quad R = \left(\frac{\hbar}{8\pi cm_{\text{O}}B}\right)^{1/2}$$

where  $I$  is moment of inertia,  $m_{\text{eff}}$  is effective mass, and  $R$  is the bond length.

$$\begin{aligned} R &= \left( \frac{(1.0546 \times 10^{-34} \text{ J s})}{8\pi(2.9979 \times 10^{10} \text{ cm s}^{-1}) \times (15.9949 \text{ u}) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1}) \times (0.39021)} \right)^{1/2} \\ &= 1.1621 \times 10^{-10} \text{ m} = \boxed{116.21 \text{ pm}} \end{aligned}$$

**E16.12(b)** This exercise is analogous to Exercise 16.12(a), but here our solution will employ a slightly different algebraic technique. Let  $R = R_{\text{OC}}$ ,  $R' = R_{\text{CS}}$ ,  $\text{O} = {}^{16}\text{O}$ ,  $\text{C} = {}^{12}\text{C}$ .

$$I = \frac{\hbar}{4\pi B} \quad [\text{Footnote 6, p. 466}]$$

$$I(\text{OC}^{32}\text{S}) = \frac{1.05457 \times 10^{-34} \text{ J s}}{(4\pi) \times (6.0815 \times 10^9 \text{ s}^{-1})} = 1.3799 \times 10^{-45} \text{ kg m}^2 = 8.3101 \times 10^{-19} \text{ u m}^2$$

$$I(\text{OC}^{34}\text{S}) = \frac{1.05457 \times 10^{-34} \text{ J s}}{(4\pi) \times (5.9328 \times 10^9 \text{ s}^{-1})} = 1.4145 \times 10^{-45} \text{ kg m}^2 = 8.5184 \times 10^{-19} \text{ u m}^2$$

The expression for the moment of inertia given in Table 16.1 may be rearranged as follows.

$$\begin{aligned} Im &= m_{\text{A}}mR^2 + m_{\text{C}}mR'^2 - (m_{\text{A}}R - m_{\text{C}}R')^2 \\ &= m_{\text{A}}mR^2 + m_{\text{C}}mR'^2 - m_{\text{A}}^2R^2 + 2m_{\text{A}}m_{\text{C}}RR' - m_{\text{C}}^2R'^2 \\ &= m_{\text{A}}(m_{\text{B}} + m_{\text{C}})R^2 + m_{\text{C}}(m_{\text{A}} + m_{\text{B}})R'^2 + 2m_{\text{A}}m_{\text{C}}RR' \end{aligned}$$

Let  $m_C = m_{32S}$  and  $m'_C = m_{34S}$

$$\frac{Im}{m_C} = \frac{m_A}{m_C}(m_B + m_C)R^2 + (m_A + m_B)R'^2 + 2m_A RR' \quad (\text{a})$$

$$\frac{I'm'}{m'_C} = \frac{m_A}{m'_C}(m_B + m'_C)R^2 + (m_A + m_B)R'^2 + 2m_A RR' \quad (\text{b})$$

Subtracting

$$\frac{Im}{m_C} - \frac{I'm'}{m'_C} = \left[ \left( \frac{m_A}{m_C} \right) (m_B + m_C) - \left( \frac{m_A}{m'_C} \right) (m_B + m'_C) \right] R^2$$

Solving for  $R^2$

$$R^2 = \frac{\left( \frac{Im}{m_C} - \frac{I'm'}{m'_C} \right)}{\left[ \left( \frac{m_A}{m_C} \right) (m_B + m_C) - \left( \frac{m_A}{m'_C} \right) (m_B + m'_C) \right]} = \frac{m'_C Im - m_C I'm'}{m_B m_A (m'_C - m_C)}$$

Substituting the masses, with  $m_A = m_O$ ,  $m_B = m_C$ ,  $m_C = m_{32S}$ , and  $m'_C = m_{34S}$

$$m = (15.9949 + 12.0000 + 31.9721) \text{ u} = 59.9670 \text{ u}$$

$$m' = (15.9949 + 12.0000 + 33.9679) \text{ u} = 61.9628 \text{ u}$$

$$\begin{aligned} R^2 &= \frac{(33.9679 \text{ u}) \times (8.3101 \times 10^{-19} \text{ u m}^2) \times (59.9670 \text{ u})}{(12.000 \text{ u}) \times (15.9949 \text{ u}) \times (33.9679 \text{ u} - 31.9721 \text{ u})} \\ &\quad - \frac{(31.9721 \text{ u}) \times (8.5184 \times 10^{-19} \text{ u m}^2) \times (61.9628 \text{ u})}{(12.000 \text{ u}) \times (15.9949 \text{ u}) \times (33.9679 \text{ u} - 31.9721 \text{ u})} \\ &= \frac{51.6446 \times 10^{-19} \text{ m}^2}{383.071} = 1.3482 \times 10^{-20} \text{ m}^2 \end{aligned}$$

$$R = 1.161\bar{1} \times 10^{-10} \text{ m} = \boxed{116.1 \text{ pm}} = R_{OC}$$

Because the numerator of the expression for  $R^2$  involves the difference between two rather large numbers of nearly the same magnitude, the number of significant figures in the answer for  $R$  is certainly no greater than 4. Having solved for  $R$ , either equation (a) or (b) above can be solved for  $R'$ . The result is

$$R' = 1.559 \times 10^{-10} \text{ m} = \boxed{155.9 \text{ pm}} = R_{CS}$$

**E16.13(b)** The wavenumber of a Stokes line in rotational Raman is

$$\tilde{\nu}_{\text{Stokes}} = \tilde{\nu}_i - 2B(2J + 3) \quad [16.49a]$$

where  $J$  is the initial (lower) rotational state. So

$$\tilde{\nu}_{\text{Stokes}} = 20\,623 \text{ cm}^{-1} - 2(1.4457 \text{ cm}^{-1}) \times [2(2) + 3] = \boxed{20\,603 \text{ cm}^{-1}}$$

**E16.14(b)** The separation of lines is  $4B$ , so  $B = \frac{1}{4} \times (3.5312 \text{ cm}^{-1}) = 0.88280 \text{ cm}^{-1}$

$$\text{Then we use } R = \left( \frac{\hbar}{4\pi m_{\text{eff}} c B} \right)^{1/2} \quad [\text{Exercise 16.11(a)}]$$

with  $m_{\text{eff}} = \frac{1}{2}m(^{19}\text{F}) = \frac{1}{2} \times (18.9984 \text{ u}) \times (1.6605 \times 10^{-27} \text{ kg u}^{-1}) = 1.577342 \times 10^{-26} \text{ kg}$

$$R = \left( \frac{1.0546 \times 10^{-34} \text{ J s}}{4\pi(1.577342 \times 10^{-26} \text{ kg}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (0.88280 \text{ cm}^{-1})} \right)^{1/2}$$

$$= 1.41785 \times 10^{-10} \text{ m} = \boxed{141.78 \text{ pm}}$$

**E16.15(b)** Polar molecules show a pure rotational absorption spectrum. Therefore, select the polar molecules based on their well-known structures. Alternatively, determine the point groups of the molecules and use the rule that only molecules belonging to  $C_n$ ,  $C_{nv}$ , and  $C_s$  may be polar, and in the case of  $C_n$  and  $C_{nv}$ , that dipole must lie along the rotation axis. Hence all are polar molecules.

Their point group symmetries are

(a)  $\text{H}_2\text{O}$ ,  $C_{2v}$ , (b)  $\text{H}_2\text{O}_2$ ,  $C_2$ , (c)  $\text{NH}_3$ ,  $C_{3v}$ , (d)  $\text{N}_2\text{O}$ ,  $C_{\infty v}$

All show a pure rotational spectrum.

**E16.16(b)** A molecule must be anisotropically polarizable to show a rotational Raman spectrum; all molecules except spherical rotors have this property. So  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CH}_3$ , and  $\text{N}_2\text{O}$  can display rotational Raman spectra;  $\text{SF}_6$  cannot.

**E16.17(b)** The angular frequency is

$$\omega = \left( \frac{k}{m} \right)^{1/2} = 2\pi\nu \quad \text{so} \quad k = (2\pi\nu)^2 m = (2\pi)^2 \times (3.0 \text{ s}^{-1})^2 \times (2.0 \times 10^{-3} \text{ kg})$$

$$k = \boxed{0.71 \text{ N m}^{-1}}$$

**E16.18(b)**  $\omega = \left( \frac{k}{m_{\text{eff}}} \right)^{1/2}$      $\omega' = \left( \frac{k}{m'_{\text{eff}}} \right)^{1/2}$  [prime =  $^2\text{H}^{37}\text{Cl}$ ]

The force constant,  $k$ , is assumed to be the same for both molecules. The fractional difference is

$$\frac{\omega' - \omega}{\omega} = \frac{\left( \frac{k}{m'_{\text{eff}}} \right)^{1/2} - \left( \frac{k}{m_{\text{eff}}} \right)^{1/2}}{\left( \frac{k}{m_{\text{eff}}} \right)^{1/2}} = \frac{\left( \frac{1}{m'_{\text{eff}}} \right)^{1/2} - \left( \frac{1}{m_{\text{eff}}} \right)^{1/2}}{\left( \frac{1}{m_{\text{eff}}} \right)^{1/2}} = \left( \frac{m_{\text{eff}}}{m'_{\text{eff}}} \right)^{1/2} - 1$$

$$\frac{\omega' - \omega}{\omega} = \left( \frac{m_{\text{eff}}}{m'_{\text{eff}}} \right)^{1/2} - 1 = \left\{ \frac{m_{\text{H}}m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} \times \frac{(m_{2\text{H}} + m_{37\text{Cl}})}{(m_{2\text{H}} \cdot m_{37\text{Cl}})} \right\}^{1/2} - 1$$

$$= \left\{ \frac{(1.0078 \text{ u}) \times (34.9688 \text{ u})}{(1.0078 \text{ u}) + (34.9688 \text{ u})} \times \frac{(2.0140 \text{ u}) + (36.9651 \text{ u})}{(2.0140 \text{ u}) \times (36.9651 \text{ u})} \right\}^{1/2} - 1$$

$$= -0.284$$

Thus the difference is 28.4 per cent

**E16.19(b)** The fundamental vibrational frequency is

$$\omega = \left( \frac{k}{m_{\text{eff}}} \right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad k = (2\pi c\tilde{\nu})^2 m_{\text{eff}}$$

We need the effective mass

$$\begin{aligned} m_{\text{eff}}^{-1} &= m_1^{-1} + m_2^{-1} = (78.9183 \text{ u})^{-1} + (80.9163 \text{ u})^{-1} = 0.025\,029\,8 \text{ u}^{-1} \\ k &= \frac{[2\pi(2.998 \times 10^{10} \text{ cm s}^{-1}) \times (323.2 \text{ cm}^{-1})]^2 \times (1.66054 \times 10^{-27} \text{ kg u}^{-1})}{0.025\,029\,8 \text{ u}^{-1}} \\ &= \boxed{245.9 \text{ N m}^{-1}} \end{aligned}$$

**E16.20(b)** The ratio of the population of the ground state ( $N_0$ ) to the first excited state ( $N_1$ ) is

$$\frac{N_0}{N_1} = \exp\left(\frac{-h\nu}{kT}\right) = \exp\left(\frac{-hc\tilde{\nu}}{kT}\right)$$

(a)  $\frac{N_0}{N_1} = \exp\left(\frac{-(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (321 \text{ cm}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}\right) = \boxed{0.212}$

(b)  $\frac{N_0}{N_1} = \exp\left(\frac{-(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^{10} \text{ cm s}^{-1}) \times (321 \text{ cm}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (800 \text{ K})}\right) = \boxed{0.561}$

**E16.21(b)** The relation between vibrational frequency and wavenumber is

$$\omega = \left( \frac{k}{m_{\text{eff}}} \right)^{1/2} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \tilde{\nu} = \frac{1}{2\pi c} \left( \frac{k}{m_{\text{eff}}} \right)^{1/2} = \frac{(km_{\text{eff}}^{-1})^{1/2}}{2\pi c}$$

The reduced masses of the hydrogen halides are very similar, but not identical

$$m_{\text{eff}}^{-1} = m_{\text{D}}^{-1} + m_{\text{X}}^{-1}$$

We assume that the force constants as calculated in Exercise 16.21(a) are identical for the deuterium halide and the hydrogen halide.

For DF

$$\begin{aligned} m_{\text{eff}}^{-1} &= \frac{(2.0140 \text{ u})^{-1} + (18.9984 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.3071 \times 10^{26} \text{ kg}^{-1} \\ \tilde{\nu} &= \frac{\left\{ (3.3071 \times 10^{26} \text{ kg}^{-1}) \times (967.04 \text{ kg s}^{-2}) \right\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{3002.3 \text{ cm}^{-1}} \end{aligned}$$

For DCI

$$\begin{aligned} m_{\text{eff}}^{-1} &= \frac{(2.0140 \text{ u})^{-1} + (34.9688 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.1624 \times 10^{26} \text{ kg}^{-1} \\ \tilde{\nu} &= \frac{\left\{ (3.1624 \times 10^{26} \text{ kg}^{-1}) \times (515.59 \text{ kg s}^{-2}) \right\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{2143.7 \text{ cm}^{-1}} \end{aligned}$$

For DBr

$$m_{\text{eff}}^{-1} = \frac{(2.0140 \text{ u})^{-1} + (80.9163 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.0646 \times 10^{26} \text{ kg}^{-1}$$

$$\tilde{\nu} = \frac{\left\{ (3.0646 \times 10^{26} \text{ kg}^{-1}) \times (411.75 \text{ kg s}^{-2}) \right\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{1885.8 \text{ cm}^{-1}}$$

For DI

$$m_{\text{eff}}^{-1} = \frac{(2.0140 \text{ u})^{-1} + (126.9045 \text{ u})^{-1}}{1.66054 \times 10^{-27} \text{ kg u}^{-1}} = 3.0376 \times 10^{26} \text{ kg}^{-1}$$

$$\tilde{\nu} = \frac{\left\{ (3.0376 \times 10^{26} \text{ kg}^{-1}) \times (314.21 \text{ kg s}^{-2}) \right\}^{1/2}}{2\pi(2.9979 \times 10^{10} \text{ cm s}^{-1})} = \boxed{1640.1 \text{ cm}^{-1}}$$

**E16.22(b)** Data on three transitions are provided. Only two are necessary to obtain the value of  $\tilde{\nu}$  and  $x_e$ . The third datum can then be used to check the accuracy of the calculated values.

$$\Delta G(v = 1 \leftarrow 0) = \tilde{\nu} - 2\tilde{\nu}x_e = 2345.15 \text{ cm}^{-1} \quad [16.64]$$

$$\Delta G(v = 2 \leftarrow 0) = 2\tilde{\nu} - 6\tilde{\nu}x_e = 4661.40 \text{ cm}^{-1} \quad [16.65]$$

Multiply the first equation by 3, then subtract the second.

$$\tilde{\nu} = (3) \times (2345.15 \text{ cm}^{-1}) - (4661.40 \text{ cm}^{-1}) = \boxed{2374.05 \text{ cm}^{-1}}$$

Then from the first equation

$$x_e = \frac{\tilde{\nu} - 2345.15 \text{ cm}^{-1}}{2\tilde{\nu}} = \frac{(2374.05 - 2345.15) \text{ cm}^{-1}}{(2) \times (2374.05 \text{ cm}^{-1})} = \boxed{6.087 \times 10^{-3}}$$

$x_e$  data are usually reported as  $x_e\tilde{\nu}$  which is

$$x_e\tilde{\nu} = 14.45 \text{ cm}^{-1}$$

$$\begin{aligned} \Delta G(v = 3 \leftarrow 0) &= 3\tilde{\nu} - 12\nu x_e = (3) \times (2374.05 \text{ cm}^{-1}) - (12) \times (14.45 \text{ cm}^{-1}) \\ &= 6948.74 \text{ cm}^{-1} \end{aligned}$$

which is close to the experimental value.

**E16.23(b)**  $\Delta G_{v+1/2} = \tilde{\nu} - 2(v+1)x_e\tilde{\nu}$  [16.64] where  $\Delta G_{v+1/2} = G(v+1) - G(v)$

Therefore, since

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

a plot of  $\Delta G_{v+1/2}$  against  $\nu$  should give a straight line which gives  $(1 - 2x_e)\tilde{\nu}$  from the intercept at  $\nu = 0$  and  $-2x_e\tilde{\nu}$  from the slope. We draw up the following table

$\nu$	0	1	2	3	4
$G(\nu)/\text{cm}^{-1}$	1144.83	3374.90	5525.51	7596.66	9588.35
$\Delta G_{v+1/2}/\text{cm}^{-1}$	2230.07	2150.61	2071.15	1991.69	



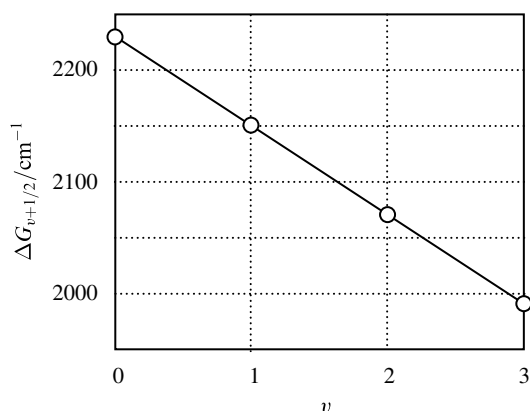


Figure 16.1

The points are plotted in Fig. 16.1.

The intercept lies at  $2230.51$  and the slope  $= -79.65 \text{ cm}^{-1}$ ; hence  $x_e \tilde{\nu} = 39.83 \text{ cm}^{-1}$ .

Since  $\tilde{\nu} - 2x_e \tilde{\nu} = 2230.51 \text{ cm}^{-1}$ , it follows that  $\tilde{\nu} = 2310.16 \text{ cm}^{-1}$ .

The dissociation energy may be obtained by assuming that the molecule is described by a Morse potential and that the constant  $D_e$  in the expression for the potential is an adequate first approximation for it. Then

$$D_e = \frac{\tilde{\nu}}{4x_e} [16.62] = \frac{\tilde{\nu}^2}{4x_e \tilde{\nu}} = \frac{(2310.16 \text{ cm}^{-1})^2}{(4) \times (39.83 \text{ cm}^{-1})} = 33.50 \times 10^3 \text{ cm}^{-1} = 4.15 \text{ eV}$$

However, the depth of the potential well  $D_e$  differs from  $D_0$ , the dissociation energy of the bond, by the zero-point energy; hence

$$\begin{aligned} D_0 &= D_e - \frac{1}{2} \tilde{\nu} = (33.50 \times 10^3 \text{ cm}^{-1}) - \left(\frac{1}{2}\right) \times (2310.16 \text{ cm}^{-1}) \\ &= \boxed{3.235 \times 10^4 \text{ cm}^{-1}} = \boxed{4.01 \text{ eV}} \end{aligned}$$

**E16.24(b)** The wavenumber of an R-branch IR transition is

$$\tilde{\nu}_R = \tilde{\nu} + 2B(J + 1) \quad [16.69c]$$

where  $J$  is the initial (lower) rotational state. So

$$\tilde{\nu}_R = 2308.09 \text{ cm}^{-1} + 2(6.511 \text{ cm}^{-1}) \times (2 + 1) = \boxed{2347.16 \text{ cm}^{-1}}$$

**E16.25(b)** See Section 16.10. Select those molecules in which a vibration gives rise to a change in dipole moment. It is helpful to write down the structural formulas of the compounds. The infrared active compounds are

(a)  $\text{CH}_3\text{CH}_3$  (b)  $\text{CH}_4(\text{g})$  (c)  $\text{CH}_3\text{Cl}$

**Comment.** A more powerful method for determining infrared activity based on symmetry considerations is described in Section 16.15.

**E16.26(b)** A nonlinear molecule has  $3N - 6$  normal modes of vibration, where  $N$  is the number of atoms in the molecule; a linear molecule has  $3N - 5$ .

- (a)  $C_6H_6$  has  $3(12) - 6 = \boxed{30}$  normal modes.  
 (b)  $C_6H_5CH_3$  has  $3(16) - 6 = \boxed{42}$  normal modes.  
 (c)  $HC\equiv C-C\equiv CH$  is linear; it has  $3(6) - 5 = \boxed{13}$  normal modes.

**E16.27(b)** (a) A planar  $AB_3$  molecule belongs to the  $D_{3h}$  group. Its four atoms have a total of 12 displacements, of which 6 are vibrations. We determine the symmetry species of the vibrations by first determining the characters of the reducible representation of the molecule formed from all 12 displacements and then subtracting from these characters the characters corresponding to translation and rotation. This latter information is directly available in the character table for the group  $D_{3h}$ . The resulting set of characters are the characters of the reducible representation of the vibrations. This representation can be reduced to the symmetry species of the vibrations by inspection or by use of the little orthogonality theorem.

$D_{3h}$	$E$	$\sigma_h$	$2C_3$	$2S_3$	$3C'_2$	$3\sigma_v$
$\chi$ (translation)	3	1	0	-2	-1	1
Unmoved atoms	4	4	1	1	2	2
$\chi$ (total, product)	12	4	0	-2	-2	2
$\chi$ (rotation)	3	-1	0	2	-1	-1
$\chi$ (vibration)	6	4	0	-2	0	2

$\chi$  (vibration) corresponds to  $A'_1 + A'_2 + 2E'$ .

Again referring to the character table of  $D_{3h}$ , we see that  $E'$  corresponds to  $x$  and  $y$ ,  $A'_2$  to  $z$ ; hence  $A'_2$  and  $E'$  are IR active. We also see from the character table that  $E'$  and  $A'_1$  correspond to the quadratic terms; hence  $A'_1$  and  $E'$  are Raman active.

(b) A trigonal pyramidal  $AB_3$  molecule belongs to the group  $C_{3v}$ . In a manner similar to the analysis in part (a) we obtain

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$\chi$ (total)	12	0	2
$\chi$ (vibration)	6	-2	2

$\chi$  (vibration) corresponds to  $2A_1 + 2E$ . We see from the character table that  $A_1$  and  $E$  are IR active and that  $A_1 + E$  are also Raman active. Thus all modes are observable in both the IR and the Raman spectra.

**E16.28(b)** (b) The boat-like bending of a benzene ring clearly changes the dipole moment of the ring, for the moving of the C—H bonds out of the plane will give rise to a non-cancelling component of their dipole moments. So the vibration is IR active.

(a) Since benzene has a centre of inversion, the exclusion rule applies: a mode which is IR active (such as this one) must be Raman inactive.

**E16.29(b)** The displacements span  $A_{1g} + A_{1u} + A_{2g} + 2E_{1u} + E_{1g}$ . The rotations  $R_x$  and  $R_y$  span  $E_{1g}$ , and the translations span  $E_{1u} + A_{1u}$ . So the vibrations span  $A_{1g} + A_{2g} + E_{1u}$

## Solutions to problems

### Solutions to numerical problems

**P16.1** Use the energy density expression in terms of wavelengths (eqn 11.5)

$$E = \rho \, d\lambda \quad \text{where } \rho = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)}.$$

Evaluate

$$E = \int_{400 \times 10^{-9} \text{ m}}^{700 \times 10^{-9} \text{ m}} \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)} d\lambda$$

at three different temperatures. Compare those results to the classical, Rayleigh–Jeans expression (eqn 11.3):

$$E_{\text{class}} = \rho_{\text{class}} d\lambda \quad \text{where } \rho_{\text{class}} = \frac{8\pi kT}{\lambda^4},$$

$$\text{so } E_{\text{class}} = \int_{400 \times 10^{-9} \text{ m}}^{700 \times 10^{-9} \text{ m}} \frac{8\pi kT}{\lambda^4} d\lambda = -\frac{8\pi kT}{3\lambda^3} \Big|_{400 \times 10^{-9} \text{ m}}^{700 \times 10^{-9} \text{ m}}.$$

$T/K$	$E/\text{J m}^{-3}$	$E_{\text{class}}/\text{J m}^{-3}$
(a) 1500	$2.136 \times 10^{-6}$	2.206
(b) 2500	$9.884 \times 10^{-4}$	3.676
(c) 5800	$3.151 \times 10^{-1}$	8.528

The classical values are very different from the accurate Planck values! Try integrating the expressions over 400–700  $\mu\text{m}$  or  $\text{mm}$  to see that the expressions agree reasonably well at longer wavelengths.

**P16.3** On the assumption that every collision deactivates the molecule we may write

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

For HCl, with  $m \approx 36 \text{ u}$ ,

$$\begin{aligned} \tau &\approx \left( \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(4) \times (0.30 \times 10^{-18} \text{ m}^2) \times (1.013 \times 10^5 \text{ Pa})} \right) \\ &\quad \times \left( \frac{\pi \times (36) \times (1.661 \times 10^{-27} \text{ kg})}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \right)^{1/2} \\ &\approx 2.3 \times 10^{-10} \text{ s} \\ \delta E &\approx h\delta\nu = \frac{\hbar}{\tau} [24] \end{aligned}$$

The width of the collision-broadened line is therefore approximately

$$\delta\nu \approx \frac{1}{2\pi\tau} = \frac{1}{(2\pi) \times (2.3 \times 10^{-10} \text{ s})} \approx \boxed{700 \text{ MHz}}$$

The Doppler width is approximately 1.3 MHz (Problem 16.2). Since the collision width is proportional to  $p$  [ $\delta\nu \propto 1/\tau$  and  $\tau \propto 1/p$ ], the pressure must be reduced by a factor of about  $\frac{1.3}{700} = 0.002$  before Doppler broadening begins to dominate collision broadening. Hence, the pressure must be reduced to below  $(0.002) \times (760 \text{ Torr}) = \boxed{1 \text{ Torr}}$

**P16.5**

$$B = \frac{\hbar}{4\pi c I} \quad [16.31]; \quad I = m_{\text{eff}} R^2; \quad R^2 = \frac{\hbar}{4\pi c m_{\text{eff}} B}$$

$$m_{\text{eff}} = \frac{m_C m_O}{m_C + m_O} = \left( \frac{(12.0000 \text{ u}) \times (15.9949 \text{ u})}{(12.0000 \text{ u}) + (15.9949 \text{ u})} \right) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1}) \\ = 1.13852 \times 10^{-26} \text{ kg}$$

$$\frac{\hbar}{4\pi c} = 2.79932 \times 10^{-44} \text{ kg m}$$

$$R_0^2 = \frac{2.79932 \times 10^{-44} \text{ kg m}}{(1.13852 \times 10^{-26} \text{ kg}) \times (1.9314 \times 10^2 \text{ m}^{-1})} = 1.2730\bar{3} \times 10^{-20} \text{ m}^2$$

$$R_0 = 1.1283 \times 10^{-10} \text{ m} = \boxed{112.83 \text{ pm}}$$

$$R_1^2 = \frac{2.79932 \times 10^{-44} \text{ kg m}}{(1.13852 \times 10^{-26} \text{ kg}) \times (1.6116 \times 10^2 \text{ m}^{-1})} = 1.52565 \times 10^{-20} \text{ m}^2$$

$$R_1 = 1.2352 \times 10^{-10} \text{ m} = \boxed{123.52 \text{ pm}}$$

**Comment.** The change in internuclear distance is roughly 10 per cent, indicating that the rotations and vibrations of molecules are strongly coupled and that it is an oversimplification to consider them independently of each other.

**P16.8**

$$\tilde{\nu} = 2B(J+1) \quad [16.44] = 2B$$

Hence,  $B(^1\text{HCl}) = 10.4392 \text{ cm}^{-1}$ ,  $B(^2\text{HCl}) = 5.3920 \text{ cm}^{-1}$

$$B = \frac{\hbar}{4\pi c I} \quad [30] \quad I = m_{\text{eff}} R^2 \quad [\text{Table 16.1}]$$

$$R^2 = \frac{\hbar}{4\pi c m_{\text{eff}} B} \quad \frac{\hbar}{4\pi c} = 2.79927 \times 10^{-44} \text{ kg m}$$

$$m_{\text{eff}}(\text{HCl}) = \left( \frac{(1.007825 \text{ u}) \times (34.96885 \text{ u})}{(1.007825 \text{ u}) + (34.96885 \text{ u})} \right) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1}) \\ = 1.62665 \times 10^{-27} \text{ kg}$$

$$m_{\text{eff}}(\text{DCl}) = \left( \frac{(2.0140 \text{ u}) \times (34.96885 \text{ u})}{(2.0140 \text{ u}) + (34.96885 \text{ u})} \right) \times (1.66054 \times 10^{-27} \text{ kg u}^{-1}) \\ = 3.1622 \times 10^{-27} \text{ kg}$$

$$R^2(\text{HCl}) = \frac{2.79927 \times 10^{-44} \text{ kg m}}{(1.62665 \times 10^{-27} \text{ kg}) \times (1.04392 \times 10^3 \text{ m}^{-1})} = 1.64848 \times 10^{-20} \text{ m}^2$$

$$R(\text{HCl}) = 1.28393 \times 10^{-10} \text{ m} = \boxed{128.393 \text{ pm}}$$

$$R^2(^2\text{HCl}) = \frac{2.79927 \times 10^{-44} \text{ kg m}}{(3.1622 \times 10^{-27} \text{ kg}) \times (5.3920 \times 10^2 \text{ m}^{-1})} = 1.6417 \times 10^{-20} \text{ m}^2$$

$$R(^2\text{HCl}) = 1.2813 \times 10^{-10} \text{ m} = \boxed{128.13 \text{ pm}}$$

The difference between these values of  $R$  is small but measurable.

**Comment.** Since the effects of centrifugal distortion have not been taken into account, the number of significant figures in the calculated values of  $R$  above should be no greater than 4, despite the fact that the data is precise to 6 figures.

**P16.10** From the equation for a linear rotor in Table 16.1 it is possible to show that  $I_m = m_a m_c (R + R')^2 + m_a m_b R^2 + m_b m_c R'^2$ .

$$\text{Thus, } I(^{16}\text{O}^{12}\text{C}^{32}\text{S}) = \left( \frac{m(^{16}\text{O})m(^{32}\text{S})}{m(^{16}\text{O}^{12}\text{C}^{32}\text{S})} \right) \times (R + R')^2 + \left( \frac{m(^{12}\text{C})\{m(^{16}\text{O})R^2 + m(^{32}\text{S})R'^2\}}{m(^{16}\text{O}^{12}\text{C}^{32}\text{S})} \right)$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S}) = \left( \frac{m(^{16}\text{O})m(^{34}\text{S})}{m(^{16}\text{O}^{12}\text{C}^{34}\text{S})} \right) \times (R + R')^2 + \left( \frac{m(^{12}\text{C})\{m(^{16}\text{O})R^2 + m(^{34}\text{S})R'^2\}}{m(^{16}\text{O}^{12}\text{C}^{34}\text{S})} \right)$$

$m(^{16}\text{O}) = 15.9949 \text{ u}$ ,  $m(^{12}\text{C}) = 12.0000 \text{ u}$ ,  $m(^{32}\text{S}) = 31.9721 \text{ u}$ , and  $m(^{34}\text{S}) = 33.9679 \text{ u}$ . Hence,

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S})/\text{u} = (8.5279) \times (R + R')^2 + (0.20011) \times (15.9949R^2 + 31.9721R'^2)$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S})/\text{u} = (8.7684) \times (R + R')^2 + (0.19366) \times (15.9949R^2 + 33.9679R'^2)$$

The spectral data provides the experimental values of the moments of inertia based on the relation  $\nu = 2c B(J + 1)$  [16.44] with  $B = \frac{\hbar}{4\pi c I}$  [16.31]. These values are set equal to the above equations which are then solved for  $R$  and  $R'$ . The mean values of  $I$  obtained from the data are

$$I(^{16}\text{O}^{12}\text{C}^{32}\text{S}) = 1.37998 \times 10^{-45} \text{ kg m}^2$$

$$I(^{16}\text{O}^{12}\text{C}^{34}\text{S}) = 1.41460 \times 10^{-45} \text{ kg m}^2$$

Therefore, after conversion of the atomic mass units to kg, the equations we must solve are

$$1.37998 \times 10^{-45} \text{ m}^2 = (1.4161 \times 10^{-26}) \times (R + R')^2 + (5.3150 \times 10^{-27} R^2) \\ + (1.0624 \times 10^{-26} R'^2)$$

$$1.41460 \times 10^{-45} \text{ m}^2 = (1.4560 \times 10^{-26}) \times (R + R')^2 + (5.1437 \times 10^{-27} R^2) \\ + (1.0923 \times 10^{-26} R'^2)$$

These two equations may be solved for  $R$  and  $R'$ . They are tedious to solve, but straightforward. Exercise 16.6(b) illustrates the details of the solution. The outcome is  $R = \boxed{116.28 \text{ pm}}$  and  $R' = \boxed{155.97 \text{ pm}}$ . These values may be checked by direct substitution into the equations.

**Comment.** The starting point of this problem is the actual experimental data on spectral line positions. Exercise 16.12(b) is similar to this problem; its starting point is, however, given values of the rotational constants  $B$ , which were themselves obtained from the spectral line positions. So the results for  $R$  and  $R'$  are expected to be essentially identical and they are.

**Question.** What are the rotational constants calculated from the data on the positions of the absorption lines?

**P16.12** The wavenumbers of the transitions with  $\Delta v = +1$  are

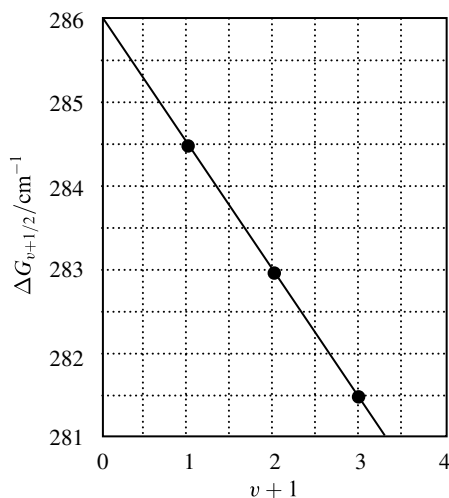
$$\Delta G_{v+1/2} = \tilde{\nu} - 2(v+1)x_e\tilde{\nu} \quad [16.64] \quad \text{and} \quad D_e = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} \quad [16.62]$$

A plot of  $\Delta G_{v+1/2}$  against  $v+1$  should give a straight line with intercept  $\tilde{\nu}$  at  $v+1 = 0$  and slope  $-2x_e\tilde{\nu}$ .

Draw up the following table

$v+1$	1	2	3
$\Delta G_{v+1/2}/\text{cm}^{-1}$	284.50	283.00	281.50

The points are plotted in Fig. 16.2.



**Figure 16.2**

The intercept is at 286.0, so  $\tilde{\nu} = 286 \text{ cm}^{-1}$ . The slope is  $-1.50$ , so  $x_e\tilde{\nu} = 0.750 \text{ cm}^{-1}$ . It follows that

$$D_e = \frac{(286 \text{ cm}^{-1})^2}{(4) \times (0.750 \text{ cm}^{-1})} = 27300 \text{ cm}^{-1}, \quad \text{or} \quad 3.38 \text{ eV}$$

The zero-point level lies at  $142.81 \text{ cm}^{-1}$  and so  $D_0 = 3.36 \text{ eV}$ . Since

$$m_{\text{eff}} = \frac{(22.99) \times (126.90)}{(22.99) + (126.90)} \text{ u} = 19.464 \text{ u}$$

the force constant of the molecule is

$$\begin{aligned} k &= 4\pi^2 m_{\text{eff}} c^2 \tilde{\nu}^2 \quad [\text{Exercise 16.19(a)}] \\ &= (4\pi^2) \times (19.464) \times (1.6605 \times 10^{-27} \text{ kg}) \times [(2.998 \times 10^{10} \text{ cm s}^{-1}) \times (286 \text{ cm}^{-1})]^2 \\ &= \boxed{93.8 \text{ N m}^{-1}} \end{aligned}$$

**P16.14** The set of peaks to the left of center are the P branch, those to the right are the R branch. Within the rigid rotor approximation the two sets are separated by  $4B$ . The effects of the interactions between vibration and rotation and of centrifugal distortion are least important for transitions with small  $J$  values hence the separation between the peaks immediately to the left and right of center will give good approximate values of  $B$  and bond length.

(a)  $\tilde{\nu}_Q(J) = \tilde{\nu}[46\text{ b}] = \boxed{2143.26\text{ cm}^{-1}}$

(b) The zero-point energy is  $\frac{1}{2}\tilde{\nu} = 1071.63\text{ cm}^{-1}$ . The molar zero-point energy in  $\text{J mol}^{-1}$  is

$$\begin{aligned} N_A h c \times (1071.63\text{ cm}^{-1}) &= N_A h c \times (1.07163 \times 10^5\text{ m}^{-1}) \\ &= 1.28195 \times 10^4\text{ J mol}^{-1} = \boxed{12.8195\text{ kJ mol}^{-1}} \end{aligned}$$

(c)  $k = 4\pi^2 \mu c^2 \tilde{\nu}^2$

$$\begin{aligned} \mu(^{12}\text{C}^{16}\text{O}) &= \frac{m_{\text{C}} m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} = \left( \frac{(12.0000\text{ u}) \times (15.9949\text{ u})}{(12.0000\text{ u}) + (15.9949\text{ u})} \right) \times (1.66054 \times 10^{-27}\text{ kg u}^{-1}) \\ &= 1.13852 \times 10^{-26}\text{ kg} \end{aligned}$$

$$k = 4\pi^2 c^2 \times (1.13852 \times 10^{-26}\text{ kg}) \times (2.14326 \times 10^5\text{ m}^{-1})^2 = \boxed{1.85563 \times 10^3\text{ N m}^{-1}}$$

(d)  $4B \approx 7.655\text{ cm}^{-1}$

$$B \approx \boxed{1.91\text{ cm}^{-1}} \text{ [4 significant figures not justified]}$$

(e)  $B = \frac{\hbar}{4\pi c I} [16.31] = \frac{\hbar}{4\pi c \mu R^2}$  [Table 16.1]

$$R^2 \frac{\hbar}{4\pi c \mu B} = \frac{\hbar}{(4\pi c) \times (1.13852 \times 10^{-26}\text{ kg}) \times (191\text{ m}^{-1})} = 1.287 \times 10^{-20}\text{ m}^2$$

$$R = 1.13 \times 10^{-10}\text{ m} = \boxed{113\text{ pm}}$$

**P16.15**  $D_0 = D_e - \tilde{\nu}'$  with  $\tilde{\nu}' = \frac{1}{2}\tilde{\nu} - \frac{1}{4}x_e\tilde{\nu}$  [Section 16.11]

(a)  $^1\text{HCl}$ :  $\tilde{\nu}' = \left\{ (1494.9) - \left( \frac{1}{4} \right) \times (52.05) \right\}, \text{ cm}^{-1} = 1481.8\text{ cm}^{-1}$ , or  $0.184\text{ eV}$

Hence,  $D_0 = 5.33 - 0.18 = \boxed{5.15\text{ eV}}$

(b)  $^2\text{HCl}$ :  $\frac{2m_{\text{eff}}\omega x_e}{\hbar} = a^2$  [16.62], so  $\tilde{\nu}x_e \propto \frac{1}{m_{\text{eff}}}$  as  $a$  is a constant. We also have  $D_e = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}}$

[Exercise 16.23(a)]; so  $\tilde{\nu}^2 \propto \frac{1}{m_{\text{eff}}}$ , implying  $\tilde{\nu} \propto \frac{1}{m_{\text{eff}}^{1/2}}$ . Reduced masses were calculated in

Exercises 16.21(a) and 16.21(b), and we can write

$$\tilde{\nu}(^2\text{HCl}) = \left( \frac{m_{\text{eff}}(^1\text{HCl})}{m_{\text{eff}}(^2\text{HCl})} \right)^{1/2} \times \tilde{\nu}(^1\text{HCl}) = (0.7172) \times (2989.7\text{ cm}^{-1}) = 2144.2\text{ cm}^{-1}$$

$$x_e\tilde{\nu}(^2\text{HCl}) = \left( \frac{m_{\text{eff}}(^1\text{HCl})}{m_{\text{eff}}(^2\text{HCl})} \right) \times x_e\tilde{\nu}(^1\text{HCl}) = (0.5144) \times (52.05\text{ cm}^{-1}) = 26.77\text{ cm}^{-1}$$

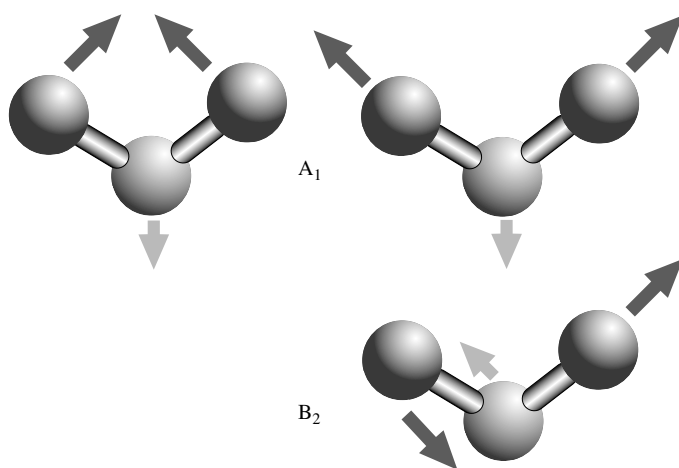
$$\tilde{\nu}'(^2\text{HCl}) = \left( \frac{1}{2} \right) \times (2144.2) - \left( \frac{1}{4} \right) \times (26.77\text{ cm}^{-1}) = 1065.4\text{ cm}^{-1}, \quad 0.132\text{ eV}$$

Hence,  $D_0(^2\text{HCl}) = (5.33 - 0.132)\text{ eV} = \boxed{5.20\text{ eV}}$

- P16.19** (a) Vibrational wavenumbers ( $\tilde{\nu}/\text{cm}^{-1}$ ) computed by PC Spartan Pro<sup>TM</sup> at several levels of theory are tabulated below, along with experimental values:

	A <sub>1</sub>	A <sub>1</sub>	B <sub>2</sub>
Semi-empirical PM3	412	801	896
SCF 6-316G**	592	1359	1569
Density functional	502	1152	1359
Experimental	525	1151	1336

The vibrational modes are shown graphically below.



**Figure 16.3**

- (b) The wavenumbers computed by density functional theory agree quite well with experiment. Agreement of the semi-empirical and SCF values with experiment is not so good. In this molecule, experimental wavenumbers can be correlated rather easily to computed vibrational modes even where the experimental and computed wavenumbers disagree substantially. Often, as in this case, computational methods that do a poor job of computing absolute transition wavenumbers still put transitions in proper order by wavenumber. That is, the modeling software systematically overestimates (as in this SCF computation) or underestimates (as in this semi-empirical computation) the wavenumbers, thus keeping them in the correct order. Group theory is another aid in the assignment of transitions: it can classify modes as forbidden, allowed only in particular polarizations, etc. Also, visual examination of the modes of motion can help to classify many modes as predominantly bond-stretching, bond-bending, or internal rotation; these different modes of vibration can be correlated to quite different ranges of wavenumbers (stretches highest, especially stretches involving hydrogen atoms, and internal rotations lowest.).

- P16.21** Summarize the six observed vibrations according to their wavenumbers ( $\tilde{\nu}/\text{cm}^{-1}$ ):

IR 870      1370   2869   3417  
Raman 877   1408   1435   3407.

- (a) If H<sub>2</sub>O<sub>2</sub> were linear, it would have  $3N - 5 = \boxed{7}$  vibrational modes.  
 (b) Follow the flow chart in Fig. 15.14. Structure **2** is not linear, there is only one  $C_n$  axis (a  $C_2$ ), and there is a  $\sigma_h$ ; the point group is  $\boxed{C_{2h}}$ . Structure **3** is not linear, there is only one  $C_n$  axis (a  $C_2$ ),



no  $\sigma_h$ , but two  $\sigma_v$ ; the point group is  $C_{2v}$ . Structure **4** is not linear, there is only one  $C_n$  axis (a  $C_2$ ), no  $\sigma_h$ , no  $\sigma_v$ ; the point group is  $C_2$ .

- (c) The exclusion rule applies to structure **2** because it has a center of inversion: no vibrational modes can be both IR and Raman active. So structure **2** is inconsistent with observation. The vibrational modes of structure **3** span  $3A_1 + A_2 + 2B_2$ . (The full basis of 12 cartesian coordinates spans  $4A_1 + 2A_2 + 2B_1 + 4B_2$ ; remove translations and rotations.) The  $C_{2v}$  character table says that five of these modes are IR active ( $3A_1 + 2B_2$ ) and all are Raman active. All of the modes of structure **4** are both IR and Raman active. (A look at the character table shows that both symmetry species are IR and Raman active, so determining the symmetry species of the normal modes does not help here.) Both structures **3** and **4** have more active modes than were observed. This is consistent with the observations. After all, group theory can only tell us whether the transition moment *must* be zero by symmetry; it does not tell us whether the transition moment is sufficiently strong to be observed under experimental conditions.

### Solutions to theoretical problems

- P16.22** The centre of mass of a diatomic molecule lies at a distance  $x$  from atom A and is such that the masses on either side of it balance

$$m_A x = m_B (R - x)$$

and hence it is at

$$x = \frac{m_B}{m} R \quad m = m_A + m_B$$

The moment of inertia of the molecule is

$$\begin{aligned} I = m_A x^2 + m_B (R - x)^2 [26] &= \frac{m_A m_B^2 R^2}{m^2} + \frac{m_B m_A^2 R^2}{m^2} = \frac{m_A m_B}{m} R^2 \\ &= \boxed{m_{\text{eff}} R^2} \quad \text{since } m_{\text{eff}} = \frac{m_A m_B}{m_A + m_B} \end{aligned}$$

- P16.23** Because the centrifugal force and the restoring force balance,

$$k(r_c - r_e) = \mu \omega^2 r_c,$$

we can solve for the distorted bond length as a function of the equilibrium bond length:

$$r_c = \frac{r_e}{1 - \mu \omega^2 / k}$$

Classically, then, the energy would be the rotational energy plus the energy of the stretched bond:

$$E = \frac{J^2}{2I} + \frac{k(r_c - r_e)^2}{2} = \frac{J^2}{2I} + \frac{k^2(r_c - r_e)^2}{2k} = \frac{J^2}{2I} + \frac{(\mu \omega^2 r_c)^2}{2k}.$$

How is the energy different from the rigid-rotor energy? Besides the energy of stretching of the bond, the larger moment of inertia alters the strictly rotational piece of the energy. Substitute  $\mu r_c^2$  for  $I$  and substitute for  $r_c$  in terms of  $r_e$  throughout:

$$\text{So} \quad E = \frac{J^2(1 - \mu \omega^2 / k)^2}{2\mu r_e^2} + \frac{\mu^2 \omega^4 r_e^2}{2k(1 - \mu \omega^2 / k)^2}.$$

Assuming that  $\mu\omega^2/k$  is small (a reasonable assumption for most molecules), we can expand the expression and discard squares or higher powers of  $\mu\omega^2/k$ :

$$E \approx \frac{J^2(1 - 2\mu\omega^2/k)}{2\mu r_e^2} + \frac{\mu^2\omega^4 r_e^2}{2k}.$$

(Note that the entire second term has a factor of  $\mu\omega^2/k$  even before squaring and expanding the denominator, so we discard all terms of that expansion after the first.) Begin to clean up the expression by using classical definitions of angular momentum:

$$J = I\omega = \mu r^2 \omega \quad \text{so} \quad \omega = J/\mu r_e^2,$$

which allows us to substitute expressions involving  $J$  for all  $\omega$ s:

$$E \approx \frac{J^2}{2\mu r_e^2} - \frac{J^4}{\mu^2 r_e^6 k} + \frac{J^4}{2\mu^2 r_e^6 k}.$$

(At the same time, we have expanded the first term, part of which we can now combine with the last term.) Continue to clean up the expression by substituting  $I/\mu$  for  $r^2$ , and then carry the expression over to its quantum mechanical equivalent by substituting  $J(J+1)\hbar^2$  for  $J^2$ :

$$E \approx \frac{J^2}{2I} - \frac{J^4\mu}{2I^3k} \Rightarrow E \approx \frac{J(J+1)\hbar^2}{2I} - \frac{J^2(J+1)^2\hbar^4\mu}{2I^3k}.$$

Dividing by  $hc$  gives the rotational term,  $F(J)$ :

$$F(J) \approx \frac{J(J+1)\hbar^2}{2hcI} - \frac{J^2(J+1)^2\hbar^4\mu}{2hcI^3k} = \frac{J(J+1)\hbar}{4\pi cI} - \frac{J^2(J+1)^2\hbar^3\mu}{4\pi cI^3k},$$

where we have used  $\hbar = h/2\pi$  to eliminate a common divisor of  $h$ . Now use the definition of the rotational constant,

$$B = \frac{\hbar}{4\pi cI} \Rightarrow F(J) \approx J(J+1)B - J^2(J+1)^2B^3 \frac{16\pi^2 c^2 \mu}{k}.$$

Finally, use the relationship between the force constant and vibrational wavenumber:

$$\left(\frac{k}{\mu}\right)^{1/2} = \omega_{\text{vib}} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \text{so} \quad \frac{\mu}{k} = \frac{1}{4\pi^2 c^2 \tilde{\nu}^2}$$

leaving  $F(J) \approx BJ(J+1) - \frac{4B^3}{\tilde{\nu}^2} J^2(J+1)^2 = BJ(J+1) - DJ^2(J+1)^2$  where  $D = \frac{4B^3}{\tilde{\nu}^2}$ .

**P16.26**

$$S(v, J) = \left(v + \frac{1}{2}\right)\tilde{\nu} + BJ(J+1) \quad [16.68]$$

$$\Delta S_J^O = \tilde{\nu} - 2B(2J-1) \quad [\Delta v = 1, \Delta J = -2]$$

$$\Delta S_J^S = \tilde{\nu} + 2B(2J+3) \quad [\Delta v = 1, \Delta J = +2]$$

The transition of maximum intensity corresponds, approximately, to the transition with the most probable value of  $J$ , which was calculated in Problem 16.25

$$J_{\text{max}} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}$$

The peak-to-peak separation is then

$$\begin{aligned}\Delta S &= \Delta S_{J_{\max}}^S - \Delta S_{J_{\max}}^O = 2B(2J_{\max} + 3) - \{-2B(2J_{\max} - 1)\} = 8B\left(J_{\max} + \frac{1}{2}\right) \\ &= 8B\left(\frac{kT}{2hcB}\right)^{1/2} = \left(\frac{32BkT}{hc}\right)^{1/2}\end{aligned}$$

To analyse the data we rearrange the relation to

$$B = \frac{hc(\Delta S)^2}{32kT}$$

and convert to a bond length using  $B = \frac{\hbar}{4\pi cI}$ , with  $I = 2m_x R^2$  (Table 16.1) for a linear rotor. This gives

$$R = \left(\frac{\hbar}{8\pi c m_x B}\right)^{1/2} = \left(\frac{1}{\pi c \Delta S}\right) \times \left(\frac{2kT}{m_x}\right)^{1/2}$$

We can now draw up the following table

	HgCl <sub>2</sub>	HgBr <sub>2</sub>	HgI <sub>2</sub>
<i>T</i> /K	555	565	565
<i>m<sub>x</sub></i> /u	35.45	79.1	126.90
$\Delta S$ /cm <sup>-1</sup>	23.8	15.2	11.4
<i>R</i> /pm	227.6	240.7	253.4

Hence, the three bond lengths are approximately 230, 240, and 250 pm

**P16.28** The energy levels of a Morse oscillator, expressed as wavenumbers, are given by:

$$G(\nu) = \left(\nu + \frac{1}{2}\right) \tilde{\nu} - \left(\nu + \frac{1}{2}\right)^2 x_e \tilde{\nu} = \left(\nu + \frac{1}{2}\right) \tilde{\nu} - \left(\nu + \frac{1}{2}\right)^2 \tilde{\nu}^2 / 4D_e.$$

States are bound only if the energy is less than the well depth,  $D_e$ , also expressed as a wavenumber:

$$G(\nu) < D_e \quad \text{or} \quad \left(\nu + \frac{1}{2}\right) \tilde{\nu} - \left(\nu + \frac{1}{2}\right)^2 \tilde{\nu}^2 / 4D_e < D_e.$$

Solve for the maximum value of  $\nu$  by making the inequality into an equality:

$$\left(\nu + \frac{1}{2}\right)^2 \tilde{\nu}^2 / 4D_e - \left(\nu + \frac{1}{2}\right) \tilde{\nu} + D_e = 0.$$

Multiplying through by  $4D_e$  results in an expression that can be factored by inspection into:

$$\left[\left(\nu + \frac{1}{2}\right) \tilde{\nu} - 2D_e\right]^2 = 0 \quad \text{so} \quad \nu + \frac{1}{2} = 2D_e / \tilde{\nu} \quad \text{and} \quad \nu = \left[2D_e / \tilde{\nu} - \frac{1}{2}\right].$$

Of course,  $\nu$  is an integer, so its maximum value is really the greatest integer less than this quantity.

### Solutions to applications

- P16.29** (a) Resonance Raman spectroscopy is preferable to vibrational spectroscopy for studying the O—O stretching mode because such a mode would be infrared inactive, or at best only weakly active. (The mode is sure to be inactive in free O<sub>2</sub>, because it would not change the molecule's dipole moment. In a complex in which O<sub>2</sub> is bound, the O—O stretch may change the dipole moment, but it is not certain to do so at all, let alone strongly enough to provide a good signal.)
- (b) The vibrational wavenumber is proportional to the frequency, and it depends on the effective mass as follows,

$$\tilde{\nu} \propto \left( \frac{k}{m_{\text{eff}}} \right)^{1/2}, \quad \text{so} \quad \frac{\tilde{\nu}({}^{18}\text{O}_2)}{\tilde{\nu}({}^{16}\text{O}_2)} = \left( \frac{m_{\text{eff}}({}^{16}\text{O}_2)}{m_{\text{eff}}({}^{18}\text{O}_2)} \right)^{1/2} = \left( \frac{16.0 \text{ u}}{18.0 \text{ u}} \right)^{1/2} = 0.943,$$

$$\text{and } \tilde{\nu}({}^{18}\text{O}_2) = (0.943)(844 \text{ cm}^{-1}) = \boxed{796 \text{ cm}^{-1}}.$$

Note the assumption that the effective masses are proportional to the isotopic masses. This assumption is valid in the free molecule, where the effective mass of O<sub>2</sub> is equal to half the mass of the O atom; it is also valid if the O<sub>2</sub> is strongly bound at one end, such that one atom is free and the other is essentially fixed to a very massive unit.

- (c) The vibrational wavenumber is proportional to the square root of the force constant. The force constant is itself a measure of the strength of the bond (technically of its stiffness, which correlates with strength), which in turn is characterized by bond order. Simple molecule orbital analysis of O<sub>2</sub>, O<sub>2</sub><sup>-</sup>, and O<sub>2</sub><sup>2-</sup> results in bond orders of 2, 1.5, and 1 respectively. Given decreasing bond order, one would expect decreasing vibrational wavenumbers (and vice versa).
- (d) The wavenumber of the O—O stretch is very similar to that of the peroxide anion, suggesting Fe<sup>3+</sup><sub>2</sub>O<sub>2</sub><sup>2-</sup>.
- (e) The detection of two bands due to <sup>16</sup>O<sup>18</sup>O implies that the two O atoms occupy non-equivalent positions in the complex. Structures **7** and **8** are consistent with this observation, but structures **5** and **6** are not.

- P16.31** (a) The molar absorption coefficient  $\varepsilon(\tilde{\nu})$  is given by

$$\varepsilon(\tilde{\nu}) = \frac{A(\tilde{\nu})}{l[\text{CO}_2]} = \frac{RTA(\tilde{\nu})}{lx_{\text{CO}_2}p} \quad (\text{eqns 16.11, 1.15, and 1.18})$$

where  $T = 298 \text{ K}$ ,  $l = 10 \text{ cm}$ ,  $p = 1 \text{ bar}$ , and  $x_{\text{CO}_2} = 0.021$ .

The absorption band originates with the 001 ← 000 transition of the antisymmetric stretch vibrational mode at 2349 cm<sup>-1</sup> (Fig. 16.48). The band is very broad because of accompanying rotational transitions and lifetime broadening of each individual absorption (also called collisional broadening or pressure broadening, Section 16.3). The spectra reveals that the Q branch is missing so we conclude that the transition ΔJ = 0 is forbidden (Section 16.12) for the D<sub>∞h</sub> point group of CO<sub>2</sub>. The P-branch (ΔJ = -1) is evident at lower energies and the R-branch (ΔJ = +1) is evident at higher energies.

- (b) <sup>16</sup>O—<sup>12</sup>C—<sup>16</sup>O has two identical nuclei of zero spin so the CO<sub>2</sub> wavefunction must be symmetric w/r/t nuclear interchange and it must obey Bose–Einstein nuclear statistics (Section 16.8). Consequently,  $J$  takes on even values only for the  $\nu = 0$  vibrational state and odd values only for the  $\nu = 1$  state. The  $(\nu, J)$  states for this absorption band are  $(1, J + 1) \leftarrow (0, J)$  for  $J = 0, 2, 4, \dots$ . According to eqn 16.68, the energy of the  $(0, J)$  state is

$$S(0, J) = \frac{1}{2}\nu + BJ(J + 1),$$

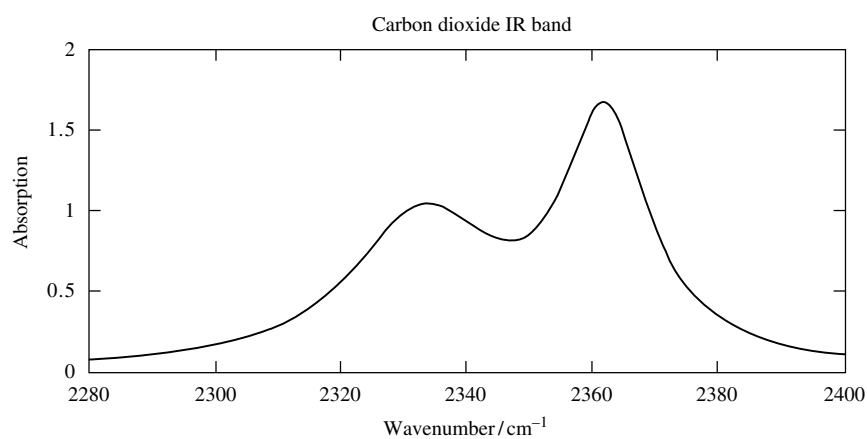


Figure 16.4(a)

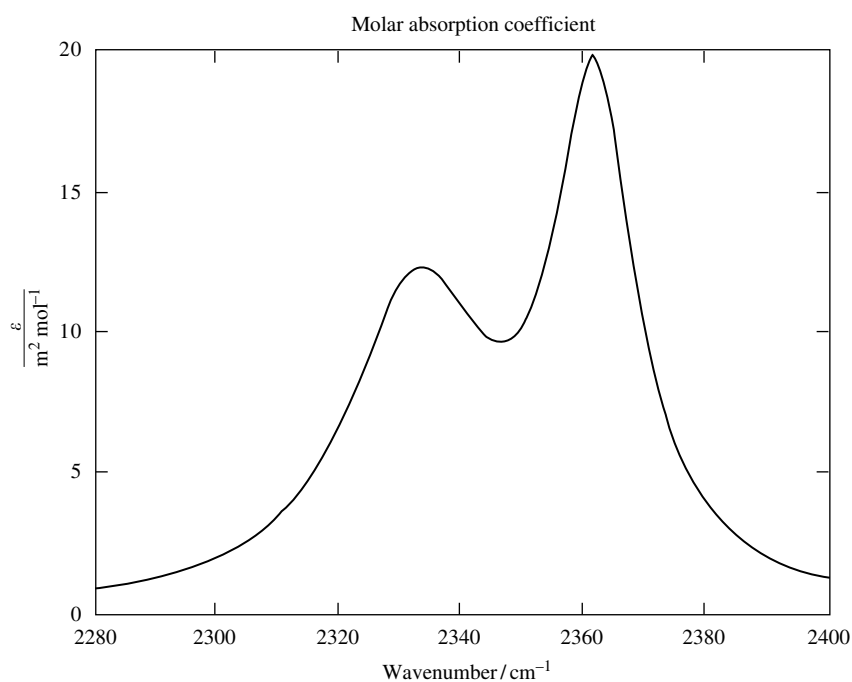


Figure 16.4(b)

where  $\nu = 2349 \text{ cm}^{-1}$

$$I = \frac{2m_{\text{O}}R^2}{N_{\text{A}}} = \frac{2(0.01600 \text{ kg mol}^{-1})(116.2 \times 10^{-12} \text{ m})^2}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$= 7.175 \times 10^{-46} \text{ kg m}^2 \quad (\text{Table 16.1})$$

$$B = \frac{h}{8\pi^2cI} \quad (\text{eqn 16.31})$$

$$= \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2(2.998 \times 10^8 \text{ m s}^{-1})(7.175 \times 10^{-46} \text{ kg m}^2)}$$

$$= 39.02 \text{ m}^{-1} = 0.3902 \text{ cm}^{-1}$$

The transitions of the P and R branches occur at

$$\tilde{\nu}_{\text{p}} = \tilde{\nu} - 2BJ \quad [16.69\text{b}]$$

and

$$\tilde{\nu}_R = \tilde{\nu} + 2B(J + 1) \quad [16.69c]$$

where  $J = 0, 2, 4, 6 \dots$

The highest energy transition of the P branch is at  $\tilde{\nu} - 4B$ ; the lowest energy transition of the R branch is at  $\tilde{\nu} + 2B$ . Transitions are separated by  $4B(1.5608 \text{ cm}^{-1})$  within each branch. The probability of each transition is proportional to the lower state population, which we assume to be given by the Boltzman distribution with a degeneracy of  $2J + 1$ . The transition probability is also proportional to both a nuclear degeneracy factor (eqn 16.50) and a transition dipole moment, which is approximately independent of  $J$ . The former factors are absorbed into the constant of proportionality.

$$\text{transition probability} \propto (2J + 1)e^{-S(0,J)hc/kT}$$

A plot of the right-hand-side of this equation, Fig. 16.4(c), against  $J$  at 298 K indicates a maximum transition probability at  $J_{\text{max}} = 16$ . We “normalize” the maximum in the predicted structure, and eliminate the constant of proportionality by examining the transition probability ratio:

$$\begin{aligned} \frac{\text{transition probability for } J\text{th state}}{\text{transition probability for } J_{\text{max}}\text{ state}} &= \frac{(2J + 1)e^{-S(0,J)hc/kT}}{33e^{-S(0,16)hc/RT}} \\ &= \left(\frac{2J + 1}{33}\right) e^{-(J^2 + J - 272)Bhc/kT} \end{aligned}$$

A plot Fig. 16.4(c) of the above ratio against predicted wavenumbers can be compared to the ratio  $A(\tilde{\nu})/A_{\text{max}}$  where  $A_{\text{max}}$  is the observed spectrum maximum (1.677). It shows a fair degree of agreement between the experimental and simple theoretical band shapes.

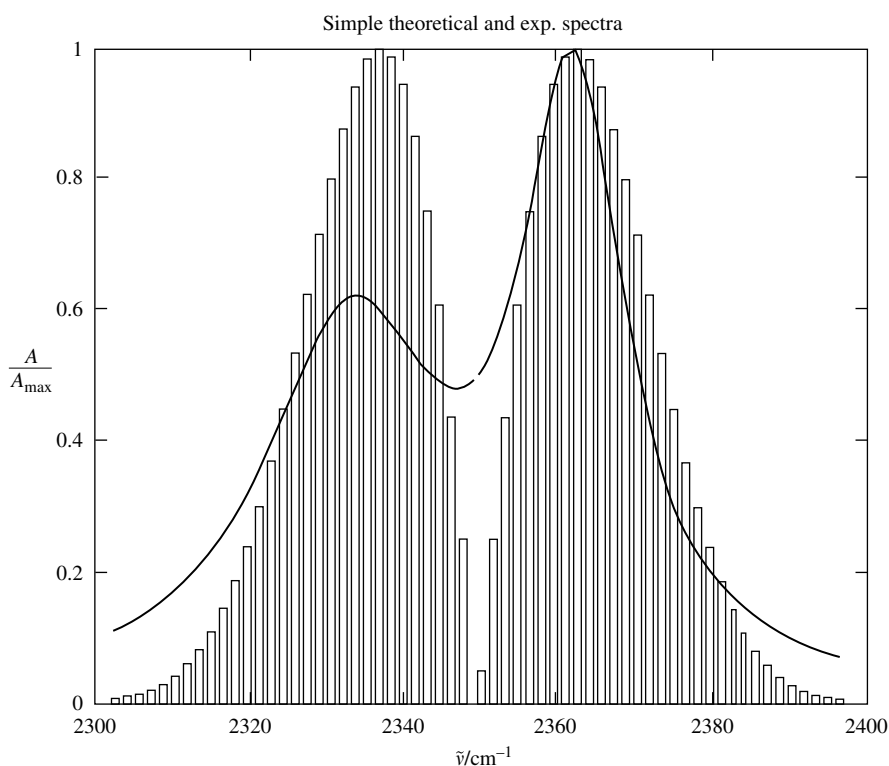


Figure 16.4(c)

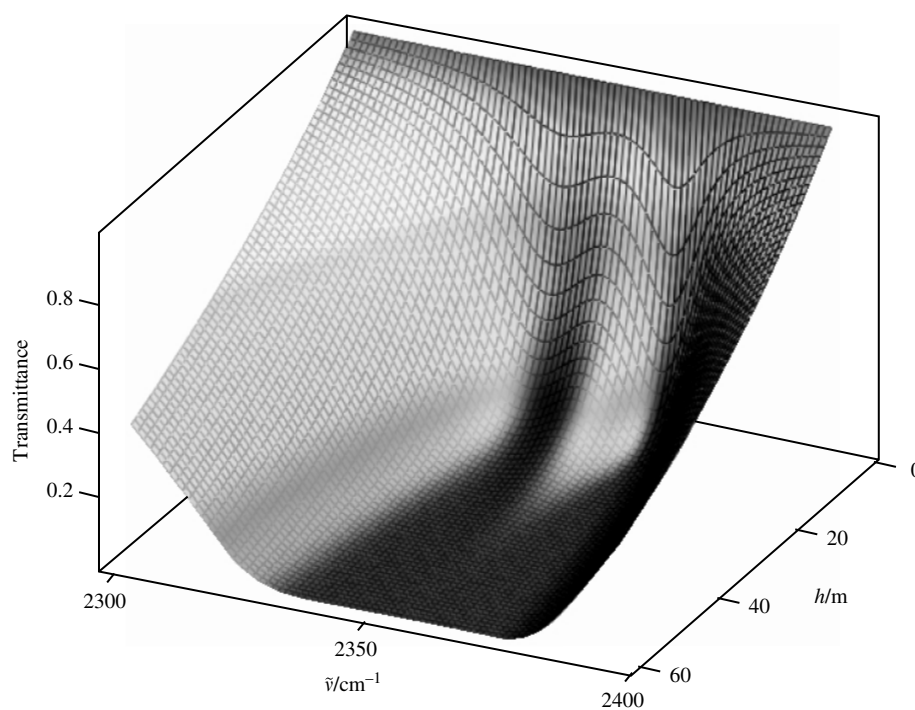


Figure 16.4(d)

(c) Using the equations of justificiant 16.1, we may write the relationship

$$A = \varepsilon(\tilde{\nu}) \int_0^h [\text{CO}_2] dh$$

The strong absorption of the band suggests that  $h$  should not be a very great length and that  $[\text{CO}_2]$  should be constant between the Earth's surface and  $h$ . Consequently, the integration gives

$$\begin{aligned} A &= \varepsilon(\tilde{\nu})[\text{CO}_2]h \\ &= \varepsilon(\tilde{\nu})h \left\{ \frac{x_{\text{CO}_2} P}{RT} \right\} \quad \text{Dalton's law of partial pressures} \end{aligned}$$

$p$  and  $T$  are not expected to change much for modest values of  $h$  so we estimate that  $p = 1$  bar and  $T = 288$  K.

$$\begin{aligned} A &= \varepsilon(\tilde{\nu})h \left\{ \frac{(3.3 \times 10^{-4}) (1 \times 10^5 \text{ Pa})}{(8.31451 \text{ J K}^{-1} \text{ mol}^{-1}) (288 \text{ K})} \right\} \\ &= (0.0138 \text{ m}^{-3} \text{ mol}) \varepsilon(\tilde{\nu})h \end{aligned}$$

$$\text{Transmittance} = 10^{-A} = 10^{-(0.0138 \text{ m}^{-3} \text{ mol})\varepsilon(\tilde{\nu})h} \quad [16.10]$$

The transmittance surface plot clearly shows that before a height of about 30 m has been reached all of the Earth's IR radiation in the  $2320 \text{ cm}^{-1} - 2380 \text{ cm}^{-1}$  range has been absorbed by atmospheric carbon dioxide.

See C.A. Meserole, F.M. Mulcalry, J. Lutz, and H.A. Yousif, *J. Chem. Ed.*, 74, 316 (1997).

- P16.34** (a) The  $\text{H}_3^+$  molecule is held together by a two-electron, three-center bond, and hence its structure is expected to be an equilateral triangle. Looking at Fig. 16.5 and using the Law of cosines

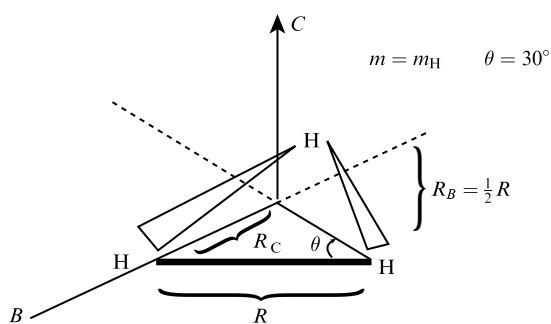
$$\begin{aligned} R^2 &= 2R_C^2 - 2R_C^2 \cos(180^\circ - 2\theta) \\ &= 2R_C^2(1 - \cos(120^\circ)) = 3R_C^2 \end{aligned}$$

Therefore

$$\begin{aligned} R_C &= R/\sqrt{3} \\ I_C &= 3mR_C^2 = 3m(R/\sqrt{3})^2 = mR^2 \\ I_B &= 2mR_B = 2m(R/2)^2 = mR^2/2 \end{aligned}$$

Therefore

$$I_C = 2I_B$$



**Figure 16.5**

$$\begin{aligned} \text{(b)} \quad B &= \frac{\hbar}{4\pi c I_B} = \frac{2\hbar}{4\pi c m R^2} = \frac{\hbar}{2\pi c m R^2} \quad [16.37] \\ R &= \left( \frac{\hbar}{2\pi c m B} \right)^{1/2} = \left( \frac{\hbar N_A}{2\pi c M_H B} \right)^{1/2} \\ &= \left( \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (6.0221 \times 10^{23} \text{ mol}^{-1}) \times \left( \frac{10^{-2} \text{ m}}{\text{cm}} \right)}{2\pi (2.998 \times 10^8 \text{ m s}^{-1}) \times (0.001008 \text{ kg mol}^{-1}) \times (43.55 \text{ cm}^{-1})} \right)^{1/2} \\ &= 8.764 \times 10^{-11} \text{ m} = \boxed{87.64 \text{ pm}} \end{aligned}$$

Alternatively the rotational constant  $C$  can be used to calculate  $R$ .

$$\begin{aligned} C &= \frac{\hbar}{4\pi c I_C} = \frac{\hbar}{4\pi c m R^2} \quad [36] \\ R &= \left( \frac{\hbar}{4\pi c m C} \right)^{1/2} = \left( \frac{\hbar N_A}{4\pi c M_H C} \right)^{1/2} \\ &= \left( \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (6.0221 \times 10^{23} \text{ mol}^{-1}) \times \left( \frac{10^{-2} \text{ m}}{\text{cm}} \right)}{4\pi (2.998 \times 10^8 \text{ m s}^{-1}) \times (0.001008 \text{ kg mol}^{-1}) \times (20.71 \text{ cm}^{-1})} \right)^{1/2} \\ &= 8.986 \times 10^{-11} \text{ m} = \boxed{89.86 \text{ pm}} \end{aligned}$$



The values of  $R$  calculated with either the rotational constant  $C$  or the rotational constant  $B$  differ slightly. We approximate the bond length as the average of these two.

$$\langle R \rangle \approx \frac{(87.64 + 89.86) \text{ pm}}{2} = \boxed{88.7 \text{ pm}}$$

$$(c) \quad B = \frac{\hbar}{2\pi cmR^2} = \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (6.0221 \times 10^{23} \text{ mol}^{-1}) \times \left(\frac{10^{-2} \text{ m}}{\text{cm}}\right)}{2\pi(2.998 \times 10^8 \text{ m s}^{-1}) \times (0.001008 \text{ kg mol}^{-1}) \times (87.32 \times 10^{-12} \text{ m})^2}$$

$$= \boxed{43.87 \text{ cm}^{-1}}$$

$$C = \frac{1}{2}B = \boxed{21.93 \text{ cm}^{-1}}$$

$$(d) \quad \frac{1}{m_{\text{eff}}} = \frac{3}{m} \quad \text{or} \quad m_{\text{eff}} = \frac{1}{3}m$$

Since  $m_{\text{D}} = 2m_{\text{H}}$ ,  $m_{\text{eff,D}} = 2m_{\text{H}}/3$

$$\tilde{\nu}_2(\text{D}_3^+) = \left(\frac{m_{\text{eff}}(\text{H}_3)}{m_{\text{eff}}(\text{D}_3)}\right)^{1/2} \tilde{\nu}_2(\text{H}_3) \quad [57]$$

$$= \left(\frac{m_{\text{H}}/3}{2m_{\text{H}}/3}\right)^{1/2} \tilde{\nu}_2(\text{H}_3) = \frac{\tilde{\nu}_2(\text{H}_2)}{2^{1/2}}$$

$$= \frac{2521.6 \text{ cm}^{-1}}{2^{1/2}} = \boxed{1783.0 \text{ cm}^{-1}}$$

Since  $B$  and  $C \propto \frac{1}{m}$ , where  $m$  = mass of H or D

$$B(\text{D}_3^+) = B(\text{H}_3^+) \times \frac{M_{\text{H}}}{M_{\text{D}}} = 43.55 \text{ cm}^{-1} \times \left(\frac{1.008}{2.014}\right) = \boxed{21.80 \text{ cm}^{-1}}$$

$$C(\text{D}_3^+) = C(\text{H}_3^+) \times \frac{M_{\text{H}}}{M_{\text{D}}} = 20.71 \text{ cm}^{-1} \times \left(\frac{1.008}{2.014}\right) = \boxed{10.37 \text{ cm}^{-1}}$$