Chapter 37
Molecules

Conceptual Problems

***1** •

Determine the Concept Yes. Because the center of charge of the positive Na ion does not coincide with the center of charge for the negative Cl ion, the NaCl molecule has a permanent dipole moment. Hence, it is a polar molecule.

2 •

Determine the Concept Because a N_2 molecule has no permanent dipole moment, it is a non-polar molecule.

3 •

Determine the Concept No. Neon occurs naturally as Ne, not Ne_2. Neon is a rare gas atom with a closed shell electron configuration.

4 •

Determine the Concept

(*a*) Because an electron is transferred from the H atom to the F atom, the bonding mechanism is ionic.

(*b*) Because an electron is transferred from the K atom to the Br atom, the bonding mechanism is ionic.

(*c*) Because the atoms share two electrons, the bonding mechanism is covalent.

(*d*) Because each valence electron is shared by many atoms, the bonding mechanism is metallic bonding.

***5** ••

Determine the Concept The diagram would consist of a non-bonding ground state with no vibrational or rotational states for ArF (similar to the upper curve in Figure 37-4) but for ArF* there should be a bonding excited state with a definite minimum with respect to inter-nuclear separation and several vibrational states as in the excited state curve of Figure 37-13.

6 •

Determine the Concept Elements similar to carbon in outer shell configurations are silicon, germanium, tin, and lead. We would expect the same hybridization for these as for carbon, and this is indeed the case for silicon and germanium whose crystal structure is the diamond structure. Tin and lead, however, are metallic and here the metallic bond is dominant.

7 •

Determine the Concept The effective force constant from Example 37-4 is 1.85×10^3 N/m. This value is about 25% larger than the given value of the force constant of the suspension springs on a typical automobile.

8 •

Determine the Concept As the angular momentum increases, the separation between the nuclei also increases (the effective force between the nuclei is similar to that of a stiff spring). Consequently, the moment of inertia also increases.

9 •

Determine the Concept For H_2, the concentration of negative charge between the two protons holds the protons together. In the H_2^+ ion, there is only one electron that is shared by the two positive charges such that most of the electronic charge is again between the two protons. However, the negative charge in the H_2^+ ion is not as effective as the larger charge in the H_2 molecule, and the protons should be farther apart. The experimental values support this argument. For H_2, $r_0 =$ 0.074 nm, while for H_2^+, $r_0 = 0.106$ nm.

10 •

Determine the Concept The energy of the first excited state of an atom is orders of magnitude greater than kT at ordinary temperatures. Consequently, practically all atoms are in the ground state. By contrast, the energy separation between the ground rotational state and nearby higher rotational states is less than or roughly equal to kT at ordinary temperatures, and so these higher states are thermally excited and occupied.

11 ••

Determine the Concept With more than two atoms in the molecule there will be more than just one frequency of vibration because there are more possible relative motions. In advanced mechanics these are known as normal modes of vibration.

Estimation and Approximation

12 ••

Picture the Problem We can estimate the value of the quantum number ν for which the improved formula corrects the original formula by 10 percent by setting the ratio of the correction term to the first term equal to 10 percent and solving for ν.

Express the ratio of the correction term to the first term of the expression for E_ν and simplify to obtain:

$$\frac{\left(\nu+\frac{1}{2}\right)^2 hf\alpha}{\left(\nu+\frac{1}{2}\right)hf}=\left(\nu+\tfrac{1}{2}\right)\alpha$$

For a correction of 10 percent:

$$\left(\nu+\tfrac{1}{2}\right)\alpha=0.1$$

Solve for ν to obtain:

$$\nu=\frac{1}{10\alpha}-\frac{1}{2}$$

Substitute numerical values and evaluate ν:

$$\nu=\frac{1}{10\left(7.6\times10^{-3}\right)}-\frac{1}{2}=12.7\approx\boxed{13}$$

13 ••

Picture the Problem We can solve Equation 37-12 for ℓ and substitute for the moment of inertia and rotational kinetic energy of the baseball to estimate the quantum number ℓ and spacing between adjacent energy levels for a baseball spinning about its own axis.

The rotational energy levels are given by Equation 37-12:

$$E=\frac{\ell(\ell+1)\hbar^2}{2I}$$

where ℓ = 0, 1, 2, … is the rotational quantum number and I is the moment of inertia of the ball.

Solve for $\ell(\ell+1)$:

$$\ell(\ell+1)=\frac{2IE}{\hbar^2}$$

Factor ℓ from the parentheses to obtain:

$$\ell^2\left(1+\frac{1}{\ell}\right)=\frac{2IE}{\hbar^2}$$

The result of our calculation of ℓ will show that $\ell \gg 1$. Assuming for the moment that this is the case:

$$\ell^2\approx\frac{2IE}{\hbar^2}\quad\text{and}\quad\ell\approx\frac{\sqrt{2IE}}{\hbar}$$

Because the energy of the ball is rotational kinetic energy:

$$E=K_{\text{rot}}=\tfrac{1}{2}I\omega^2$$

Substitute for E in the expression for ℓ to obtain:

$$\ell\approx\frac{\sqrt{2I\left(\frac{1}{2}I\omega^2\right)}}{\hbar}=\frac{\sqrt{\left(I^2\omega^2\right)}}{\hbar}=\frac{I\omega}{\hbar}$$

The moment of inertia of a ball about an axis through its diameter is (see Table 9-1):

$$I=\tfrac{2}{5}mr^2$$

Substitute for I to obtain:

$$\ell\approx\frac{2mr^2\omega}{5\hbar}$$

Substitute numerical values and evaluate ℓ:

$$\ell \approx \frac{2(0.3\,\text{kg})(0.03\,\text{m})^2\left(\frac{20\,\text{rev}}{\text{min}}\times\frac{2\pi\,\text{rad}}{\text{rev}}\times\frac{1\,\text{min}}{60\,\text{s}}\right)}{5\left(1.05\times10^{-34}\,\text{J}\cdot\text{s}\right)} = \boxed{2.15\times10^{30}}$$

Set $\ell = 0$ to express the spacing between adjacent energy levels:

$$E_{0\text{r}} = \frac{\hbar^2}{2I} = \frac{5\hbar^2}{4mr^2}$$

Substitute numerical values and evaluate $E_{0\text{r}}$:

$$E_{0\text{r}} = \frac{5\left(1.05\times10^{-34}\,\text{J}\cdot\text{s}\right)^2}{4(0.3\,\text{kg})(0.03\,\text{m})^2} = \boxed{5.10\times10^{-65}\,\text{J}}$$

Remarks: Note that our value for ℓ justifies our assumption that ℓ >> 1.

***14** ••

Picture the Problem We can solve Equation 37-18 for v and substitute for the frequency of the mass-and-spring oscillator to estimate the quantum number v and spacing between adjacent energy levels for this system.

The vibrational energy levels are given by Equation 37-18:

$$E_v = \left(v + \tfrac{1}{2}\right)hf$$

where $v = 0, 1, 2, \ldots$

Solve for v:

$$v = \frac{E_v}{hf} - \frac{1}{2}$$

or, because $v >> 1$,

$$v \approx \frac{E_v}{hf}$$

The vibrational energy of the object attached to the spring is:

$$E_v = \tfrac{1}{2}kA^2$$

where A is the amplitude of its motion.

Substitute for E_v in the expression for v to obtain:

$$v = \frac{kA^2}{2hf}$$

The frequency of oscillation f of the mass-and-spring oscillator is given by:

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$v = \frac{\pi kA^2}{h}\sqrt{\frac{m}{k}} = \frac{\pi A^2}{h}\sqrt{mk}$$

Substitute numerical values and evaluate ν:

$$\nu = \frac{\pi(0.02\,\text{m})^2}{6.63\times10^{-34}\,\text{J}\cdot\text{s}}\sqrt{(5\,\text{kg})(1500\,\text{N/m})} = \boxed{1.64\times10^{32}}$$

Set $\nu = 0$ in Equation 37-18 to express the spacing between adjacent energy levels:

$$E_{0\nu} = \frac{1}{2}hf = \frac{h}{4\pi}\sqrt{\frac{k}{m}}$$

Substitute numerical values and evaluate $E_{0\nu}$:

$$E_{0\nu} = \frac{6.63\times10^{-34}\,\text{J}\cdot\text{s}}{4\pi}\sqrt{\frac{1500\,\text{N/m}}{5\,\text{kg}}}$$
$$= \boxed{9.14\times10^{-34}\,\text{J}}$$

Remarks: Note that our value for ν justifies our assumption that ν >> 1.

Molecular Bonding

15 •

Picture the Problem The electrostatic potential energy with U at infinity is given by $U = -ke^2/r$.

Relate the electrostatic potential energy of the ions to their separation:

$$U_\text{e} = -\frac{ke^2}{r}$$

Solve for r:

$$r = -\frac{ke^2}{U_\text{e}}$$

Substitute numerical values and evaluate r:

$$r = -\frac{(8.99\times10^9\,\text{N}\cdot\text{m}^2/\text{C}^2)(1.6\times10^{-19}\,\text{C})^2}{(-1.52\,\text{eV})(1.6\times10^{-19}\,\text{J/eV})} = \boxed{0.946\,\text{nm}}$$

16 •

Picture the Problem We can find the energy absorbed or released per molecule by computing the difference between dissociation energy of Cl and the binding energy of NaCl.

Noting that the dissociation energy per Cl atom is 1.24 eV, express the net energy change per molecule ΔE:

$$\Delta E = 1.24\,\text{eV} - E_{\text{binding, NaCl}}$$

The binding energy of NaCl is (see page 1210):

4.27 eV

Substitute and evaluate ΔE:

$$\Delta E = 1.24\,\text{eV} - 4.27\,\text{eV} = \boxed{-3.03\,\text{eV}}$$

$$\boxed{\text{Because } \Delta E < 0, \text{ energy is released. The reaction is } \textit{exothermic}.}$$

17 •

Picture the Problem We can use conversion factors to convert eV/molecule into kcal/mol.

(*a*)
$$1\frac{\text{eV}}{\text{molecule}} = 1\frac{\text{eV}}{\text{molecule}} \times \frac{1\,\text{kcal}}{4184\,\text{J}} \times \frac{6.02\times10^{23}\ \text{molecules}}{\text{mole}} \times \frac{1.60\times10^{-19}\ \text{J}}{\text{eV}}$$
$$= \boxed{23.0\,\text{kcal/mol}}$$

(*b*) The dissociation energy of NaCl, in eV/molecule, is (see page 1205):

4.27 eV/molecule

Using the conversion factor in (*a*), express this energy in kcal/mol:

$$\frac{4.27\,\text{eV}}{\text{molecule}} \times \frac{23.0\,\text{kcal}}{\text{mol}} = \boxed{98.2\,\text{kcal/mol}}$$

***18** •

Picture the Problem The percentage of the bonding that is ionic is given by $100\left(\frac{p_{\text{meas}}}{p_{100}}\right)$.

Express the percentage of the bonding that is ionic:

$$\text{Percent ionic bonding} = 100\left(\frac{p_{\text{meas}}}{p_{100}}\right)$$

Express the dipole moment for 100% ionic bonding:

$$p_{100} = er$$

Substitute to obtain:

$$\text{Percent ionic bonding} = 100\left(\frac{p_{\text{meas}}}{er}\right)$$

Substitute numerical values and evaluate the percent ionic bonding:

$$\text{Percent ionic bonding} = 100\left[\frac{6.40\times10^{-30}\ \text{C}\cdot\text{m}}{\left(1.60\times10^{-19}\ \text{C}\right)\left(0.0917\ \text{nm}\right)}\right] = \boxed{43.6\%}$$

19 ••

Picture the Problem If we choose the potential energy at infinity to be ΔE, the total potential energy is $U_{\text{tot}} = U_{\text{e}} + \Delta E + U_{\text{rep}}$, where U_{rep} is the energy of repulsion, which is found by setting the dissociation energy equal to $-U_{\text{tot}}$.

Express the total potential energy of the molecule:

$$U_{\text{tot}} = U_{\text{e}} + \Delta E + U_{\text{rep}}$$

The core-repulsive energy is :

$$U_{\text{rep}} = -\left(\Delta E + U_{\text{e}} + E_{\text{d}}\right)$$

Calculate the energy ΔE needed to form Rb^+ and F^- ions from neutral rubidium and fluorine atoms:

$$\Delta E = 4.18\,\text{eV} - 3.40\,\text{eV} = 0.78\,\text{eV}$$

Express the electrostatic potential energy is:

$$U_{\text{e}} = -\frac{ke^2}{r}$$

Substitute numerical values and evaluate U_{e}:

$$U_{\text{e}} = -\frac{\left(8.99\times10^{9}\ \text{N}\cdot\text{m}^2/\text{C}^2\right)\left(1.60\times10^{-19}\ \text{C}\right)^2}{\left(0.227\ \text{nm}\right)\left(1.60\times10^{-19}\ \text{J/eV}\right)} = -6.34\,\text{eV}$$

Substitute numerical values and evaluate U_{rep}:

$$U_{\text{rep}} = -\left(0.78\,\text{eV} - 6.34\,\text{eV} + 5.12\,\text{eV}\right) = \boxed{0.44\,\text{eV}}$$

20 ••

Picture the Problem The potential energy of attraction of the ions is $U_{\text{e}} = -ke^2/r$. We can find the dissociation energy from the negative of the sum of the potential energy of attraction and the difference between the ionization energy of potassium and the electron affinity of chlorine.

(*a*) The potential energy of attraction of the ions is given by:

$$U_{\mathrm{e}} = -\frac{ke^2}{r}$$

where $ke^2 = 1.44\ \mathrm{eV\cdot nm}$

Substitute numerical values and evaluate U_{e}:

$$U_{\mathrm{e}} = -\frac{1.44\,\mathrm{eV\cdot nm}}{0.267\,\mathrm{nm}} = \boxed{-5.39\,\mathrm{eV}}$$

(*b*) Express the total potential energy of the molecule:

$$U_{\mathrm{tot}} = U_{\mathrm{e}} + \Delta E + U_{\mathrm{rep}}$$

or, neglecting any energy of repulsion,

$$U_{\mathrm{tot}} = U_{\mathrm{e}} + \Delta E$$

The dissociation energy is the negative of the total potential energy:

$$E_{\mathrm{d,calc}} = -U_{\mathrm{tot}} = -\left(U_{\mathrm{e}} + \Delta E\right)$$

ΔE is the difference between the ionization energy of potassium and the electron affinity of Cl:

$$\Delta E = 4.34\,\mathrm{eV} - 3.62\,\mathrm{eV} = 0.72\,\mathrm{eV}$$

Substitute numerical values and evaluate $E_{\mathrm{d,calc}}$:

$$E_{\mathrm{d,calc}} = -\left(-5.39\,\mathrm{eV} + 0.72\,\mathrm{eV}\right) = \boxed{4.67\,\mathrm{eV}}$$

The energy due to repulsion of the ions at equilibrium separation is given by:

$$U_{\mathrm{rep}} = E_{\mathrm{d,calc}} - E_{\mathrm{d,meas}}$$

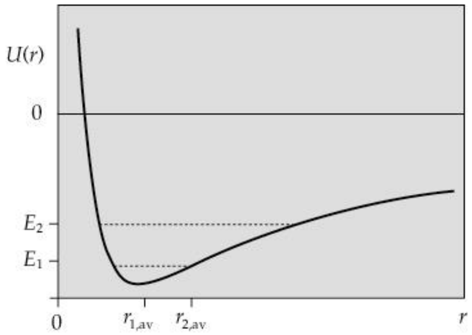
Substitute numerical values and evaluate U_{rep}:

$$U_{\mathrm{rep}} = 4.67\,\mathrm{eV} - 4.49\,\mathrm{eV} = \boxed{0.18\,\mathrm{eV}}$$

21 ••

Picture the Problem Assume that $U(r)$ is of the form given in Problem 24 with $n = 6$.

The potential energy curve is shown in the figure. The turning points for vibrations of energy E_1 and E_2 are at the values of r, where the energies equal $U(r)$. It is apparent that the average value of r depends on the energy and that $r_{2,\text{av}}$ is greater than $r_{1,\text{av}}$.



22 ••

Picture the Problem We can use $U_e = -ke^2/r_0$ to calculate the potential energy of attraction between the Na^+ and Cl^- ions at the equilibrium separation r_0 = 0.236 nm. We can find the energy due to repulsion of the ions at the equilibrium separation from $U_{\text{rep}} = -(U_e + E_d + \Delta E)$.

The potential energy of attraction between the Na^+ and Cl^- ions at the equilibrium separation r_0 is given by:

$$U_e = -\frac{ke^2}{r_0}$$

where ke^2 = 1.44 eV·nm.

Substitute numerical values and evaluate U_e:

$$U_e = -\frac{1.44\,\text{eV}\cdot\text{nm}}{0.236\,\text{nm}} = \boxed{-6.10\,\text{eV}}$$

From Figure 37-1:

$$E_d = 4.27\,\text{eV}$$

The ratio of the magnitude of the potential energy of attraction to the dissociation energy is:

$$\frac{|U_e|}{E_d} = \frac{6.10\,\text{eV}}{4.27\,\text{eV}} = \boxed{1.43}$$

U_{rep} is related to U_e, E_d, and ΔE according to:

$$U_{\text{rep}} = -(U_e + E_d + \Delta E)$$

From Figure 37-1:

$$\Delta E = 1.52\,\text{eV}$$

Substitute numerical values and evaluate U_{rep}:

$$U_{\text{rep}} = -(-6.10\,\text{eV} + 4.27\,\text{eV} + 1.52\,\text{eV}) = \boxed{0.310\,\text{eV}}$$

23 ••

Picture the Problem The potential energy of attraction of the ions is $U_e = -ke^2/r$. We can find the dissociation energy from the negative of the sum of the potential energy of attraction and the difference between the ionization energy of potassium and the electron affinity of fluorine.

(*a*) The potential energy of attraction between the K^+ and F^- ions at the equilibrium separation r_0 is given by:

$$U_e = -\frac{ke^2}{r_0}$$

where $ke^2 = 1.44\ \text{eV}\cdot\text{nm}$.

Substitute numerical values and evaluate U_e:

$$U_e = -\frac{1.44\,\text{eV}\cdot\text{nm}}{0.217\,\text{nm}} = \boxed{-6.64\,\text{eV}}$$

(*b*) Express the total potential energy of the molecule:

$$U_{tot} = U_e + \Delta E + U_{rep}$$

or, neglecting any energy of repulsion,

$$U_{tot} = U_e + \Delta E$$

The dissociation energy is the negative of the total potential energy:

$$E_{d,calc} = -U_{tot} = -\left(U_e + \Delta E\right)$$

ΔE is the difference between the ionization energy of potassium and the electron affinity of fluorine:

$$\Delta E = 4.34\,\text{eV} - 3.40\,\text{eV} = 0.94\,\text{eV}$$

Substitute numerical values and evaluate $E_{d,calc}$:

$$E_{d,calc} = -\left(-6.64\,\text{eV} + 0.94\,\text{eV}\right) = \boxed{5.70\,\text{eV}}$$

The energy due to repulsion of the ions at equilibrium separation is given by:

$$U_{rep} = E_{d,calc} - E_{d,meas}$$

Substitute numerical values and evaluate U_{rep}:

$$U_{rep} = 5.70\,\text{eV} - 5.07\,\text{eV} = \boxed{0.63\,\text{eV}}$$

***24** •••

Picture the Problem $U(r)$ is the potential energy of the two ions as a function of separation distance r. $U(r)$ is chosen so $U(\infty) = -\Delta E$, where ΔE is the negative of the energy required to form two ions at infinite separation from two neutral atoms also at infinite separation. $U_{rep}(r)$ is the potential energy of the two ions due to the repulsion of the two closed-shell cores. E_d is the disassociation energy, the energy required to separate the two ions plus the energy ΔE required to form two neutral atoms from the two ions at infinite separation. The net force acting on the ions is the sum of F_{rep} and F_{e}. We can find F_{rep} from U_{rep} and F_{e} from Coulomb's law and then use $dU/dr = F_{\text{net}} = 0$ at $r = r_0$ to solve for n.

Express the net force acting on the ions:

$$F_{\text{net}} = F_{\text{rep}} + F_{\text{e}} \qquad (1)$$

Find F_{rep} from U_{rep}:

$$F_{\text{rep}} = \frac{dU_{\text{rep}}}{dr} = \frac{d}{dr}\left[Cr^{-n}\right] = -nCr^{-n-1} = -\frac{nC}{r^{n+1}}$$

The electrostatic potential energy of the two ions as a function of separation distance is given by:

$$U_{\text{e}} = -\frac{ke^2}{r}$$

Find the electrostatic force of attraction F_{e} from U_{e}:

$$F_{\text{e}} = \frac{dU_{\text{e}}}{dr} = \frac{d}{dr}\left[-\frac{ke^2}{r}\right] = \frac{ke^2}{r^2}$$

Substitute for F_{rep} and F_{e} in equation (1) to obtain:

$$F_{\text{net}} = -\frac{nC}{r^{n+1}} + \frac{ke^2}{r^2}$$

Because $dU/dr = F_{\text{net}} = 0$ at $r = r_0$:

$$0 = -\frac{nC}{r_0^{n+1}} + \frac{ke^2}{r_0^2}$$

Multiply both sides of this equation by r_0 to obtain:

$$0 = -\frac{nC}{r_0^n} + \frac{ke^2}{r_0} = -nU_{\text{rep}}(r_0) + \left|U_{\text{e}}(r_0)\right|$$

Solve for n to obtain:

$$n = \boxed{\frac{\left|U_{\text{e}}(r_0)\right|}{U_{\text{rep}}(r_0)}}$$

25 •••

Picture the Problem U_{rep} at $r = r_0$ is related to U_{e}, E_{d}, and ΔE through $U_{\text{rep}} = -\left(U_{\text{e}} + E_{\text{d}} + \Delta E\right)$. The net force is the sum of F_{rep} and F_{e}. We can find F_{rep} from U_{rep} and F_{e} from Coulomb's law. Because $F_{\text{net}} = 0$ at $r = r_0$, we can obtain simultaneous equations in C and n that we can solve for each of these quantities.

(*a*) U_{rep} is related to U_{e}, E_{d}, and ΔE according to:

$$U_{\text{rep}} = -\left(U_{\text{e}} + E_{\text{d}} + \Delta E\right)$$

where $\Delta E_{\text{NaCl}} = 1.52$ eV

$U_e(r_0)$ is given by:

$$U_e = -\frac{ke^2}{r_0}$$

where $ke^2 = 1.44$ eV·nm

Substitute numerical values and evaluate U_e:

$$U_e = -\frac{1.44\,\text{eV}\cdot\text{nm}}{0.236\,\text{nm}} = -6.10\,\text{eV}$$

Substitute numerical values and evaluate U_{rep}:

$$U_{\text{rep}} = -\left(-6.10\,\text{eV} + 4.27\,\text{eV} + 1.52\,\text{eV}\right)$$
$$= \boxed{0.31\,\text{eV}}$$

(*b*) Express the net force acting on the Na^+ and Cl^- ions:

$$F_{\text{net}} = F_{\text{rep}} + F_e \qquad (1)$$

Find F_{rep} from U_{rep}:

$$F_{\text{rep}} = \frac{dU_{\text{rep}}}{dr} = \frac{d}{dr}\left[Cr^{-n}\right] = -nCr^{-n-1}$$
$$= -\frac{nC}{r^{n+1}}$$

The electrostatic force of attraction is:

$$F_e = \frac{ke^2}{r^2}$$

Substitute for F_{rep} and F_e in equation (1) to obtain:

$$F_{\text{net}} = -\frac{nC}{r^{n+1}} + \frac{ke^2}{r^2}$$

Because $F_{\text{net}} = 0$ at $r = r_0$:

$$0 = -\frac{nC}{r_0^{n+1}} + \frac{ke^2}{r_0^2}$$

or

$$\left|U_e(r_0)\right| = n\frac{C}{r_0^n} = nU_{\text{rep}}(r_0)$$

Solve for n and C to obtain:

$$n = \frac{\left|U_e(r_0)\right|}{U_{\text{rep}}(r_0)}$$

and

$$C = U_{\text{rep}}(r_0)r_0^n$$

From (*a*):

$$U_e(r_0) = -6.10\,\text{eV}$$
$$U_{\text{rep}}(r_0) = 0.31\,\text{eV}$$

and, from Figure 37-1,

$$r_0 = 0.236\,\text{nm}$$

Substitute for $U_e(r_0)$ and $U_{rep}(r_0)$ and evaluate n and C:

$$n = \frac{6.10\,\text{eV}}{0.31\,\text{eV}} = \boxed{19.7}$$

and

$$C = (0.31\,\text{eV})(0.236\,\text{nm})^{19.7}$$
$$= \boxed{1.37\times10^{-13}\,\text{eV}\cdot\text{nm}^{19.7}}$$

Energy Levels of Spectra of Diatomic Molecules

26 •

Picture the Problem We can relate the characteristic rotational energy E_{0r} to the moment of inertia of the molecule and model the moment of inertia of the N_2 molecule as two point objects separated by a distance r.

The characteristic rotational energy of a molecule is given by:

$$E_{0r} = \frac{\hbar^2}{2I}$$

Express the moment of inertia of the molecule:

$$I = 2M_N\left(\frac{r}{2}\right)^2 = \tfrac{1}{2}M_N r^2$$

Substitute for I to obtain:

$$E_{0r} = \frac{\hbar^2}{2\left(\frac{1}{2}M_N r^2\right)} = \frac{\hbar^2}{M_N r^2} = \frac{\hbar^2}{14 m_p r^2}$$

Solve for r:

$$r = \hbar\sqrt{\frac{1}{14E_{0r}m_p}}$$

Substitute numerical values and evaluate r:

$$r = (1.055\times10^{-34}\,\text{J}\cdot\text{s})\sqrt{\frac{1}{14(2.48\times10^{-4}\,\text{eV})(1.602\times10^{-19}\,\text{J/eV})(1.673\times10^{-27}\,\text{kg})}}$$
$$= \boxed{0.109\,\text{nm}}$$

***27** •

Picture the Problem We can relate the characteristic rotational energy E_{0r} to the moment of inertia of the molecule and model the moment of inertia of the O_2 molecule as two point objects separated by a distance r.

The characteristic rotational energy of a molecule is given by:

$$E_{0r}=\frac{\hbar^2}{2I}$$

Express the moment of inertia of the molecule:

$$I=2M_{\mathrm{O}}\left(\frac{r}{2}\right)^2=\tfrac{1}{2}M_{\mathrm{O}}r^2$$

Substitute for *I* to obtain:

$$E_{0r}=\frac{\hbar^2}{2\left(\frac{1}{2}M_{\mathrm{O}}r^2\right)}=\frac{\hbar^2}{M_{\mathrm{O}}r^2}=\frac{\hbar^2}{16m_{\mathrm{p}}r^2}$$

Solve for *r*:

$$r=\frac{\hbar}{4}\sqrt{\frac{1}{E_{0r}m_{\mathrm{p}}}}$$

Substitute numerical values and evaluate *r*:

$$r=\left(\frac{1.055\times10^{-34}\ \mathrm{J\cdot s}}{4}\right)\sqrt{\frac{1}{(1.78\times10^{-4}\ \mathrm{eV})(1.6\times10^{-19}\ \mathrm{J/eV})(1.67\times10^{-27}\ \mathrm{kg})}}$$
$$=\boxed{0.121\mathrm{nm}}$$

28 ••

Picture the Problem We can use the definition of the reduced mass to show that the reduced mass is smaller than either mass in a diatomic molecule.

Express the reduced mass of a two-body system:

$$\mu=\frac{m_1m_2}{m_1+m_2}$$

Divide the numerator and denominator of this expression by m_2 to obtain:

$$\mu=\frac{m_1}{1+\dfrac{m_1}{m_2}}\qquad(1)$$

Divide the numerator and denominator of this expression by m_1 to obtain:

$$\mu=\frac{m_2}{1+\dfrac{m_2}{m_1}}\qquad(2)$$

Because the denominator is greater than 1 in equations (1) and (2):

$$\boxed{\mu<m_1}\ \text{and}\ \boxed{\mu<m_2}$$

(*a*) For H_2, $m_1 = m_2 = 1$ u:

$$\mu_{\mathrm{H_2}}=\frac{(1\,\mathrm{u})(1\,\mathrm{u})}{1\,\mathrm{u}+1\,\mathrm{u}}=\boxed{0.500\,\mathrm{u}}$$

(*b*) For N_2, $m_1 = m_2 = 14$ u:

$$\mu_{N_2} = \frac{(14\,\text{u})(14\,\text{u})}{14\,\text{u} + 14\,\text{u}} = \boxed{7.00\,\text{u}}$$

(*c*) For CO, $m_1 = 12$ u and $m_2 = 16$ u:

$$\mu_{CO} = \frac{(12\,\text{u})(16\,\text{u})}{12\,\text{u} + 16\,\text{u}} = \boxed{6.86\,\text{u}}$$

(*d*) For HCl, $m_1 = 1$ u and $m_2 = 35.5$ u:

$$\mu_{HCl} = \frac{(1\,\text{u})(35.5\,\text{u})}{1\,\text{u} + 35.5\,\text{u}} = \boxed{0.973\,\text{u}}$$

29 ••

Picture the Problem We can solve Equation 37-18 for ν and substitute for the frequency of the CO molecule (see Example 37-4) and its binding energy to estimate the quantum number ν.

The vibrational energy levels are given by Equation 37-18:

$$E_\nu = \left(\nu + \tfrac{1}{2}\right)hf$$

where $\nu = 0, 1, 2, \ldots$

Solve for ν:

$$\nu = \frac{E_\nu}{hf} - \frac{1}{2}$$

Substitute numerical values and evaluate ν:

$$\nu = \frac{11\,\text{eV} \times \dfrac{1.60\times10^{-19}\,\text{J}}{\text{eV}}}{(6.63\times10^{-34}\,\text{J}\cdot\text{s})(6.42\times10^{13}\,\text{Hz})} - \frac{1}{2} = 40.8 \approx \boxed{41}$$

***30** ••

Picture the Problem We can use the expression for the rotational energy levels of the diatomic molecule to express the energy separation Δ*E* between the $\ell = 3$ and $\ell = 2$ rotational levels and model the moment of inertia of the LiH molecule as two point objects separated by a distance r_0.

The energy separation between the $\ell = 3$ and $\ell = 2$ rotational levels of this diatomic molecule is given by:

$$\Delta E = E_{\ell=3} - E_{\ell=2}$$

Express the rotational energy levels $E_{\ell=3}$ and $E_{\ell=2}$ in terms of E_{0r}:

$$E_{\ell=3} = 3(3+1)E_{0r} = 12E_{0r}$$

and

$$E_{\ell=2} = 2(2+1)E_{0r} = 6E_{0r}$$

Substitute for $E_{\ell=3}$ and $E_{\ell=2}$ to

$$\Delta E = 12E_{0r} - 6E_{0r} = 6E_{0r}$$

obtain:

or

$$E_{0r} = \tfrac{1}{6}\Delta E$$

The characteristic rotational energy of a molecule is given by:

$$E_{0r} = \frac{\hbar^2}{2I} = \tfrac{1}{6}\Delta E \Rightarrow \Delta E = \frac{3\hbar^2}{I}$$

Express the moment of inertia of the molecule:

$$I = \mu r_0^2$$

where μ is the reduced mass of the molecule.

Substitute for I to obtain:

$$\Delta E = \frac{3\hbar^2}{\mu r_0^2} = \frac{3\hbar^2}{\dfrac{m_{\text{Li}} m_{\text{H}}}{m_{\text{Li}} + m_{\text{H}}} r_0^2} = \frac{3\hbar^2 \left(m_{\text{Li}} + m_{\text{H}}\right)}{m_{\text{Li}} m_{\text{H}}\ r_0^2}$$

Substitute numerical values and evaluate ΔE:

$$\Delta E = \frac{3\left(1.055\times10^{-34}\ \text{J}\cdot\text{s}\right)^2\left(6.94\,\text{u} + 1\,\text{u}\right)}{\left(6.94\,\text{u}\right)\left(1\,\text{u}\right)\left(0.16\,\text{nm}\right)^2\left(1.602\times10^{-19}\ \text{J/eV}\right)\left(1.660\times10^{-27}\ \text{kg/u}\right)} = \boxed{5.61\,\text{meV}}$$

***31** ••

Picture the Problem Let the origin of coordinates be at the point mass m_1 and point mass m_2 be at a distance r_0 from the origin. We can express the moment of inertia of a diatomic molecule with respect to its center of mass using the definitions of the center of mass and the moment of inertia of point particles.

Express the moment of inertia of a diatomic molecule:

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad (1)$$

The r coordinate of the center of mass is:

$$r_{\text{CM}} = \frac{m_2}{m_1 + m_2} r_0$$

The distances of m_1 and m_2 from the center of mass are:

$$r_1 = r_{\text{CM}}$$

and

$$r_2 = r_0 - r_{\text{CM}} = r_0 - \frac{m_2}{m_1 + m_2} r_0 = \frac{m_1}{m_1 + m_2} r_0$$

Substitute for r_1 and r_2 in equation (1) to obtain:

$$I = m_1\left(\frac{m_2}{m_1+m_2}r_0\right)^2 + m_2\left(\frac{m_1}{m_1+m_2}r_0\right)^2$$

Simplifying this expression leads to:

$$I = \frac{m_1m_2}{m_1+m_2}r_0^2$$

or

$$\boxed{I = \mu r_0^2} \qquad 36\text{-}14$$

where

$$\boxed{\mu = \frac{m_1m_2}{m_1+m_2}} \qquad 36\text{-}15$$

32 ••

Picture the Problem We can relate the characteristic rotational energy $E_{0\mathrm{r}}$ to the moment of inertia of the molecule and model the moment of inertia of the KCl molecule as two point objects of reduced mass μ separated by a distance r.

The characteristic rotational energy of a molecule is given by:

$$E_{0r} = \frac{\hbar^2}{2I}$$

Express the moment of inertia of the molecule:

$$I = \mu r_0^2$$

where $\mu = \dfrac{m_\mathrm{K}m_\mathrm{Cl}}{m_\mathrm{K}+m_\mathrm{Cl}}$

Substitute for I to obtain:

$$E_{0r} = \frac{\hbar^2}{2\mu r_0^2} = \frac{\hbar^2(m_\mathrm{K}+m_\mathrm{Cl})}{2m_\mathrm{k}m_\mathrm{Cl}r_0^2}$$

Substitute numerical values and evaluate E_{0r}:

$$E_{0r} = \frac{(1.055\times10^{-34}\,\mathrm{J\cdot s})^2(39.1\,\mathrm{u}+35.5\,\mathrm{u})}{2(39.1\,\mathrm{u})(35.5\,\mathrm{u})(0.267\,\mathrm{nm})^2(1.660\times10^{-27}\,\mathrm{kg/u})}$$
$$= 2.53\times10^{-24}\,\mathrm{J}\times\frac{1}{1.602\times10^{-19}\,\mathrm{J/eV}} = \boxed{0.0158\,\mathrm{meV}}$$

33 ••

Picture the Problem We can use the expression for the vibrational energies of a molecule to find the lowest vibrational energy. Because the difference in the vibrational energy levels depends on both Δf and the moment of inertia I of the molecule, we can relate these quantities and solve for I. Finally, we can use $I = \mu r^2$, with μ representing the reduced mass of the molecule, to find the equilibrium separation of the atoms.

(*a*) The vibrational energy levels are given by:

$$E_\nu = \left(\nu + \tfrac{1}{2}\right)hf, \quad \nu = 0,1,2,...$$

The lowest vibrational energy corresponds to $\nu = 0$:

$$E_0 = \tfrac{1}{2}hf$$

Substitute numerical values and evaluate E_0:

$$E_0 = \tfrac{1}{2}\left(6.63\times10^{-34}\ \text{J}\cdot\text{s}\right)\left(8.66\times10^{13}\ \text{Hz}\right) = 2.87\times10^{-20}\,\text{J}\times\frac{1}{1.6\times10^{-19}\ \text{J/eV}}$$

$$= \boxed{0.179\,\text{eV}}$$

(*b*) For $\Delta\ell = \pm1$:

$$\Delta E_\ell = \frac{\ell\hbar^2}{I} = \ell h\Delta f$$

Solve for *I*:

$$I = \frac{\hbar^2}{h\Delta f} = \frac{h^2}{4\pi^2 h\Delta f} = \frac{h}{4\pi^2\Delta f}$$

Substitute numerical values and evaluate *I*:

$$I = \frac{6.63\times10^{-34}\ \text{J}\cdot\text{s}}{4\pi^2\left(6\times10^{11}\ \text{Hz}\right)}$$

$$= \boxed{2.80\times10^{-47}\ \text{kg}\cdot\text{m}^2}$$

(*c*) The moment of inertia of a HCL molecule is given by:

$$I = \mu r^2$$

Replace μ by the reduced mass of a HCl molecule and *r* by r_0 to obtain:

$$I = \frac{m_\text{H} m_\text{Cl}}{m_\text{H} + m_\text{Cl}} r_0^2$$

Solve for r_0:

$$r_0 = \sqrt{\frac{m_\text{H} + m_\text{Cl}}{m_\text{H} m_\text{Cl}} I}$$

Substitute numerical values and evaluate r_0:

$$r_0 = \sqrt{\left[\frac{1\,\text{u} + 34.453\,\text{u}}{(1\,\text{u})(34.453\,\text{u})}\right]\frac{\left(2.80\times10^{-47}\ \text{kg}\cdot\text{m}^2\right)}{1.66\times10^{-27}\ \text{kg/u}}} = \boxed{0.132\,\text{nm}}$$

34 ••

Picture the Problem Let the numeral 1 refer to the H^+ and the numeral 2 to the Cl^- ion. For a two-mass and spring system on which no external forces are acting, the center of mass must remain fixed. We can use this condition to express the net force acting on either the H^+ or Cl^- ion. Because this force is a linear restoring force, we can conclude that the motion of the object whose mass is m_1 will be simple harmonic with an angular frequency given by $\omega = \sqrt{K_{\text{eff}}/m_1}$. Substitution for K_{eff} will lead us to the result given in (*b*).

If the particle whose mass is m_1 moves a distance r_1 from (or toward) the center of mass, then the particle whose mass is m_2 must move a distance:

$\Delta r_2 = \dfrac{m_1}{m_2}\Delta r_1$ from (or toward) the center of mass.

Express the force exerted by the spring:

$$F = -K\Delta r = -K(\Delta r_1 + \Delta r_2)$$

Substitute for Δr_2 to obtain:

$$F = -K\left(\Delta r_1 + \frac{m_1}{m_2}\Delta r_1\right) = -K\left(\frac{m_1+m_2}{m_2}\right)\Delta r_1$$

A displacement Δr_1 of m_1 results in a restoring force:

$$F = -K\left(\frac{m_1+m_2}{m_2}\right)\Delta r_1 = -K_{\text{eff}}\Delta r_1$$

where $K_{\text{eff}} = K\left(\dfrac{m_1+m_2}{m_2}\right)$

Because this is a linear restoring force, we know that the motion will be simple harmonic with:

$$\omega = \sqrt{\frac{K_{\text{eff}}}{m_1}}$$

or

$$f = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{K_{\text{eff}}}{m_1}}$$

Substitute for K_{eff} and simplify to obtain:

$$f = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{K\left(\frac{m_1+m_2}{m_1m_2}\right)}$$

or, because $\mu = \dfrac{m_1m_2}{m_1+m_2}$ is the reduced mass of the two-particle system,

$$f = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

Solve for K:

$$K = 4\pi^2 f^2\mu = 4\pi^2 f^2\frac{m_{\mathrm{H}}m_{\mathrm{Cl}}}{m_{\mathrm{H}} + m_{\mathrm{Cl}}}$$

Substitute numerical values and evaluate K:

$$K = \frac{4\pi^2\left(8.66\times10^{13}\ \mathrm{Hz}\right)^2(1\,\mathrm{u})(35.453\,\mathrm{u})\left(1.66\times10^{-27}\ \mathrm{kg/u}\right)}{(1\,\mathrm{u} + 35.453\,\mathrm{u})} = \boxed{478\ \mathrm{N/m}}$$

35 ••

Picture the Problem

We're given the population of rotational states function:

$$f(\ell) = (2\ell + 1)e^{-E_l/kT}$$

where

$$E_\ell = \ell(\ell + 1)E_{0r} \text{ and } E_{0\mathrm{r}} = \frac{\hbar^2}{2I}$$

The moment of inertia I of an oxygen molecule is given by:

$$I = \tfrac{1}{2}mr_0^2$$

where m is the reduced mass and r_0 is the separation of the atoms in a molecule.

We'll assume, as in Example 37-3, that:

$$r_0 = 0.1\,\mathrm{nm}$$

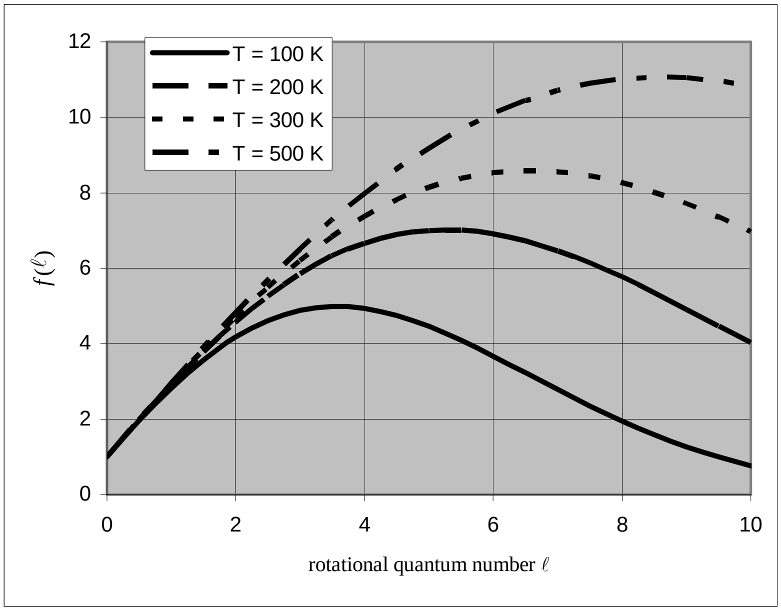
A spreadsheet program to plot $f(\ell)$ is shown below. The formulas used to calculate the quantities in the columns are as follows:

Cell	Formula/Content	Algebraic Form
B1	1.00E–10	r_0
B2	16	m (u)
B3	2.66E–26	m (kg)
B4	1.05E–34	$\hbar$
B5	1.38E–23	k
B6	4.15E–23	$E_{0\mathrm{r}}$
B7	100	T (K)
B8	200	T (K)
B9	300	T (K)
B10	500	T (K)
A13	0	ℓ

B13	A13*(A13+1)*B6	$\ell(\ell+1)E_{0r}$
C13	(2*A13 + 1)*EXP(–B13/(B5*B7))	$f(\ell, T = 100\text{ K})$
D13	(2*A13 + 1)*EXP(–B13/(B5*B8))	$f(\ell, T = 200\text{ K})$
E13	(2*A13 + 1)*EXP(–B13/(B5*B9))	$f(\ell, T = 300\text{ K})$
F13	(2*A13 + 1)*EXP(–B13/(B5*B10))	$f(\ell, T = 500\text{ K})$

	A	B	C	D	E	F
1	r_0=	1.00E–10	m			
2	m=	16	u			
3	m=	2.656E–26	kg			
4	h_bar=	1.05E–34	J.s			
5	k=	1.38E–23	J/K			
6	E_0r=	4.15E–23	eV			
7	T=	100	K			
8	T=	200	K			
9	T=	300	K			
10	T=	500	K			
11						
12	l	E_l	E_100 K	E_200 K	E_300 K	E_500 K
13	0.0	0.00E+00	1.00	1.00	1.00	1.00
14	0.5	3.11E–23	1.96	1.98	1.99	1.99
15	1.0	8.30E–23	2.82	2.91	2.94	2.96
16	1.5	1.56E–22	3.57	3.78	3.85	3.91
17	2.0	2.49E–22	4.17	4.57	4.71	4.82
29	8.0	2.99E–21	1.95	5.76	8.26	11.02
30	8.5	3.35E–21	1.59	5.34	8.01	11.07
31	9.0	3.74E–21	1.27	4.91	7.71	11.06
32	9.5	4.14E–21	1.00	4.46	7.36	10.98
33	10.0	4.57E–21	0.77	4.02	6.97	10.83

The following graph shows $f(\ell)$ as a function of temperature.



***36** ••

Picture the Problem For a two-mass and spring system on which no external forces are acting, the center of mass must remain fixed. We can use this condition to express the net force acting on either object. Because this force is a linear restoring force, we can conclude that the motion of the object whose mass is m_1 will be simple harmonic with an angular frequency given by $\omega = \sqrt{\frac{k_{\text{eff}}}{m_1}}$. Substitution for k_{eff} will lead us to the result given in (*b*).

(*a*) If the particle whose mass is m_1 moves a distance Δr_1 from (or toward) the center of mass, then the particle whose mass is m_2 must move a distance:

$\Delta r_2 = \frac{m_1}{m_2}\Delta r_1$ from (or toward) the center of mass.

Express the force exerted by the spring:

$$F = -k\Delta r = -k(\Delta r_1 + \Delta r_2)$$

Substitute for Δr_2 to obtain:

$$F = -k\left(\Delta r_1 + \frac{m_1}{m_2}\Delta r_1\right)$$

$$= \boxed{-k\left(\frac{m_1 + m_2}{m_2}\right)\Delta r_1}$$

(*b*) A displacement Δr_1 of m_1 results in a restoring force:

$$F = -k\left(\frac{m_1 + m_2}{m_2}\right)\Delta r_1 = -k_{\text{eff}}\Delta r_1$$

where $k_{\text{eff}} = k\left(\frac{m_1 + m_2}{m_2}\right)$

Because this is a linear restoring force, we know that the motion will be simple harmonic with:

$$\omega = \sqrt{\frac{k_{\text{eff}}}{m_1}}$$

or

$$f = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{k_{\text{eff}}}{m_1}}$$

Substitute for k_{eff} and simplify to obtain:

$$f = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{k\left(\frac{m_1 + m_2}{m_1 m_2}\right)}$$

or, because $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the two-particle system,

$$f = \boxed{\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}}\,.$$

37 •••

Picture the Problem We can use the definition of the reduced mass to find the reduced mass for the $H^{35}Cl$ and $H^{37}Cl$ molecules and the fractional difference $\Delta\mu/\mu$. Because the rotational frequency is proportional to 1/*I*, where *I* is the moment of inertia of the system, and *I* is proportional to μ, we can obtain an expression for *f* as a function of μ that we differentiate implicitly to show that $\Delta f/f = -\Delta\mu/\mu$.

For $H^{35}Cl$:

$$\mu = \frac{(35\,\text{u})(1\,\text{u})}{35\,\text{u} + 1\,\text{u}} = \frac{35}{36}\,\text{u} = \boxed{0.9722\,\text{u}}$$

For $H^{37}Cl$:

$$\mu = \frac{(37\,\text{u})(1\,\text{u})}{37\,\text{u} + 1\,\text{u}} = \frac{37}{38}\,\text{u} = \boxed{0.9737\,\text{u}}$$

The fractional difference is:

$$\frac{\Delta\mu}{\mu} = \frac{\frac{37}{38}\,\text{u} - \frac{35}{36}\,\text{u}}{\frac{1}{2}\left(\frac{35}{36}\,\text{u} + \frac{37}{38}\,\text{u}\right)} = \frac{\frac{36\times 37 - 35\times 38}{36\times 38}\,\text{u}}{\frac{35\times 38 + 36\times 37}{2(36)(38)}\,\text{u}} = \boxed{0.00150}$$

The rotational frequency is proportional to 1/*I*, where *I* is the moment of inertia of the system. Because *I* is proportional to μ:

$$f=\frac{C}{\mu}$$

and

$$df=-C\mu^{-2}d\mu$$

Divide *df* by *f* to obtain:

$$\frac{df}{f}=-\frac{d\mu}{\mu}\text{ and }\frac{\Delta f}{f}\approx-\frac{\Delta\mu}{\mu}$$

From Figure 36-17:

$$\Delta f\approx0.01\times10^{13}\text{ Hz}=10^{11}\text{ Hz}$$

For $f=8.40\times10^{13}$ Hz:

$$\frac{\Delta f}{f}\approx\frac{10^{11}\text{ Hz}}{8.40\times10^{13}\text{ Hz}}=\boxed{0.00119}$$

$$\boxed{\begin{array}{l}\text{This result is in fair agreement (about 21\% difference) with the calculated}\\ \text{result. Note that }\Delta f\text{ is difficult to determine precisely from Figure 36-17.}\end{array}}$$

General Problems

38 •

Picture the Problem We can use the definition of the reduced mass to show that when one atom in a diatomic molecule is much more massive than the other the reduced mass is approximately equal to the mass of the lighter atom.

Express the reduced mass of a two-body system:

$$\mu=\frac{m_1m_2}{m_1+m_2}$$

Divide the numerator and denominator of this expression by m_2 to obtain:

$$\mu=\frac{m_1}{1+\frac{m_1}{m_2}}$$

If $m_2>>m_1$, then:

$$\frac{m_1}{m_2}<<1\text{ and }\boxed{\mu\approx m_1}$$

39 ••

Picture the Problem The rotational energy levels are given by $E=\frac{\ell(\ell+1)\hbar^2}{2I},\ell=0,1,2,....$

Express the energy difference between these rotational energy

$$\Delta E_{1,2}=E_2-E_1$$

levels:

Express E_2 and E_1:

$$E_2 = \frac{2(2+1)\hbar^2}{2I} = \frac{3\hbar^2}{I}$$

and

$$E_1 = \frac{1(1+1)\hbar^2}{2I} = \frac{\hbar^2}{I}$$

Substitute to obtain:

$$\Delta E_{1,2} = \frac{3\hbar^2}{I} - \frac{\hbar^2}{I} = \frac{2\hbar^2}{I}$$

The moment of inertia of the molecule is:

$$I = \mu r_0^2$$

where μ is the reduced mass of the molecule.

Substitute for I to obtain:

$$\Delta E_{1,2} = \frac{2\hbar^2}{\mu r_0^2} = \frac{2\hbar^2}{\frac{m_\mathrm{C} m_\mathrm{O}}{m_\mathrm{C} + m_\mathrm{O}} r_0^2} = \frac{2\hbar^2 (m_\mathrm{C} + m_\mathrm{O})}{m_\mathrm{C} m_\mathrm{O} r_0^2}$$

Substitute numerical values and evaluate $\Delta E_{1,2}$:

$$\Delta E_{1,2} = \frac{2(1.055\times10^{-34}\ \mathrm{J\cdot s})^2 (12\,\mathrm{u} + 16\,\mathrm{u})}{(16\,\mathrm{u})(12\,\mathrm{u})(0.113\,\mathrm{nm})^2 (1.66\times10^{-27}\ \mathrm{kg/u})} = \frac{1.53\times10^{-22}\ \mathrm{J}}{1.6\times10^{-19}\ \mathrm{J/eV}} = \boxed{0.955\ \mathrm{meV}}$$

***40** ••

Picture the Problem We can use the result of Problem 36 to find the frequency of vibration of the HF molecule.

In Problem 36 it was established that:

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

The reduced mass is:

$$\mu = \frac{m_\mathrm{H} m_\mathrm{F}}{m_\mathrm{H} + m_\mathrm{F}}$$

Substitute for μ to obtain:

$$f=\frac{1}{2\pi}\sqrt{\frac{k}{\frac{m_\mathrm{H}m_\mathrm{F}}{m_\mathrm{H}+m_\mathrm{F}}}}=\frac{1}{2\pi}\sqrt{\frac{k(m_\mathrm{H}+m_\mathrm{F})}{m_\mathrm{H}m_\mathrm{F}}}$$

Substitute numerical values and evaluate *f*:

$$f=\frac{1}{2\pi}\sqrt{\frac{(970\,\mathrm{N/m})(1\,\mathrm{u}+19\,\mathrm{u})}{(1\,\mathrm{u})(19\,\mathrm{u})(1.66\times10^{-27}\,\mathrm{kg/u})}}=\boxed{1.25\times10^{14}\,\mathrm{Hz}}$$

41 ••

Picture the Problem We can use the result of Problem 36 to find the effective force constant for NO.

In Problem 36 it was established that:

$$f=\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Solve for *k*:

$$k=4\pi^2f^2\mu$$

The reduced mass is:

$$\mu=\frac{m_\mathrm{N}m_\mathrm{O}}{m_\mathrm{N}+m_\mathrm{O}}$$

Substitute for μ to obtain:

$$k=\frac{4\pi^2f^2m_\mathrm{N}m_\mathrm{O}}{m_\mathrm{N}+m_\mathrm{O}}$$

Substitute numerical values and evaluate *k*:

$$k=\frac{4\pi^2\left(5.63\times10^{13}\,\mathrm{s}^{-1}\right)^2(14\,\mathrm{u})(16\,\mathrm{u})(1.66\times10^{-27}\,\mathrm{kg/u})}{14\,\mathrm{u}+16\,\mathrm{u}}=\boxed{1.55\,\mathrm{kN/m}}$$

42 ••

Picture the Problem We can use the expression for the vibrational energy levels of a molecule and the expression for the frequency of oscillation from Problem 36 to find the four lowest vibrational levels of the given molecules.

The vibrational energy levels are given by:

$$E_\nu=\left(\nu+\tfrac{1}{2}\right)hf, \nu=0,1,2,\ldots$$

In Problem 36 we showed that the frequency of oscillation is:

$$f=\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Substitute for f and μ to obtain:

$$E_\nu = \frac{\left(\nu + \tfrac{1}{2}\right)h}{2\pi}\sqrt{\frac{(m_1 + m_2)k}{m_1 m_2}} = \frac{\left(\nu + \tfrac{1}{2}\right)h}{2\pi}\sqrt{k}\sqrt{\frac{(m_1 + m_2)}{m_1 m_2}}$$

Substitute numerical values to obtain:

$$E_\nu = \frac{\left(\nu + \tfrac{1}{2}\right)\left(4.136\times10^{-15}\ \text{eV}\cdot\text{s}\right)}{2\pi}\sqrt{\frac{580\,\text{N/m}}{1.661\times10^{-27}\ \text{kg/u}}}\sqrt{\frac{(m_1 + m_2)}{m_1 m_2}}$$
$$= \left(\nu + \tfrac{1}{2}\right)(0.389\,\text{eV}\cdot\text{u})\sqrt{\frac{(m_1 + m_2)}{m_1 m_2}}$$

Substitute for m_1 and m_2 and evaluate E_0 for H_2:

$$E_0 = \tfrac{1}{2}(0.389\,\text{eV}\cdot\text{u})\sqrt{\frac{(1\text{u} + 1\text{u})}{(1\text{u})(1\text{u})}} = 0.275\,\text{eV}$$

Proceed similarly to complete the table to the right:

	H_2	HD	D_2
	(eV)	(eV)	(eV)
0	$\boxed{0.275}$	$\boxed{0.238}$	$\boxed{0.195}$
1	$\boxed{0.825}$	$\boxed{0.715}$	$\boxed{0.584}$
2	$\boxed{1.375}$	$\boxed{1.191}$	$\boxed{0.973}$
3	$\boxed{1.925}$	$\boxed{1.667}$	$\boxed{1.362}$

The energies of the photons resulting from transitions between adjacent vibrational levels of these molecules are given by:

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

Solve for λ:

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

Evaluate $\lambda(H_2)$:

$$\lambda(H_2)=\frac{1240\,\text{eV}\cdot\text{nm}}{0.550\,\text{eV}}=\boxed{2.25\,\mu\text{m}}$$

Evaluate $\lambda(\text{HD})$:

$$\lambda(\text{HD})=\frac{1240\,\text{eV}\cdot\text{nm}}{0.477\,\text{eV}}=\boxed{2.60\,\mu\text{m}}$$

Evaluate $\lambda(D_2)$:

$$\lambda(D_2)=\frac{1240\,\text{eV}\cdot\text{nm}}{0.389\,\text{eV}}=\boxed{3.19\,\mu\text{m}}$$

43 ••

Picture the Problem We can set the derivative of the potential energy function equal to zero to find the value of *r* for which it is either a maximum or a minimum. Examination of the second derivative of this function at the value for *r* obtained from setting the first derivative equal to zero will establish whether the function is a relative maximum or relative minimum at this point.

Differentiate the potential energy function with respect to *r*:

$$\frac{dU}{dr}=\frac{d}{dr}\left\{U_0\left[\left(\frac{a}{r}\right)^{12}-2\left(\frac{a}{r}\right)^{6}\right]\right\}$$
$$=-\frac{U_0}{r}\left[12\left(\frac{a}{r}\right)^{11}-12\left(\frac{a}{r}\right)^{5}\right]$$

Set the derivative equal to zero:

$$\frac{dU}{dr}=-\frac{U_0}{r_0}\left[12\left(\frac{a}{r_0}\right)^{11}-12\left(\frac{a}{r_0}\right)^{5}\right]$$
$$=0\text{ for extrema}$$

Solve for r_0 to obtain, as our candidate for *r* that minimizes the Lenard-Jones potential:

$$r_0=\boxed{a}$$

To show that $r_0 = a$ corresponds to a minimum, differentiate *U* a second time to obtain:

$$\frac{d^2U}{dr^2}=\frac{d}{dr}\left\{-\frac{U_0}{r}\left[12\left(\frac{a}{r}\right)^{11}-12\left(\frac{a}{r}\right)^{5}\right]\right\}$$
$$=\frac{U_0}{r^2}\left[132\left(\frac{a}{r}\right)^{10}-60\left(\frac{a}{r}\right)^{4}\right]$$

Evaluate this second derivative of the potential at $r_0 = a$:

$$\left.\frac{d^2U}{dr^2}\right|_{r=a}=\frac{U_0}{a^2}[132-60]=\frac{72U_0}{a^2}>0$$

Therefore, we can conclude that $r_0 = a$

minimizes the potential function.

Evaluate $U_{\min}$:

$$U_{\min} = U(a) = U_0\left[\left(\frac{a}{a}\right)^{12} - 2\left(\frac{a}{a}\right)^{6}\right]$$

$$= \boxed{-U_0}$$

From Figure 37-4:

$$r_0 = \boxed{0.074\,\text{nm}}$$

and

$$U_0 = \boxed{4.52\,\text{eV}}$$

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Picture the Problem We can use Equation 21-10 to establish the dependence of E on x and the dependence of an induced dipole on the field that induces it to establish the dependence of p and U on x.

(*a*) In terms of the dipole moment, the electric field on the axis of the dipole at a point a great distance $|x|$ away has the magnitude (see Equation 21-10):

$$E = \frac{2kp}{|x|^3}$$

or

$$E \propto \boxed{\frac{1}{|x|^3}}$$

(*b*) Because the induced dipole moment is proportional to the field that induces it:

$$p \propto \boxed{\frac{1}{x^3}}$$

and

$$U = -\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{E}} \propto \boxed{\frac{1}{x^6}}$$

(*c*) Differentiate U with respect to x to obtain:

$$F_x = -\frac{dU}{dx} \propto \boxed{\frac{1}{x^7}}$$

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Picture the Problem the case of two polar molecules, p does not depend on the field E.

Because p does not depend on the electric field in which the polar molecules find themselves:

$$U \propto \frac{1}{x^3}$$

Differentiate U with respect to x to obtain:

$$F_x = -\frac{dU}{dx} \propto \boxed{\frac{1}{x^4}}$$

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Picture the Problem We can use the expression for the vibrational and rotational energies of a molecule, in conjunction with Figure 37-17 to find E_{0r}, f, and hf.

(*a*) Except for a gap of $4E_{0r}/h$ at the vibrational frequency f, the absorption spectrum contains frequencies equally spaced at:

$$f = \frac{2E_{0r}}{h}$$

Solve for E_{0r}:

$$E_{0r} = \tfrac{1}{2}hf$$

From Figure 37-17:

$$f = 8.66\times10^{13}\text{ Hz}$$

Substitute numerical values and evaluate E_{0r}:

$$E_{0r} = \tfrac{1}{2}\left(6.63\times10^{-34}\text{ J}\cdot\text{s}\right)\left(8.66\times10^{13}\text{ Hz}\right) = 2.87\times10^{-20}\text{ J}\times\frac{1}{1.6\times10^{-19}\text{ J/eV}}$$

$$= \boxed{0.179\,\text{eV}}$$

(*b*) The vibrational energy levels are given by:

$$E_\nu = \left(\nu + \tfrac{1}{2}\right)hf, \quad \nu = 0,1,2,\ldots$$

The lowest vibrational energy corresponds to $\nu = 0$:

$$E_0 = \tfrac{1}{2}hf$$

and

$$hf = 2E_0 \qquad (1)$$

Determine f from Figure 37-17:

$$f = \boxed{8.66\times10^{13}\text{ Hz}}$$

Substitute for f and h and evaluate E_0:

$$E_0 = \tfrac{1}{2}\left(6.63\times10^{-34}\text{ J}\cdot\text{s}\right)\left(8.66\times10^{13}\text{ Hz}\right) = 2.87\times10^{-20}\text{ J}\times\frac{1}{1.6\times10^{-19}\text{ J/eV}}$$

$$= 0.179\text{ eV}$$

Substitute in equation (1) and evaluate hf:

$$hf = 2\left(0.179\,\text{eV}\right) = \boxed{0.358\,\text{eV}}$$

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Picture the Problem We can find the reduced mass of CO and the moment of inertia of a CO molecule from their definitions. The energy level diagram for the rotational levels for $\ell = 0$ to $\ell = 5$ can be found using $\Delta E_{\ell,\ell-1} = 2\ell E_{0r}$. Finally, we can find the wavelength of the photons emitted for each transition using $\lambda_{\ell,\ell-1} = \frac{hc}{\Delta E_{\ell,\ell-1}} = \frac{hc}{2\ell\Delta E_{0r}}$.

(*a*) Express the moment of inertia of CO:

$$I = \mu r_0^2$$

where μ is the reduced mass of the CO molecule.

Find μ:

$$\mu = \frac{m_C m_O}{m_C + m_O} = \frac{(12\,\text{u})(16\,\text{u})}{12\,\text{u} + 16\,\text{u}} = 6.86\,\text{u}$$

In Problem 39 it was established that $r_0 = 0.113$ nm. Use this result to evaluate I:

$$I = (6.86\,\text{u})(1.66\times10^{-27}\ \text{kg/u})(0.113\,\text{nm})^2 = \boxed{1.45\times10^{-46}\ \text{kg}\cdot\text{m}^2}$$

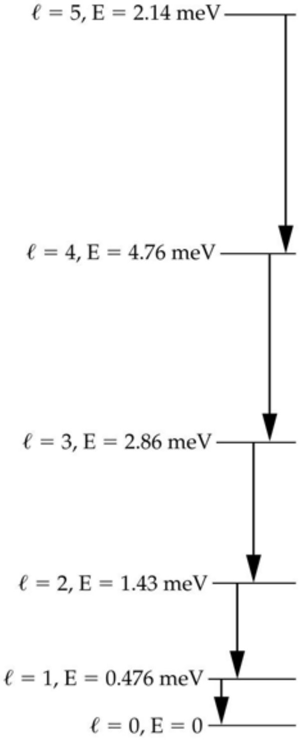
The characteristic rotational energy E_{0r} is given by:

$$E_{0r} = \frac{\hbar^2}{2I}$$

Substitute numerical values and evaluate E_{0r}:

$$E_{0r} = \frac{(6.58\times10^{-16}\ \text{eV}\cdot\text{s})^2(1.6\times10^{-19}\ \text{J/eV})}{2(1.45\times10^{-46}\ \text{kg}\cdot\text{m}^2)} = \boxed{0.239\,\text{meV}}$$

(*b*) The energy level diagram is shown to the right. Note that $\Delta E_{\ell,\ell-1}$, the energy difference between adjacent levels for $\Delta\ell = -1$, is $\Delta E_{\ell,\ell-1} = 2\ell E_{0r}$.



(*c*) Express the energy difference $\Delta E_{\ell.\ell-1}$ between energy levels in terms of the frequency of the emitted radiation:

$$\Delta E_{\ell,\ell-1} = hf_{\ell,\ell-1}$$

Because $c = f_{\ell,\ell-1}\lambda_{\ell,\ell-1}$:

$$\lambda_{\ell,\ell-1} = \frac{hc}{\Delta E_{\ell,\ell-1}} = \frac{hc}{2\ell\Delta E_{0r}}$$

Substitute numerical values to obtain:

$$\lambda_{\ell,\ell-1} = \frac{\left(4.136\times10^{-15}\ \text{eV}\cdot\text{s}\right)\left(3\times10^{8}\ \text{m/s}\right)}{2\ell\left(0.239\,\text{meV}\right)} = \frac{2596\,\mu\text{m}}{\ell}$$

For $\ell = 1$:

$$\lambda_{1,0} = \frac{2596\,\mu\text{m}}{1} = \boxed{2596\,\mu\text{m}}$$

For $\ell = 2$:

$$\lambda_{2,1} = \frac{2596\,\mu\text{m}}{2} = \boxed{1298\,\mu\text{m}}$$

For $\ell = 3$:

$$\lambda_{3,2} = \frac{2596\,\mu\text{m}}{3} = \boxed{865\,\mu\text{m}}$$

For $\ell = 4$:

$$\lambda_{4,3} = \frac{2596\,\mu\text{m}}{4} = \boxed{649\,\mu\text{m}}$$

For $\ell = 5$:

$$\lambda_{5,4} = \frac{2596\,\mu\text{m}}{5} = \boxed{519\,\mu\text{m}}$$

$$\boxed{\text{These wavelengths fall in the microwave region of the spectrum.}}$$

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Picture the Problem The wavelength resulting from transitions between adjacent harmonic oscillator levels of a LiCl molecule is given by $\lambda = \dfrac{2\pi c}{\omega}$. We can find an expression for ω by following the procedure outlined in the problem statement.

The wavelength resulting from transitions between adjacent harmonic oscillator levels of this molecule is given by:

$$\lambda = \frac{hc}{\Delta E} = \frac{hc}{\hbar\omega} = \frac{2\pi c}{\omega} \qquad (1)$$

From Problem 24 we have:

$$U(r) = -\frac{ke^2}{r} + \frac{C}{r^n}\text{, where } \Delta E \text{ is constant.}$$

The Taylor expansion of $U(r)$ about $r = r_0$ is:

$$U(r) = U(r_0) + \left(\frac{dU}{dr}\right)_{r_0}(r - r_0) + \frac{1}{2}\left(\frac{d^2U}{dr^2}\right)_{r_0}(r - r_0)^2 + \ldots$$

Because $U(r_0)$ is a constant, it can be dropped without affecting the physical results and because $\left(\dfrac{dU}{dr}\right)_{r_0} = 0$:

$$U(r) \approx \frac{1}{2}\left(\frac{d^2U}{dr^2}\right)_{r_0}(r - r_0)^2 \qquad (2)$$

Differentiate $U(r)$ twice to obtain:

$$\frac{d^2U}{dr^2} = -2\frac{ke^2}{r^3} + n(n-1)\frac{C}{r^{n+2}}$$

Because $dU/dr = F_{\text{net}} = 0$ at $r = r_0$:

$$0 = -\frac{nC}{r_0^{n+1}} + \frac{ke^2}{r_0^2}$$

Solving for C yields:

$$C = \frac{ke^2 r_0^{n+1}}{n r_0^2} = \frac{ke^2 r_0^{n-1}}{n}$$

Substitute for C and evaluate $\left(\frac{d^2U}{dr^2}\right)_{r_0}$ to obtain:

$$\left(\frac{d^2U}{dr^2}\right)_{r_0} = -2\frac{ke^2}{r_0^3}(n-1) + \frac{n(n-1)}{r_0^{n+2}}\frac{ke^2 r_0^{n-1}}{n}$$
$$= \frac{ke^2}{r_0^3}(n-1)$$

Substitute for $\left(\frac{d^2U}{dr^2}\right)_{r_0}$ in equation (2):

$$U(r) \approx \frac{1}{2}\left[\frac{ke^2}{r_0^3}(n-1)\right](r-r_0)^2$$

Because the potential energy of a simple harmonic oscillator is given by $U_{\text{SHO}} = \frac{1}{2}m\omega^2(r-r_0)^2$:

$$\frac{1}{2}m\omega^2(r-r_0)^2 \approx \frac{1}{2}\left[\frac{ke^2}{r_0^3}(n-1)\right](r-r_0)^2$$

Solve for ω to obtain:

$$\omega \approx \sqrt{\frac{(n-1)ke^2}{mr_0^3}}$$

Substitute μ_{LiCl} for m to obtain:

$$\omega \approx \sqrt{\frac{(n-1)ke^2}{\frac{m_{\text{Li}}m_{\text{Cl}}}{m_{\text{Li}}+m_{\text{Cl}}}r_0^3}} = \sqrt{\frac{(n-1)(m_{\text{Li}}+m_{\text{Cl}})ke^2}{m_{\text{Li}}m_{\text{Cl}}r_0^3}} \qquad (3)$$

From Problem 24:

$$n = \frac{|U_{\text{e}}(r_0)|}{U_{\text{rep}}(r_0)} \qquad (4)$$

U_{rep} is related to U_{e}, E_{d}, and ΔE according to:

$$U_{\text{rep}} = -(U_{\text{e}} + E_{\text{d}} + \Delta E) \qquad (5)$$

The energy needed to form Li^+ and Cl^- from neutral lithium and chlorine atoms is:

$$\Delta E = E_{\text{ionization}} - E_{\text{electron affinity}}$$
$$= 5.39\,\text{eV} - 3.62\,\text{eV} = 1.77\,\text{eV}$$

$U_{\text{e}}(r_0)$ is given by:

$$U_{\text{e}} = -\frac{ke^2}{r_0} = -\frac{1.44\,\text{eV}\cdot\text{nm}}{r_0}$$

Substitute r_0 and evaluate U_e:

$$U_e = -\frac{1.44\,\mathrm{eV\cdot nm}}{0.202\,\mathrm{nm}} = -7.13\,\mathrm{eV}$$

Substitute numerical values in equation (5) and evaluate U_{rep}:

$$U_{rep} = -\left(-7.13\,\mathrm{eV} + 4.86\,\mathrm{eV} + 1.77\,\mathrm{eV}\right)$$
$$= 0.500\,\mathrm{eV}$$

Substitute for $U_{rep}(r_0)$ and $U_e(r_0)$ in equation (4) and evaluate n:

$$n = \frac{\left|-7.13\,\mathrm{eV}\right|}{0.500\,\mathrm{eV}} = 14.3$$

Substitute numerical values in equation (3) and evaluate ω:

$$\omega \approx \sqrt{\frac{(14.3-1)(6.941\,\mathrm{u} + 35.453\,\mathrm{u})(1.44\,\mathrm{eV\cdot nm})\left(1.60\times10^{-19}\ \mathrm{J/eV}\right)}{(6.941\,\mathrm{u})(35.453\,\mathrm{u})\left(1.66\times10^{-27}\ \mathrm{kg/u}\right)(0.202\,\mathrm{nm})^3}}$$
$$= \boxed{1.96\times10^{14}\ \mathrm{s^{-1}}}$$

Substitute numerical values in equation (1) and evaluate λ:

$$\lambda = \frac{2\pi\left(3\times10^{8}\ \mathrm{m/s}\right)}{1.96\times10^{14}\ \mathrm{s^{-1}}} = \boxed{9.62\,\mu\mathrm{m}}$$