

Solutions to assignment 6

1. The dipole moment for a fully ionic bond involves a transfer of one complete unit of charge over a distance r_0 :

$$\begin{aligned} p_{\text{ionic}} &= er_0 \\ &= (1.60 \times 10^{-30} \text{ C})(0.0917 \text{ nm}) \\ &= 1.47 \times 10^{-20} \text{ C m}. \end{aligned}$$

Since the measured value is $6.4 \times 10^{-30} \text{ C}$, the HF bond is

$$\frac{6.4 \times 10^{-30} \text{ C}}{1.47 \times 10^{-20} \text{ C m}} = 0.44$$

or 44% ionic.

2. For N_2 , the fundamental rotational energy is

$$E_{0r} = 2.48 \times 10^{-4} \text{ eV} = \frac{\hbar^2}{2I},$$

where $I = \frac{1}{2}mr_0^2$ and $m = 14.0067 \text{ u}$. Hence,

$$r_0^2 = \frac{\hbar^2}{(2.48 \times 10^{-4} \text{ eV})(14.0067 \text{ u})}$$

and

$$r_0 = \left[\frac{(1.055 \times 10^{-34} \text{ J s})^2}{(2.48 \times 10^{-4} \text{ eV})(1.60 \times 10^{-10} \text{ J/eV})(14.0067 \text{ u})(1.66 \times 10^{-27} \text{ kg/u})} \right]^{1/2} = 1.61 \times 10^{-10} \text{ m} = 0.110 \text{ nm}.$$

3. (a) For CO , the atomic separation is $r_0 = 0.113 \text{ nm}$; the masses of the two species are 12.0112 u and 15.994 u . Consequently, the reduced mass of the molecule is

$$\mu = \frac{m_{\text{C}}m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} = \frac{12.0112 \text{ u} \cdot 15.994 \text{ u}}{12.0112 \text{ u} + 15.994 \text{ u}} = 6.861 \text{ u},$$

the moment of inertia is

$$\begin{aligned} I &= \mu r_0^2 \\ &= (6.861 \text{ u})(1.66 \times 10^{-27} \text{ kg/u}) \\ &\quad \times (0.133 \times 10^{-9} \text{ m})^2 = 1.454 \times 10^{-46} \text{ kg m}^2, \end{aligned}$$

and the fundamental rotational energy is

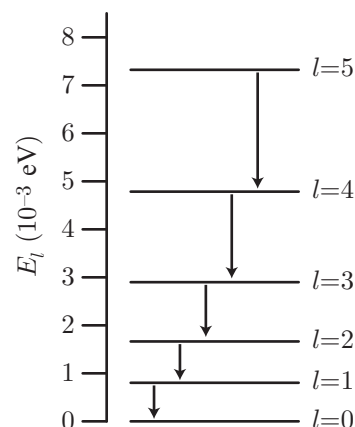
$$\begin{aligned} E_{0r} &= \frac{\hbar^2}{2I} = \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2(1.454 \times 10^{-46} \text{ kg m}^2)} \\ &= 3.827 \times 10^{-23} \text{ J} \\ &= 2.39 \times 10^{-4} \text{ eV}. \end{aligned}$$

- (b) Since, $E_l = l(l+1)E_{0r}$, we have

$$\begin{aligned} E_0 &= 0 \\ E_1 &= 2E_{0r} = 4.78 \times 10^{-4} \text{ eV} \\ E_2 &= 6E_{0r} = 1.43 \times 10^{-3} \text{ eV} \\ E_3 &= 12E_{0r} = 2.87 \times 10^{-3} \text{ eV} \\ E_4 &= 20E_{0r} = 4.78 \times 10^{-3} \text{ eV} \\ E_5 &= 30E_{0r} = 7.17 \times 10^{-3} \text{ eV} \end{aligned}$$

- (c) The transitions $E_{l+1} - E_l$ (see diagram) have energies

$$\begin{aligned} E_5 - E_4 &= 2.39 \times 10^{-3} \text{ eV} \\ E_4 - E_3 &= 1.91 \times 10^{-3} \text{ eV} \\ E_3 - E_2 &= 1.44 \times 10^{-3} \text{ eV} \\ E_2 - E_1 &= 0.95 \times 10^{-3} \text{ eV} \\ E_1 - E_0 &= 4.78 \times 10^{-4} \text{ eV} \end{aligned}$$



- (d) The corresponding wavelength of the photon emitted is given by $\lambda = hc/\epsilon$, where $\epsilon = E_{l+1} - E_l$ is the energy released in the transition from level

$l + 1$ to l .

$$\begin{aligned}\lambda_{54} &= \frac{1240 \text{ eV nm}}{2.39 \times 10^{-3} \text{ eV}} = 5.19 \times 10^5 \text{ nm} = 0.519 \text{ mm} \\ \lambda_{43} &= \frac{1240 \text{ eV nm}}{1.91 \times 10^{-3} \text{ eV}} = 6.49 \times 10^5 \text{ nm} = 0.649 \text{ mm} \\ \lambda_{32} &= \frac{1240 \text{ eV nm}}{1.44 \times 10^{-3} \text{ eV}} = 8.61 \times 10^5 \text{ nm} = 0.861 \text{ mm} \\ \lambda_{21} &= \frac{1240 \text{ eV nm}}{0.95 \times 10^{-3} \text{ eV}} = 13.05 \times 10^5 \text{ nm} = 1.31 \text{ mm} \\ \lambda_{10} &= \frac{1240 \text{ eV nm}}{4.78 \times 10^{-4} \text{ eV}} = 25.9 \times 10^5 \text{ nm} = 2.59 \text{ mm}\end{aligned}$$

Wavelengths on the scale of millimetres are in the microwave region of the spectrum.

4. (a) The position of the n th atom in a linear crystal is $u_n = u \cos(\omega t - nKa)$. Its velocity is the time derivative $\dot{u}_n = du_n/dt$, and thus its kinetic energy is $\frac{1}{2}M\dot{u}_n^2$. The total kinetic energy of *all* the atoms is the sum $\sum_n \frac{1}{2}M\dot{u}_n^2$.

The Hooke's law forces acting on the n th atom, pulling it to the right and to the left, are $F_n = +C(u_{n+1} - u_n) - C(u_n - u_{n-1})$. The corresponding potential is

$$V_n = \frac{1}{2}C(u_{n+1} - u_n)^2 + \frac{1}{2}C(u_n - u_{n-1})^2.$$

This has been constructed so that $F_n = -dV_n/du_n$.

The total potential is $\frac{1}{2}\sum_n V_n$, where the factor $\frac{1}{2}$ is necessary to prevent double counting:

$$\begin{aligned}\frac{1}{2}\sum_n V_n &= \frac{1}{4}C\sum_n [(u_{n+1} - u_n)^2 + (u_n - u_{n-1})^2] \\ &= \frac{1}{2}C\sum_n (u_{n+1} - u_n)^2.\end{aligned}$$

Finally, the total kinetic and potential energies sum

to give

$$E = \frac{1}{2}\sum_n [M\dot{u}_n^2 + C(u_{n+1} - u_n)^2].$$

(b) Since $\dot{u}_n = -u\omega \sin(\omega t - nKa)$, we have

$$\begin{aligned}E &= \frac{1}{2}Mu^2\omega^2\sum_n \sin^2\phi \\ &\quad + \frac{1}{2}Cu^2\sum_n [\cos(\phi - Ka) - \cos\phi]^2,\end{aligned}$$

where $\phi = \omega t - nKa$. The functions that depend on ϕ oscillate with a period $P = 2\pi/\omega$; this leads to the time average

$$\langle \cos^2\phi \rangle = \frac{1}{P}\int_0^P \cos^2(\omega t - Ka) dt = \frac{1}{2},$$

which is nothing more than the observation that $\cos^2\phi$ oscillates uniformly between 0 and 1, averaging to $\frac{1}{2}$. Similarly, $\langle \sin^2\phi \rangle = \frac{1}{2}$. On the other hand $\langle \cos\phi \rangle = \langle \sin\phi \rangle = \langle \sin\phi \cos\phi \rangle = 0$, since these functions oscillate between -1 and 1 , averaging to 0.

This tells us that the kinetic energy per particle is $\frac{1}{2}M\omega^2u^2\langle \sin^2\phi \rangle = \frac{1}{4}M\omega^2u^2$. To get the potential energy, we can make use of the identity

$$\cos(\phi - Ka) = \cos\phi \cos Ka + \sin\phi \sin Ka$$

to write

$$\begin{aligned}\langle [\cos(\phi - Ka) - \cos\phi]^2 \rangle &= \underbrace{\langle \cos^2\phi \rangle}_{=\frac{1}{2}}(1 - \cos Ka)^2 + 2\underbrace{\langle \cos\phi \sin\phi \rangle}_{=0}\cos Ka(1 - \cos Ka) + \underbrace{\langle \sin^2\phi \rangle}_{=\frac{1}{2}}\sin^2 Ka \\ &= \frac{1}{2}(1 - 2\cos Ka + \underbrace{\cos^2 Ka + \sin^2 Ka}_{=1}) \\ &= 1 - \cos Ka.\end{aligned}$$

The two contributions together give

$$\frac{1}{2}M\omega^2u^2 + \frac{1}{2}C(1 - \cos Ka)u^2 = \frac{1}{2}M\omega^2u^2.$$

The final simplification comes about because

$$\omega = (4C/M)^{1/2}|\sin \frac{1}{2}Ka| = (2C/M)(1 - \cos Ka)^{1/2},$$

which tells us that the kinetic and potential energy

terms are equal:

$$\frac{1}{2}C(1 - \cos Ka)u^2 = \frac{1}{4}M\omega^2u^2.$$