Chapter 10

Molecular Structure. Selected Problems

10.1 Problem 10.3

Use the data in Table 10.2 to calculate the maximum amplitude of vibration for

(a) the HI molecule and

(b) the HF molecule. Which molecule has the weaker bond?

Solution

At maximum displacement (amplitude), all kinetic energy of vibration will be transformed into potential energy, i.e.

$$\frac{1}{2}\hbar\omega = \frac{1}{2}K\,A^2$$

where ω is the angular frequency of vibration, K is the force constant of the molecule, and A is the amplitude of the vibration. The force constant K is given by:

$$K = \mu\,\omega^2$$

where $\mu = (m_1\, m_2)/(m_1 + m_2)$ is the reduced mass of a diatomic molecule. The amplitude of the vibration is then:

$$\begin{aligned} A &= \sqrt{\frac{\hbar\,\omega}{K}} \\ &= \sqrt{\frac{\hbar\,\omega}{\mu\,\omega^2}} \\ &= \sqrt{\frac{\hbar}{\mu\,\omega}} \\ &= \sqrt{\frac{\hbar}{\mu\,(2\pi\,f)}} \end{aligned}$$

where f is the frequency, given in Table 10.2.

(a) The Hydrogen mass $= 1.6605 \times 10^{-27}\,kg$ and the mass of Iodine is $127 \times 1.6605^{-27}\,kg$, so the reduced mass of HI is $\mu = 127 \times 1.6605 \times 10^{-27}/128\,kg$. The frequency of HI molecules as given Table 10.2 is $f = 6.69 \times 10^{13}\,Hz$.

$$\begin{aligned} A &= \sqrt{\frac{\hbar}{\mu\,(2\pi\,f)}} \\ &= \sqrt{\frac{1.055 \times 10^{-34} \times 128}{2\pi \times 6.69 \times 10^{13} \times 127 \times 1.6605 \times 10^{-27}}} \\ &= 1.23 \times 10^{-11}\,m \\ &= 0.0123\,nm \end{aligned}$$

The force constant of the HI molecule is:

$$\begin{aligned} K &= \mu\,\omega^2 \\ &= (2\pi\,f)^2\,\mu \\ &= \frac{(2\pi \times 6.69 \times 10^{13})^2 \times 127 \times 1.6605 \times 10^{-27}}{128} \\ &= 291\,N/m \end{aligned}$$

(b) The mass of Fluorin is $19 \times 6.66 \times 10^{-27}\,kg$ and its frequency from Table 10.2 is $f =$

$8.72 \times 10^{13}\, Hz$.

$$\begin{aligned} A &= \sqrt{\frac{\hbar}{\mu\,(2\pi\, f)}} \\ &= \sqrt{\frac{1.055 \times 10^{-34} \times 20}{2\pi \times 8.72 \times 10^{13} \times 19 \times 1.6605 \times 10^{-27}}} \\ &= 1.23 \times 10^{-11}\, m \\ &= 0.0110\, nm \end{aligned}$$

The force constant of the HF molecule is:

$$\begin{aligned} K &= \mu\, \omega^2 \\ &= (2\pi\, f)^2\, \mu \\ &= \frac{(2\pi \times 8.72 \times 10^{13})^2 \times 19 \times 1.6605 \times 10^{-27}}{20} \\ &= 472\, N/m \end{aligned}$$

The HI molecule has weaker bond due to its smaller force constant.

10.2 Problem 10.4

The $\ell = 5$ to $\ell = 6$ rotational absorption line of a diatomic molecule occurs at a wavelength of 1.35 cm (in the vapor phase).

(a) Calculate the wavelength and frequency of the $\ell = 0$ to $\ell = 1$ rotational absorption line.

(b) Calculate the moment of inertia of the molecule.

Solution

(a) The energy change, $\Delta E_{\ell_1,\ell_2}$ in a rotational transition from ℓ_1 to ℓ_2 is:

$$\begin{aligned}
\Delta E_{\ell_1,\ell_2} &= \frac{\hbar^2}{I}\,\ell_2 \\
&= h\,f \\
&= \frac{h\,c}{\lambda_{\ell_1,\ell_2}} \\
\lambda_{\ell_1,\ell_2} &= \frac{h\,c\,I}{\hbar^2\,\ell_2} \\
&= \frac{2\pi\,c\,I}{\hbar\,\ell_2} \\
\lambda_{0,1} &= \frac{2\pi\,c\,I}{\hbar} \\
\lambda_{5,6} &= \frac{2\pi\,c\,I}{6\,\hbar} \\
\lambda_{0,1} &= 6\lambda_{5,6} \\
&= 6 \times 1.35 \\
&= 8.1\,cm
\end{aligned}$$

(b) The moment of inertia I can be calculated from one of the wavelngth:

$$\begin{aligned}
\lambda_{0,1} &= \frac{2\pi\,c\,I}{\hbar} \\
I &= \frac{\hbar\,\lambda_{0,1}}{2\pi\,c} \\
&= \frac{1.055 \times 10^{-34} \times 8.1 \times 10^{-2}}{2\pi \times 3^8} \\
&= 4.53 \times 10^{-45}\,kg \cdot m^2
\end{aligned}$$

10.3 Problem 10.7

The $\nu = 0$ to $\nu = 1$ vibrational transition of the HI molecule occurs at a frequency of $6.69 \times 10^{13}\ Hz$. The same transition for the NO molecule occurs at a frequency of $5.63 \times 10^{13}\ Hz$. Calculate

(a) the effective force constant and

(b) the amplitude of vibration for each molecule.

(c) Explain why the force constant of the NO molecule is so much larger than that of the HI molecule.

Solution

Vibrational energy of a molecule is:

$$\begin{aligned} E_{vib} &= (\nu + \frac{1}{2})\,\hbar\,\omega \\ \omega &= \sqrt{\frac{K}{\mu}} \\ \Delta E_{0,1} &= E_1 - E_0 \\ &= h\,f \\ &= \sqrt{\frac{\hbar^2\,K}{\mu}} \\ f &= \sqrt{\frac{K}{4\pi^2\mu}} \\ K &= 4\pi^2\,f^2\,\mu \end{aligned}$$

where K is the force constant, μ is the reduced mass of the molecule, and f is the frequency of the radiation emitted in the transition.

(a) the reduced mass of the the HI molecule is $127 \times 1.6605 \times 10^{-27}/128$ and that of NO molecule is $14 \times 16 \times 1.6605 \times 10^{-27}/30$. Using the frequencies given in the problem we

get:

$$\begin{aligned} K_{HI} &= (2\pi \times 6.69 \times 10^{13})^2 \times \frac{127 \times 1.6605 \times 10^{-27}}{128} \\ &= 291.1\, N/m \\ K_{NO} &= (2\pi \times 5.63 \times 10^{13})^2 \times \frac{14 \times 16 \times 1.6605 \times 10^{-27}}{30} \\ &= 1551\, N/m \end{aligned}$$

(b) Tha mplitude of vibration is:

$$\begin{aligned} A &= \sqrt{\frac{\hbar}{\mu\,(2\pi\, f)}} \\ A_{HI} &= \sqrt{\frac{1.055 \times 10^{-34} \times 128}{127 \times 1.6605 \times 10^{-27} \times 2 \times \pi \times 6.69 \times 10^{13}}} \\ &= 1.23 \times 10^{-11}\, m \\ A_{NO} &= \sqrt{\frac{1.055 \times 10^{-34} \times 30}{16 \times 14 \times 1.6605 \times 10^{-27} \times 2 \times \pi \times 5.63 \times 10^{13}}} \\ &= 4.90 \times 10^{-12}\, m \end{aligned}$$

(c) The reduced mass of the NO molecules is 7.5 times the reduced mass of the HI molecules, as a result the force constant of NO is much larger than that of HI.

10.4 Problem 10.9

The hydrogen molecule comes apart (dissociates) when it is excited internally by 4.5 eV. Assuming that this molecule behaves exactly like a harmonic oscillator with classical frequency $\omega = 8.277 \times 10^{14}\ rad/s$, find the vibrational quantum number corresponding to its 4.5-eV dissociation energy.

Solution

The vibrational energy of the molecule is:

$$E_{vib} = (\nu + \frac{1}{2})\,\hbar\,\omega$$

If we take E_{vib} to be $4.5eV$and the given value of ω, we get:

$$\begin{aligned} \nu &= \frac{E_{vib}}{\hbar\,\omega} - \frac{1}{2} \\ &= \frac{4.5}{6.582 \times 10^{-16} \times 8.277 \times 10^{14}} - \frac{1}{2} \\ &= 7.76 \end{aligned}$$

But ν has to be a an integer number, so $\nu = 7$ is the highest vibrational state that the hydrogen molecule can attain without dissociating. In other words the $\nu = 8$ state is unstable.

10.5 Problem 10.13

As an alternative to harmonic interactions, the *Morse potential*

$$U(r) = U_\circ \left\{1 - e^{-\beta(r-R_\circ)}\right\}^2$$

can be used to describe the vibrations of a diatomic molecule. The parameters $R_\circ$, $U_\circ$ and β are chosen to fit the data for a particular atom pair.

(a) Show that $R_\circ$ is the equilibrium separation, and that the potential energy far from equilibrium approaches $U_\circ$.

(b) Show that near equilibrium ($r \approx R_\circ$) the Morse potential is harmonic, with force constant $K = m\omega^2 = 2U_\circ\beta^2$.

(c) The lowest vibrational energy for the Morse oscillator can be shown to be

$$E_{vib} = \frac{1}{2}\hbar\omega - \frac{(\hbar\omega)^2}{16U_\circ}$$

Obtain from this an expression for the dissociation energy of the molecule.

(d) Apply the results of parts (b) and (c) to deduce the Morse parameters $U_\circ$ and β for the hydrogen molecule. Use the experimental values 573 N/m and 4.52 eV for the effective spring constant and dissociation energy respectively. (The measured value of $R_\circ$ for H_2 is 0.074 nm).

Solution

(a) The condition for equilibrium is:

$$\begin{aligned}\frac{dU}{dr} &= 0 \\ &= 2U_\circ \left\{1 - e^{-\beta(r-R_\circ)}\right\} \left\{\beta e^{-\beta(r-R_\circ)}\right\}\end{aligned}$$

The values of r that satisfies the above equation are $r = \infty$ and $r = R_\circ$, so obviously the finite solution is $r = R_\circ$. When $r \gg R_\circ$, the exponent of the exponential term is large and $U(r) \approx U_\circ$.

(b) Near equilibrium, $(r - R_\circ)$ is very small and we can use the expansion $e^x = 1 + x + \cdots$ to write:

$$1 - e^{-\beta(r-R_\circ)} \approx \beta(r - R_\circ)$$

and this gives:

$$U(r) \approx U_\circ[\beta(r - R_\circ)]^2$$

The above equation can be written as:

$$U(r) = \frac{1}{2}K(r - R_\circ)^2$$

this is the form of a harmonic oscillator where;

$$K = 2U_\circ\beta^2 \tag{10.1}$$

(c) To dissociate a molecule an energy of $E_{diss} = U(\infty) - E_{vib}$ must be given to the molecule. Since $U(\infty) = U_\circ$, we then have:

$$E_{diss} = U_\circ - \frac{1}{2}\hbar\omega + \frac{(\hbar\omega)^2}{16U_\circ} \tag{10.2}$$

(d) Equation (10.2) can be used to find $U_\circ$ and then Equation (10.1) is used to fin β. In addition we need:

$$\omega = \sqrt{\frac{K}{\mu}} \tag{10.3}$$

where μ is the reduced mass of the hydrogen molecule, $\mu = m_p m_p/(m_p + m_p) = m_p/2$, and $m_p = 938.28 \times 10^3\ keV/c^2$ is the mass of the proton. We then get:

$$\begin{aligned} K &= 573\ N/m \\ &= 573\ J/m^2 \\ &= \frac{573}{1.602 \times 10^{-19}}\ eV/m^2 \\ &= \frac{573}{1.602 \times 10^{-16} \times 10^{18}}\ keV/(nm)^2 \\ &= 3.58\ keV/(nm)^2 \end{aligned}$$

then ω becomes:

$$\begin{aligned} \omega &= \sqrt{\frac{K}{\mu}} \\ &= \sqrt{\frac{3.5}{\frac{1}{2} \times 938.28 \times 10^3}} \end{aligned}$$

Using $\hbar = 197.3\ eV \cdot nm/c$ then $\hbar\omega$ is:

$$\begin{aligned} \hbar\omega &= 197.3\sqrt{\frac{3.5}{\frac{1}{2} \times 938.28 \times 10^3}} \\ &= 0.545\ eV \end{aligned}$$

Substituting in Equation (10.2), we get:

$$\begin{aligned} 4.52 &= U_\circ - 0.272 + \frac{0.0186}{U_\circ} \\ 0 &= U_\circ^2 - 4.792U_\circ + 0.0186 \end{aligned}$$

Solving the above equation we get $U_\circ = 4.788$ or $0.004\ eV$. The second solution is unrealistically small so $U_\circ = 4.79\ eV$.

Now substituting K and $U_\circ$ in Equation (10.1) we get:

$$\begin{aligned} \beta &= \sqrt{\frac{K}{2U_\circ}} \\ &= \sqrt{\frac{3.58 \times 10^3}{2 \times 4.79}} \\ &= 19.3\ nm^{-1} \end{aligned}$$