Suggested Solutions for Tutorial 8

Optical sensors

Atomic and molecular spectra

Q1: *(a)* From the notes we have that the difference between two adjacent rotational energy levels is

$$\begin{aligned}\Delta E &= E_{l+1} - E_l \\ &= (l+1)\frac{\hbar^2}{mR_{eq}^2}\end{aligned}$$

which, since $I = mR_{eq}^2$, can be written as

$$\Delta E = \frac{\hbar^2}{I}$$

where I is the moment of inertia about the centre of mass, and since $l = 0$ for this transition. Equating this to the energy of the absorbed photon we get

$$\frac{\hbar^2}{I} = \hbar\omega$$

The angular frequency ω of the absorbed radiation is

$$\omega = 2\pi f = 2\pi(1.15 \times 10^{11}) = 7.23 \times 10^{11} \text{ rad/s}$$

so that I becomes

$$I = \frac{\hbar}{\omega} = \frac{1.055 \times 10^{-34}}{7.23 \times 10^{11}} = 1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2$$

Q1: *(b)* Again, in the notes we have that the moment of inertia is related to the bond length (equilibrium separation) via the reduced mass i.e.

$$I = mR_{eq}^2$$

The atomic masses of carbon and oxygen are 12 u and 16 u respectively
(1 u $= 1.66 \times 10^{-27}$ kg) so the reduced mass of CO is

$$m = \frac{12 \times 16}{12 + 16} = 6.857 \text{ u} = 1.14 \times 10^{-26} \text{ kg}$$

Then

$$R_{eq} = \sqrt{\frac{I}{m}} = \sqrt{\frac{1.46 \times 10^{-46}}{1.14 \times 10^{-26}}} = 1.13 \times 10^{-10} \text{ m} = 0.113 \text{ nm}$$

Note the immense power of spectroscopic measurements to determine molecular properties.

Q2: *(a)* The absorption process is accompanied by a molecular transition from the $\nu = 0$ to the $\nu = 1$ vibrational level. Since the energy difference between these levels is $\Delta E_{vib} = \hbar\omega$, the absorbed photon must have carried this much energy. It follows that the photon frequency is just $\Delta E_{vib}/\hbar = \omega$, which is the frequency of the CO oscillator. From the information given in the question, we calculate the angular frequency

$$\omega = 2\pi f = 2\pi(6.42 \times 10^{13}) = 4.03 \times 10^{14} \text{ rad/s}$$

Using 12 u and 16 u for the carbon and oxygen atomic masses (1 u = 1.66×10^{-27} kg), we find that the reduced mass is $m = 6.857$ u $= 1.14 \times 10^{-26}$ kg. Then the spring constant (force constant) is

$$k = m\omega^2 = (1.14 \times 10^{-26})(4.03 \times 10^{14})^2 = 1.86 \times 10^3 \text{ N/m}$$

Thus, infrared spectroscopy furnishes useful information on the elastic properties (bond strengths) of molecules.

Q2: *(b)* The total vibrational energy for the molecule is $E_{vib} = \frac{1}{2}\hbar\omega$. At maximum displacement the CO molecule has transformed all this into elastic energy of the spring

$$\frac{1}{2}\hbar\omega = \frac{1}{2}kA^2$$

where A is the vibration amplitude. Using $k = m\omega^2$ and $m = 1.14 \times 10^{-26}$ kg, we get

$$A = \left(\frac{\hbar}{m\omega}\right)^{\frac{1}{2}} = \left\{\frac{1.055 \times 10^{-34}}{(1.14 \times 10^{-26})(4.03 \times 10^{14})}\right\}^{\frac{1}{2}} = 4.79 \times 10^{-12} \text{ m} = 0.00479 \text{ nm}$$

Comparing this to the bond length of CO (0.113 nm), we see that the vibration amplitude is only about 4% of the bond length.

Q3: *(a)* The maximum amplitude occurs when the (in this case) ground state energy is equal to the amplitude of a spring of spring constant K. Mathematically this is

$$\begin{aligned} \frac{1}{2}\hbar\omega &= \frac{1}{2}KA^2 \\ \Rightarrow A &= \sqrt{\frac{\hbar\omega}{K}} \\ &= \sqrt{\frac{hf}{K}} \end{aligned}$$

where A is the amplitude and ω is the angular frequency of the exciting radiation, note that we have used the fact that $\omega = 2\pi f$. For HI this amplitude is

$$\begin{aligned} A &= \sqrt{\frac{6.626 \times 10^{-34} \times 6.69 \times 10^{13}}{320}} \\ &= 1.2 \times 10^{-11} \text{ m} \end{aligned}$$

Q3: *(b)* For HF plugging the numbers into the equation gives

$$\begin{aligned} A &= \sqrt{\frac{6.626 \times 10^{-34} \times 8.72 \times 10^{13}}{970}} \\ &= 7.7 \times 10^{-12} \text{ m} \end{aligned}$$

Q3: *(c)* HI has the weaker bond since the bond distance is greater.

Q4: The difference in energy between two nearby rotational states is

$$\Delta E = E_l - E_{l-1} = \frac{\hbar^2 l}{I} = \frac{\hbar^2 l}{mR_{eq}^2}$$

this must be equal to the excitation energy

$$E_{rot} = hf = \hbar\omega$$

therefore

$$\begin{aligned} \hbar\omega &= \frac{\hbar^2 l}{mR_{eq}^2} \\ \Rightarrow \omega &= \frac{\hbar l}{mR_{eq}^2} \\ &= \frac{6.626 \times 10^{-34} \times 1}{2 \times \pi \times 1.61 \times 10^{-27} \times (0.1275 \times 10^{-9})^2} \\ &= 4.02 \times 10^{12} \text{ rad/s} \end{aligned}$$

Q5: *(a)* We know that the effective force (spring) constant is given by

$$K = m\omega^2$$

where m is the reduced mass and we know that

$$\omega = 2\pi f$$

hence the force constant can be rewritten as

$$K = 4\pi^2 m f^2$$

The reduced mass for HI is

$$\begin{aligned} m &= \frac{1\text{u} \times 127\text{u}}{1\text{u} + 127\text{u}} \\ &= 0.992\text{u} \\ &= 0.992 \times 1.66 \times 10^{-27} \\ &= 1.647 \times 10^{-27} \text{ kg} \end{aligned}$$

Hence the force constant is

$$\begin{aligned} K &= 1.647 \times 10^{-27} \times 4 \times \pi^2 \times (6.69 \times 10^{13})^2 \\ &= 291 \text{ N/m} \end{aligned}$$

For NO we have a reduced mass of

$$\begin{aligned} m &= \frac{14\text{u} \times 16\text{u}}{14\text{u} + 16\text{u}} \\ &= 7.467\text{u} \\ &= 7.467 \times 1.66 \times 10^{-27} \\ &= 1.239 \times 10^{-26} \text{ kg} \end{aligned}$$

and so the force constant is

$$\begin{aligned} K &= 1.239 \times 10^{-26} \times 4 \times \pi^2 \times (5.63 \times 10^{13})^2 \\ &= 1550 \text{ N/m} \end{aligned}$$

Q5: *(b)* The maximum amplitude is given (in this case) by the ground state energy being equal to the amplitude of a spring of force constant K. This is

$$\begin{aligned}\frac{1}{2}\hbar\omega &= \frac{1}{2}KA^2\\ \Rightarrow A &= \sqrt{\frac{\hbar\omega}{K}}\\ &= \sqrt{\frac{hf}{K}}\end{aligned}$$

for HI we have

$$\begin{aligned}A &= \sqrt{\frac{6.626\times10^{-34}\times6.69\times10^{13}}{291}}\\ &= 1.23\times10^{-11}\ \mathrm{m}\end{aligned}$$

for NO we have

$$\begin{aligned}A &= \sqrt{\frac{6.626\times10^{-34}\times5.63\times10^{13}}{1550}}\\ &= 4.91\times10^{-12}\ \mathrm{m}\end{aligned}$$

Q5: *(c)* The force constant of NO is much larger than that of HI because of the relative sizes of the atoms involved in bonding. N and O are basically the same size, whereas H is tiny and I is huge. The relative sizes means that the overlap of the electron clouds used for bonding is much higher for NO than for HI hence the bonding is stronger and hence the force constant is much larger.