Chapter 8 - Molecules

8-1:   The nuclear charge of $+2e$ is concentrated at the nucleus, while the electron charges' densities are spread out in (presumably) the $1s$ subshell. This means that the additional attractive force of the two protons exceeds the mutual repulsion of the electrons to increase the binding energy.

8-3:   Using 4.5 eV for the binding energy of hydrogen,

$$\frac{3}{2}\, kT = 4.5 \text{ eV} \qquad \text{or} \qquad T = \frac{2}{3}\, \frac{4.5 \text{ eV}}{8.617 \times 10^{-5} \text{ eV/K}} = 3.5 \times 10^4 \text{ K}.$$

8-5:   The increase in bond lengths in the molecule increases its moment of inertia and accordingly decreases the frequencies in its rotational spectrum (see Equation (8.9)). In addition, the higher the quantum number J (and hence the greater the angular momentum), the faster the rotation and the greater the distortion, so the spectral lines are no longer evenly spaced.

Quantitatively, the parameter I (the moment of inertia of the molecule) is a function of J, with I larger for higher J. Thus, all of the levels as given by Equation (8.11) are different, so that the spectral lines are not evenly spaced. (It should be noted that if I depends on J, the algebraic steps that lead to Equation (8.11) will not be valid.)

8-7:   From Equation (8.11), the ratios of the frequencies will be the ratio of the moments of inertia. For the different isotopes, the atomic separation, which depends on the charges of the atoms, will be essentially the same. The ratio of the moments of inertia will then be the ratio of the reduced masses. Denoting the unknown mass number by x and the ratio of the frequencies as r, r in terms of x is

$$r = \frac{\dfrac{x \cdot 16}{x + 16}}{\dfrac{12 \cdot 16}{12 + 16}}.$$

Solving for x in terms of r,

$$x = \frac{48\, r}{7 - 3\, r}.$$

Using $r = (1.153)/(1.102)$ in the above expression gives $x = 13.007$, or the integer 13 to three significant figures.

8-9: The corresponding frequencies are, from $\nu = \dfrac{c}{\lambda}$, and keeping an extra significant figure, in multiples of 10^{12} Hz:

$$2.484, \qquad 3.113, \qquad 4.337, \qquad 4.947$$

The average spacing of these frequencies is $\Delta\nu = 0.616 \times 10^{12}$ Hz. (A least-squares fit from a spreadsheet program gives 0.6151 if $c = 2.998 \times 10^8$ m/s is used.) From Equation (8.11), the spacing of the frequencies should be $\Delta\nu = \dfrac{\hbar}{2\pi I}$; Solving for I and using $\Delta\nu$ as found above,

$$I = \frac{\hbar}{2\pi\Delta\nu} = \frac{\left(1.055 \times 10^{-34}\ \text{J·s}\right)}{2\pi\left(0.6151 \times 10^{-12}\ \text{Hz}\right)} = 2.73 \times 10^{-47}\ \text{kg·m}^2.$$

The reduced mass of the HCl molecule is $(35/36)m_H$, and so the distance between the nuclei is

$$R = \sqrt{\frac{I}{m'}} = \sqrt{\frac{(36)\left(2.73 \times 10^{-47}\ \text{kg·m}^2\right)}{(35)\left(1.6736 \times 10^{-27}\ \text{kg}\right)}} = 0.129\ \text{nm}$$

(keeping extra significant figures in the intermediate calculation gives a result that is rounded to 0.130 nm to three significant figures).

8-11: Using $\nu_{1\to 0} = \dfrac{c}{\lambda}$ and $I = m'R^2$ in Equation (8.11) and solving for R,

$$R^2 = \frac{\hbar\lambda}{2\pi\,m'\,c}.$$

For this atom, $m' = m_H(200 \cdot 35)/(200 + 35)$, and

$$R = \sqrt{\frac{\left(1.055 \times 10^{-34}\ \text{J·s}\right)\left(4.4 \times 10^{-2}\ \text{m}\right)}{2\pi\left(1.6736 \times 10^{-27}\ \text{kg}\right)\left(2.998 \times 10^8\ \text{m/s}\right)}\frac{235}{200 \cdot 35}} = 0.223\ \text{nm},$$

or 0.22 nm to two significant figures.

8-13: Equation (8.11) may be re-expressed in terms of the frequency of the emitted photon when the molecule drops from the J rotational level to the $J - 1$ rotational level,

$$\nu_{J\to J-1} = \frac{\hbar J}{2\pi I}.$$

For large J, the angular momentum of the molecule in its initial state is

$$L = \hbar\sqrt{J(J+1)} = \hbar J\sqrt{1 + \frac{1}{J}} \approx \hbar J.$$

Thus, for large J,

$$\nu \approx \frac{L}{2\pi I}, \qquad \text{or} \qquad L = \omega I,$$

the classical expression.

8-15: The shape of the curve in Figure 8.18 will be the same for either isotope; that is, the value of k in Equation (8.14) will be the same. HD has the greater reduced mass, and hence the smaller frequency of vibration ν_0 and the smaller zero-point energy. HD is the more tightly bound, and has the greater binding energy since its zero-point energy contributes less energy to the splitting of the molecule.

8-17: (a) Using $m' = (19/20)m_H$ in Equation (8.15),

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{966 \text{ N/m}}{(1.6736 \times 10^{-27} \text{ kg})}\frac{20}{19}} = 1.24 \times 10^{14} \text{ Hz.}$$

(b) $E_0 = (1/2)\hbar\sqrt{\dfrac{k}{m'}} = 4.11 \times 10^{-20}$ J. The levels are shown below, where the vertical scale is in units of 10^{-20} J and the horizontal scale is in units of 10^{-11} m.
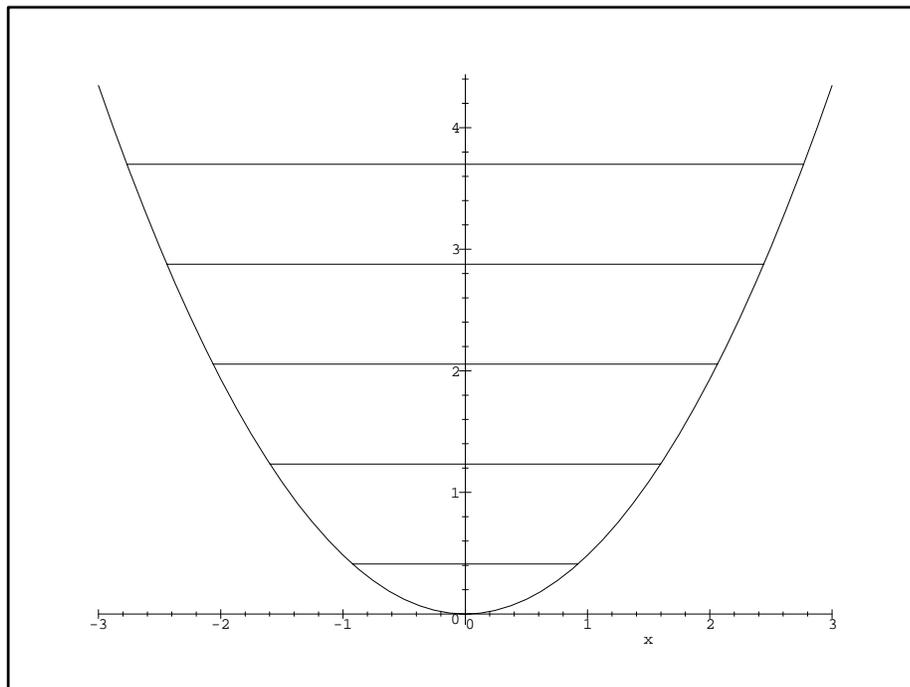
8-19: From Equation (8.16), the lower energy levels are separated by $\Delta E = h\nu_0$, and $\nu_0 = \Delta E/h$. Solving Equation (8.15) for k,

$$k = m' \left(2\pi\,\nu_0\right)^2 = m' \left(\frac{\Delta E}{\hbar}\right).$$

Using $m' = m_H(23 \cdot 35)/(23 + 35)$,

$$k = \frac{23 \cdot 35}{58} \left(1.6736 \times 10^{-27} \text{ kg}\right) \left(\frac{(0.063 \text{ eV}) \left(1.602 \times 10^{-19} \text{ J/eV}\right)}{\left(4.136 \times 10^{-15} \text{ eV·s}\right)}\right) = 213 \text{ N/m},$$

or 2.1×10^2 N/m to the given two significant figures.

8-21: Using

$$\Delta E = h\,\nu_0 = \hbar \sqrt{\frac{k}{m'}} \qquad \text{and} \qquad m' = m_H \frac{35}{36},$$

$$\Delta E = \left(1.055 \times 10^{-34} \text{ J·s}\right) \sqrt{\frac{516 \text{ N/m}}{1.6736 \times 10^{-27} \text{ kg}} \frac{36}{35}} = 5.94 \times 10^{-20} \text{ J} = 0.371 \text{ eV}.$$

At room temperature of about 300 K,

$$k\,T = \left(8.617 \times 10^{-5} \text{ eV/K}\right) (300 \text{ K}) = 0.026 \text{ eV}.$$

An individual atom is not likely to be vibrating in its first excited level, but in a large collection of atoms, it is likely that some of these atoms will be in the first excited state.

It's important to note that in the above calculations, the symbol "k" has been used for both a spring constant and Boltzmann's constant, quantities that are not interchangeable.