Answers to the Problems in Chapter 10

Problem 10.1.

Equation 10.2.2 $\quad x = X \sin(2\pi\nu_c t + \phi)$

$\partial x/\partial t = X\, 2\pi\nu_c \cos(2\pi\nu_c t + \phi)$

$\partial^2 x/\partial^2 t = -\; X\,(2\pi\nu_c)^2 \sin(2\pi\nu_c t + \phi) = -\,(2\pi\nu_c)^2\, x$

Equation 10.2.1 $\quad F = -kx = m\partial^2 x/\partial^2 t \;=\; -m\,(2\pi\nu_c)^2\, x$

Therefore, $\quad k = m\,(2\pi\nu_c)^2$ or $\nu_c = (1/2\pi)\sqrt{(k/m)}$

Problem 10.2.

The completed table is:

Molecule	X–H stretch	Reduced mass	Force constant
OH_2	365 200	0.941	739
NH_3	333 400	0.933	611
CH_4	291 400	0.923	461

The reduced mass is given by Equation B10.1.8. Since this is a simplified view of the stretching of one bond in molecules with several bonds there is no point in using highly exact data for the atomic masses. Thus, for the O–H bond, in atomic units, we have $\mu = 16\times 1/(16+1) = 0.941$ a.u.

When the reduced mass is used we have (Section 10.2), $\nu_c = (1/2\pi)\sqrt{(k/\mu)}$. Converting to wavenumbers, in m^{-1}, gives $\bar{\nu} = (1/2\pi c)\sqrt{(k/\mu)}$ or $k = (2\pi c\bar{\nu})^2\mu$

If μ is entered in amu, $k = (2\pi c\bar{\nu})^2\mu \times 1.660 \times 10^{-27}\ Nm^{-1}$

For the O-H stretching of water, for example,

$k = (2 \times 3.142\times 2.997\times 10^8 \times 3.652\times 10^5)^2 \times 0.941\times 1.660\times 10^{-27}\ Nm^{-1}$

$= 739\ Nm^{-1}$

Problem 10.3.

Expanding the Morse potential:

$$V = D_e[1-\exp\{a(r_e - R)\}]^2$$

$$= D_e[1-1-a(r_e-R)-a^2(r_e-R)^2/2!-a^3(r_e-R)^3/3!-...]^2$$

$$= D_e[a^2(r_e-R)^2+a^3(r_e-R)^3+\frac{7}{12}a^4(r_e-R)^4+...]$$

$$= D_e a^2(R-r_e)^2 - D_e a^3(R-r_e)^3+\frac{7}{12}D_e a^4(R-r_e)^4-...$$

For the simple harmonic oscillator we have: $V = \frac{1}{2}k(R-r_e)^2$ which, on comparison with the above result, gives: $k = 2D_e a^2$.

Problem 10.4.

At a temperature of 25°C effectively all the HCl molecules are in their ground vibrational state (v = 0) so that this absorption must be due to the v = 0 to v = 1 vibrational transition with associated structure due to changes in rotational state. Figure 10.7 (p. 296) is the required energy-level diagram, though the numbers given there are not sufficiently precise for the present purposes.

The band is centred at 2990 cm^{-1} which corresponds to the vibrational transition from $J'' = 0$ to $J' = 0$ which is not allowed because there is no change of angular momentum and a photon has angular momentum. The transition immediately above the centre to higher energy must be the $J'' = 0$ to $J' = 1$ transition having an energy of $h\nu + B'J'(J'+1)$. The band immediately below must be the $J'' = 1$ to $J' = 0$ with an energy of $h\nu - B''J''(J''+1)$. The difference in their wavenumbers is 3010.8 – 2969.2 = 41.6 cm^{-1}, which is equal to $2B' + 2B''$. If we assume that the change of the rotational constant in going from v = 0 to v = 1 can be neglected we have $4B = 10.4$ cm^{-1}.

According to Equation 10.4.1a:

$$B = \frac{h}{8\pi^2 cI} = \frac{6.6262\times10^{-34}}{8\times(3.1416)^2\times2.9979\times10^8\times I} = \frac{2.7993}{I}\times10^{-44}$$

Rearranging the last equation and introducing our value for B (in m^{-1}) we have:

$$I = \frac{2.7993}{1040}\times10^{-44} = 2.6916\times10^{-47} = \mu R^2 = 1.6275\times10^{-27}(\text{kg})R^2$$

Therefore

$$R = \sqrt{\frac{2.6916}{1.6275}}\times10^{-10}\,\text{m} = 128.6\ \text{pm}$$

Problem 10.5.

$$\Omega_0 = \left[\frac{\gamma}{\pi}\right]^{\frac{1}{4}} \exp\left(-\tfrac{1}{2}\gamma q^2\right)$$

$$\Omega_1 = \left[\frac{\gamma}{\pi}\right]^{\frac{1}{4}} \sqrt{2\gamma}\, q \exp\left(-\tfrac{1}{2}\gamma q^2\right)$$

$$\Gamma_{10} = \left[\frac{\gamma}{\pi}\right]^{\frac{1}{2}} \sqrt{2\gamma}\, x \exp\left(-\tfrac{1}{2}\gamma[x^2 + y^2]\right)$$

$$\Gamma_{01} = \left[\frac{\gamma}{\pi}\right]^{\frac{1}{2}} \sqrt{2\gamma}\, y \exp\left(-\tfrac{1}{2}\gamma[x^2 + y^2]\right)$$

Converting to plane polar co-ordinates we have:

$$\Gamma_{10} = \gamma\left[\frac{2}{\pi}\right]^{\frac{1}{2}} r\cos\phi \exp\left(-\tfrac{1}{2}\gamma r^2\right)$$

$$\Gamma_{01} = \gamma\left[\frac{2}{\pi}\right]^{\frac{1}{2}} r\sin\phi \exp\left(-\tfrac{1}{2}\gamma r^2\right)$$

Combining the above functions gives:

$$\frac{1}{\sqrt{2}}(\Gamma_{10} + i\Gamma_{01}) = \frac{\gamma r}{\sqrt{\pi}}\exp(-\tfrac{1}{2}\gamma r^2)\exp(+i\phi)$$

$$\frac{1}{\sqrt{2}}(\Gamma_{10} - i\Gamma_{01}) = \frac{\gamma r}{\sqrt{\pi}}\exp(-\tfrac{1}{2}\gamma r^2)\exp(-i\phi)$$

Clearly, these functions are eigenfunctions of the operator $\hat{l}_z = -i\hbar\partial/\partial\phi$ with eigenvalues of ± 1.

Problem 10.6.

The two C–Br bonds of CH_2Br_2 are identical, and if it were not for the interaction of their stretching vibrations those two vibrations would have identical energies and intensities. But they mix strongly because they have the same energy (frequency) and the asymmetric combination gives a much larger dipole change, and therefore intensity, than the symmetric.

The two C–halogen bonds in CH_2BrCl are quite different and the two stretching vibrations do not mix strongly. Each has essentially its own frequency and intensity, though the Cl stretching is more intense than the Br.