

# Chapter 10

## Molecular Structure. Home Work Solutions

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

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

The force constant of the  $HI$  molecule is:

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

- (b) The mass of Fluorin is  $19 \times 1.66 \times 10^{-27} \text{ kg}$  and its frequency from Table 10.2 is  $f =$

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

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

The force constant of the  $HF$  molecule is:

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

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  $1.35 \text{ cm}$  (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  $\ell_1$  to  $\ell_2$  is:

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

- (b) The moment of inertia  $I$  can be calculated from one of the wavelength:

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

### 10.3 Problem 10.7

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

- the effective force constant and
- the amplitude of vibration for each molecule.
- 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:

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

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

- 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:

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

(b) The amplitude of vibration is:

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

(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  $4.5 \text{ eV}$ . Assuming that this molecule behaves exactly like a harmonic oscillator with classical frequency  $\omega = 8.277 \times 10^{14} \text{ rad/s}$ , find the vibrational quantum number corresponding to its  $4.5\text{-eV}$  dissociation energy.

### Solution

The vibrational energy of the molecule is:

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

If we take  $E_{vib}$  to be  $4.5\text{eV}$  and the given value of  $\omega$ , 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  $\nu$  has to be 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 10.14

The allowed energies of vibration for the Morse oscillator can be shown to be

$$E_{vib} = \left(\nu + \frac{1}{2}\right) \hbar\omega - \left(\nu + \frac{1}{2}\right)^2 \frac{(\hbar\omega)^2}{4U_0} \quad \text{where } \nu = 0, 1, \dots$$

Obtain from this an expression for the interval separating successive levels of the Morse oscillator, and show that this interval diminishes steadily at higher energies, as illustrated in Figure 10.9b. From your result, deduce an upper limit for the vibrational quantum number  $\nu$ . What is the largest vibrational energy permitted for the Morse oscillator?

### Solution

The excitation energy from state  $\nu$  to state  $\nu + 1$  is:

$$\begin{aligned} \Delta E_{vib} &= \left(\nu + \frac{3}{2}\right) \hbar\omega - \left(\nu + \frac{3}{2}\right)^2 \frac{(\hbar\omega)^2}{4U_0} - \left(\nu + \frac{1}{2}\right) \hbar\omega + \left(\nu + \frac{1}{2}\right)^2 \frac{(\hbar\omega)^2}{4U_0} \\ &= \hbar\omega - \left\{ \left(\nu + \frac{3}{2}\right)^2 - \left(\nu + \frac{1}{2}\right)^2 \right\} \frac{(\hbar\omega)^2}{4U_0} \\ &= \hbar\omega - \{2(\nu + 1)\} \frac{(\hbar\omega)^2}{4U_0} \\ &= \hbar\omega \left\{ 1 - (\nu + 1) \frac{\hbar\omega}{2U_0} \right\} \end{aligned}$$

It is clear from the last equation that the excitation energy depends on  $\nu$ . It gets smaller with increasing  $\nu$ . Moreover, the excitation energy can never be negative, so the second term in the curly brackets can not exceed "1". This condition gives the highest vibrational state:

$$\begin{aligned} 1 &= (\nu + 1) \frac{\hbar\omega}{2U_0} \\ \nu_{max} &= \frac{2U_0}{\hbar\omega} - 1 \end{aligned}$$

The maximum vibrational excitation energy is then given by:

$$\begin{aligned} E_{vib_{max}} &= \left(\frac{2U_0}{\hbar\omega} + \frac{1}{2} - 1\right) \hbar\omega - \left(\frac{2U_0}{\hbar\omega} + \frac{1}{2} - 1\right)^2 \frac{(\hbar\omega)^2}{4U_0} \\ &= U_0 - \frac{(\hbar\omega)^2}{16U_0} \end{aligned}$$