10

Molecular spectroscopy

Answers to worked examples

W.E. 10.1 Using the Beer-Lambert law (on p. 462 in *Chemistry*^{3})

What concentration of the solution is required to absorb 35% of the light at the same wavelength in an identical cell?

Strategy

Rearrange Equation 10.8 to give an expression for the concentration of the solution in terms of the absorbance, path length and absorption coefficient. Calculate the absorbance and substitute, along with the values given in the example.

Solution

The absorbance of the solution is given by Equation 10.7

$$A = \log_{10}(I_0/I_t) = \log_{10}(1.00/0.65) = +0.187$$

because if 35% of the incident radiation is absorbed, 65% must be transmitted. We may rearrange Equation 10.8 and substitute the values directly

$$\begin{aligned} c &= A/(\epsilon l) \\ &= +0.187/\{(15.1\ \mathrm{m^2 mol^{-1}}) \times (0.0100\ \mathrm{m})\} \\ &= 1.24\ \mathrm{mol\ m^{-3}} = 1.24 \times 10^{-3} \mathrm{mol\ dm^{-3}} \end{aligned}$$

W.E. 10.2 Using the Boltzmann distribution (on p. 463 in *Chemistry*^{3})

Calculate the relative populations of the two energy levels, each with a degeneracy of one, separated by 5.0 kJ mol^{-1} at: (a) 200 K; (b) 300 K; (c) 500 K. What is the effect of temperature on the relative populations in the two levels?

Strategy

Use Equation 10.9, which shows how the Boltzmann distribution affects the relative populations of two energy levels.

Solution

The separation between the energy levels is quoted as a molar value and should be expressed as an equivalent value per molecule by dividing by Avogadro's number, N_A. Thus, using Equation 10.9,

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{g_{\text{upper}}}{g_{\text{lower}}} e^{-[(\Delta E/\, N_A)\,/k_B T]}$$

directly for the different temperatures gives:

(a)

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{1}{1} e^{-[(5.0\times10^3\ \text{kJ mol}^{-1}/6.022\times10^{23}\text{mol}^{-1})/(1.381\times10^{-23}\ \text{J K}^{-1}\times200\ \text{K})]}$$

$$= 0.050$$

(b)

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{1}{1} e^{-[(5.0\times10^3\ \text{kJ mol}^{-1}/6.022\times10^{23}\text{mol}^{-1})/(1.381\times10^{-23}\ \text{J K}^{-1}\times300\ \text{K})]}$$

$$= 0.135$$

(c)

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{1}{1} e^{-[(5.0\times10^3\ \text{kJ mol}^{-1}/6.022\times10^{23}\text{mol}^{-1})/(1.381\times10^{-23}\ \text{J K}^{-1}\times500\ \text{K})]}$$

$$= 0.300$$

Thus, as the temperature increases the population of the upper level relative to that of the lower level increases from 5.0%, to 13.5% to 30.0%.

Note that the solution given in the printed text for part (c) corresponds to a temperature of 600 K and not 500 K.

W.E. 10.3 Calculating moments of inertia (on p. 467 in *Chemistry*^{3})

The moment of inertia of $^1H^{35}Cl$ is 2.639×10^{-47} kg m^2. Calculate the bond length.

Strategy

Calculate the reduced mass of $^1H^{35}Cl$ from Equation 10.13. Rearrange Equation

10.12 to give an expression for the bond length of a molecule in terms of its moment of inertia and reduced mass and substitute the values.

Solution

The molar mass of a ^{1}H atom is 1.00 g mol^{-1}, and of a ^{35}Cl chlorine atom is 35.00 g mol^{-1} so that

$$m_{\mathrm{H}} = (1.00 \times \overbrace{10^{-3}\ \mathrm{kg\ mol^{-1}}}^{1\ \mathrm{g}=10^{-3}\mathrm{kg}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 1.661 \times 10^{-27}\mathrm{kg}$$
$$m_{\mathrm{Cl}} = (35.00 \times 10^{-3}\mathrm{kg\ mol^{-1}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 5.814 \times 10^{-26}\mathrm{kg}$$

The reduced mass of a ^{1}H^{35}Cl molecule is, from Equation 10.13,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_{\mathrm{H}} m_{\mathrm{Cl}}}{m_{\mathrm{H}} + m_{\mathrm{Cl}}}$$
$$= \frac{(1.661 \times 10^{-27}\mathrm{kg}) \times (5.814 \times 10^{-26}\mathrm{kg})}{(1.661 \times 10^{-27}\mathrm{kg}) + (5.814 \times 10^{-26}\mathrm{kg})}$$
$$= 1.615 \times 10^{-27}\mathrm{kg}$$

Then, if the moment of inertia is 2.639 × 10^{-47} kg m^2, rearranging and applying Equation 10.12 gives

$$r_0 = (I/\mu)^{1/2} = \{(2.639 \times 10^{-47}\ \mathrm{kg\ m^2})/(1.615 \times 10^{-27}\mathrm{kg})\}^{1/2}$$
$$= 1.28 \times 10^{-10}\mathrm{m} = 0.128\ \mathrm{nm} = 1.28\ \mathrm{Å}$$

W.E. 10.4 Calculating rotational energies (on p. 470 in *Chemistry*^{3})

Calculate the energies of the J =7 and J = 8 levels. At what wavenumber does the J = 7 → 8 transition occur?

Strategy

Use Equation 10.16 to calculate the energies of the two levels. Calculate the difference and convert the answer to a wavenumber using Equation 10.11.

Solution

If B = 5.77 × 10^{10} s^{-1}, then using Equation 10.16,

$$E_J = hBJ(J+1)$$
$$E_{J=7} = hB \times 7 \times (7+1) = hB \times 7 \times 8 = 56\ hB$$
$$= 56 \times (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (5.77 \times 10^{10}\mathrm{s^{-1}}) = 2.141 \times 10^{-21}\mathrm{J}$$

$$E_{J=8} = hB \times 8 \times (8+1) = hB \times 8 \times 9 = 72\ hB$$

$$= 72 \times (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (5.77 \times 10^{10}\mathrm{s}^{-1}) = 2.753 \times 10^{-21}\mathrm{J}$$

The difference in energy between these levels is

$$\Delta E = E_{J=8} - E_{J=7} = 2.753 \times 10^{-21}\mathrm{J} - 2.141 \times 10^{-21}\mathrm{J} = 6.04 \times 10^{-22}\mathrm{J}$$

But, from Equation 10.11,

$$\Delta E = hc\tilde{\nu}$$

so that

$$\nu = \Delta E/hc = (6.04 \times 10^{-22}\mathrm{J})/\{(6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s}^{-1})\}$$

$$= 3040\ \mathrm{m}^{-1}$$

The wavenumbers of spectroscopic transitions are usually quoted in units of cm^{-1} rather than m^{-1}. Remembering that 3040 m^{-1} means 3040 wavelengths per metre, this must be equivalent to 30.4 wavelengths per centimetre and therefore 30.4 cm^{-1}.

W.E. 10.5 Selection rules in rotational spectroscopy (on p. 471 in *Chemistry*^{3})

Which of the following show rotational spectra: D_2; HCl; ClO; CN?

Strategy

Consider which of the molecules listed have a permanent electric dipole moment.

Solution

Of the molecules listed, HCl, ClO and CN all have permanent electric dipole moments. These are heteronuclear diatomic molecules, and the difference in the electronegativities of the different atoms results in an asymmetric distribution of electrons around the nuclei and hence a permanent electric dipole moment. We shall see in Chapter 17 that dipole moments are measured in units of debye, symbol D. The permanent electric dipole moment is greatest for HCl at 1.08 D, so we might expect the microwave rotational spectrum of this molecule to be the most intense.

The only molecule that does not show a rotational spectrum is D_2. This is a homonuclear diatomic molecule. The electronegativities of the atoms are identical, so the molecule is not polarised.

W.E. 10.6 Calculating bond lengths from rotational spectra (on p. 473 in *Chemistry*^{3})

In the rotational spectrum of $^1H^{35}Cl$ recorded at 298 K, consecutive lines were observed at the following frequencies (measured in GHz): 621, 1245, 1869, 2493. Calculate the rotational constant, B, and the bond length in $^1H^{35}Cl$.

Strategy

Calculate the average spacing between the transitions and hence determine the rotational constant. Use Equation 10.15 to determine the moment of inertia of the molecule and then Equation 10.12 to find the bond length.

Solution

The separation between consecutive lines in the spectrum of simple diatomic molecules such as $^1H^{35}Cl$ is $2B$. For the transitions given, the difference between each pair of consecutive lines is

$$(2493 - 1869)\ \text{GHz} = 624\ \text{GHz}$$

$$(1869 - 1245)\ \text{GHz} = 624\ \text{GHz}$$

$$(1245 - 621)\ \text{GHz} = 624\ \text{GHz}$$

Thus,

$$2B = 624\ \text{GHz}$$

and so

$$B = 312\ \text{GHz} = 312 \times 10^9\ \text{s}^{-1}$$

In reality, we might expect some variation in the separations between the measured frequencies of the lines because of experimental error, and we should determine the average spacing by plotting a graph.

Rearranging Equation 10.15 gives a moment of inertia of

$$I = \frac{h}{8\pi^2 B} = \frac{(6.626 \times 10^{-34}\ \text{J s})}{8\pi^2 \times (312 \times 10^9\ \text{s}^{-1})} = 2.69 \times 10^{-47}\ \text{J s}^2 = 2.69 \times 10^{-47}\ \text{kg m}^2$$

The molar mass of a ^{1}H atom is 1.00 g mol^{-1}, and of a ^{35}Cl chlorine atom is 35.00 g mol^{-1} so that

$$m_\mathrm{H} = (1.00 \times \overbrace{10^{-3}\ \mathrm{kg\ mol^{-1}}}^{1\ \mathrm{g} = 10^{-3}\mathrm{kg}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 1.661 \times 10^{-27}\mathrm{kg}$$
$$m_\mathrm{Cl} = (35.00 \times 10^{-3}\ \mathrm{kg\ mol^{-1}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 5.814 \times 10^{-26}\mathrm{kg}$$

The reduced mass of a ^{1}H^{35}Cl molecule is, from Equation 10.13,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_\mathrm{H} m_\mathrm{Cl}}{m_\mathrm{H} + m_\mathrm{Cl}}$$
$$= \frac{(1.661 \times 10^{-27}\mathrm{kg}) \times (5.814 \times 10^{-26}\mathrm{kg})}{(1.661 \times 10^{-27}\mathrm{kg}) + (5.814 \times 10^{-26}\mathrm{kg})}$$
$$= 1.615 \times 10^{-27}\mathrm{kg}$$

Then, if the moment of inertia is 2.69 × 10^{-47} kg m^2, rearranging and applying Equation 10.12 gives

$$r_0 = (I/\mu)^{1/2} = (2.69 \times 10^{-47}\ \mathrm{kg\ m^2}/1.615 \times 10^{-27}\mathrm{kg})^{1/2}$$
$$= 1.29 \times 10^{-10}\mathrm{m} = 0.129\ \mathrm{nm} = 1.29\ \mathrm{Å}$$

W.E 10.7 Force constants from infrared data (on p. 482 in *Chemistry*^{3})

The force constant of the bond in ^{12}C^{16}O is 1902 N m^{-1}. Calculate the wavenumber of the transition corresponding to the vibration of this bond.

Strategy

Determine the reduced mass of ^{12}C^{16}O from Equation 10.13. Substitute the values for the reduced mass and force constant into Equation 10.18 to determine the vibrational frequency. Express this value as a wavenumber using Equation 10.10(b).

Solution

The molar mass of a ^{12}C carbon atom is 12.00 g mol^{-1} and of ^{16}O is 16.00 g mol^{-1} so that

$$m_\mathrm{C} = (12.00 \times \overbrace{10^{-3}\ \mathrm{kg\ mol^{-1}}}^{1\ \mathrm{g} = 10^{-3}\mathrm{kg}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 1.993 \times 10^{-26}\mathrm{kg}$$
$$m_\mathrm{O} = (16.00 \times 10^{-3}\ \mathrm{kg\ mol^{-1}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 2.657 \times 10^{-26}\mathrm{kg}$$

The reduced mass of a $^{12}C^{16}O$ molecule is, from Equation 10.13,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_C m_O}{m_C + m_O}$$
$$= \frac{(1.993 \times 10^{-26}\ \mathrm{kg}) \times (2.657 \times 10^{-26}\ \mathrm{kg})}{(1.993 \times 10^{-26}\ \mathrm{kg}) + (2.657 \times 10^{-26}\ \mathrm{kg})}$$
$$= 1.139 \times 10^{-26}\ \mathrm{kg}$$

The frequency of vibration is given by Equation 10.18

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} = \frac{1}{2\pi}\left(\frac{\overbrace{1902\ \mathrm{kg\ s^{-2}}}^{1\ \mathrm{N\ m^{-1}} = 1\ \mathrm{kg\ s^{-2}}}}{1.139 \times 10^{-26}\ \mathrm{kg}}\right)^{1/2} = 6.50 \times 10^{13}\mathrm{s^{-1}}$$

This is equivalent to a wavenumber of

$$\nu = \nu/c = (6.50 \times 10^{13}\mathrm{s^{-1}})/(2.998 \times 10^{8}\ \mathrm{m\ s^{-1}}) = 217000\ \mathrm{m^{-1}} = 2170\ \mathrm{cm^{-1}}$$

because 1 $\mathrm{m^{-1}}$ = 0.01 $\mathrm{cm^{-1}}$.

W.E. 10.8 Explaining the splittings in ^{19}F and ^{31}P spectra (on p. 506 in *Chemistry*^{3})

Predict the ^{19}F and ^{31}P spectra of PF_3.

Strategy

Use the same rules for predicting the splitting pattern of ^1H spectra.

Solution

There is just one ^{31}P nucleus. Because for ^{31}P, I = ½, the multiplicity of the signal is N + 1 = 1 + 1 = 2. The multiplicity of the ^{31}P nuclei affects the appearance of the ^{19}F spectrum, which therefore consists of a doublet.

In contrast, there are N = 3 magnetically equivalent ^{19}F nuclei. Since I = ½, the N = 3 equivalent nuclei give rise to N + 1 = 4 peaks in the ^{31}P NMR spectrum.

There are N = 3 magnetically equivalent ^{19}F nuclei. Since I = ½, the N = 3 equivalent nuclei give rise to N + 1 = 4 peaks, i.e. a quartet, in the ^{31}P NMR spectrum.

Answers to boxes

Box 10.1 Particle in a one-dimensional box (on p. 454 in *Chemistry*^{3})

Write an expression for the energy level, E, when n = 6 and sketch the shape of the wavefunction.

Strategy

Consider the form of the wavefunctions shown, paying attention to the relationship between the quantum number and the number of nodes.

Solution

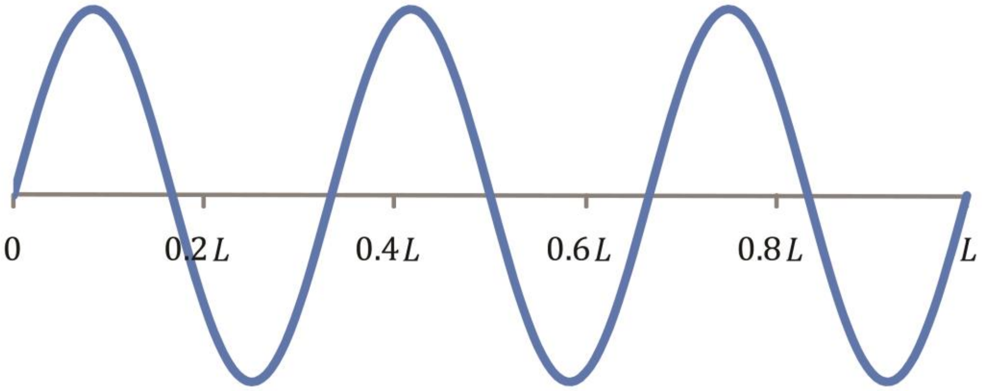
The energy levels of a one-dimensional particle in a box are given by

$$E_n = \frac{n^2h^2}{8mL^2}$$

so that for n = 6

$$E_6 = \frac{6^2h^2}{8mL^2} = \frac{36h^2}{8mL^2} = \frac{9h^2}{2mL^2}$$

Nodes are points at which the wavefunction passes through zero and changes sign. In general, a wavefunction with quantum number n has n – 1 nodes. Thus, we should expect the wavefunction for the level with n = 6 to have 5 nodes and thus be of the form



Box 10.2 Lasers (on p. 464 in *Chemistry*^{3})

(a) In which region of the electromagnetic spectrum does the emission from the

Nd-YAG laser occur?

(b) For a helium-neon laser, calculate the energy of (i) a single photon and (ii) 1 mol of photons.

Strategy

Compare the wavelength for a Nd-YAG laser quoted with the regions of the electromagnetic spectrum shown in Figure3.5 or Appendix 11. Apply a combination of Equations 3.1 and 3.2 to calculate the energy of a photon of known wavelength.

Solution

(a) It can be seen from the figures in Chapter 3 and Appendix 11 that a wavelength of 1064 nm falls in the infrared region of the spectrum. The emission from a Nd-YAG laser is thus of lower frequency than visible light.

(b) Combining Equations 3.1 and 3.2,

$$E = h\nu$$

with

$$c = \lambda\nu$$

so that

$$\nu = c/\lambda$$

and therefore

$$E = hc/\lambda$$

and remembering that a wavelength of 1064 nm is equivalent to 1064×10^{-9} m,

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})}{(1064 \times 10^{-9}\mathrm{m})} = 1.867 \times 10^{-19}\ \mathrm{J}$$

This is equivalent to a molar energy of

$$N_\mathrm{A}E = (6.022\ \times 10^{23}\mathrm{mol^{-1}}) \times (1.867 \times 10^{-19}\ \mathrm{J})$$
$$= 112.4 \times 10^{3}\mathrm{J\ mol^{-1}} = 112.4\ \mathrm{kJ\ mol^{-1}}$$

Box 10.3 Using rotational spectroscopy to monitor ClO· radicals in the atmosphere (on p. 474 in *Chemistry*^{3})

The rotational constant, *B*, for $^{35}\text{Cl}^{16}\text{O}$ is 18.69 GHz. Calculate the ClO bond length.

Strategy

Use Equation 10.15 to determine the moment of inertia from the rotational constant. Determine the reduced mass of the molecule from Equation 10.13. Combine the two results and use Equation 10.12 to find the bond length.

Solution

A rotational constant of 18.69 GHz may be written as $18.69 \times 10^{-9}\ \text{s}^{-1}$.

Rearranging Equation 10.15 thus gives a moment of inertia of

$$I = \frac{h}{8\pi^2 B} = \frac{(6.626 \times 10^{-34}\ \text{J s})}{8\pi^2 \times (18.69 \times 10^{9}\text{s}^{-1})} = 4.49 \times 10^{-46}\text{J s}^2 = 4.49 \times 10^{-46}\text{kg m}^2$$

The molar mass of a ^{35}Cl chlorine atom is 35.00 g mol^{-1} and of ^{16}O is 16.00 g mol^{-1} so that

$$m_{\text{Cl}} = (35.00 \times \overbrace{10^{-3}}^{1\ \text{g}=10^{-3}\text{kg}}\ \text{kg mol}^{-1})/(6.022\ \times 10^{23}\text{mol}^{-1}) = 5.814 \times 10^{-26}\text{kg}$$

$$m_{\text{O}} = (16.00 \times 10^{-3}\ \text{kg mol}^{-1})/(6.022\ \times 10^{23}\text{mol}^{-1}) = 2.657 \times 10^{-26}\text{kg}$$

The reduced mass of a $^{35}\text{Cl}^{16}\text{O}$ molecule is, from Equation 10.13,

$$\begin{aligned}\mu &= \frac{m_1 m_2}{m_1 + m_2} = \frac{m_{\text{Cl}} m_{\text{O}}}{m_{\text{Cl}} + m_{\text{O}}}\\ &= \frac{(5.814 \times 10^{-26}\text{kg}) \times (2.657 \times 10^{-26}\text{kg})}{(5.814 \times 10^{-26}\text{kg}) + (2.657 \times 10^{-26}\text{kg})}\\ &= 1.824 \times 10^{-26}\text{kg}\end{aligned}$$

Then, if the moment of inertia is $2.639 \times 10^{-47}\ \text{kg m}^2$, rearranging and applying Equation 10.12 gives

$$\begin{aligned}r_0 &= (I/\mu)^{1/2} = (4.49 \times 10^{-46}\text{kg m}^2/1.824 \times 10^{-26}\text{kg})^{1/2}\\ &= 1.57 \times 10^{-10}\text{m} = 1.57\ \text{Å}\end{aligned}$$

Box 10.5 Atmospheric concentrations of carbon dioxide (on p. 485 in *Chemistry*^{3})

(a) Suggest explanations for:

(i) the steady rise in CO_2 concentration from 1959 to 2007;

(ii) the zigzag nature of the plot.

(b) Why is the concentration of CO_2 increasing in Mauna Loa where there is little traffic or local industry?

Strategy

Consider the possible sources of carbon dioxide and their variation.

Solution

(a) (i) The steady rise in carbon dioxide concentrations is consistent with the increase in the use of fossil fuels during this period.

(ii) The zigzag variation arises because of the seasonal nature of the carbon dioxide emissions. Vegetation absorbs carbon dioxide as part of photosynthesis. The absorption of carbon dioxide is greatest during the spring and summer months, when plants are growing, creating a six-monthly cycle in the carbon dioxide profile.

(b) The gases in the Earth's troposphere are mixed by transport processes such as diffusion and air currents.

Box 10.6 Degrees of freedom and normal modes of vibration (on p. 486 in *Chemistry*^{3})

For a molecule of methane, CH_4, what are: (a) the total number of degrees of freedom; (b) the number of vibrational modes?

Strategy

Count the number of atoms and hence determine the number of degrees of freedom. Subtract the modes that correspond to translation and rotation to calculate the number of vibrational modes.

Solution

(a) A molecule with N atoms has $3N$ degrees of freedom. For methane, CH_4, there are $N = 5$ atoms, resulting in $3 \times 5 = 15$ degrees of freedom.

(b) Methane is a non-linear molecule, so has 3 translational and 3 rotational modes. There are thus 15 – 3 – 3 = 9 modes that correspond to vibrations.

Box 10.7 Electronic spectroscopy and colour (on p. 491 in *Chemistry*^{3})

Figure 2 shows the visible spectra of two types of chlorophyll and the ultraviolet spectrum of butanone.

(a) Explain why grass is green but butanone is colourless.

(b) Calculate the energies corresponding to the absorption maxima in: (i) $KMnO_4$, λ_{max} = 520 nm; (ii) chlorophyll b, λ_{max} =456 nm; (iii) butanone, λ_{max} = 273 nm.

(c) Compare the absorption spectrum of chlorophyll with the spectrum of sunlight reaching the surface of the Earth in Box 3.1 (p. 120). Can you make any connections?

Strategy

Consider the importance of the wavelength of maximum absorption on colour.

Solution

(a) The absorption spectra of chlorophyll a and b show absorptions in both the red (λ_{max} = 625 and 660 nm) and in the blue (λ_{max} = 428 and 456 nm) regions of the spectrum. Thus, whilst read and blue light is absorbed, green light is transmitted or reflected. Plants, which contain significant quantities of chlorophyll appear to be green in colour. In contrast, the principal absorption in butanone falls in the ultraviolet region of the spectrum at λ_{max} = 273 nm. No visible light is absorbed, so that butanone appears colourless.

(b) The molar energy that corresponds to photons of wavelength λ is

$$E = N_A \times hc/\lambda$$

Thus for potassium permanganate, $KMnO_4$, the absorption at 520 nm corresponds to an energy

$$E = \frac{(6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (2.998 \times 10^{8}\,\mathrm{m\,s^{-1}})}{(520 \times 10^{-9}\,\mathrm{m})}$$

$$= 230 \times 10^{3}\,\mathrm{J\,mol^{-1}} = 230\,\mathrm{kJ\,mol^{-1}}$$

for chlorophyll b, at 456 nm,

$$E = \frac{(6.022 \times 10^{23} \text{mol}^{-1}) \times (6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^{8}\ \text{m s}^{-1})}{(456 \times 10^{-9} \text{m})}$$

$$= 262 \times 10^{3} \text{J mol}^{-1} = 262\ \text{kJ mol}^{-1}$$

and for butanone at 273 nm,

$$E = \frac{(6.022 \times 10^{23} \text{mol}^{-1}) \times (6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^{8}\ \text{m s}^{-1})}{(273 \times 10^{-9} \text{m})}$$

$$= 438 \times 10^{3} \text{J mol}^{-1} = 438\ \text{kJ mol}^{-1}$$

(c) The spectra show that the two principal absorptions for chlorophyll lie in the most intense region of the spectrum of sunlight falling on the Earth's surface. Chlorophyll thus acts as a very efficient ways of harvesting the energy from the Sun.

Box 10.9 Magnetic Resonance Imaging, MRI (on p. 507 in *Chemistry*^{3})

Why were the ^{1}H nuclei, rather than other NMR active nuclei, chosen for monitoring in the MRI technique?

Strategy

Consider the abundance and magnetic properties of the ^{1}H nucleus.

Solution

The sensitivity of NMR spectroscopy, or MRI imaging, depends upon the total number of magnetically active nuclei present and the relative populations of the spin states. The most abundant magnetically active nucleus is ^{1}H. Not only is hydrogen present in most organic molecules, but it is the most common isotope, ^{1}H, that is magnetically active. Carbon is also highly abundant, but the ^{12}C isotope, which is the most abundant, is not magnetically active, because it has $I = 0$.

Sensitivity improves as the difference between the populations of the spin states increases. The greater the imbalance in the populations of the states, the more nuclei can be made to undergo a spectroscopic transition. The Boltzmann equation, Equation 10.9

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{g_{\text{upper}}}{g_{\text{lower}}} \mathrm{e}^{-[(\Delta E/\, N_{\text{A}})\;/k_{\text{B}}T]}$$

shows that the relative populations of the states depends exponentially on the difference in energy, ΔE, between the levels. The greater the separation, the greater the difference in population and the more sensitive the technique will become. The difference in energy depends upon the magnetic field applied and the magnetogyric ratio, through Equation 10.23

$$\Delta E = (h/2\pi)\gamma B$$

i.e.

$$\Delta E \propto \gamma$$

A large value for the magnetogyric ratio therefore promotes sensitivity. Consideration of the magnetogyric ratios for various magnetically active nuclei shows that the value for hydrogen is larger than that for all other commonly occurring isotopes.

Answers to end of chapter questions

1. Convert a wavelength of 450 nm to (a) wavenumber, (b) frequency and (c) energy.

Strategy

Use Equations 10.10, 3.1 and 3.2, which express how wavelength is related to wavenumber, frequency and energy.

Solution

(a) Wavenumber is the reciprocal of wavelength. It is usual to express wavenumbers in units of cm^{-1} rather than m^{-1}. Thus, because

1 m^{-1} ≡ 10^{-2} cm^{-1},

$$\tilde{\nu} = 1/\lambda = 1/(450 \times 10^{-9}\ \mathrm{m}) = 2.22 \times\ 10^{6}\ \mathrm{m^{-1}} = 2.22 \times 10^{4}\ \mathrm{cm^{-1}}$$

(b) Frequency is related to wavelength through Equation 3.1, so that

$$\nu = c/\lambda = (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})/(450 \times 10^{-9}\mathrm{m}) = 6.66 \times 10^{14}\mathrm{Hz} = 666\ \mathrm{THz}$$

(c) The energy of a photon depends upon its wavelength according to Equation 3.2,

$$\begin{aligned} E &= hc/\lambda \\ &= (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})/(450 \times 10^{-9}\ \mathrm{m}) \\ &= 4.41 \times\ 10^{-19}\ \mathrm{J} \end{aligned}$$

This may be expressed as a molar quantity by multiplying by Avogadro's number.

$$\begin{aligned} E_{\mathrm{m}} &= N_{\mathrm{A}}E \\ &= (6.022 \times 10^{23}\mathrm{mol^{-1}}) \times (4.41 \times 10^{-19}\mathrm{J}) \\ &= 266 \times 10^{3}\mathrm{J\ mol^{-1}} = 266\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

2. The yellow colour of sodium emission in a flame is due to emission at 589.0 nm and 589.6 nm. Calculate the difference in energy between the photons emitted at these two wavelengths.

Strategy

Use Equation 3.2 to calculate the energy of the photons.

Solution

The energy of a photon depends upon its wavelength through

$$E = hc/\lambda$$

Thus, the difference in energy between the two photons is

$$\begin{aligned}\Delta E &= E_1 - E_2\\ &= hc(1/\lambda_1 - 1/\lambda_2)\\ &= (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})\\ &\qquad \times \left(\frac{1}{589.0 \times 10^{-9}\mathrm{m}} - \frac{1}{589.6 \times 10^{-9}\mathrm{m}}\right)\\ &= 3.432 \times\ 10^{-22}\ \mathrm{J}\end{aligned}$$

3. What wavelength of radiation would provide sufficient energy to break a C–H bond in methane, where the bond dissociation energy is +439 kJ mol^{-1}?

$$\mathrm{CH_4 \longrightarrow CH_3\cdot + H\cdot}$$

Strategy

Rearrange Equation 3.2 to provide an expression for the wavelength of a photon in terms of its wavelength. Remember that the energy is expressed as a molar quantity.

Solution

The molar energy of photons of wavelength λ is

$$E_\mathrm{m} = N_\mathrm{A}hc/\lambda$$

which may be rearranged to give

$$\begin{aligned}\lambda &= \frac{N_\mathrm{A}hc}{E_\mathrm{m}}\\ &= \frac{(6.022 \times 10^{23}\mathrm{mol^{-1}}) \times (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})}{(439 \times 10^{3}\ \mathrm{J\ mol^{-1}})}\\ &= 272 \times 10^{-9}\mathrm{m} = 272\ \mathrm{nm}\end{aligned}$$

4. Calculate the energy difference between the $n = 1$ and $n = 2$ levels for an electron in a one-dimensional box with a length of 4.0×10^{-10} m. At what wavelength would a transition between these levels appear? (Section 10.2)

Strategy

Use Equation 10.4 to derive an expression for the difference in energy between a particle with a quantum number $n + 1$ and a particle with quantum number n. Rearrange Equation 3.2 to obtain an expression for the wavelength in terms of the energy of the photon.

Solution

Applying Equation 10.4, the difference in the energy of the adjacent levels is

$$\begin{aligned}\Delta E &= E_{n+1} - E_n = \frac{(n+1)^2h^2}{8mL^2} - \frac{n^2h^2}{8mL^2} = \{(n^2 + 2n + 1) - n^2\}\frac{h^2}{8mL^2} \\ &= \frac{(2n+1)h^2}{8mL^2} = \frac{\{(2 \times 1) + 1\}h^2}{8mL^2} = \frac{3h^2}{8mL^2}\end{aligned}$$

Substituting for the mass of the electron and length of the box gives the difference in energy as

$$\Delta E = \frac{3 \times (6.626 \times 10^{-34}\,\mathrm{J\ s})^2}{8 \times (9.109 \times 10^{-31}\ \mathrm{kg}) \times (4.0 \times 10^{-10}\ \mathrm{m})^2} = 1.1 \times 10^{-18}\ \mathrm{J}$$

Using Equation 3.2, this corresponds to a wavelength of

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})}{1.1 \times 10^{-18}\ \mathrm{J}} = 1.8 \times 10^{-7}\ \mathrm{m} = 180\ \mathrm{nm}$$

5. Using the one-dimensional particle-in-a-box model, calculate the first four electronic energy levels of 1,3,5-hexatriene. Assume that a 2p electron can move freely along the delocalized system. At what wavelength would the lowest energy electronic transition appear? Assume the average carbon–carbon distance to be 0.15 nm.

Strategy

Use the expression given in Box 10.1 for the energy levels of a one-dimensional particle in a box.

Solution

The energy levels of a one-dimensional particle in a box are given by

$$E_n = \frac{n^2h^2}{8mL^2}$$

with quantum numbers n =1, 2, 3, 4, … . For 1,3,5-hexatriene, there are six carbon atoms in the π system, so we might expect the length of the equivalent box to be

$$L = 5 \times 0.15\ \mathrm{nm}\ = \ 0.75\ \mathrm{nm} = 0.75 \times 10^{-9}\mathrm{m}$$

because there are five bonds between the six atoms. The energies of the first four levels are thus

$$E_1 = 1^2 \times \frac{h^2}{8m_\mathrm{e}L^2} = 1^2 \times \frac{(6.626 \times 10^{-34}\ \mathrm{J\ s})^2}{8 \times (9.110 \times 10^{-31}\mathrm{kg}) \times (0.75 \times 10^{-9}\mathrm{m})^2}$$

$$= 1^2 \times (1.071 \times 10^{-20}\ \mathrm{J}) = 1.071 \times 10^{-20}\ \mathrm{J}$$

$$E_2 = 2^2 \times (1.071 \times 10^{-20}\ \mathrm{J}) = 4.28 \times 10^{-19}\mathrm{J}$$

$$E_3 = 3^2 \times (1.071 \times 10^{-20}\ \mathrm{J}) = 9.64 \times 10^{-19}\mathrm{J}$$

$$E_4 = 4^2 \times (1.071 \times 10^{-20}\ \mathrm{J}) = 1.71 \times 10^{-18}\mathrm{J}$$

Each carbon atom contributes one electron to the π system. The electrons are, however, paired in the energy levels because of the two different spin states. Thus the highest occupied level is that with n = 3, and the lowest energy electronic transition will be that from $n = 3 \rightarrow n = 4$. The difference in energy between a level with quantum number n and n + 1 is these levels is

$$\begin{aligned}\Delta E &= E_{n+1} - E_n \\ &= [(n+1)^2 - n^2] \times \frac{h^2}{8m_\mathrm{e}L^2} \\ &= [(n^2 + 2n + 1) - n^2] \times \frac{h^2}{8m_\mathrm{e}L^2} \\ &= (2n+1) \times \frac{h^2}{8m_\mathrm{e}L^2}\end{aligned}$$

The wavelength of the transition is

$$\lambda = hc/\Delta E = hc \times \frac{8m_\mathrm{e}L^2}{(2n+1)h^2} = \frac{8m_\mathrm{e}L^2c}{(2n+1)h}$$

Substituting the appropriate values gives

$$\lambda = \frac{8 \times (9.110 \times 10^{-31}\,\mathrm{kg}) \times (0.75 \times 10^{-9}\ \mathrm{m})^2 \times (2.998 \times 10^8\ \mathrm{m\ s^{-1}})}{\{(2 \times 3) + 1\} \times 6.626 \times 10^{-34}\ \mathrm{J\ s}}$$
$$= 265 \times 10^{-9}\mathrm{m} = 265\ \mathrm{nm}$$

6. Calculate the energy difference, ΔE, and the relative populations of the upper and lower energy levels for transitions giving rise to absorption of the following at 298 K.

(a) an IR photon with wavenumber 2000 $\mathrm{cm^{-1}}$;

(b) a microwave photon with frequency 20 GHz;

(c) visible light with wavelength 500 nm

(d) an X-ray with wavelength 4 nm;

(e) a radio wave with frequency 10 MHz.

(Assume the degeneracy of all levels is $g = 1$.)

Strategy

Calculate the difference in energy between the levels and apply the Boltzmann equation, Equation 10.9

$$\frac{n_{\mathrm{upper}}}{n_{\mathrm{lower}}} = \frac{g_{\mathrm{upper}}}{g_{\mathrm{lower}}} \mathrm{e}^{-[\Delta E\ /k_{\mathrm{B}}T]}$$

Solution

(a) A wavenumber of 2000 $\mathrm{cm^{-1}}$ is equivalent to an energy

$$\Delta E = hc\tilde{\nu} = (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^8\ \mathrm{m\ s^{-1}}) \times (2000 \times 10^2\mathrm{m^{-1}})$$
$$= 3.97 \times 10^{-20}\mathrm{J}$$

where it is important to remember to express the wavenumber in units of $\mathrm{m^{-1}}$. Thus, the relative populations between non-degenerate levels of this separation is

$$\frac{n_{\mathrm{upper}}}{n_{\mathrm{lower}}} = \mathrm{e}^{-[3.97\times10^{-20}\mathrm{J}/\{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})\}]} = 6.4 \times 10^{-5}$$

The population of the upper level is, essentially, negligible in comparison with that of the lower level.

(b) A frequency of 20 GHz = 20 × 10^9 Hz = 20 × 10^9 $\mathrm{s^{-1}}$ corresponds to an energy

$$\Delta E = h\nu = (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (20 \times 10^{9}\ \mathrm{s^{-1}}) = 1.33 \times 10^{-23}\mathrm{J}$$

and so

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \mathrm{e}^{-[1.33\times10^{-23}\mathrm{J}/\{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})\}]} = 0.997$$

(c) The energy of a photon of wavelength 500 nm = 500 × 10^{-9} m is

$$\Delta E = hc/\lambda$$
$$= (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})/(500 \times 10^{-9}\mathrm{m}) = 3.97 \times 10^{-19}\mathrm{J}$$

and so

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \mathrm{e}^{-[3.97\times10^{-19}\mathrm{J}/1.381\times10^{-23}\ \mathrm{J\ K^{-1}}\times298\ \mathrm{K}]} = 1.3 \times 10^{-42}$$

(d) Similarly, an X-ray with wavelength 4 nm = 4 × 10^{-9} m has an energy

$$\Delta E = hc/\lambda$$
$$= (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})/(4 \times 10^{-9}\mathrm{m}) = 4.97 \times 10^{-17}\mathrm{J}$$

and so

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \mathrm{e}^{-[4.97\times10^{-17}\mathrm{J}/\{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})\}]} = 0$$

(e) A radio wave with a frequency of 10 MHz = 20 × 10^6 Hz = 20 × 10^6 $\mathrm{s^{-1}}$ corresponds to an energy

$$\Delta E = h\nu = 6.626 \times 10^{-34}\ \mathrm{J\ s} \times 10 \times 10^{6}\ \mathrm{s^{-1}} = 6.63 \times 10^{-27}\mathrm{J}$$

and so

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \mathrm{e}^{-[6.63\times10^{-27}\mathrm{J}/\{(1.381\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})\}]} = 1.00$$

7. What are the transmittance and absorbance of a solution that absorbs: (a) 10%; (b) 90%; (c) 99% of the incident radiation?

Strategy

Calculate the intensity of light that is transmitted and use Equations 10.6 and 10.7 to determine the transmittance and absorbance.

Solution

(a) If 10% of the incident radiation is absorbed, then 90% is transmitted. Thus, from Equation 10.6, the transmittance is

$$T = (I_\mathrm{t}/I_0) = 90/100 = 0.9$$

and, from Equation 10.7, the absorbance is

$$A = -\log_{10} T = -\log_{10}(0.9) = 0.046$$

(b) In the same way, if 90% of the radiation is absorbed, 10% is transmitted, so that

$$T = (I_\mathrm{t}/I_0) = 10/100 = 0.1$$

and

$$A = -\log_{10} T = -\log_{10}(0.1) = 1.000$$

(c) If 99% of the intensity of the incident radiation is absorbed, then 1% is transmitted, and so

$$T = (I_\mathrm{t}/I_0) = 1/100 = 0.01$$

and

$$A = -\log_{10} T = -\log_{10}(0.01) = 2.000$$

8. A 5.0×10^{-4} mol dm^{-3} solution of Br_2 in CCl_4 absorbed 64% of the incident light when placed in a 2.0 cm cell at a wavelength where CCl_4 does not absorb. Calculate the molar absorption coefficient of Br_2.

Strategy

Rearrange Equation 10.8 to give an expression for the concentration of the solution in terms of the absorbance, path length and absorption coefficient. Calculate the absorbance and substitute, along with the values given in the example.

Solution

The absorbance of the solution is given by Equation 10.7

$$A = \log_{10}(I_0/I_\mathrm{t}) = \log_{10}(1.00/0.36) = +0.444$$

because if 64% of the incident radiation is absorbed, 36% must be transmitted. We may rearrange Equation 10.8 and substitute the values directly

$$\begin{aligned}\epsilon &= A/(cl)\\ &= +0.444/\{(5.0\times10^{-1}\ \text{mol m}^{-3})\times(0.020\ \text{m})\}\\ &= 44.4\ \text{m}^2\text{mol}^{-1}\end{aligned}$$

9. Naphthalene ($C_{10}H_8$) absorbs around 310 nm in solution. The absorbance of a 1.00×10^{-3} mol dm^{-3} solution is 0.29 in 1.0 cm cell. Find the molar absorption coefficient.

Strategy

Use Equation 10.8, which relates the absorbance to the concentration, path length and molar absorption coefficient of a solution.

Solution

Rearranging Equation 10.8, and noting that a concentration of 1.00×10^{-3} mol dm^{-3} is equivalent to 1.00 mol m^{-3}, because 1 dm^3 ≡ 10^{-3} m^3, and 1.0 cm ≡ 10^{-2} m,

$$\begin{aligned}\epsilon = A/cl &= 0.29/(1.00\ \text{mol m}^{-3}\times10^{-2}\ \text{m}) = 0.29\times10^{2}\ \text{m}^2\ \text{mol}^{-1}\\ &= 29\ \text{m}^2\ \text{mol}^{-1}\end{aligned}$$

10. The percentage transmission of an aqueous solution of fumaric acid is 19.2% for a 0.00050 mol dm^{-3} solution in a 1.0 cm cell. Calculate the absorbance and the molar absorption coefficient. What percentage of light would be transmitted through a solution with double the concentration of this one? (Section 10.3)

Strategy

Express the absorbance in terms of the percentage transmission using Equation 10.7. Rearrange the Beer–Lambert law, Equation 10.8, to obtain an expression for the molar absorption coefficient. Combine the two equations and use the result to calculate relative intensity of light transmitted in terms of the new concentration of the solution.

Solution

Using Equation 10.7, the absorbance is

$$A = \log_{10}(I_0/I_t)$$

We may express this in terms of the relative transmission, $I_t/I_0 = 0.192$, using the rules for the manipulation of logarithms, $\log x = -\log(x^{-1})$,

$$A = -\log_{10}(I_t/I_0)$$

so that

$$A = -\log_{10} 0.192 = 0.717$$

Combining Equations 10.7 and 10.8,

$$\log_{10}(I_0/I_t) = \epsilon c l$$

Thus, rearranging and substituting,

$$\epsilon = -\frac{\log_{10}(I_t/I_0)}{cl} = -\frac{\log_{10} 0.192}{(0.00050 \text{ mol dm}^{-3}) \times (1.0 \text{ cm})} = 1400 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$$

For a solution with a different concentration, c', we may rearrange the combined expression as

$$I_t'/I_0 = 10^{-\epsilon c' l}$$

and so calculate the relative intensity of light transmitted for a solution of double this concentration, $c' = 2c$, as

$$I_t'/I_0 = 10^{-\epsilon(2c)l} = 10^{-2\times(\epsilon c l)} = 10^{-2A} = 10^{-2\times 0.717} = 0.0368$$

which is equivalent to 3.68 per cent.

11. The molar absorption coefficient for the cobalt and nickel complexes with the ligand 2,3-quinoxalinedithiol are given below at two different wavelengths. When 2,3-quinoxalinedithiol was added to a solution containing both cobalt and nickel, the solution had an absorbance of 0.446 at 510 nm and 0.326 at 656 nm in a 1.00 cm cell. Calculate the concentrations of both metals in the solution. Assume that the absorbances are independent of one another. (Section 10.3)

	ε / dm^3 mol^{-1} cm^{-1} at 510 nm	ε / dm^3 mol^{-1} cm^{-1} at 656 nm
Co complex	36400	1240
Ni complex	5520	17500

Strategy

Write expressions for the absorbance at each wavelength using the Beer–Lambert law, Equation 10.8, by treating the absorbance of light by the solution as the sum of the absorbances resulting from the two separate components. Solve the two equations simultaneously for the concentrations of the two complexes.

Solution

The absorbance at 510 nm is

$$A_{510} = A_{\mathrm{Co},510} + A_{\mathrm{Ni},510} = \epsilon_{\mathrm{Co},510} c_{\mathrm{Co}} l + \epsilon_{\mathrm{Ni},510} c_{\mathrm{Ni}} l =$$
$$= (36400\ \mathrm{mol^{-1}\ dm^3 cm^{-1}} \times 1\ \mathrm{cm}) c_{\mathrm{Co}} + (5520\ \mathrm{mol^{-1}\ dm^3 cm^{-1}} \times 1\ \mathrm{cm}) c_{\mathrm{Ni}}$$
$$= 0.446$$

and at 656 nm

$$A_{656} = A_{\mathrm{Co},656} + A_{\mathrm{Ni},656} = \epsilon_{\mathrm{Co},656} c_{\mathrm{Co}} l + \epsilon_{\mathrm{Ni},656} c_{\mathrm{Ni}} l =$$
$$= (1240\ \mathrm{mol^{-1}\ dm^3 cm^{-1}} \times 1\ \mathrm{cm}) c_{\mathrm{Co}} + (17500\ \mathrm{mol^{-1}\ dm^3 cm^{-1}} \times 1\ \mathrm{cm}) c_{\mathrm{Ni}}$$
$$= 0.326$$

These expressions are simultaneous linear equations in the two unknown concentrations, c_{Co} and c_{Ni}

$$36400\ (c_{\mathrm{Co}}/\mathrm{mol\ dm^{-3}}) + 5520\ (c_{\mathrm{Ni}}/\mathrm{mol\ dm^{-3}}) = 0.446$$
$$1240\ (c_{\mathrm{Co}}/\mathrm{mol\ dm^{-3}}) + 17500\ (c_{\mathrm{Ni}}/\mathrm{mol\ dm^{-3}}) = 0.326$$

and solving gives

$$c_{\mathrm{Co}} = 9.53 \times 10^{-6}\ \mathrm{mol\ dm^{-3}}$$
$$c_{\mathrm{Ni}} = 1.78 \times 10^{-6}\ \mathrm{mol\ dm^{-3}}$$

12. Calculate the relative populations of two non-degenerate energy levels separated at 298 K by (Section 10.3):

(a) an energy corresponding to a frequency of 4.3×10^{13} Hz;

(b) an energy corresponding to a wavelength of 254 nm;

(c) an energy corresponding to a wavenumber of 5 $\mathrm{cm^{-1}}$.

In each case, comment on the value that you calculate.

Strategy

Apply Equation 10.9,

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{g_{\text{upper}}}{g_{\text{lower}}} \mathrm{e}^{-(\Delta E/k_{\mathrm{B}}T)}$$

which gives the relative populations of energy levels according to the Boltzmann distribution. If the energy levels are non degenerate, then $g_{\text{upper}} = g_{\text{lower}} = 1$.

Solution

(a) A frequency ν is equivalent, from Equation 3.2, to a difference in energy of $\Delta E = h\nu$, so that

$$\frac{\Delta E}{k_{\mathrm{B}}T} = \frac{h\nu}{k_{\mathrm{B}}T} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\ s}) \times (4.3 \times 10^{13}\,\mathrm{Hz})}{(1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (298\ \mathrm{K})} = 6.9$$

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{1}{1}\mathrm{e}^{-6.9} = 9.8 \times 10^{-4}$$

The frequency given is characteristic of the stretching vibrations of molecules. The result implies that, a temperature of 298 K, the populations of excited vibrational states are negligible.

(b) In the same way, a wavelength λ corresponds to a difference in energy $\Delta E = hc/\lambda$, so that

$$\frac{\Delta E}{k_{\mathrm{B}}T} = \frac{hc}{\lambda k_{\mathrm{B}}T} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})}{(254 \times 10^{-9}\ \mathrm{m}) \times (1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (298\ \mathrm{K})} = 190$$

$$\frac{n_{\text{upper}}}{n_{\text{lower}}} = \frac{1}{1}\mathrm{e}^{-190} = 2.94 \times 10^{-83}$$

A photon of wavelength 254 nm is characteristic of an electronic transition in an atom or molecule. Thus, the Boltzmann distribution implies that at 298 K the population of excited electronic states is negligible. We may thus assume that for sample at this temperature, all atoms or molecules are in their ground electronic state.

(c) A wavenumber $\tilde{\nu}$ corresponds to a difference in energy, $\Delta E = hc\tilde{\nu}$, so that

$$\frac{\Delta E}{k_\mathrm{B}T} = \frac{hc\tilde{\nu}}{k_\mathrm{B}T} = \frac{(6.626 \times 10^{-34}\,\mathrm{J\ s}) \times (2.998 \times 10^{8}\,\mathrm{m\ s^{-1}}) \times \overbrace{(5 \times 10^{2}\,\mathrm{m^{-1}})}^{1\ \mathrm{cm^{-1}} = 10^{2}\ \mathrm{m^{-1}}}}{(1.381 \times 10^{-23}\,\mathrm{J\ K^{-1}}) \times (298\,\mathrm{K})} = 0.02$$

$$\frac{n_\mathrm{upper}}{n_\mathrm{lower}} = \frac{1}{1}\mathrm{e}^{-0.02} = 0.976$$

The result implies that the populations of states separated by 5 cm^{-1} are almost equal at 298 K. This separation is typical of rotational states. However, we shall discover later in Section 10.4 that excited rotational states are not degenerate. If we allow for this degeneracy, we find that the populations of excited rotational energy levels are sometimes greater than that of the lowest level.

13. Explain why the rotational spectrum is observed for ICl but not for I_2 or Cl_2.

Strategy

Consider the requirement that a molecule must possess a permanent electric dipole moment to exhibit a rotational spectrum.

Solution

A molecule must possess a permanent electric dipole moment for a rotational spectrum to be observed. ICl is a polar molecule because the electronegativities of the iodine and chlorine atoms are different. It therefore possesses a permanent electric dipole moment and a rotational spectrum is observed. In contrast, I_2 and Cl_2 are homonuclear diatomic molecules and are therefore non-polar. They do not have a permanent electric dipole moment and thus no rotational spectrum.

14. The $J = 2 \rightarrow J = 3$ transition occurs in a rotational spectrum at 30 cm^{-1}. At what wavenumber will the $J = 0 \rightarrow J = 1$ transition be seen? What is the rotational constant for the molecule?

Strategy

Use Equation 10.16 to derive an expression for the wavenumbers of the two transitions in terms of the rotational constant.

Solution

The rotational energy levels of a linear molecule are given by Equation 10.16

$$E_J = hBJ(J+1)$$

The difference in energy between levels with rotational quantum numbers $J + 1$ and J is thus

$$\begin{aligned}\Delta E &= E_{J+1} - E_J \\ &= hB(J+1)(J+2) - hBJ(J+1) \\ &= hB[(J^2+3J+2) - (J^2+J)] \\ &= 2hB(J+1)\end{aligned}$$

The wavenumber of a transition is related to the difference between energy levels through Equation 10.11

$$\Delta E = hc\tilde{\nu}$$

Combining these two equations gives an expression for the wavenumber of a transition from $J \rightarrow J + 1$

$$\tilde{\nu} = \frac{\Delta E}{hc} = \frac{2hB(J+1)}{hc} = (2B/c)(J+1)$$

For the $J = 2 \rightarrow J = 3$ transition at a wavenumber of 30 cm^{-1}

$$\tilde{\nu} = (2B/c)(J+1) = (2B/c)(2+1) = 6B/c$$

Thus, if

$$6B/c = 30\ \mathrm{cm}^{-1}$$

then

$$B/c = 5\ \mathrm{cm}^{-1} = \overbrace{5 \times 10^2\ \mathrm{m}^{-1}}^{1\ \mathrm{cm}^{-1} = 10^2\ \mathrm{m}^{-1}}$$

and

$$B = 5\ \text{cm}^{-1} \times c = (5 \times 10^2 \text{m}^{-1}) \times (2.998 \times 10^8\ \text{m s}^{-1})$$
$$= 1500 \times 10^8\ \text{s}^{-1} = 150\ \text{GHz}$$

In the same way, we expect the $J = 0 \rightarrow J = 1$ transition to be observed at a wavenumber of

$$\tilde{\nu} = (2B/c)(J+1) = (2B/c)(0+1) = 2B/c = 2 \times 5\ \text{cm}^{-1} = 10\ \text{cm}^{-1}$$

15. The $J = 0 \rightarrow J = 1$ transition for $^1H^{79}Br$ occurs at a frequency of 500.7216 GHz.

(a) Calculate the bond length for this molecule.

(b) Calculate the relative populations of the $J = 0$ and $J = 1$ levels.

Strategy

Use Equation 10.15 to determine the moment of inertia from the rotational constant. Calculate the reduced mass of $^1H^{79}Br$ from Equation 10.13. Rearrange Equation 10.12 to give an expression for the bond length of a molecule in terms of its moment of inertia and reduced mass and substitute the values.

Calculate the difference in energy between the levels and use Equation 10.9 to determine the relative populations.

Solution

The $J = 0 \rightarrow J = 1$ transition occurs at a frequency of $2B$. Thus,

$$B = (500.7216 \times 10^9 \text{Hz})\ /2 = 250.3608 \times 10^9\ \text{s}^{-1}$$

Rearranging Equation 10.15 gives a moment of inertia

$$I = \frac{h}{8\pi^2 B} = \frac{6.626176 \times 10^{-34}\ \text{J s}}{8\pi^2 \times (250.3608 \times 10^9 \text{s}^{-1})}$$
$$= 3.352022 \times 10^{-47} \text{J s}^2 = 3.352022 \times 10^{-47} \text{kg m}^2$$

The molar mass of a ^1H atom is 1.00 g mol^{-1}, and of a ^{79}Br chlorine atom is 79.00 g mol^{-1} so that

$$m_{\text{H}} = (1.00 \times \overbrace{10^{-3}\ \text{kg mol}^{-1}}^{1\ \text{g}=10^{-3}\text{kg}})/(6.022\ \times 10^{23}\text{mol}^{-1}) = 1.661 \times 10^{-27}\text{kg}$$
$$m_{\text{Br}} = (79.00 \times 10^{-3}\ \text{kg mol}^{-1})/(6.022\ \times 10^{23}\text{mol}^{-1}) = 1.312 \times 10^{-25}\text{kg}$$

The reduced mass of a $^1H^{79}Br$ molecule is, from Equation 10.13,

$$\begin{aligned}\mu &= \frac{m_1 m_2}{m_1 + m_2} = \frac{m_\mathrm{H} m_\mathrm{Br}}{m_\mathrm{H} + m_\mathrm{Br}} \\ &= \frac{(1.661 \times 10^{-27}\,\mathrm{kg}) \times (1.312 \times 10^{-25}\,\mathrm{kg})}{(1.661 \times 10^{-27}\,\mathrm{kg}) + (1.312 \times 10^{-25}\,\mathrm{kg})} \\ &= 1.640 \times 10^{-27}\,\mathrm{kg}\end{aligned}$$

Then, if the moment of inertia is 3.352022×10^{-47} kg m^2, rearranging and applying Equation 10.12 gives

$$\begin{aligned}r_0 &= (I/\mu)^{1/2} = (3.352022 \times 10^{-47}\,\mathrm{kg\,m^2}/1.640 \times 10^{-27}\,\mathrm{kg})^{1/2} \\ &= 1.43 \times 10^{-10}\,\mathrm{m} = 0.143\,\mathrm{nm} = 1.43\,\mathrm{Å}\end{aligned}$$

For rotational energy levels, the relative populations are given by Equation 10.9, with the degeneracy of a given level being

$$g_J = 2J + 1$$

The difference in energy between the levels is, from Equation 3.2,

$$\Delta E = h\nu$$

so that Equation 10.9 becomes

$$\begin{aligned}\frac{n_{J\,=\,1}}{n_{J\,=\,0}} &= \frac{g_{J\,=\,1}}{g_{J\,=\,0}} \mathrm{e}^{-[\Delta E/k_\mathrm{B}T]} \\ &= \frac{\overbrace{\{(2 \times 1) + 1\}}^{g_J\,=\,2J+1}}{\{(2 \times 0) + 1\}} \mathrm{e}^{-[h\nu/k_\mathrm{B}T]} \\ &= \frac{3}{1} \mathrm{e}^{-[(6.626 \times 10^{-34}\,\mathrm{J\,s}) \times (500.7216 \times 10^9\,\mathrm{s^{-1}})/\{(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})\}]} \\ &= 2.77\end{aligned}$$

16. The bond length of $^1H^{35}Cl$ is 0.129 nm. Calculate the rotational constant and the separation between peaks (in cm^{-1} and Hz) in the rotational spectrum.

Strategy

Calculate the reduced mass using Equation 10.13 and hence the moment of inertia from Equation 10.12. Then determine the rotational constant using the definition in Equation 10.15.

Solution

The moment of inertia depends upon the reduced mass and the bond length through Equation 10.12

$$I = \mu r_0^2$$

The molar mass of a ^{1}H atom is 1.00 g mol^{-1}, and of a ^{35}Cl chlorine atom is 35.00 g mol^{-1} so that

$$m_{\mathrm{H}} = (1.00 \times \overbrace{10^{-3}\ \mathrm{kg\ mol^{-1}}}^{1\ \mathrm{g}=10^{-3}\mathrm{kg}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 1.661 \times 10^{-27}\mathrm{kg}$$

$$m_{\mathrm{Cl}} = (35.00\ \times 10^{-3}\ \mathrm{kg\ mol^{-1}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 5.814 \times 10^{-26}\mathrm{kg}$$

The reduced mass of a ^{1}H^{35}Cl molecule is, from Equation 10.13,

$$\begin{aligned}\mu &= \frac{m_1 m_2}{m_1 + m_2} = \frac{m_{\mathrm{H}} m_{\mathrm{Cl}}}{m_{\mathrm{H}} + m_{\mathrm{Cl}}} \\ &= \frac{(1.661 \times 10^{-27}\mathrm{kg}) \times (5.814 \times 10^{-26}\mathrm{kg})}{(1.661 \times 10^{-27}\mathrm{kg}) + (5.814 \times 10^{-26}\mathrm{kg})} \\ &= 1.615 \times 10^{-27}\mathrm{kg}\end{aligned}$$

so that the moment of inertia is

$$I = (1.615 \times 10^{-27}\mathrm{kg}) \times (0.129 \times 10^{-9}\ \mathrm{m})^2 = 2.689 \times 10^{-47}\mathrm{kg\ m^2}$$

and, from Equation 10.15, the rotational constant is

$$B = \frac{h}{8\pi^2 I} = \frac{(6.626 \times 10^{-34}\ \mathrm{J\ s})}{8\pi^2 \times (2.689 \times 10^{-47}\mathrm{kg\ m^2})} = 3.123 \times 10^{11}\mathrm{s^{-1}} = 312.3\ \mathrm{GHz}$$

Figure 10.13 shows that the peaks in the rotational spectrum of a linear molecule such as ^{1}H^{35}Cl are separated by an energy of $2hB$. This is equivalent, through Equation 3.2, to a frequency of $2B$,

$$\nu = 2B = 2 \times (312.3\ \mathrm{GHz}) = 624.5\ \mathrm{GHz}$$

or through Equation 10.11 to a wavenumber of $2B/c$

$$\nu = 2B/c = 2 \times (312.3 \times 10^{11}\mathrm{s^{-1}})/c = (624.5 \times 10^{11}\mathrm{s^{-1}})/(2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})$$

$$= \underbrace{2083\ \mathrm{m^{-1}}}_{1\ \mathrm{cm^{-1}}=10^2\mathrm{m^{-1}}} = 20.83\ \mathrm{cm^{-1}}$$

17. The lines in the rotational spectrum of HF are separated by 41.90 cm^{-1}. Calculate the bond length. What will be the separation between lines in DF (^{2}HF)? (Section 10.4)

Strategy

To determine the bond length, we follow the method used in worked example 10.6. Use the separation between the observed lines to determine the value of the rotational constant. Combine Equation 10.12, 10.13 and 10.15 and use the resulting expression to calculate the bond length from the rotational constant.

To calculate the equivalent spacing in the spectrum of DF, assume that the bond length remains constant upon isotopic substitution, and use the combined expression to calculate the value of the rotational constant.

Solution

Figure 10.16 shows that lines in the rotational spectrum are separated by an energy of $2hB$. The separation between lines is expressed in this example as a wavenumber, $\tilde{\nu} = \nu/c$, so that for HF, $B = (41.90\ \text{cm}^{-1}/2) \times c$. The rotational constant is, however, defined in terms of the moment of inertia using Equation 10.15

$$B = \frac{h}{8\pi^2 I}$$

with the moment of inertia from Equations 10.12 and 10.13

$$I = \mu r_0^2 = \overbrace{\left(\frac{m_\text{H} m_\text{F}}{m_\text{H} + m_\text{F}}\right)}^{\text{reduced mass},\mu} r_0^2$$

Combining these equations, and rearranging,

$$r_0^2 = \frac{h}{8\pi^2 B} \times \frac{m_\text{H} + m_\text{F}}{m_\text{H} m_\text{F}}$$

The mass of a ^{1}H hydrogen atom is

$$m_\text{H} = (1.00 \times \overbrace{10^{-3}\ \text{kg}}^{1\ \text{g}=10^{-3}\text{kg}}\ \text{mol}^{-1})/(6.022 \times 10^{23}\ \text{mol}^{-1}) = 1.68 \times 10^{-27}\text{kg}$$

and a^{19}F fluorine atom is

$$m_\text{F} = (19.00 \times 10^{-3}\ \text{kg mol}^{-1})/(6.022 \times 10^{23}\ \text{mol}^{-1}) = 3.155 \times 10^{-26}\text{kg}$$

Thus, substituting,

$$r_0^2 = \frac{6.626\times10^{-34}\,\mathrm{J\ s}}{8\pi^2\times(41.90\times10^2\ \mathrm{m^{-1}}/2)\times(2.998\times10^8\ \mathrm{m\ s^{-1}})} \times\frac{(1.68\times10^{-27}\mathrm{kg})+(3.155\times10^{-26}\mathrm{kg})}{(1.68\times10^{-27}\mathrm{kg})\times(3.155\times10^{-26}\mathrm{kg})}$$

$$= 8.377\times\ 10^{-21}\mathrm{m}^2$$

so that

$$r_0 = 0.922\times10^{-10}\mathrm{m} = 0.922\ \mathrm{Å}$$

In the same way, it follows that the rotational constant for DF is given by

$$B = \frac{h}{8\pi^2 I} = \frac{h}{8\pi^2\mu r_0^2} = \frac{h}{8\pi^2 r_0^2}\times\frac{m_\mathrm{D}+m_\mathrm{F}}{m_\mathrm{D}m_\mathrm{F}}$$

The mass of a ^{2}H deuterium atom is

$$m_\mathrm{D} = (2.00\times10^{-3}\ \mathrm{kg\ mol^{-1}})/(6.022\times10^{23}\ \mathrm{mol^{-1}}) = 3.54\times10^{-27}\mathrm{kg}$$

so that

$$B = \frac{6.626\times10^{-34}\mathrm{J\ s}}{8\pi^2\times(0.922\times10^{-10}\mathrm{m})^2}\times\frac{(3.35\times10^{-27}\mathrm{kg})+(3.155\times10^{-26}\mathrm{kg})}{(3.35\times10^{-27}\mathrm{kg})\times(3.155\times10^{-26}\mathrm{kg})}$$

$$= 3.31\times\ 10^{11}\mathrm{Hz}$$

Using Equation 3.2, this is equivalent to a wavenumber of

$$B/c = (3.31\times10^{11}\mathrm{Hz})/(2.998\times10^8\ \mathrm{m\ s^{-1}}) = 11.0\times10^2\ \mathrm{m^{-1}} = 11.0\ \mathrm{cm^{-1}}$$

The lines in the spectrum are therefore separated by

$$2B = 2\times11.0\ \mathrm{cm^{-1}} = 21.9\ \mathrm{cm^{-1}}$$

18. Which of the following molecules is (are) IR active: NO; HBr; O_2?

Strategy

Use Figure 10.21 to decide if there is a change in dipole moment on vibration.

Solution

Nitric oxide, NO, and hydrogen bromide, HBr, are both polar molecules and so have a permanent electric dipole moment. The magnitude of the dipole moment depends upon the fractional charges on the atoms and the bond length. Figure 18.11 shows that, for fractional charges ±q and bond length r, the electric dipole moment is

$$\mu = q \times r$$

Excitation of the vibrational mode causes a change in the bond length of the molecule and hence, for polar molecules such as nitric oxide, NO, and hydrogen bromide, HBr, that have

$$q \neq 0$$

a change in the electric dipole moment. This is a necessary requirement for a vibrational mode to be infrared active.

In contrast, oxygen, O_2 is not polar. The molecule does not have a permanent dipole moment. Even when the vibrational mode is excited, the charge distribution remains symmetrical. Thus O_2 is not IR active.

19. Calculate the number of normal modes of (a) benzene (C_6H_6) and (b) cyclohexane (C_6H_{12}).

Strategy

Count the number of atoms in each molecule and apply the rules given in Box 10.6

Solution

Both benzene and cyclohexane are non-linear polyatomic molecules. Of the 3N degrees of freedom, 3 correspond to translation, 3 to rotation and the remaining 3N – 6 to vibration. For benzene, there are N = 12 atoms, resulting in

$$3 \times 12 - 6 = 30$$

vibrational modes. In the same way, for cyclohexane, there are

$$3 \times 18 - 6 = 48$$

vibrational modes.

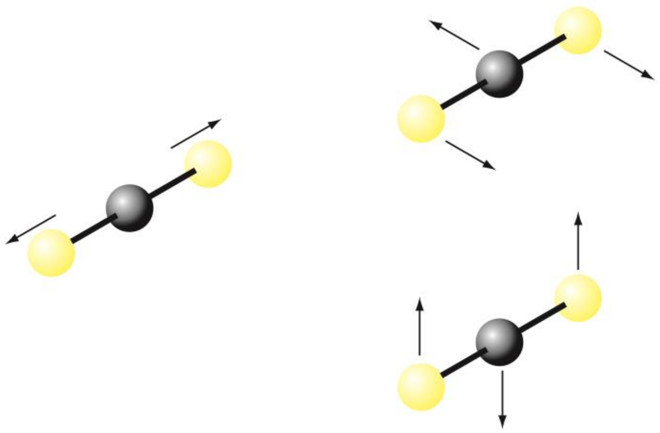
20. Draw diagrams to represent the normal modes of vibration of CS_2 and OCS. Indicate which modes will show in the IR spectrum.

Strategy

Consider the vibrational modes for carbon dioxide, CO_2, shown in Figure 10.24. Determine whether there is a change in electric dipole moment for each vibration.

Solution

CS_2



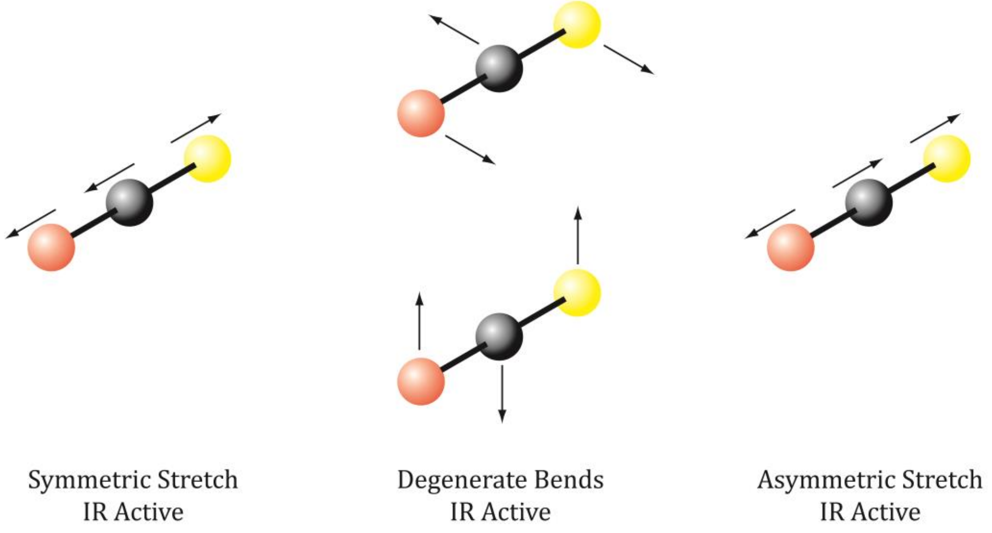
Symmetric Stretch
Not IR Active

Degenerate Bends
IR Active

Asymmetric Stretch
IR Active

There are $3N - 6 = 4$ vibrational modes. The symmetric stretch is not IR active. The molecule is symmetric and does not have a permanent electric dipole moment. This does not change when the two carbon–sulphur bonds stretch in phase. The bending and asymmetric stretching modes are IR active, because distortion of the molecule in this way results in the creation of an electric dipole moment. The two bending modes, corresponding to vibration in two perpendicular planes are degenerate and have the same frequency.

OCS



Once again, there are $3N - 6 = 4$ vibrational modes. However, an OCS molecule has a permanent electric dipole moment, which changes for all of the modes. All of the vibrational modes are therefore IR active. The centre of mass of the molecule is between the carbon and sulphur atoms. Thus, unlike for CS_2, in OCS the central carbon atom is displaced in the two stretching vibrations.

21. HBr shows an absorption at 2650 cm^{-1}. The HBr bond length is 0.141 nm. Calculate the force constant of the bond.

Strategy

Assume that the wavenumber is that for the most abundant isotopomer, $^{1}H^{79}Br$. Calculate the reduced mass from Equation 10.13 and substitute it, together with the value for the wavenumber of the vibrational mode, into a rearranged version of Equation 10.18. The bond length is not required to calculate the force constant.

Solution

We may rearrange Equation 10.18 to express the force constant of a bond in terms of the frequency of vibration

$$k = (2\pi\nu)^2\mu$$

The wavenumber of a transition is related to the frequency through Equation 10.10(b)

$$\nu = \tilde{\nu} \times c$$

and combining these two expressions gives

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

The molar mass of a ^{1}H hydrogen atom is 1.00 g mol^{-1} and of ^{79}Br is 16.00 g mol^{-1} so that

$$m_{\mathrm{H}} = (1.00 \times \overbrace{10^{-3}\ \mathrm{kg\ mol^{-1}}}^{1\ \mathrm{g}=10^{-3}\mathrm{kg}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 1.661 \times 10^{-27}\mathrm{kg}$$
$$m_{\mathrm{Br}} = (79.00 \times 10^{-3}\ \mathrm{kg\ mol^{-1}})/(6.022\ \times 10^{23}\mathrm{mol^{-1}}) = 1.312 \times 10^{-26}\mathrm{kg}$$

The reduced mass of a ^{1}H^{79}Br molecule is, from Equation 10.13,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_{\mathrm{H}} m_{\mathrm{Br}}}{m_{\mathrm{H}} + m_{\mathrm{Br}}}$$
$$= \frac{(1.661 \times 10^{-27}\mathrm{kg}) \times (1.312 \times 10^{-26}\mathrm{kg})}{(1.661 \times 10^{-27}\mathrm{kg}) + (1.312 \times 10^{-26}\mathrm{kg})}$$
$$= 1.640 \times 10^{-27}\ \mathrm{kg}$$

Thus, remembering to express the wavenumber of the transition in units of m^{-1} rather than cm^{-1}

$$k = \{2\pi \times \overbrace{(2650 \times 10^2\ \mathrm{m^{-1}})}^{1\ \mathrm{cm^{-1}}=10^2\ \mathrm{m^{-1}}} \times (2.998 \times 10^8\ \mathrm{m\ s^{-1}})\}^2 \times 1.640 \times 10^{-27}\mathrm{kg}$$
$$= 409\ \mathrm{kg\ s^{-2}} = 409\ \mathrm{N\ m^{-1}}$$

22. How many normal modes of vibration would you expect for cyclopentane, C_5H_{10}? Why would they not all give rise to peaks in the infrared spectrum? (Section 10.5)

Strategy

Use the general rules for the number of degrees of freedom presented in Box 10.6.

Solution

Cyclopentane is a non-linear polyatomic molecule with N = 15 atoms. In general, such a molecule has 3N – 6 vibrational normal modes. Thus, for cyclopentane, there are $(3 \times 15) - 6 = 29$ normal modes in total. The symmetry of the molecule does, however, mean that some of these modes are degenerate, so that vibrational transitions occur at exactly the same frequency (or wavenumber) in the spectrum. Furthermore, some modes will not be infrared active, because the vibration does not lead to a change in the dipole moment of the molecule. Thus, we should not expect to observe 29 fundamental bands in the infrared spectrum.

23. Calculate the vibrational frequency of a bond between a hydrogen atom and a solid surface if the bond has a force constant of 5 kg s^{-2}. (Section 10.5)

Strategy

Calculate the vibrational frequency using Equation 10.18, treating the solid surface as having an effectively infinite mass, and therefore as stationary.

Solution

If we assume that the mass of the solid is so large that it is effectively stationary, and that only the hydrogen atom moves, then, Equation 10.18 reduces to

$$\nu = \frac{1}{2\pi}\left(\frac{k}{m_\text{H}}\right)^{1/2}$$

We can prove this result by manipulating the expression for the reduced mass, Equation 10.19. Dividing all terms by the mass of the surface, m_S, the reduced mass becomes

$$\mu = \frac{m_\text{H} m_\text{S}}{m_\text{H} + m_\text{S}} = \frac{m_\text{H}}{(m_\text{H}/m_\text{S}) + 1} = m_\text{H}$$

The molar mass of a ^{1}H hydrogen atom is 1.00 g mol^{-1} so that

$$m_\text{H} = (1.00 \times \overbrace{10^{-3}\ \text{kg mol}^{-1}}^{1\ \text{g}=10^{-3}\text{kg}})/(6.022 \times 10^{23}\text{mol}^{-1}) = 1.66 \times 10^{-27}\text{kg}$$

and substituting, gives a vibrational frequency of

$$\nu = \frac{1}{2\pi}\left(\frac{5\ \text{kg s}^{-2}}{1.66 \times 10^{-27}\text{kg}}\right)^{1/2} = 9 \times 10^{12}\ \text{s}^{-1} = 9 \times 10^{12}\ \text{Hz}$$

24. The radiation absorbed by ^{12}C^{16}O during a vibrational transition occurs at 2168 cm^{-1}. (Section 10.5)

(a) Calculate the ground-state vibrational energy in kJ mol^{-1}.

(b) What is the ratio of the number of molecules in the first vibrational excited state (v = 1) compared with the ground state (v = 0) at 298 K?

(c) Calculate the force constant of the bond, assuming $^{12}C^{16}O$ behaves as a simple harmonic oscillator.

(d) Estimate the change in the position of the peak if ^{12}C was replaced by ^{13}C.

Strategy

Use the observed wavenumber for the fundamental transition in CO to calculate the frequency of vibration. The energies of the vibrational states then follow from Equation 10.20, and the populations from Equation 10.9. The force constant of the bond may be calculated by rearranging Equation 10.18. Assume that the force constant of the bond remains unchanged upon isotopic substitution and calculate the frequency of $^{13}C^{16}O$ by calculating the reduced mass using Equation 10.19 and reapplying Equation 10.19.

Solution

(a) The energy levels of a harmonic oscillator are given by Equation 10.20.

$$E_v = (v + ½)h\nu$$

Thus, the separation in energy between adjacent vibrational levels of a harmonic oscillator is $h\nu$. Transitions in the vibrational spectrum are therefore observed at a frequency ν, which, if we use Equation 3.2, may be expressed in terms of wavenumber as $\nu = c\tilde{\nu}$. Hence, for $^{12}C^{16}O$, the energy of the lowest level, with $v = 0$, is

$$\begin{aligned} E_0 &= (0 + ½)hc\tilde{\nu} \\ &= ½ \times (6.626 \times 10^{-34}\ \mathrm{J\ s}) \times (2.998 \times 10^{8}\ \mathrm{m\ s^{-1}}) \times (2168 \times 10^{2}\ \mathrm{m^{-1}}) \\ &= 2.153 \times 10^{-20}\ \mathrm{J} \end{aligned}$$

which is equivalent to a molar energy of

$$\begin{aligned} E_{0,\mathrm{m}} &= N_A E_0 = (6.022 \times 10^{23}\ \mathrm{mol^{-1}}) \times (2.153 \times 10^{-20}\ \mathrm{J}) \\ &= 12.97 \times 10^{3}\ \mathrm{J\ mol^{-1}} = 12.97\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

(b) Using Equation 10.9, the relative population of the first vibrational excited state (v = 1) compared with the ground state (v = 0) at 298 K is

$$\frac{n_{v=1}}{n_{v=0}} = \frac{g_{v=1}}{g_{v=0}}\mathrm{e}^{-\Delta E/k_\mathrm{B}T} = \frac{g_{v=1}}{g_{v=0}}\mathrm{e}^{-hc\tilde{v}/k_\mathrm{B}T}$$

Substituting, and remembering that the vibrational levels of diatomic molecules are non-degenerate, so that $g_{v=0} = g_{v=1} = 1$,

$$\frac{n_{v=1}}{n_{v=0}} = \frac{1}{1}\mathrm{e}^{-(6.626\times10^{-34}\ \mathrm{J\ s})\times(2.998\times10^{8}\ \mathrm{m\ s^{-1}})\times(2168\times10^{2}\ \mathrm{m^{-1}})/\{(1.38\times10^{-23}\ \mathrm{J\ K^{-1}})\times(298\ \mathrm{K})\}}$$

$$= 2.92\times10^{-5}$$

(c) We may calculate the force constant of the bond by rearranging Equation 10.18,

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

The mass of a ^{12}C atom and a ^{16}O atom are

$$m_{^{12}\mathrm{C}} = (12.00\times\overbrace{10^{-3}\ \mathrm{kg\ mol^{-1}}}^{1\ \mathrm{g}=10^{-3}\mathrm{kg}})/(6.022\times10^{23}\ \mathrm{mol^{-1}}) = 1.993\times10^{-26}\ \mathrm{kg}$$

$$m_{^{16}\mathrm{O}} = (16.00\times10^{-3}\ \mathrm{kg\ mol^{-1}})/(6.022\times10^{23}\ \mathrm{mol^{-1}}) = 2.657\times10^{-26}\ \mathrm{kg}$$

so that

$$\mu = \frac{m_{^{12}\mathrm{C}}m_{^{16}\mathrm{O}}}{m_{^{12}\mathrm{C}} + m_{^{16}\mathrm{O}}} = \frac{(1.993\times10^{-26}\ \mathrm{kg})\times(2.657\times10^{-26}\ \mathrm{kg})}{(1.993\times10^{-26}\ \mathrm{kg}) + (2.657\times10^{-26}\ \mathrm{kg})} = 1.139\times10^{-26}\mathrm{kg}$$

Thus, the force constant is

$$k = \{2\pi\times(2.998\times10^{8}\ \mathrm{m\ s^{-1}})\times(2168\times10^{2}\ \mathrm{m^{-1}})\}^2\times(1.139\times10^{-26}\mathrm{kg})$$

$$= 1890\ \mathrm{kg\ s^{-2}}$$

(d) The mass of a ^{13}C atom is

$$m_{^{13}\mathrm{C}} = (13.00\times\overbrace{10^{-3}\ \mathrm{kg\ mol^{-1}}}^{1\ \mathrm{g}=10^{-3}\mathrm{kg}})/(6.022\times10^{23}\ \mathrm{mol^{-1}}) = 2.158\times10^{-26}\ \mathrm{kg}$$

so that

$$\mu = \frac{m_{^{13}\mathrm{C}}m_{^{16}\mathrm{O}}}{m_{^{13}\mathrm{C}} + m_{^{16}\mathrm{O}}} = \frac{(2.158\times10^{-26}\ \mathrm{kg})\times(2.657\times10^{-26}\ \mathrm{kg})}{(2.158\times10^{-26}\ \mathrm{kg}) + (2.657\times10^{-26}\ \mathrm{kg})} = 1.191\times10^{-26}\mathrm{kg}$$

Thus, assuming that the force constant does not change on isotopic substitution, and applying Equation 10.18, the vibrational frequency in $^{13}C^{16}O$ is

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} = \frac{1}{2\pi}\left(\frac{1890\ \mathrm{kg\ s^{-2}}}{1.191 \times 10^{-26}\mathrm{kg}}\right)^{1/2} = 6.340 \times 10^{13}\mathrm{s^{-1}}$$

which is equivalent to a wavenumber of

$$\tilde{\nu} = \nu/c = (6.340 \times 10^{13}\mathrm{s^{-1}})/(2.998 \times 10^{8}\ \mathrm{m\ s^{-1}})$$
$$= 2115 \times 10^{2}\ \mathrm{m^{-1}} = 2115\ \mathrm{cm^{-1}}$$

25. Phenolphthalein is used as an indicator in acid base titrations. In solutions at high pH, it is a bright magenta colour with a peak at 553 nm in the absorption spectrum; at low pH, phenolphthalein is colourless, (Section 10.6)

(a) In terms of absorption and transmission of light, explain the colour of phenolphthalein at high pH.

(b) At high pH, phenolphthalein is ionized; it is unionized at low pH. Suggest a reason for the colour change.

(c) Does the absorption move to a higher energy or lower energy at low pH?

Strategy

Consider the examples given in Box 10.7 on the origins of electronic transitions.

Solution

(a) The maximum in the absorption spectrum of phenolphthalein is observed at a wavelength of 553 nm, which falls in the green region of the visible spectrum. Thus, a sample of phenolphthalein will absorb green light, and reflect or transit all other colours, appearing magenta.

(b) At high pH, the ionization of phenolphthalein increases some of the conjugation within the molecule. In general, we can infer from Table 10.3 that increased conjugation shifts the wavelength of a transition to longer wavelength. The transition responsible for the colour in phenolphthalein at low pH therefore shifts out of the visible region of the spectrum, so that it appears colourless at high pH.

(c) Wavelength is inversely proportional to the difference in energy between the energy levels. Thus, the observation that in changing from high to low pH, the peak in the absorption spectrum shifts to shorter wavelength implies that the energy of the transition must increase.

26. Find the nuclear spin quantum number of the following isotopes: ^{2}H; ^{3}H; ^{14}N; ^{15}N; ^{16}O.

Strategy

Consult an on-line or printed database or specialist text book on NMR spectroscopy.

Solution

The data given in, for example, Lide, D.R. (ed.) (2006–07), *CRC handbook of chemistry and physics,* 87th edn. CRC Press, Boca Raton, Florida, shows the isotopes to have nuclear spin quantum numbers:

	H	^{3}H	^{14}N	^{15}N	^{16}O
I	1	½	1	½	0

27. Predict the form (approximate chemical shifts, integrals and splitting patterns) of the ^{1}H and ^{13}C NMR spectrum of pentan-2-one.

Strategy

Draw out the structure of pentan-2-one, and decide which of the nuclei are chemically and magnetically equivalent. Estimate the chemical shift using the data

Determine the spin–spin coupling patterns between non-equivalent protons using the principles explained in Box 10.8.

Solution

The ^{13}C-NMR spectrum will consist of five peaks, corresponding to the five chemically different carbon atoms. The natural abundance of ^{13}C is less than 1%, so that the probability of an individual molecule containing two ^{13}C nuclei is negligibly small. The resonances are therefore not split by coupling between carbon atoms.

28. Predict the splitting patterns of the ^{1}H NMR spectrum of the following molecules:

(a) propanone (CH_3COCH_3);

(b) 1-bromopropane ($CH_3CH_2CH_2Br$);

(c) 1,1-dichloroethene ($CCl_2=CH_2$);

(d) *E*-1,2-dichloroethene ($CHCl=CHCl$); (*Z* and *E* isomers);

(e) nitrobenzene;

(f) 1,2-dinitrobenzene;

(g) 1,3-dinitrobenzene;

(h) 1,4-dinitrobenzene.

Strategy

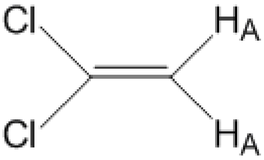
Determine which of the protons are chemically and magnetically equivalent. Use the principles explained in Box 10.8 to determine the spin–spin coupling patterns between non-equivalent protons.

Solution

(a) propanone (CH_3COCH_3): The methyl groups in propanone may rotate about the C–C bond so that all of the protons are chemically and magnetically equivalent. The ^{1}H-NMR spectrum will therefore appear as just a single peak, because magnetically equivalent nuclei do not couple.

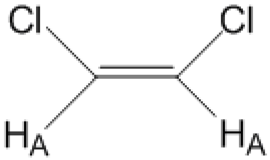
(b) 1-bromopropane ($CH_3CH_2CH_2Br$); There are three chemically different types of proton. Internal rotation means that the protons within each chemically different set are all magnetically equivalent. The terminal protons in the methyl, CH_3, group will couple to both pairs of intermediate ethyl, CH_2, protons, resulting in splitting into a triplet of triplets. The intermediate ethyl protons will be split by the terminal methyl protons into a triplet and by the other ethyl group into a doublet. The pattern for these protons will therefore appear as either a doublet of triplets or a triplet of doublets, depending upon the magnitude of the coupling constants.

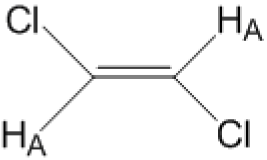
(c) 1,1-dichloroethene ($CCl_2=CH_2$);



The two protons are chemically and magnetically equivalent. The ^{1}H-NMR spectrum will therefore appear as a single peak, because there is no coupling.

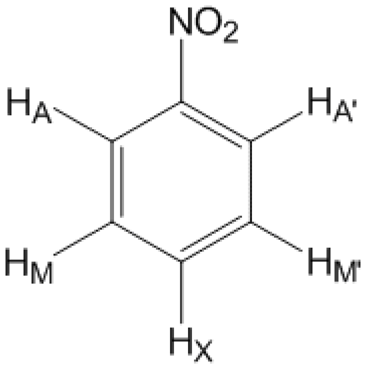
(d) *E*-1,2-dichloroethene (CHCl=CHCl); (*Z* and *E* isomers);





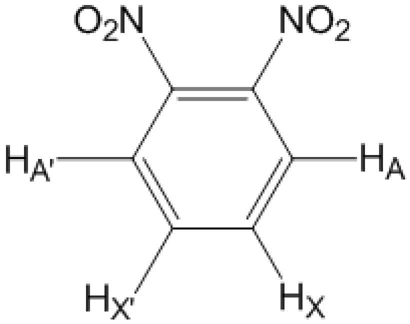
In both the *Z* and *E* isomers, the protons are both chemically and magnetically equivalent. There will thus be no coupling, and the ^{1}H-NMR spectra of both will appear as a single peak.

(e) nitrobenzene;



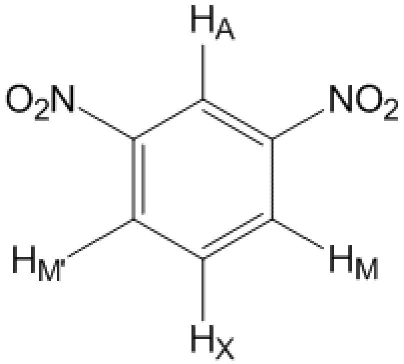
There are three chemically different types of proton: H_A, $H_{A'}$, H_M, $H_{M'}$ and H_X. The pair H_A and $H_{A'}$ are not magnetically equivalent, because they have a different relationship to other magnetically active nuclei, such as H_B, within the molecule. Thus the pair will couple not only with H_M and $H_{M'}$, and H_X, but also with each other. Coupling with H_M and $H_{M'}$ should result in a triplet, whilst coupling with H_X a doublet. Splitting of H_A by $H_{A'}$ (and $H_{A'}$ by H_A) should result in a doublet. the exact appearance of the spectrum will depend upon the magnitudes of the coupling constants. Second-order effects, which become important when the magnitude of a coupling constant is comparable with the difference in resonance frequencies, may also perturb the predicted pattern.

(f) 1,2-dinitrobenzene:



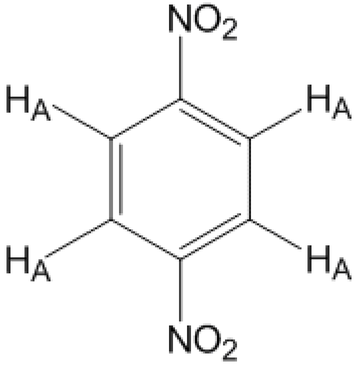
There are two pairs of chemically equivalent protons, H_A, $H_{A'}$ and H_X and $H_{X'}$, that resonate at different frequencies. However, although protons H_A and $H_{A'}$ are chemically equivalent, they are not magnetically equivalent, because their relationship to other magnetically active nuclei within the molecule is different. The coupling between proton H_A and H_X is different from that between H_A and $H_{X'}$. Thus, the peak due to H_A is split into a triplet by coupling to H_X and $H_{X'}$ and into a doublet by coupling to $H_{A'}$. The pattern for $H_{A'}$ will be identical. It is difficult to predict which coupling will be strongest; if $J_{AX} > J_{AA'}$, so that the coupling to between H_A and H_X is stronger than that with $H_{A'}$, then the pattern will appear as a triplet of doublets. If, however, $J_{AA'} > J_{AX}$, so that the coupling of H_A to the chemically equivalent $H_{A'}$ is stronger than that to H_X or $H_{X'}$ in the other set, then the pattern will appear as a doublet of triplets. In practice, the magnitude of the coupling constants are comparable, both with each other and with the separation between the resonant frequencies, leading to second-order effects that perturb the appearance of the spectrum.

(g) 1,3-dinitrobenzene:



There are three distinct types of proton, H_A, H_B, and a pair H_X and $H_{X'}$. The resonance due to H_A will be split into a triplet by protons H_X and $H_{X'}$, with each of these peaks being further split into a doublet by proton H_B. The pattern for H_A therefore appears as a triplet of doublets. The same will be true for H_B. The pair H_X and $H_{X'}$ are both chemically and magnetically equivalent, because they couple in the same way to the other protons, H_A and H_B. Thus, whilst these protons will couple to both H_A and H_B, they will not couple with each other. Coupling to H_B will split the resonance into a doublet and coupling to H_A will further split each of these components into another doublet. The resonances due to H_X and $H_{X'}$ therefore appears as a doublet of doublets.

(h) 1,4-dinitrobenzene:



All of the protons are chemically and magnetically equivalent. The ^{1}H-NMR spectrum therefore appears as a single peak, because magnetically equivalent nuclei do not couple.

29. The magnetogyric ratio for a ^{1}H nucleus is 26.7519×10^7 T^{-1} s^{-1}. Calculate the magnetic field strength (in tesla) required to give a Larmor frequency of 400 MHz. (Section 10.7)

Strategy

Combine Equation 10.23 with Equation 3.2, which expresses how a difference in energy relates to a transition frequency.

Solution

The difference in energy between the two ^{1}H spin states is, from Equation 10.23,

$$\Delta E = \frac{\gamma B h}{2\pi}$$

This difference in energy may be expressed in terms of the Larmor frequency using Equation 3.2,

$$\Delta E = h\nu$$

Combining these two equations, and rearranging,

$$B = 2\pi\nu/\gamma = 2\pi \times (400 \times 10^6\ \mathrm{s}^{-1})/(26.7519 \times 10^{-7}\ \mathrm{T}^{1}\ \mathrm{s}^{-1}) = 9.39 \times 10^{14}\ \mathrm{T}$$