

MOLECULES AND CONDENSED MATTER

42.1. IDENTIFY: The minimum energy the photon must have is the energy of the covalent bond.

SET UP: The energy of the photon is $E = \frac{hc}{\lambda}$. Visible light has wavelengths between 400 nm and 700 nm.

EXECUTE: The photon must have energy 4.48 eV. Solving for the wavelength gives

$$\lambda = \frac{hc}{E} = \frac{1.24 \times 10^{-6} \text{ eV} \cdot \text{m}}{4.48 \text{ eV}} = 277 \text{ nm}.$$

EVALUATE: This wavelength is shorter than the wavelengths of visible light so lies in the ultraviolet.

42.2. IDENTIFY and SET UP: $U = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$. The binding energy of the molecule is equal to U plus the ionization energy of K minus the electron affinity of Br.

EXECUTE: (a) $U = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -5.0 \text{ eV}.$

(b) $-5.0 \text{ eV} + (4.3 \text{ eV} - 3.5 \text{ eV}) = -4.2 \text{ eV}.$

EVALUATE: We expect the magnitude of the binding energy to be somewhat less than this estimate. At this separation the two ions don't behave exactly like point charges and U is smaller in magnitude than our estimate. The experimental value for the binding energy is -4.0 eV , which is smaller in magnitude than our estimate.

42.3. IDENTIFY: Set $\frac{3}{2}kT$ equal to the specified bond energy E .

SET UP: $k = 1.38 \times 10^{-23} \text{ J/K}.$

EXECUTE: (a) $E = \frac{3}{2}kT \Rightarrow T = \frac{2E}{3k} = \frac{2(7.9 \times 10^{-4} \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{3(1.38 \times 10^{-23} \text{ J/K})} = 6.1 \text{ K}.$

(b) $T = \frac{2(4.48 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{3(1.38 \times 10^{-23} \text{ J/K})} = 34,600 \text{ K}.$

EVALUATE: (c) The thermal energy associated with room temperature (300 K) is much greater than the bond energy of He_2 (calculated in part (a)), so the typical collision at room temperature will be more than enough to break up He_2 . However, the thermal energy at 300 K is much less than the bond energy of H_2 , so we would expect it to remain intact at room temperature.

42.4. IDENTIFY: If the photon has too little energy, it cannot alter atomic energy levels.

SET UP: $\Delta E = \frac{hc}{\lambda}$. Atomic energy levels are separated by a few eV. Vibrational levels are separated by a few tenths of an eV. Rotational levels are separated by a few thousandths of an eV or less.

EXECUTE: (a) $\Delta E = \frac{hc}{\lambda} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{3.10 \times 10^{-3} \text{ m}} = 4.00 \times 10^{-4} \text{ eV}.$ This is a typical transition energy for a rotational transition.

$$(b) \Delta E = \frac{hc}{\lambda} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{207 \times 10^{-9} \text{ m}} = 5.99 \text{ eV. This is a typical transition energy for a}$$

transition between atomic energy levels.

EVALUATE: As the transition energy increases, the photon requires a shorter and shorter wavelength to cause transitions.

- 42.5. IDENTIFY:** The energy of the photon is equal to the energy difference between the $l = 1$ and $l = 2$ states. This energy determines its wavelength.

SET UP: The reduced mass of the molecule is $m_r = \frac{m_H m_H}{m_H + m_H} = \frac{1}{2} m_H$, its moment of inertia is $I = m_r r_0^2$,

the photon energy is $\Delta E = \frac{hc}{\lambda}$, and the energy of the state l is $E_l = l(l+1) \frac{\hbar^2}{2I}$.

EXECUTE: $I = m_r r_0^2 = \frac{1}{2} (1.67 \times 10^{-27} \text{ kg})(0.074 \times 10^{-9} \text{ m})^2 = 4.57 \times 10^{-48} \text{ kg} \cdot \text{m}^2$. Using $E_l = l(l+1) \frac{\hbar^2}{2I}$,

the energy levels are $E_2 = 6 \frac{\hbar^2}{2I} = 6 \frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(4.57 \times 10^{-48} \text{ kg} \cdot \text{m}^2)} = 6(1.218 \times 10^{-21} \text{ J}) = 7.307 \times 10^{-21} \text{ J}$ and

$E_1 = 2 \frac{\hbar^2}{2I} = 2(1.218 \times 10^{-21} \text{ J}) = 2.436 \times 10^{-21} \text{ J}$. $\Delta E = E_2 - E_1 = 4.87 \times 10^{-21} \text{ J}$. Using $\Delta E = \frac{hc}{\lambda}$ gives

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{4.871 \times 10^{-21} \text{ J}} = 4.08 \times 10^{-5} \text{ m} = 40.8 \mu\text{m}.$$

EVALUATE: This wavelength is much longer than that of visible light.

- 42.6. IDENTIFY:** The energy decrease of the molecule or atom is equal to the energy of the emitted photon. From this energy, we can calculate the wavelength of the photon.

SET UP: $\Delta E = \frac{hc}{\lambda}$.

EXECUTE: (a) $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{0.250 \text{ eV}} = 4.96 \mu\text{m}.$

EVALUATE: This radiation is in the infrared.

(b) $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{8.50 \text{ eV}} = 146 \text{ nm}.$

EVALUATE: This radiation is in the ultraviolet.

(c) $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{3.20 \times 10^{-3} \text{ eV}} = 388 \mu\text{m}.$

EVALUATE: This radiation is in the microwave region.

- 42.7. IDENTIFY:** The energy given to the photon comes from a transition between rotational states.

SET UP: The rotational energy of a molecule is $E = l(l+1) \frac{\hbar^2}{2I}$ and the energy of the photon is $E = hc/\lambda$.

EXECUTE: Use the energy formula, the energy difference between the $l = 3$ and $l = 1$ rotational levels of

the molecule is $\Delta E = \frac{\hbar^2}{2I} [3(3+1) - 1(1+1)] = \frac{5\hbar^2}{I}$. Since $\Delta E = hc/\lambda$, we get $hc/\lambda = 5\hbar^2/I$. Solving for I gives

$$I = \frac{5\hbar\lambda}{2\pi c} = \frac{5(1.055 \times 10^{-34} \text{ J} \cdot \text{s})(1.780 \text{ nm})}{2\pi(3.00 \times 10^8 \text{ m/s})} = 4.981 \times 10^{-52} \text{ kg} \cdot \text{m}^2.$$

Using $I = m_r r_0^2$, we can solve for r_0 :

$$r_0 = \sqrt{\frac{I(m_N + m_H)}{m_N m_H}} = \sqrt{\frac{(4.981 \times 10^{-52} \text{ kg} \cdot \text{m}^2)(2.33 \times 10^{-26} \text{ kg} + 1.67 \times 10^{-27} \text{ kg})}{(2.33 \times 10^{-26} \text{ kg})(1.67 \times 10^{-27} \text{ kg})}} \quad r_0 = 5.65 \times 10^{-13} \text{ m}$$

EVALUATE: This separation is much smaller than the diameter of a typical atom and is not very realistic. But we are treating a *hypothetical* NH molecule.

42.8. IDENTIFY: The transition energy E and the frequency f of the absorbed photon are related by $E = hf$.

EXECUTE: The energy of the emitted photon is 1.01×10^{-5} eV, and so its frequency and wavelength are

$$f = \frac{E}{h} = \frac{(1.01 \times 10^{-5} \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})} = 2.44 \text{ GHz} = 2440 \text{ MHz and}$$

$$\lambda = \frac{c}{f} = \frac{(3.00 \times 10^8 \text{ m/s})}{(2.44 \times 10^9 \text{ Hz})} = 0.123 \text{ m.}$$

EVALUATE: This frequency corresponds to that given for a microwave oven.

42.9. IDENTIFY: Apply Eq. (42.5).

SET UP: Let 1 refer to C and 2 to O. $m_1 = 1.993 \times 10^{-26}$ kg, $m_2 = 2.656 \times 10^{-26}$ kg, $r_0 = 0.1128$ nm.

EXECUTE: (a) $r_1 = \left(\frac{m_2}{m_1 + m_2} \right) r_0 = 0.0644 \text{ nm (carbon)}$; $r_2 = \left(\frac{m_1}{m_1 + m_2} \right) r_0 = 0.0484 \text{ nm (oxygen)}$

(b) $I = m_1 r_1^2 + m_2 r_2^2 = 1.45 \times 10^{-46} \text{ kg} \cdot \text{m}^2$; yes, this agrees with Example 42.2.

EVALUATE: $I = m_1 r_1^2 + m_2 r_2^2$ and $I = m_r r_0^2$ give equivalent results.

42.10. IDENTIFY: $I = m_1 r_1^2 + m_2 r_2^2$. Since the two atoms are identical, the center of mass is midway between them.

SET UP: Each atom has a mass m and is at a distance $L/2$ from the center of mass.

EXECUTE: The moment of inertia is $2(m) = (L/2)^2 = mL^2/2 = 2.21 \times 10^{-44} \text{ kg} \cdot \text{m}^2$.

EVALUATE: $r_0 = L$ and $m_r = m/2$, so $I = m_r r_0^2$ gives the same result.

42.11. IDENTIFY and SET UP: Set $K = E_1$ from Example 42.2. Use $K = \frac{1}{2} I \omega^2$ to solve for ω and $v = r\omega$ to solve for v .

EXECUTE: (a) From Example 42.2, $E_1 = 0.479 \text{ meV} = 7.674 \times 10^{-23} \text{ J}$ and $I = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2$

$$K = \frac{1}{2} I \omega^2 \text{ and } K = E \text{ gives } \omega = \sqrt{2E_1/I} = 1.03 \times 10^{12} \text{ rad/s}$$

(b) $v_1 = r_1 \omega_1 = (0.0644 \times 10^{-9} \text{ m})(1.03 \times 10^{12} \text{ rad/s}) = 66.3 \text{ m/s (carbon)}$

$v_2 = r_2 \omega_2 = (0.0484 \times 10^{-9} \text{ m})(1.03 \times 10^{12} \text{ rad/s}) = 49.8 \text{ m/s (oxygen)}$

(c) $T = 2\pi/\omega = 6.10 \times 10^{-12} \text{ s}$

EVALUATE: Even for fast rotation rates, $v \ll c$.

42.12. IDENTIFY: For a $n \rightarrow n-1$ vibrational transition, $\Delta E = \hbar \sqrt{\frac{k'}{m_r}}$. ΔE is related to λ of the photon by $\Delta E = \frac{hc}{\lambda}$.

SET UP: $m_r = \frac{m_{\text{Na}} m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}}$.

EXECUTE: $\Delta E = \frac{hc}{\lambda} = \hbar \sqrt{k'/m_r}$, and solving for k' , $k' = \left(\frac{2\pi c}{\lambda} \right)^2 m_r = 205 \text{ N/m}$.

EVALUATE: The value of k' we calculated for NaCl is comparable to that of a fairly stiff lab spring.

42.13. IDENTIFY and SET UP: The energy of a rotational level with quantum number l is $E_l = l(l+1)\hbar^2/2I$

(Eq. (42.3)). $I = m_r r^2$, with the reduced mass m_r given by Eq. (42.4). Calculate I and ΔE and then use $\Delta E = hc/\lambda$ to find λ .

EXECUTE: (a) $m_r = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_{\text{Li}} m_{\text{H}}}{m_{\text{Li}} + m_{\text{H}}} = \frac{(1.17 \times 10^{-26} \text{ kg})(1.67 \times 10^{-27} \text{ kg})}{1.17 \times 10^{-26} \text{ kg} + 1.67 \times 10^{-27} \text{ kg}} = 1.461 \times 10^{-27} \text{ kg}$

$I = m_r r^2 = (1.461 \times 10^{-27} \text{ kg})(0.159 \times 10^{-9} \text{ m})^2 = 3.694 \times 10^{-47} \text{ kg} \cdot \text{m}^2$

$l = 3: E = 3(4) \left(\frac{\hbar^2}{2I} \right) = 6 \left(\frac{\hbar^2}{I} \right)$

$$l = 4: E = 4(5) \left(\frac{\hbar^2}{2I} \right) = 10 \left(\frac{\hbar^2}{I} \right)$$

$$\Delta E = E_4 - E_3 = 4 \left(\frac{\hbar^2}{I} \right) = 4 \left(\frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{3.694 \times 10^{-47} \text{ kg} \cdot \text{m}^2} \right) = 1.20 \times 10^{-21} \text{ J} = 7.49 \times 10^{-3} \text{ eV}$$

$$\text{(b) } \Delta E = hc/\lambda \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV})(2.998 \times 10^8 \text{ m/s})}{7.49 \times 10^{-3} \text{ eV}} = 166 \mu\text{m}$$

EVALUATE: LiH has a smaller reduced mass than CO and λ is somewhat smaller here than the λ calculated for CO in Example 42.2

- 42.14. IDENTIFY:** The vibrational energy of the molecule is related to its force constant and reduced mass, while the rotational energy depends on its moment of inertia, which in turn depends on the reduced mass.

SET UP: The vibrational energy is $E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}}$ and the rotational energy is

$$E_l = l(l+1) \frac{\hbar^2}{2I}.$$

EXECUTE: For a vibrational transition, we have $\Delta E_v = \hbar\sqrt{\frac{k'}{m_r}}$, so we first need to find m_r . The energy

for a rotational transition is $\Delta E_R = \frac{\hbar^2}{2I}[2(2+1) - 1(1+1)] = \frac{2\hbar^2}{I}$. Solving for I and using the fact that

$I = m_r r_0^2$, we have $m_r r_0^2 = \frac{2\hbar^2}{\Delta E_R}$, which gives

$$m_r = \frac{2\hbar^2}{r_0^2 \Delta E_R} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})(6.583 \times 10^{-16} \text{ eV} \cdot \text{s})}{(0.8860 \times 10^{-9} \text{ m})^2 (8.841 \times 10^{-4} \text{ eV})} = 2.0014 \times 10^{-28} \text{ kg}$$

Now look at the vibrational transition to find the force constant.

$$\Delta E_v = \hbar\sqrt{\frac{k'}{m_r}} \Rightarrow k' = \frac{m_r (\Delta E_v)^2}{\hbar^2} = \frac{(2.0014 \times 10^{-28} \text{ kg})(0.2560 \text{ eV})^2}{(6.583 \times 10^{-16} \text{ eV} \cdot \text{s})^2} = 30.27 \text{ N/m}$$

EVALUATE: This would be a rather weak spring in the laboratory.

- 42.15. IDENTIFY and SET UP:** The energy of a rotational level is given in Eq. (42.3). The transition energy ΔE and the frequency f of the photon are related by $\Delta E = hf$.

$$\text{EXECUTE: (a) } E_l = \frac{l(l+1)\hbar^2}{2I}, E_{l-1} = \frac{l(l-1)\hbar^2}{2I} \Rightarrow \Delta E = \frac{\hbar^2}{2I}(l^2 + l - l^2 + l) = \frac{l\hbar^2}{I}$$

$$\text{(b) } f = \frac{\Delta E}{h} = \frac{\Delta E}{2\pi\hbar} = \frac{l\hbar}{2\pi I}.$$

EVALUATE: ΔE and f increase with l because the separation between adjacent energy levels increases with l .

- 42.16. IDENTIFY:** Find ΔE for the transition and compute λ from $\Delta E = hc/\lambda$.

SET UP: From Example 42.2, $E_l = l(l+1) \frac{\hbar^2}{2I}$, with $\frac{\hbar^2}{2I} = 0.2395 \times 10^{-3} \text{ eV}$. $\Delta E = 0.2690 \text{ eV}$ is the

spacing between vibrational levels. Thus $E_n = (n + \frac{1}{2})\hbar\omega$, with $\hbar\omega = 0.2690 \text{ eV}$. By Eq. (42.9),

$$E = E_n + E_l = (n + \frac{1}{2})\hbar\omega + l(l+1) \frac{\hbar^2}{2I}.$$

EXECUTE: (a) $n = 0 \rightarrow n = 1$ and $l = 1 \rightarrow l = 2$

$$\text{For } n = 0, l = 1, E_i = \frac{1}{2}\hbar\omega + 2 \left(\frac{\hbar^2}{2I} \right).$$

$$\text{For } n=1, l=2, E_f = \frac{3}{2}\hbar\omega + 6\left(\frac{\hbar^2}{2I}\right).$$

$$\Delta E = E_f - E_i = \hbar\omega + 4\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} + 4(0.2395 \times 10^{-3} \text{ eV}) = 0.2700 \text{ eV}$$

$$\frac{hc}{\lambda} = \Delta E \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2700 \text{ eV}} = 4.592 \times 10^{-6} \text{ m} = 4.592 \mu\text{m}$$

(b) $n=0 \rightarrow n=1$ and $l=2 \rightarrow l=1$

$$\text{For } n=0, l=2, E_i = \frac{1}{2}\hbar\omega + 6\left(\frac{\hbar^2}{2I}\right).$$

$$\text{For } n=1, l=1, E_f = \frac{3}{2}\hbar\omega + 2\left(\frac{\hbar^2}{2I}\right).$$

$$\Delta E = E_f - E_i = \hbar\omega - 4\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} - 4(0.2395 \times 10^{-3} \text{ eV}) = 0.2680 \text{ eV}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2680 \text{ eV}} = 4.627 \times 10^{-6} \text{ m} = 4.627 \mu\text{m}$$

(c) $n=0 \rightarrow n=1$ and $l=3 \rightarrow l=2$

$$\text{For } n=0, l=3, E_i = \frac{1}{2}\hbar\omega + 12\left(\frac{\hbar^2}{2I}\right).$$

$$\text{For } n=1, l=2, E_f = \frac{3}{2}\hbar\omega + 6\left(\frac{\hbar^2}{2I}\right).$$

$$\Delta E = E_f - E_i = \hbar\omega - 6\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} - 6(0.2395 \times 10^{-3} \text{ eV}) = 0.2676 \text{ eV}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2676 \text{ eV}} = 4.634 \times 10^{-6} \text{ m} = 4.634 \mu\text{m}$$

EVALUATE: All three transitions are for $n=0 \rightarrow n=1$. The spacing between vibrational levels is larger than the spacing between rotational levels, so the difference in λ for the various rotational transitions is small. When the transition is to a larger l , $\Delta E > \hbar\omega$ and when the transition is to a smaller l , $\Delta E < \hbar\omega$.

42.17. IDENTIFY and SET UP: Find the volume occupied by each atom. The density is the average mass of Na and Cl divided by this volume.

EXECUTE: Each atom occupies a cube with side length 0.282 nm. Therefore, the volume occupied by each atom is $V = (0.282 \times 10^{-9} \text{ m})^3 = 2.24 \times 10^{-29} \text{ m}^3$. In NaCl there are equal numbers of Na and Cl atoms, so the average mass of the atoms in the crystal is

$$m = \frac{1}{2}(m_{\text{Na}} + m_{\text{Cl}}) = \frac{1}{2}(3.82 \times 10^{-26} \text{ kg} + 5.89 \times 10^{-26} \text{ kg}) = 4.855 \times 10^{-26} \text{ kg}$$

$$\text{The density then is } \rho = \frac{m}{V} = \frac{4.855 \times 10^{-26} \text{ kg}}{2.24 \times 10^{-29} \text{ m}^3} = 2.17 \times 10^3 \text{ kg/m}^3.$$

EVALUATE: The density of water is $1.00 \times 10^3 \text{ kg/m}^3$, so our result is reasonable.

42.18. IDENTIFY and SET UP: For an average spacing a , the density is $\rho = m/a^3$, where m is the average of the ionic masses.

$$\text{EXECUTE: } a^3 = \frac{m}{\rho} = \frac{(6.49 \times 10^{-26} \text{ kg} + 1.33 \times 10^{-25} \text{ kg})/2}{(2.75 \times 10^3 \text{ kg/m}^3)} = 3.60 \times 10^{-29} \text{ m}^3, \text{ and}$$

$$a = 3.30 \times 10^{-10} \text{ m} = 0.330 \text{ nm}.$$

EVALUATE: (b) Exercise 42.17 says that the average spacing for NaCl is 0.282 nm. The larger (higher atomic number) atoms have the larger spacing.

42.19. IDENTIFY: The energy gap is the energy of the maximum-wavelength photon.

SET UP: The energy difference is equal to the energy of the photon, so $\Delta E = hc/\lambda$.

EXECUTE: (a) Using the photon wavelength to find the energy difference gives

$$\Delta E = hc/\lambda = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})/(1.11 \times 10^{-6} \text{ m}) = 1.12 \text{ eV}$$

(b) A wavelength of $1.11 \mu\text{m} = 1110 \text{ nm}$ is in the infrared, shorter than that of visible light.

EVALUATE: Since visible photons have more than enough energy to excite electrons from the valence to the conduction band, visible light will be absorbed, which makes silicon opaque.

42.20. IDENTIFY and SET UP: $\Delta E = \frac{hc}{\lambda}$, where ΔE is the band gap.

EXECUTE: (a) $\lambda = \frac{hc}{\Delta E} = 2.27 \times 10^{-7} \text{ m} = 227 \text{ nm}$, in the ultraviolet.

EVALUATE: (b) Visible light lacks enough energy to excite the electrons into the conduction band, so visible light passes through the diamond unabsorbed.

(c) Impurities can lower the gap energy making it easier for the material to absorb shorter wavelength visible light. This allows longer wavelength visible light to pass through, giving the diamond color.

42.21. IDENTIFY and SET UP: The energy ΔE deposited when a photon with wavelength λ is absorbed is

$$\Delta E = \frac{hc}{\lambda}.$$

EXECUTE: $\Delta E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{9.31 \times 10^{-13} \text{ m}} = 2.14 \times 10^{-13} \text{ J} = 1.34 \times 10^6 \text{ eV}$. So the number

of electrons that can be excited to the conduction band is $n = \frac{1.34 \times 10^6 \text{ eV}}{1.12 \text{ eV}} = 1.20 \times 10^6$ electrons.

EVALUATE: A photon of wavelength

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.13 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{1.12 \text{ eV}} = 1.11 \times 10^{-6} \text{ m} = 1110 \text{ nm}$$
 can excite one electron. This

photon is in the infrared.

42.22. IDENTIFY: Set $\frac{3}{2}kT = \frac{1}{2}mv_{\text{rms}}^2$.

SET UP: $k = 1.38 \times 10^{-23} \text{ J/K}$. $m = 9.11 \times 10^{-31} \text{ kg}$.

EXECUTE: $v_{\text{rms}} = \sqrt{3kT/m} = 1.17 \times 10^5 \text{ m/s}$, as found in Example 42.8.

EVALUATE: Temperature plays a very small role in determining the properties of electrons in metals. Instead, the average energies and corresponding speeds are determined almost exclusively by the exclusion principle.

42.23. IDENTIFY: $g(E)$ is given by Eq. (42.10).

SET UP: $m = 9.11 \times 10^{-31} \text{ kg}$, the mass of an electron.

EXECUTE: $g(E) = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3} E^{1/2} = \frac{(2(9.11 \times 10^{-31} \text{ kg}))^{3/2}(1.0 \times 10^{-6} \text{ m}^3)(5.0 \text{ eV})^{1/2}(1.60 \times 10^{-19} \text{ J/eV})^{1/2}}{2\pi^2(1.054 \times 10^{-34} \text{ J} \cdot \text{s})^3}$.

$$g(E) = (9.5 \times 10^{40} \text{ states/J})(1.60 \times 10^{-19} \text{ J/eV}) = 1.5 \times 10^{22} \text{ states/eV}.$$

EVALUATE: For a metal the density of states expressed as states/eV is very large.

42.24. IDENTIFY and SET UP: Combine Eqs. (42.11) and (42.12) to eliminate n_{fs} .

EXECUTE: Eq. (42.12) may be solved for $n_{\text{fs}} = (2mE)^{1/2} (L/\hbar\pi)$, and substituting this into Eq. (42.11), using $L^3 = V$, gives Eq. (42.13).

EVALUATE: n is the total number of states with energy of E or less.

42.25. (a) IDENTIFY and SET UP: The electron contribution to the molar heat capacity at constant volume of a

$$\text{metal is } C_V = \left(\frac{\pi^2 KT}{2E_F} \right) R.$$

EXECUTE: $C_V = \frac{\pi^2(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})}{2(5.48 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})} R = 0.0233R.$

(b) EVALUATE: The electron contribution found in part (a) is $0.0233R = 0.194 \text{ J/mol} \cdot \text{K}$. This is $0.194/25.3 = 7.67 \times 10^{-3} = 0.767\%$ of the total C_V .

(c) Only a small fraction of C_V is due to the electrons. Most of C_V is due to the vibrational motion of the ions.

42.26. IDENTIFY: Eq. (42.21) relates E_{av} and E_{F0} , the Fermi energy at absolute zero. The speed v is related to E_{av} by $\frac{1}{2}mv^2 = E_{\text{av}}$.

SET UP: $k = 1.38 \times 10^{-23} \text{ J/K}$.

EXECUTE: (a) $E_{\text{av}} = \frac{3}{5}E_{\text{F}} = 1.94 \text{ eV}.$

(b) $v = \sqrt{2E_{\text{av}}/m} = \sqrt{\frac{2(1.94 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{9.11 \times 10^{-31} \text{ kg}}} = 8.25 \times 10^5 \text{ m/s}.$

(c) $\frac{E_{\text{F}}}{k} = \frac{(3.23 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{(1.38 \times 10^{-23} \text{ J/K})} = 3.74 \times 10^4 \text{ K}.$

EVALUATE: The Fermi energy of sodium is less than that of copper. Therefore, the values of E_{av} and v we have calculated for sodium are less than those calculated for copper in Example 42.7.

42.27. IDENTIFY: The probability is given by the Fermi-Dirac distribution.

SET UP: The Fermi-Dirac distribution is $f(E) = \frac{1}{e^{(E-E_{\text{F}})/kT} + 1}.$

EXECUTE: We calculate the value of $f(E)$, where $E = 8.520 \text{ eV}$, $E_{\text{F}} = 8.500 \text{ eV}$,

$k = 1.38 \times 10^{-23} \text{ J/K} = 8.625 \times 10^{-5} \text{ eV/K}$, and $T = 20^\circ\text{C} = 293 \text{ K}$. The result is $f(E) = 0.312 = 31.2\%$.

EVALUATE: Since the energy is close to the Fermi energy, the probability is quite high that the state is occupied by an electron.

42.28. IDENTIFY and SET UP: Follow the procedure of Example 42.9. Evaluate $f(E)$ in Eq. (42.16) for $E - E_{\text{F}} = E_{\text{g}}/2$, where E_{g} is the band gap.

EXECUTE: (a) The probabilities are 1.78×10^{-7} , 2.37×10^{-6} , and 1.51×10^{-5} .

(b) The Fermi distribution, Eq. (42.16), has the property that $f(E_{\text{F}} - E) = 1 - f(E)$ (see Problem (42.50)), and so the probability that a state at the top of the valence band is occupied is the same as the probability that a state of the bottom of the conduction band is filled (this result depends on having the Fermi energy in the middle of the gap). Therefore, the probabilities at each T are the same as in part (a).

EVALUATE: The probabilities increase with temperature.

42.29. IDENTIFY: Use Eq. (42.16), $f(E) = \frac{1}{e^{(E-E_{\text{F}})/kT} + 1}$. Solve for $E - E_{\text{F}}$.

SET UP: $e^{(E-E_{\text{F}})/kT} = \frac{1}{f(E)} - 1$

The problem states that $f(E) = 4.4 \times 10^{-4}$ for E at the bottom of the conduction band.

EXECUTE: $e^{(E-E_{\text{F}})/kT} = \frac{1}{4.4 \times 10^{-4}} - 1 = 2.272 \times 10^3.$

$E - E_{\text{F}} = kT \ln(2.272 \times 10^3) = (1.3807 \times 10^{-23} \text{ J/K})(300 \text{ K}) \ln(2.272 \times 10^3) = 3.201 \times 10^{-20} \text{ J} = 0.20 \text{ eV}$

$E_{\text{F}} = E - 0.20 \text{ eV}$; the Fermi level is 0.20 eV below the bottom of the conduction band.

EVALUATE: The energy gap between the Fermi level and bottom of the conduction band is large compared to kT at $T = 300 \text{ K}$ and as a result $f(E)$ is small.

42.30. IDENTIFY: The wavelength of the photon to be detected depends on its energy.

SET UP: $\Delta E = \frac{hc}{\lambda}$.

EXECUTE: (a) $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{0.67 \text{ eV}} = 1.9 \text{ } \mu\text{m}$.

(b) $\lambda = (1.9 \text{ } \mu\text{m}) \left(\frac{0.67 \text{ eV}}{1.14 \text{ eV}} \right) = 1.1 \text{ } \mu\text{m}$.

EVALUATE: Both of these photons are in the infrared.

42.31. IDENTIFY: Knowing the saturation current of a p - n junction at a given temperature, we want to find the current at that temperature for various voltages.

SET UP: $I = I_S(e^{eV/kT} - 1)$.

EXECUTE: (a) (i) For $V = 1.00 \text{ mV}$, $\frac{eV}{kT} = \frac{(1.602 \times 10^{-19} \text{ C})(1.00 \times 10^{-3} \text{ V})}{(1.381 \times 10^{-23} \text{ J/K})(290 \text{ K})} = 0.0400$.

$I = (0.500 \text{ mA})(e^{0.0400} - 1) = 0.0204 \text{ mA}$.

(ii) For $V = -1.00 \text{ mV}$, $\frac{eV}{kT} = -0.0400$. $I = (0.500 \text{ mA})(e^{-0.0400} - 1) = -0.0196 \text{ mA}$.

(iii) For $V = 100 \text{ mV}$, $\frac{eV}{kT} = 4.00$. $I = (0.500 \text{ mA})(e^{4.00} - 1) = 26.8 \text{ mA}$.

(iv) For $V = -100 \text{ mV}$, $\frac{eV}{kT} = -4.00$. $I = (0.500 \text{ mA})(e^{-4.00} - 1) = -0.491 \text{ mA}$.

EXECUTE: (b) For small V , between $\pm 1.00 \text{ mV}$, $R = V/I$ is approximately constant and the diode obeys Ohm's law to a good approximation. For larger V the deviation from Ohm's law is substantial.

42.32. IDENTIFY: The current depends on the voltage across the diode and its temperature, so the resistance also depends on these quantities.

SET UP: The current is $I = I_S(e^{eV/kT} - 1)$ and the resistance is $R = V/I$.

EXECUTE: (a) The resistance is $R = \frac{V}{I} = \frac{V}{I_S(e^{eV/kT} - 1)}$. The exponent is

$\frac{eV}{kT} = \frac{e(0.0850 \text{ V})}{(8.625 \times 10^{-5} \text{ eV/K})(293 \text{ K})} = 3.3635$, giving $R = \frac{85.0 \text{ mV}}{(0.750 \text{ mA})(e^{3.3635} - 1)} = 4.06 \text{ } \Omega$.

(b) In this case, the exponent is $\frac{eV}{kT} = \frac{e(-0.050 \text{ V})}{(8.625 \times 10^{-5} \text{ eV/K})(293 \text{ K})} = -1.979$

which gives $R = \frac{-50.0 \text{ mV}}{(0.750 \text{ mA})(e^{-1.979} - 1)} = 77.4 \text{ } \Omega$

EVALUATE: Reversing the voltage can make a considerable change in the resistance of a diode.

42.33. IDENTIFY and SET UP: The voltage-current relation is given by Eq. (42.22): $I = I_S(e^{eV/kT} - 1)$. Use the current for $V = +15.0 \text{ mV}$ to solve for the constant I_S .

EXECUTE: (a) Find I_S : $V = +15.0 \times 10^{-3} \text{ V}$ gives $I = 9.25 \times 10^{-3} \text{ A}$

$\frac{eV}{kT} = \frac{(1.602 \times 10^{-19} \text{ C})(15.0 \times 10^{-3} \text{ V})}{(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.5800$

$I_S = \frac{I}{e^{eV/kT} - 1} = \frac{9.25 \times 10^{-3} \text{ A}}{e^{0.5800} - 1} = 1.177 \times 10^{-2} = 11.77 \text{ mA}$

Then can calculate I for $V = 10.0 \text{ mV}$: $\frac{eV}{kT} = \frac{(1.602 \times 10^{-19} \text{ C})(10.0 \times 10^{-3} \text{ V})}{(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.3867$

$I = I_S(e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{0.3867} - 1) = 5.56 \text{ mA}$

(b) $\frac{eV}{kT}$ has the same magnitude as in part (a) but not V is negative so $\frac{eV}{kT}$ is negative.

$$V = -15.0 \text{ mV}: \frac{eV}{kT} = -0.5800 \text{ and } I = I_s(e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{-0.5800} - 1) = -5.18 \text{ mA}$$

$$V = -10.0 \text{ mV}: \frac{eV}{kT} = -0.3867 \text{ and } I = I_s(e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{-0.3867} - 1) = -3.77 \text{ mA}$$

EVALUATE: There is a directional asymmetry in the current, with a forward-bias voltage producing more current than a reverse-bias voltage of the same magnitude, but the voltage is small enough for the asymmetry not be pronounced.

42.34. IDENTIFY: Apply Eq. (42.22).

SET UP: $I_s = 3.60 \text{ mA}$. $\ln e^x = x$

EXECUTE: (a) Solving Eq. (42.22) for the voltage as a function of current,

$$V = \frac{kT}{e} \ln \left(\frac{I}{I_s} + 1 \right) = \frac{kT}{e} \ln \left(\frac{40.0 \text{ mA}}{3.60 \text{ mA}} + 1 \right) = 0.0645 \text{ V}.$$

(b) From part (a), the quantity $e^{eV/kT} = 12.11$, so far a reverse-bias voltage of the same magnitude,

$$I = I_s(e^{-eV/kT} - 1) = I_s \left(\frac{1}{12.11} - 1 \right) = -3.30 \text{ mA}.$$

EVALUATE: The reverse bias current for a given magnitude of voltage is much less than the forward bias current.

42.35. IDENTIFY: During the transition, the molecule emits a photon of light having energy equal to the energy difference between the two vibrational states of the molecule.

SET UP: The vibrational energy is $E_n = \left(n + \frac{1}{2}\right)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m_r}}$.

EXECUTE: (a) The energy difference between two adjacent energy states is $\Delta E = \hbar\sqrt{\frac{k'}{m_r}}$, and this is the energy of the photon, so $\Delta E = hc/\lambda$. Equating these two expressions for ΔE and solving for k' , we have

$$k' = m_r \left(\frac{\Delta E}{\hbar} \right)^2 = \frac{m_H m_O}{m_H + m_O} \left(\frac{\Delta E}{\hbar} \right)^2, \text{ and using } \frac{\Delta E}{\hbar} = \frac{hc/\lambda}{\hbar} = \frac{2\pi c}{\lambda} \text{ with the appropriate numbers gives us}$$

$$k' = \frac{(1.67 \times 10^{-27} \text{ kg})(2.656 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 2.656 \times 10^{-26} \text{ kg}} \left[\frac{2\pi(3.00 \times 10^8 \text{ m/s})}{2.39 \times 10^{-6} \text{ m}} \right]^2 = 977 \text{ N/m}$$

(b) $f = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k'}{m_r}} = \frac{1}{2\pi} \sqrt{\frac{m_H m_O}{m_H + m_O} \frac{k'}{k'}}$. Substituting the appropriate numbers gives us

$$f = \frac{1}{2\pi} \sqrt{\frac{(1.67 \times 10^{-27} \text{ kg})(2.656 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 2.656 \times 10^{-26} \text{ kg}} \frac{977 \text{ N/m}}{977 \text{ N/m}}} = 1.25 \times 10^{14} \text{ Hz}$$

EVALUATE: The frequency is close to, but not quite in, the visible range.

42.36. IDENTIFY and SET UP: $E_l = l(l+1)\frac{\hbar^2}{2I}$. ΔE for the molecule is related to λ for the photon by $\Delta E = \frac{hc}{\lambda}$.

EXECUTE: $E_2 = 3\frac{\hbar^2}{I}$ and $E_1 = \frac{\hbar^2}{I}$, so $\Delta E = \frac{2\hbar^2}{I}$. $I = \frac{2\hbar^2}{\Delta E} = \frac{h\lambda}{2\pi^2 c} = 7.14 \times 10^{-48} \text{ kg} \cdot \text{m}^2$.

EVALUATE: The I we calculated is approximately a factor of 20 times smaller than I calculated for the CO molecule in Example 42.2.

- 42.37. IDENTIFY and SET UP:** Eq. (21.14) gives the electric dipole moment as $p = qd$, where the dipole consists of charges $\pm q$ separated by distance d .

EXECUTE: (a) Point charges $+e$ and $-e$ separated by distance d , so

$$p = ed = (1.602 \times 10^{-19} \text{ C})(0.24 \times 10^{-9} \text{ m}) = 3.8 \times 10^{-29} \text{ C} \cdot \text{m}$$

$$\text{(b) } p = qd \text{ so } q = \frac{p}{d} = \frac{3.0 \times 10^{-29} \text{ C} \cdot \text{m}}{0.24 \times 10^{-9} \text{ m}} = 1.3 \times 10^{-19} \text{ C}$$

$$\text{(c) } \frac{q}{e} = \frac{1.3 \times 10^{-19} \text{ C}}{1.602 \times 10^{-19} \text{ C}} = 0.81$$

$$\text{(d) } q = \frac{p}{d} = \frac{1.5 \times 10^{-30} \text{ C} \cdot \text{m}}{0.16 \times 10^{-9} \text{ m}} = 9.37 \times 10^{-21} \text{ C}$$

$$\frac{q}{e} = \frac{9.37 \times 10^{-21} \text{ C}}{1.602 \times 10^{-19} \text{ C}} = 0.058$$

EVALUATE: The fractional ionic character for the bond in HI is much less than the fractional ionic character for the bond in NaCl. The bond in HI is mostly covalent and not very ionic.

- 42.38. IDENTIFY:** The electric potential energy U , the binding energy E_B , the electron affinity E_A , and the ionization energy E_I , where E_B , E_A and E_I are positive and U is negative, are related by

$$E_B = -U + E_A - E_I.$$

SET UP: For two point charges q_1 and q_2 separated by a distance r , the electric potential energy is given

$$\text{by } U = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}.$$

EXECUTE: The electrical potential energy is $U = -5.13 \text{ eV}$, and $r = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{U} = 2.8 \times 10^{-10} \text{ m}$.

EVALUATE: We have neglected the kinetic energy of the ions in the molecule. Also, it is an approximation to treat the two ions as point charges.

- 42.39. (a) IDENTIFY:** $E(\text{Na}) + E(\text{Cl}) = E(\text{Na}^+) + E(\text{Cl}^-) + U(r)$. Solving for $U(r)$ gives

$$U(r) = -[E(\text{Na}^+) - E(\text{Na})] + [E(\text{Cl}) - E(\text{Cl}^-)].$$

SET UP: $[E(\text{Na}^+) - E(\text{Na})]$ is the ionization energy of Na, the energy required to remove one electron, and is equal to 5.1 eV. $[E(\text{Cl}) - E(\text{Cl}^-)]$ is the electron affinity of Cl, the magnitude of the decrease in energy when an electron is attached to a neutral Cl atom, and is equal to 3.6 eV.

EXECUTE: $U = -5.1 \text{ eV} + 3.6 \text{ eV} = -1.5 \text{ eV} = -2.4 \times 10^{-19} \text{ J}$, and $-\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -2.4 \times 10^{-19} \text{ J}$

$$r = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{2.4 \times 10^{-19} \text{ J}} = (8.988 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \frac{(1.602 \times 10^{-19} \text{ C})^2}{2.4 \times 10^{-19} \text{ J}}$$

$$r = 9.6 \times 10^{-10} \text{ m} = 0.96 \text{ nm}$$

(b) ionization energy of K = 4.3 eV; electron affinity of Br = 3.5 eV

Thus $U = -4.3 \text{ eV} + 3.5 \text{ eV} = -0.8 \text{ eV} = -1.28 \times 10^{-19} \text{ J}$, and $-\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -1.28 \times 10^{-19} \text{ J}$

$$r = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{1.28 \times 10^{-19} \text{ J}} = (8.988 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \frac{(1.602 \times 10^{-19} \text{ C})^2}{1.28 \times 10^{-19} \text{ J}}$$

$$r = 1.8 \times 10^{-9} \text{ m} = 1.8 \text{ nm}$$

EVALUATE: K has a smaller ionization energy than Na and the electron affinities of Cl and Br are very similar, so it takes less energy to make $\text{K}^+ + \text{Br}^-$ from K + Br than to make $\text{Na}^+ + \text{Cl}^-$ from Na + Cl. Thus, the stabilization distance is larger for KBr than for NaCl.

42.40. IDENTIFY: The rotational energy levels are given by Eq. (42.3). The photon wavelength λ is related to the transition energy of the atom by $\Delta E = \frac{hc}{\lambda}$.

SET UP: For emission, $\Delta l = -1$. For such a transition, from state l to state $l-1$,

$$\Delta E_l = [l(l+1) - (l-1)l] \frac{\hbar^2}{2I} = \frac{l\hbar^2}{I}. \text{ The difference in transition energies for adjacent lines in the spectrum is}$$

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

EXECUTE: The transition energies corresponding to the observed wavelengths are 3.29×10^{-21} J, 2.87×10^{-21} J, 2.47×10^{-21} J, 2.06×10^{-21} J and 1.65×10^{-21} J. The average spacing of these energies is

$$0.410 \times 10^{-21} \text{ J. Then, } \frac{\hbar^2}{I} = 0.410 \times 10^{-21} \text{ J, from which } I = 2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2.$$

EVALUATE: With $\frac{\hbar^2}{I} = 0.410 \times 10^{-21} \text{ J}$ and $\Delta E_l = \frac{l\hbar^2}{I}$, we find that these wavelengths correspond to transitions from levels 8, 7, 6, 5 and 4 to the respective next lower levels.

42.41. (a) IDENTIFY: The rotational energies of a molecule depend on its moment of inertia, which in turn depends on the separation between the atoms in the molecule.

SET UP: Problem 42.40 gives $I = 2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2$. $I = m_r r^2$. Calculate m_r and solve for r .

$$\text{EXECUTE: } m_r = \frac{m_H m_{\text{Cl}}}{m_H + m_{\text{Cl}}} = \frac{(1.67 \times 10^{-27} \text{ kg})(5.81 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 5.81 \times 10^{-26} \text{ kg}} = 1.623 \times 10^{-27} \text{ kg}$$

$$r = \sqrt{\frac{I}{m_r}} = \sqrt{\frac{2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2}{1.623 \times 10^{-27} \text{ kg}}} = 1.29 \times 10^{-10} \text{ m} = 0.129 \text{ nm}$$

EVALUATE: This is a typical atomic separation for a diatomic molecule; see Example 42.2 for the corresponding distance for CO.

(b) IDENTIFY: Each transition is from the level l to the level $l-1$. The rotational energies are given by Eq. (42.3). The transition energy is related to the photon wavelength by $\Delta E = hc/\lambda$.

$$\text{SET UP: } E_l = l(l+1)\hbar^2/2I, \text{ so } \Delta E = E_l - E_{l-1} = [l(l+1) - l(l-1)] \left(\frac{\hbar^2}{2I} \right) = l \left(\frac{\hbar^2}{I} \right).$$

$$\text{EXECUTE: } l \left(\frac{\hbar^2}{I} \right) = \frac{hc}{\lambda}$$

$$l = \frac{2\pi c I}{\hbar \lambda} = \frac{2\pi(2.998 \times 10^8 \text{ m/s})(2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2)}{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})\lambda} = \frac{4.843 \times 10^{-4} \text{ m}}{\lambda}$$

$$\text{For } \lambda = 60.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{60.4 \times 10^{-6} \text{ m}} = 8.$$

$$\text{For } \lambda = 69.0 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{69.0 \times 10^{-6} \text{ m}} = 7.$$

$$\text{For } \lambda = 80.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{80.4 \times 10^{-6} \text{ m}} = 6.$$

$$\text{For } \lambda = 96.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{96.4 \times 10^{-6} \text{ m}} = 5.$$

$$\text{For } \lambda = 120.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{120.4 \times 10^{-6} \text{ m}} = 4.$$

EVALUATE: In each case l is an integer, as it must be.

(c) **IDENTIFY and SET UP:** Longest λ implies smallest ΔE , and this is for the transition from $l=1$ to $l=0$.

$$\text{EXECUTE: } \Delta E = l \left(\frac{\hbar^2}{I} \right) = (1) \frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2} = 4.099 \times 10^{-22} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{4.099 \times 10^{-22} \text{ J}} = 4.85 \times 10^{-4} \text{ m} = 485 \mu\text{m}.$$

EVALUATE: This is longer than any wavelengths in part (b).

(d) **IDENTIFY:** What changes is m_r , the reduced mass of the molecule.

SET UP: The transition energy is $\Delta E = l \left(\frac{\hbar^2}{I} \right)$ and $\Delta E = \frac{hc}{\lambda}$, so $\lambda = \frac{2\pi c I}{l\hbar}$ (part (b)). $I = m_r r^2$, so λ is

$$\text{directly proportional to } m_r. \quad \frac{\lambda(\text{HCl})}{m_r(\text{HCl})} = \frac{\lambda(\text{DCl})}{m_r(\text{DCl})} \quad \text{so} \quad \lambda(\text{DCl}) = \lambda(\text{HCl}) \frac{m_r(\text{DCl})}{m_r(\text{HCl})}$$

EXECUTE: The mass of a deuterium atom is approximately twice the mass of a hydrogen atom, so $m_D = 3.34 \times 10^{-27} \text{ kg}$.

$$m_r(\text{DCl}) = \frac{m_D m_{\text{Cl}}}{m_D + m_{\text{Cl}}} = \frac{(3.34 \times 10^{-27} \text{ kg})(5.81 \times 10^{-27} \text{ kg})}{3.34 \times 10^{-27} \text{ kg} + 5.81 \times 10^{-26} \text{ kg}} = 3.158 \times 10^{-27} \text{ kg}$$

$$\lambda(\text{DCl}) = \lambda(\text{HCl}) \left(\frac{3.158 \times 10^{-27} \text{ kg}}{1.623 \times 10^{-27} \text{ kg}} \right) = (1.946) \lambda(\text{HCl})$$

$$l=8 \rightarrow l=7; \lambda = (60.4 \mu\text{m})(1.946) = 118 \mu\text{m}$$

$$l=7 \rightarrow l=6; \lambda = (69.0 \mu\text{m})(1.946) = 134 \mu\text{m}$$

$$l=6 \rightarrow l=5; \lambda = (80.4 \mu\text{m})(1.946) = 156 \mu\text{m}$$

$$l=5 \rightarrow l=4; \lambda = (96.4 \mu\text{m})(1.946) = 188 \mu\text{m}$$

$$l=4 \rightarrow l=3; \lambda = (120.4 \mu\text{m})(1.946) = 234 \mu\text{m}$$

EVALUATE: The moment of inertia increases when H is replaced by D, so the transition energies decrease and the wavelengths increase. The larger the rotational inertia the smaller the rotational energy for a given l (Eq. 42.3).

42.42. IDENTIFY: Problem 42.15b shows that for the $l \rightarrow l-1$ transition, $\Delta E = \frac{l\hbar^2}{I}$. $I = m_r r_0^2$.

$$\text{SET UP: } m_r = \frac{(3.82 \times 10^{-26} \text{ kg})(3.15 \times 10^{-26} \text{ kg})}{3.82 \times 10^{-26} \text{ kg} + 3.15 \times 10^{-26} \text{ kg}} = 1.726 \times 10^{-26} \text{ kg}.$$

$$\text{EXECUTE: } I = \frac{\hbar^2 l}{\Delta E} = \frac{h l \lambda}{4\pi^2 c} = 6.43 \times 10^{-46} \text{ kg} \cdot \text{m}^2 \quad \text{and from Eq. (42.6) the separation is}$$

$$r_0 = \sqrt{\frac{I}{m_r}} = 0.193 \text{ nm}.$$

EVALUATE: Section 42.1 says $r_0 = 0.24 \text{ nm}$ for NaCl. Our result for NaF is smaller than this. This makes sense, since F is a smaller atom than Cl.

42.43. IDENTIFY: $E_{\text{ex}} = \frac{L^2}{2I} = \frac{\hbar^2 l(l+1)}{2I}$. $E_g = 0$ ($l=0$), and there is an additional multiplicative factor of $2l+1$ because for each l state there are really $(2l+1)$ m_l -states with the same energy.

SET UP: From Example 42.3, $I = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2$.

$$\text{EXECUTE: (a) } \frac{n_l}{n_0} = (2l+1) e^{-\hbar^2 l(l+1)/(2IkT)}.$$

$$(b) (i) E_{l=1} = \frac{\hbar^2(1)(1+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)} = 7.67 \times 10^{-23} \text{ J}. \quad \frac{E_{l=1}}{kT} = \frac{7.67 \times 10^{-23} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.0185.$$

$$(2l+1) = 3, \text{ so } \frac{n_{l=1}}{n_0} = (3)e^{-0.0185} = 2.95.$$

$$(ii) \frac{E_{l=2}}{kT} = \frac{\hbar^2(2)(2+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.0556. \quad (2l+1) = 5, \text{ so}$$

$$\frac{n_{l=1}}{n_0} = (5)(e^{-0.0556}) = 4.73.$$

$$(iii) \frac{E_{l=10}}{kT} = \frac{\hbar^2(10)(10+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 1.02.$$

$$(2l+1) = 21, \text{ so } \frac{n_{l=10}}{n_0} = (21)(e^{-1.02}) = 7.57.$$

$$(iv) \frac{E_{l=20}}{kT} = \frac{\hbar^2(20)(20+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 3.89. \quad (2l+1) = 41, \text{ so}$$

$$\frac{n_{l=20}}{n_0} = (41)e^{-3.89} = 0.838.$$

$$(v) \frac{E_{l=50}}{kT} = \frac{\hbar^2(50)(50+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 23.6. \quad (2l+1) = 101, \text{ so}$$

$$\frac{n_{l=50}}{n_0} = (101)e^{-23.6} = 5.69 \times 10^{-9}.$$

EVALUATE: (c) There is a competing effect between the $(2l+1)$ term and the decaying exponential. The $2l+1$ term dominates for small l , while the exponential term dominates for large l .

42.44. IDENTIFY: The rotational energy levels are given by Eq. (42.3). The transition energy ΔE for the molecule and λ for the photon are related by $\Delta E = \frac{hc}{\lambda}$.

SET UP: From Example 42.2, $I_{\text{CO}} = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2$.

$$\text{EXECUTE: (a)} \quad E_{l=1} = \frac{\hbar^2 l(l+1)}{2I} = \frac{(1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2 (1)(1+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)} = 7.67 \times 10^{-23} \text{ J}. \quad E_{l=0} = 0.$$

$$\Delta E = 7.67 \times 10^{-23} \text{ J} = 4.79 \times 10^{-4} \text{ eV}. \quad \lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(7.67 \times 10^{-23} \text{ J})} =$$

$$2.59 \times 10^{-3} \text{ m} = 2.59 \text{ mm}.$$

EVALUATE: (b) Let's compare the value of kT when $T = 20 \text{ K}$ to that of ΔE for the $l=1 \rightarrow l=0$ rotational transition: $kT = (1.38 \times 10^{-23} \text{ J/K})(20 \text{ K}) = 2.76 \times 10^{-22} \text{ J}$.

$$\Delta E = 7.67 \times 10^{-23} \text{ J (from part (a)). So } \frac{kT}{\Delta E} = 3.60. \text{ Therefore, although } T \text{ is quite small, there is still plenty}$$

of energy to excite CO molecules into the first rotational level. This allows astronomers to detect the 2.59 mm wavelength radiation from such molecular clouds.

42.45. IDENTIFY and SET UP: $E_l = l(l+1)\hbar^2/2I$, so E_l and the transition energy ΔE depend on I . Different isotopic molecules have different I .

EXECUTE: (a) Calculate I for Na^{35}Cl :

$$m_r = \frac{m_{\text{Na}} m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}} = \frac{(3.8176 \times 10^{-26} \text{ kg})(5.8068 \times 10^{-26} \text{ kg})}{3.8176 \times 10^{-26} \text{ kg} + 5.8068 \times 10^{-26} \text{ kg}} = 2.303 \times 10^{-26} \text{ kg}$$

$$I = m_r r^2 = (2.303 \times 10^{-26} \text{ kg})(0.2361 \times 10^{-9} \text{ m})^2 = 1.284 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

$l = 2 \rightarrow l = 1$ transition

$$\Delta E = E_2 - E_1 = (6 - 2) \left(\frac{\hbar^2}{2I} \right) = \frac{2\hbar^2}{I} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.284 \times 10^{-45} \text{ kg} \cdot \text{m}^2} = 1.734 \times 10^{-23} \text{ J}$$

$$\Delta E = \frac{hc}{\lambda} \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{1.734 \times 10^{-23} \text{ J}} = 1.146 \times 10^{-2} \text{ m} = 1.146 \text{ cm}$$

$l = 1 \rightarrow l = 0$ transition

$$\Delta E = E_1 - E_0 = (2 - 0) \left(\frac{\hbar^2}{2I} \right) = \frac{\hbar^2}{I} = \frac{1}{2}(1.734 \times 10^{-23} \text{ J}) = 8.67 \times 10^{-24} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{8.67 \times 10^{-24} \text{ J}} = 2.291 \text{ cm}$$

(b) Calculate I for Na^{37}Cl : $m_r = \frac{m_{\text{Na}}m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}} = \frac{(3.8176 \times 10^{-26} \text{ kg})(6.1384 \times 10^{-26} \text{ kg})}{3.8176 \times 10^{-26} \text{ kg} + 6.1384 \times 10^{-26} \text{ kg}} = 2.354 \times 10^{-26} \text{ kg}$

$$I = m_r r^2 = (2.354 \times 10^{-26} \text{ kg})(0.2361 \times 10^{-9} \text{ m})^2 = 1.312 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

$l = 2 \rightarrow l = 1$ transition

$$\Delta E = \frac{2\hbar^2}{I} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.312 \times 10^{-45} \text{ kg} \cdot \text{m}^2} = 1.697 \times 10^{-23} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{1.697 \times 10^{-23} \text{ J}} = 1.171 \times 10^{-2} \text{ m} = 1.171 \text{ cm}$$

$l = 1 \rightarrow l = 0$ transition

$$\Delta E = \frac{\hbar^2}{I} = \frac{1}{2}(1.697 \times 10^{-23} \text{ J}) = 8.485 \times 10^{-24} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{8.485 \times 10^{-24} \text{ J}} = 2.341 \text{ cm}$$

The differences in the wavelengths for the two isotopes are:

$$l = 2 \rightarrow l = 1 \text{ transition: } 1.171 \text{ cm} - 1.146 \text{ cm} = 0.025 \text{ cm}$$

$$l = 1 \rightarrow l = 0 \text{ transition: } 2.341 \text{ cm} - 2.291 \text{ cm} = 0.050 \text{ cm}$$

EVALUATE: Replacing ^{35}Cl by ^{37}Cl increases I , decreases ΔE and increases λ . The effect on λ is small but measurable.

42.46. IDENTIFY: $\Delta E = hf = \hbar \sqrt{\frac{k'}{m_r}}$.

SET UP: $m_r = \frac{m_{\text{O}}m_{\text{H}}}{m_{\text{O}} + m_{\text{H}}} = 1.57 \times 10^{-27} \text{ kg}$

EXECUTE: The vibration frequency is $f = \frac{\Delta E}{h} = 1.12 \times 10^{14} \text{ Hz}$. The force constant is

$$k' = (2\pi f)^2 m_r = 777 \text{ N/m}.$$

EVALUATE: This would be a fairly stiff spring in an ordinary physics lab.

42.47. IDENTIFY: The vibrational energy levels are given by $E_n = \left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{k'}{m_r}}$. The zero-point energy is

$$E_0 = \frac{1}{2} \hbar \sqrt{\frac{2k'}{m_{\text{H}}}}.$$

SET UP: For H_2 , $m_r = \frac{m_{\text{H}}}{2}$.

EXECUTE: $E_0 = \frac{1}{2}(1.054 \times 10^{-34} \text{ J} \cdot \text{s}) \sqrt{\frac{2(576 \text{ N/m})}{1.67 \times 10^{-27} \text{ kg}}} = 4.38 \times 10^{-20} \text{ J} = 0.274 \text{ eV}.$

EVALUATE: This is much less than the magnitude of the H_2 bond energy.

- 42.48. IDENTIFY:** The frequency is proportional to the reciprocal of the square root of the reduced mass. The transition energy ΔE and the wavelength of the light emitted are related by $\Delta E = \frac{hc}{\lambda}$.

SET UP: $f_0 = 1.24 \times 10^{14} \text{ Hz}.$

EXECUTE: (a) In terms of the atomic masses, the frequency of the isotope with the deuterium atom is

$$f = f_0 \left(\frac{m_F m_H / (m_H + m_F)}{m_F m_D / (m_D + m_F)} \right)^{1/2} = f_0 \left(\frac{1 + (m_F / m_D)}{1 + (m_F / m_H)} \right)^{1/2}. \text{ Using } f_0 \text{ and the given masses, } f = 8.99 \times 10^{13} \text{ Hz.}$$

(b) For the molecule, $\Delta E = hf$. $hf = \frac{hc}{\lambda}$, so $\lambda = \frac{c}{f} = \frac{3.00 \times 10^8 \text{ m/s}}{8.99 \times 10^{13} \text{ Hz}} = 3.34 \times 10^{-6} \text{ m} = 3340 \text{ nm}.$ This wavelength is in the infrared.

EVALUATE: The vibrational frequency of the molecule equals the frequency of the light that is emitted.

- 42.49. IDENTIFY and SET UP:** Use Eq. (42.6) to calculate I . The energy levels are given by Eq. (42.9). The transition energy ΔE is related to the photon wavelength by $\Delta E = hc/\lambda$.

EXECUTE: (a) $m_r = \frac{m_H m_I}{m_H + m_I} = \frac{(1.67 \times 10^{-27} \text{ kg})(2.11 \times 10^{-25} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 2.11 \times 10^{-25} \text{ kg}} = 1.657 \times 10^{-27} \text{ kg}$

$$I = m_r r^2 = (1.657 \times 10^{-27} \text{ kg})(0.160 \times 10^{-9} \text{ m})^2 = 4.24 \times 10^{-47} \text{ kg} \cdot \text{m}^2$$

(b) The energy levels are $E_{nl} = l(l+1) \left(\frac{\hbar^2}{2I} \right) + \left(n + \frac{1}{2} \right) \hbar \sqrt{\frac{k'}{m_r}}$ (Eq. (42.9))

$$\sqrt{\frac{k'}{m}} = \omega = 2\pi f \text{ so } E_{nl} = l(l+1) \left(\frac{\hbar^2}{2I} \right) + \left(n + \frac{1}{2} \right) hf$$

(i) transition $n=1 \rightarrow n=0, l=1 \rightarrow l=0$

$$\Delta E = (2-0) \left(\frac{\hbar^2}{2I} \right) + \left(1 + \frac{1}{2} - \frac{1}{2} \right) hf = \frac{\hbar^2}{I} + hf$$

$$\Delta E = \frac{hc}{\lambda} \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{hc}{(\hbar^2/I) + hf} = \frac{c}{(\hbar/2\pi I) + f}$$

$$\frac{\hbar}{2\pi I} = \frac{1.055 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi(4.24 \times 10^{-47} \text{ kg} \cdot \text{m}^2)} = 3.960 \times 10^{11} \text{ Hz}$$

$$\lambda = \frac{c}{(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{3.960 \times 10^{11} \text{ Hz} + 6.93 \times 10^{13} \text{ Hz}} = 4.30 \mu\text{m}$$

(ii) transition $n=1 \rightarrow n=0, l=2 \rightarrow l=1$

$$\Delta E = (6-2) \left(\frac{\hbar^2}{2I} \right) + hf = \frac{2\hbar^2}{I} + hf$$

$$\lambda = \frac{c}{2(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{2(3.960 \times 10^{11} \text{ Hz}) + 6.93 \times 10^{13} \text{ Hz}} = 4.28 \mu\text{m}$$

(iii) transition $n=2 \rightarrow n=1, l=2 \rightarrow l=3$

$$\Delta E = (6-12) \left(\frac{\hbar^2}{2I} \right) + hf = -\frac{3\hbar^2}{I} + hf$$

$$\lambda = \frac{c}{-3(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{-3(3.960 \times 10^{11} \text{ Hz}) + 6.93 \times 10^{13} \text{ Hz}} = 4.40 \mu\text{m}$$

EVALUATE: The vibrational energy change for the $n = 1 \rightarrow n = 0$ transition is the same as for the $n = 2 \rightarrow n = 1$ transition. The rotational energies are much smaller than the vibrational energies, so the wavelengths for all three transitions don't differ much.

42.50. IDENTIFY and SET UP: $P(E) = f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$.

EXECUTE: The sum of the probabilities is

$$f(E_F - \Delta E) + f(E_F + \Delta E) = \frac{1}{e^{-\Delta E/kT} + 1} + \frac{1}{e^{\Delta E/kT} + 1} = \frac{1}{e^{-\Delta E/kT} + 1} + \frac{e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}} = 1. \text{ Therefore,}$$

$$f(E_F - \Delta E) = 1 - f(E_F + \Delta E).$$

EVALUATE: This result is true for all T , even though P is strongly dependent on temperature.

42.51. IDENTIFY: E_{F0} is given by Eq. (42.20). Since potassium is a metal and E does not change much with T for metals, we approximate E_F by E_{F0} , so $E_F = \frac{3^{2/3} \pi^{4/3} \hbar^2 n^{2/3}}{2m}$.

SET UP: The number of atoms per m^3 is ρ/m . If each atom contributes one free electron, the electron concentration is $n = \frac{\rho}{m} = \frac{851 \text{ kg/m}^3}{6.49 \times 10^{-26} \text{ kg}} = 1.31 \times 10^{28} \text{ electrons/m}^3$.

EXECUTE: $E_F = \frac{3^{2/3} \pi^{4/3} (1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2 (1.31 \times 10^{28} / \text{m}^3)^{2/3}}{2(9.11 \times 10^{-31} \text{ kg})} = 3.24 \times 10^{-19} \text{ J} = 2.03 \text{ eV}.$

EVALUATE: The E_F we calculated for potassium is about a factor of three smaller than the E_F for copper that was calculated in Example 42.7.

42.52. IDENTIFY: The only difference between the two isotopes is their mass, which will affect their reduced mass and hence their moment of inertia.

SET UP: The rotational energy states are given by $E = l(l+1) \frac{\hbar^2}{2I}$ and the reduced mass is given by

$$m_1 = m_1 m_2 / (m_1 + m_2).$$

EXECUTE: (a) If we call m the mass of the H-atom, the mass of the deuterium atom is $2m$ and the reduced masses of the molecules are

$$\text{H}_2 \text{ (hydrogen): } m_r(\text{H}) = mm/(m+m) = m/2$$

$$\text{D}_2 \text{ (deuterium): } m_r(\text{D}) = (2m)(2m)/(2m+2m) = m$$

Using $I = m_r r_0^2$, the moments of inertia are $I_H = m r_0^2 / 2$ and $I_D = m r_0^2$. The ratio of the rotational energies

is then $\frac{E_H}{E_D} = \frac{l(l+1)(\hbar^2/2I_H)}{l(l+1)(\hbar^2/2I_D)} = \frac{I_D}{I_H} = \frac{m r_0^2}{\frac{m}{2} r_0^2} = 2.$

(b) The ratio of the vibrational energies is $\frac{E_H}{E_D} = \frac{\left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{k'}{m_r(\text{H})}}}{\left(n + \frac{1}{2}\right) \hbar \sqrt{\frac{k'}{m_r(\text{D})}}} = \sqrt{\frac{m_r(\text{D})}{m_r(\text{H})}} = \sqrt{\frac{m}{m/2}} = \sqrt{2}.$

EVALUATE: The electrical force is the same for both molecules since both H and D have the same charge, so it is reasonable that the force constant would be the same for both of them.

42.53. IDENTIFY and SET UP: Use the description of the bcc lattice in Fig. 42.11c in the textbook to calculate the number of atoms per unit cell and then the number of atoms per unit volume.

EXECUTE: (a) Each unit cell has one atom at its center and 8 atoms at its corners that are each shared by 8 other unit cells. So there are $1 + 8/8 = 2$ atoms per unit cell.

$$\frac{n}{V} = \frac{2}{(0.35 \times 10^{-9} \text{ m})^3} = 4.66 \times 10^{-8} \text{ atoms/m}^3$$

$$(b) E_{F0} = \frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \left(\frac{N}{V} \right)^{2/3}$$

In this equation N/V is the number of free electrons per m^3 . But the problem says to assume one free electron per atom, so this is the same as n/V calculated in part (a).

$$m = 9.109 \times 10^{-31} \text{ kg (the electron mass), so } E_{F0} = 7.563 \times 10^{-19} \text{ J} = 4.7 \text{ eV}$$

EVALUATE: Our result for metallic lithium is similar to that calculated for copper in Example 42.7.

42.54. IDENTIFY and SET UP: At r where U_{tot} is a minimum, $\frac{d}{dr} U_{\text{tot}} = 0$.

$$\text{EXECUTE: (a) } \frac{d}{dr} U_{\text{tot}} = \frac{\alpha e^2}{4\pi\epsilon_0} \frac{1}{r^2} - 8A \frac{1}{r^9}. \text{ Setting this equal to zero when } r = r_0 \text{ gives } r_0^7 = \frac{8A4\pi\epsilon_0}{\alpha e^2} \text{ and}$$

$$\text{so } U_{\text{tot}} = \frac{\alpha e^2}{4\pi\epsilon_0} \left(-\frac{1}{r} + \frac{r_0^7}{8r^8} \right). \text{ At } r = r_0, U_{\text{tot}} = -\frac{7\alpha e^2}{32\pi\epsilon_0 r_0} = -1.26 \times 10^{-18} \text{ J} = -7.85 \text{ eV}.$$

(b) To remove a Na^+Cl^- ion pair from the crystal requires 7.85 eV. When neutral Na and Cl atoms are formed from the Na^+ and Cl^- atoms there is a net release of energy $-5.14 \text{ eV} + 3.61 \text{ eV} = -1.53 \text{ eV}$, so the net energy required to remove a neutral Na Cl pair from the crystal is $7.85 \text{ eV} - 1.53 \text{ eV} = 6.32 \text{ eV}$.

EVALUATE: Our calculation is in good agreement with the experimental value.

42.55. (a) IDENTIFY and SET UP: $p = -\frac{dE_{\text{tot}}}{dV}$. Relate E_{tot} to E_{F0} and evaluate the derivative.

$$\text{EXECUTE: } E_{\text{tot}} = NE_{\text{av}} = \frac{3N}{5} E_{F0} = \frac{3}{5} \left(\frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \right) N^{5/3} V^{-2/3}$$

$$\frac{dE_{\text{tot}}}{dV} = \frac{3}{5} \left(\frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \right) N^{5/3} \left(-\frac{2}{3} V^{-5/3} \right) \text{ so } p = \left(\frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \right) \left(\frac{N}{V} \right)^{5/3}, \text{ as was to be shown.}$$

$$(b) N/V = 8.45 \times 10^{28} \text{ m}^{-3}$$

$$p = \left(\frac{3^{2/3} \pi^{4/3} (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{5(9.109 \times 10^{-31} \text{ kg})} \right) (8.45 \times 10^{28} \text{ m}^{-3})^{5/3} = 3.81 \times 10^{10} \text{ Pa} = 3.76 \times 10^5 \text{ atm}.$$

(c) **EVALUATE:** Normal atmospheric pressure is about 10^5 Pa , so these pressures are extremely large. The electrons are held in the metal by the attractive force exerted on them by the copper ions.

42.56. (a) IDENTIFY and SET UP: From Problem 42.53, $p = \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \left(\frac{N}{V} \right)^{5/3}$. Use this expression to calculate dp/dV .

$$\text{EXECUTE: (a) } B = -V \frac{dp}{dV} = -V \left[\frac{5}{3} \cdot \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \cdot \left(\frac{N}{V} \right)^{2/3} \cdot \left(\frac{-N}{V^2} \right) \right] = \frac{5}{3} p.$$

$$(b) \frac{N}{V} = 8.45 \times 10^{28} \text{ m}^{-3}. B = \frac{5}{3} \cdot \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} (8.45 \times 10^{28} \text{ m}^{-3})^{5/3} = 6.33 \times 10^{10} \text{ Pa}.$$

EVALUATE: (c) The fraction of B due to the free electrons is $\frac{6.33 \times 10^{10} \text{ Pa}}{1.4 \times 10^{11} \text{ Pa}} = 0.45$. The copper ions themselves make up the remaining fraction.

42.57. IDENTIFY and SET UP: Follow the steps specified in the problem.

$$\text{EXECUTE: (a) } E_{F0} = \frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \left(\frac{N}{V} \right)^{2/3}. \text{ Let } E_{F0} = \frac{1}{100} mc^2.$$

$$\left(\frac{N}{V} \right) = \left[\frac{2m^2 c^2}{(100) 3^{2/3} \pi^{4/3} \hbar^2} \right]^{3/2} = \frac{2^{3/2} m^3 c^3}{100^{3/2} 3\pi^2 \hbar^3} = \frac{2^{3/2} m^3 c^3}{3000 \pi^2 \hbar^3} = 1.67 \times 10^{33} \text{ m}^{-3}.$$

(b) $\frac{8.45 \times 10^{28} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3}} = 5.06 \times 10^{-5}$. Since the real concentration of electrons in copper is less than one part in 10^{-4} of the concentration where relativistic effects are important, it is safe to ignore relativistic effects for most applications.

(c) The number of electrons is $N_e = \frac{6(2 \times 10^{30} \text{ kg})}{1.99 \times 10^{-26} \text{ kg}} = 6.03 \times 10^{56}$. The concentration is

$$\frac{N_e}{V} = \frac{6.03 \times 10^{56}}{\frac{4}{3}\pi(6.00 \times 10^6 \text{ m})^3} = 6.66 \times 10^{35} \text{ m}^{-3}.$$

EVALUATE: (d) Comparing this to the result from part (a) $\frac{6.66 \times 10^{35} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3}} \cong 400$ so relativistic effects

will be very important.

42.58. IDENTIFY: The current through the diode is related to the voltage across it.

SET UP: The current through the diode is given by $I = I_S (e^{eV/kT} - 1)$.

EXECUTE: (a) The current through the resistor is $(35.0 \text{ V})/(125 \Omega) = 0.280 \text{ A} = 280 \text{ mA}$, which is also the current through the diode. This current is given by

$I = I_S (e^{eV/kT} - 1)$, giving $280 \text{ mA} = 0.625 \text{ mA}(e^{eV/kT} - 1)$ and $1 + (280/0.625) = 449 = e^{eV/kT}$. Solving for V

$$\text{at } T = 293 \text{ K gives } V = \frac{kT \ln 449}{e} = \frac{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) \ln 449}{1.60 \times 10^{-19} \text{ C}} = 0.154 \text{ V}$$

(b) $R = V/I = (0.154 \text{ V})/(0.280 \text{ A}) = 0.551 \Omega$

EVALUATE: At a different voltage, the diode would have different resistance.

42.59. IDENTIFY and SET UP: For a pair of point charges q_1 and q_2 separated by a distance r_{12} the electric

potential energy is $U = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r_{12}}$. Sum over all pairs of charges.

EXECUTE: (a)

$$U = \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{q_i q_j}{r_{ij}} = \frac{q^2}{4\pi\epsilon_0} \left(\frac{-1}{d} + \frac{1}{r} - \frac{1}{r+d} - \frac{1}{r-d} + \frac{1}{r} - \frac{1}{d} \right) = \frac{q^2}{4\pi\epsilon_0} \left(\frac{2}{r} - \frac{2}{d} - \frac{1}{r+d} - \frac{1}{r-d} \right).$$

$$\text{But } \frac{1}{r+d} + \frac{1}{r-d} = \frac{1}{r} \left(\frac{1}{1+\frac{d}{r}} + \frac{1}{1-\frac{d}{r}} \right) \approx \frac{1}{r} \left(1 - \frac{d}{r} + \frac{d^2}{r^2} + \dots + 1 + \frac{d}{r} + \frac{d^2}{r^2} \right) \approx \frac{2}{r} + \frac{2d^2}{r^3}$$

$$\Rightarrow U = \frac{-2q^2}{4\pi\epsilon_0} \left(\frac{1}{d} + \frac{d^2}{r^3} \right) = \frac{-2p^2}{4\pi\epsilon_0 r^3} - \frac{2p^2}{4\pi\epsilon_0 d^3}.$$

$$\text{(b) } U = \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{q_i q_j}{r_{ij}} = \frac{q^2}{4\pi\epsilon_0} \left(\frac{-1}{d} - \frac{1}{r} + \frac{1}{r+d} + \frac{1}{r-d} - \frac{1}{r} - \frac{1}{d} \right) = \frac{q^2}{4\pi\epsilon_0} \left(\frac{-2}{d} - \frac{2}{r} + \frac{2}{r} + \frac{2d^2}{r^3} \right) = \frac{-2q^2}{4\pi\epsilon_0} \left(\frac{1}{d} - \frac{d^2}{r^3} \right) \Rightarrow U = \frac{-2p^2}{4\pi\epsilon_0 d^3} + \frac{2p^2}{4\pi\epsilon_0 r^3}.$$

If we ignore the potential energy involved in forming each individual molecule, which just involves a different choice for the zero of potential energy, then the answers are:

(a) $U = \frac{-2p^2}{4\pi\epsilon_0 r^3}$. The interaction is attractive.

(b) $U = \frac{+2p^2}{4\pi\epsilon_0 r^3}$. The interaction is repulsive.

EVALUATE: In each case the interactions between the two dipoles involve two interactions between like charges and two between unlike charges. But in part (a) the two closest charges are unlike and in (b) the two closest charges are alike.

42.60. IDENTIFY: Follow the procedure specified in the hint.

SET UP: According to Eq. (42.8), the vibrational level spacing is $\Delta E = \hbar\omega = \hbar\sqrt{k'/m}$.

EXECUTE: (a) Following the hint, $k'dr = -d\left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}\right)_{r=r_0} = \frac{1}{2\pi\epsilon_0} \frac{e^2}{r_0^3} dr$ and $k' = \frac{1}{2\pi\epsilon_0} \frac{e^2}{r_0^3}$. The energy

level spacing therefore is $\hbar\omega = \hbar\sqrt{2k'/m} = \hbar\sqrt{\frac{1}{\pi\epsilon_0} \frac{e^2}{mr_0^3}} = 1.23 \times 10^{-19} \text{ J} = 0.77 \text{ eV}$, where $(m/2)$ has been used for the reduced mass.

(b) The reduced mass is doubled, and the energy is reduced by a factor of $\sqrt{2}$ to 0.54 eV.

EVALUATE: The vibrational level spacing is inversely proportional to the square root of the reduced mass of the molecule. The force constant depends on the bond between the two atoms.

