Chapter 9 – Molecular Structure and Spectra

9-1. (a) $$1\,\frac{eV}{molecule} = \left(1\,\frac{eV}{molecule}\right)\left(\frac{1.602\times 10^{-19}J}{eV}\right)\left(\frac{6.022\times 10^{23}molecules}{mole}\right)$$

$$= \left(96472\,\frac{J}{mole}\right)\left(\frac{1\,cal}{4.184\,J}\right) = 23057\,\frac{cal}{mole} = 23.06\,\frac{kcal}{mole}$$

(b) $$E_d = \left(4.27\,\frac{eV}{molecule}\right)\left(\frac{23.06\,kcal/mole}{1\,eV/molecule}\right) = 98.5\,kcal/mole$$

(c) $$E_d = \left(106\,\frac{kJ}{mole}\right)\left(\frac{1\,eV/molecule}{96.47\,kJ/mole}\right) = 1.08\,eV/molecule$$

9-2. Dissociation energy of *NaCl* is 4.27 eV, which is the energy released when the *NaCl* molecule is formed from neutral *Na* and *Cl* atoms. Because this is more than enough energy to dissociate a Cl_2 molecule, the reaction is exothermic. The net energy release is 4.27 eV – 2.48 eV = 1.79 eV.

9-3. From *Cs* to *F*: 3.89 eV – 3.40 eV = 0.49 eV

From *Li* to *I*: 5.39 eV – 3.06 eV = 2.33 eV

From *Rb* to *Br*: 4.18 eV – 3.36 eV = 0.82 eV

9-4. $$E_d = |U_C| = -\frac{ke^2}{r_0} + E_{ion}$$

CsI: $$-\frac{ke^2}{r_0} + E_{ion} = -\frac{1.440\,eV\cdot nm}{0.337\,nm} + (3.89\,eV - 3.06\,eV) \rightarrow E_d = 3.44\,eV$$

NaF: $$-\frac{ke^2}{r_0} + E_{ion} = -\frac{1.440\,eV\cdot nm}{0.193\,nm} + (5.14\,eV - 3.40\,eV) \rightarrow E_d = 5.72\,eV$$

(Problem 9-4 continued)

LiI: $-\frac{ke^2}{r_0} + E_{ion} = -\frac{1.440\,eV\cdot nm}{0.238\,nm} + (5.39\,eV - 3.06\,eV) \rightarrow E_d = 3.72\,eV$

While E_d for CsI is very close to the experimental value, the other two are both high. Exclusion principle repulsion was ignored.

9-5. (a) Total potential energy: $U(r) = -\frac{ke^2}{r} + E_{ex} + E_{ion}$ (Equation 9 – 1)

attractive part of $U(r_0) = -\frac{ke^2}{r_0} = -\frac{1.44\,eV\cdot nm}{0.267\,nm} = -5.39\,eV$

(b) The net ionization energy is:

$$E_{ion} = (ionization\ energy\ of\ Rb) - (electron\ affinity\ of\ Cl)$$

$$= 4.18\,eV - 3.62\,eV = 0.56\,eV$$

Neglecting the exclusion principle repulsion energy E_{ex},

$$dissociation\ energy = -U(r_0) = 5.39\,eV - 0.56\,eV = 4.83\,eV$$

(c) Including exclusion principle repulsion,

$$dissociation\ energy = 4.37\,eV = -U(r_0) = 5.39\,eV - 0.56\,eV - E_{ex}$$

$$E_{ex} = 5.39\,eV - 4.37\,eV - 0.56\,eV = 0.46\,eV$$

9-6. $U_c = -\frac{ke^2}{r_0} + E_{ion} = -\frac{1.440\,eV\cdot nm}{0.282\,nm} + (4.34\,eV - 3.36\,eV) = -4.13\,eV$

The dissociation energy is 3.94 eV.

$$E_d = |U_c + E_{ex}| = 3.94\,eV = |-4.13\,eV + E_{ex}|$$

$$E_{ex} = 0.19\,eV \text{ at } r_0 = 0.282\,nm$$

9-7. $E_{ex} = \dfrac{A}{r^n}$ (Equation 9-2) $0.19\,eV = \dfrac{A}{(0.282\,nm)^n}$

At r_0 the net force on each ion is zero, so we have (from Example 9-2)

$$\frac{U_c(r_0)}{r_0} = \frac{ke^2}{r_0^2} = 18.11\,eV/nm = \frac{nA}{r_0^{n+1}} = \frac{n}{r_0} \times \frac{A}{r_0^n} = \frac{n}{r_0}(0.19\,eV)$$

$$n = \frac{(18.11\,eV/nm)(0.282\,nm)}{0.19\,eV} = 26.9 \approx 27$$

$$A = E_{ex} r_0^n = (0.19\,eV)(0.282\,nm)^{27} = 2.73 \times 10^{-16}\,eV \cdot nm^{27}$$

9-8. $E_d = 3.76\,eV$ per molecule of *NaBr* (from Table 9-2)

$$1\,eV/molecule = (1\,eV/molecule)(1.60 \times 10^{-19}\,J/eV) \times$$

$$(6.02 \times 10^{23}\,molecules/mol)/(1\,cal/4.186\,J) = 23.0\,kcal/mol$$

$$E_d(NaBr) = (3.76\,eV/moelcule)(23.0\,kcal/mol)/(1\,eV/molecule) = 86.5\,kcal/mol$$

9-9. For *KBr*: $U_C = \dfrac{1.440\,eV \cdot nm}{0.282\,nm} + (4.34\,eV - 3.36\,eV) = -4.13\,eV$

$$E_d = 3.94\,eV = |U_c + E_{ex}| = |-4.13\,eV + E_{ex}|$$

$$E_{ex} = 0.19\,eV$$

For *RbCl*: $U_C = \dfrac{1.440\,eV \cdot nm}{0.279\,nm} + (4.18\,eV - 3.62\,eV) = -4.60\,eV$

$$E_d = 4.37\,eV = |U_c + E_{ex}| = |-4.60\,eV + E_{ex}|$$

$$E_{ex} = 0.23\,eV$$

9-10. H_2S, H_2Te, H_3P, H_3Sb

9-11. (a) KCl should exhibit ionic bonding.

(b) O_2 should exhibit covalent bonding.

(c) CH_4 should exhibit covalent bonding.

9-12. Dipole moment $p_{ionic} = er_0$ (Equation 9-3)

$$= (1.60\times10^{-19}C)(0.0917\,nm)$$

$$= 1.47\times10^{-20}C\cdot nm \times 10^{-9}\,m/nm$$

$$= 1.47\times10^{-29}\,C\cdot m$$

if the *HF* molecule were a pure ionic bond. The measured value is $6.4\times10^{-30}C\cdot m$, so the *HF* bond is $\dfrac{6.40\times10^{-30}C\cdot m}{1.47\times10^{-29}C\cdot m} = 0.44 \text{ or } 44\% \text{ ionic}$.

9-13. $p_{ionic} = er_0 = (1.60\times10^{-19}C)(0.2345\times10^{-9}m) \quad (\text{Equation } 9-3)$

$$= 3.757\times10^{-29}\,C\cdot m, \text{ if purely ionic.}$$

The measured value should be:

$$p_{ionic}(\text{measured}) = 0.70p_{ionic} = 0.70(3.757\times10^{-29}\,C\cdot m) = 2.630\times10^{-29}\,C\cdot m$$

9-14. $p_{ionic} = er_0 = (1.60\times10^{-19}C)(0.193\times10^{-9}m) \quad (\text{Equation } 9-3)$

$$= 3.09\times10^{-29}\,C\cdot m$$

The measured value is $2.67\times10^{-19}C\cdot m$, so the *BaO* bond is

$$\frac{2.67\times10^{-29}C\cdot m}{2.09\times10^{-29}C\cdot m} = 0.86 \text{ or } 86\% \text{ ionic}$$

9-15. Silicon, germanium, tin, and lead have the same outer shell configuration as carbon. Silicon and germanium have the same hybrid bonding as carbon (their crystal structure is diamond, like carbon); however, tin and lead are metallic bonded. (See Chapter 10.)

9-16. $\boldsymbol{p} = \boldsymbol{p_1} + \boldsymbol{p_2}$ and $p = 6.46\times10^{-30}C\cdot m$ and $p = p_1\cos52.25° + p_2\cos52.25° = 2p_1\cos52.25°$

If bonding were ionic, $p_{ionic} = er_0 = (1.60\times10^{-19}C)(0.0956\times10^{-9}m) = 1.532\times10^{-29}C\cdot m$

$p_1(\text{actual}) = p/2(\cos52.25°) = 6.46\times10^{-30}C\cdot m/2(\cos52.25°) = 5.276\times10^{-30}C\cdot nm$

Ionic fraction = fraction of charge transferred = $\dfrac{5.276\times10^{-30}C\cdot m}{1.532\times10^{-29}C\cdot m} = 0.34 \text{ or } 34\%$

9-17. $U = \alpha k^2 p_1^2/r^2$ (Equation 9-10)

(a) Kinetic energy of $N_2 = 0.026\,eV$, so when $|U| = 0.026\,eV$ the bond will be broken.

$$0.026eV = \frac{(1.1\times10^{-37}m\cdot C^2/N)(9\times10^9N\cdot m^2/C^2)^2(6.46\times10^{-30}C\cdot m)^2}{r^6}$$

$$r^6 = \frac{(1.1\times10^{-37}m\cdot C^2/N)(9\times10^9N\cdot m^2/C^2)^2(6.46\times10^{-30}C\cdot m)^2}{0.026eV(1.60\times10^{-19}J/eV)}$$

$$= 8.94\times10^{-56}m^6$$

$$r = 6.7\times10^{-10}m = 0.67\,nm$$

(b) $U \approx -\dfrac{ke^2}{r} \rightarrow |U| = 0.026eV = \dfrac{1.440\,eV\cdot nm}{r} \rightarrow r \approx 55\,nm$

(c) H_2O-Ne bonds in the atmosphere would be very unlikely. The individual molecules will, on the average, be about 4 nm apart, but if a H_2O-Ne molecule should form, its $U \approx 0.003\,eV$ at $r = 0.95nm$, a typical (large) separation. Thus, a N_2 molecule with the average kinetic energy could easily dissociate the H_2O-Ne bond.

9-18. (a) $\Delta E = 0.3\,eV = hc/\lambda = 1240\,eV\cdot nm/\lambda \rightarrow \lambda = 1240\,eV\cdot nm/0.3\,eV = 4.13\times10^3\,nm$

(b) infrared

(c) The infrared is absorbed causing increased molecular vibrations (heat) long before it gets to the DNA.

9-19. (a) NaCl is polar. The Na^+ ion is the positive charge center, the Cl^- ion is the negative charge center.

(b) O_2 is nonpolar. The covalent bond involves no separation of charges, hence no polarization of the molecule.

9-20. For N_2 $E_{0r} = 2.48 \times 10^{-4} eV = \hbar^2/2I$ where $I = \frac{1}{2}mr_0^2$ and $m = 14.0067u$

$$2.48 \times 10^{-4} eV(2I) = \hbar^2$$

$$r_0^2 = \frac{\hbar^2}{(2.48 \times 10^{-4} eV)(14.0067u)}$$

$$r_0 = \left[\frac{(1.055 \times 10^{-34} J \cdot s)^2}{(2.48 \times 10^{-4} eV)(1.60 \times 10^{-19} J/eV)(14.0067u)(1.66 \times 10^{-27} kg/u)}\right]^{1/2}$$

$$= 1.61 \times 10^{-10} m = 0.161 nm$$

9-21. $E_v = \frac{\hbar^2}{2I}$ (Equation 9-14) *where* $I = \frac{1}{2}mr_0^2$ for a symmetric molecule.

$$E_v = \frac{\hbar^2}{mr_0^2} = \frac{(\hbar c)^2}{mc^2 r_0^2)} = \frac{(197.3\, eV \cdot nm)^2}{(16uc^2)(931.5 \times 10^6\, eV/uc^2)(0.121\, nm)^2} = 1.78 \times 10^{-4}\, eV$$

9-22. For $H\,^{35}Cl$: $\mu = \frac{mm_2}{m_1 + m_2}$ (Equation 9-17)

$$\mu = \frac{(1.0078u)(34.9689u)}{1.0078u + 34.9689u} = 0.980u$$

(b) For $H\,^{37}Cl$: $\mu = \frac{(1.0078u)(36.9659u)}{1.0078u + 36.9659u} = 0.981u$

9-23. The reduced mass μ allows us to treat one mass as fixed and to replace the other with μ. For a spring, the force is $F = -Kx = \mu a$. The displacement x is given by:

$$x = A\cos\omega t = A\cos 2\pi f t \text{ and } a = -(2\pi f)^2 A\cos 2\pi f t$$

So, $-Kx = -KA\cos 2\pi f t = \mu a = -\mu(2\pi f)^2 A\cos 2\pi f t$

Or, $K = \mu(2\pi f^2) \rightarrow f = \dfrac{1}{2\pi}\sqrt{\dfrac{K}{\mu}}$

9-24. (a) For H_2: $\mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{(1.0078u)^2}{2(1.0078u)} = 0.504u$

(b) For N_2: $\mu = \dfrac{(14.0067u)^2}{2(14.0067u)} = 7.0034u$

(c) For CO: $\mu = \dfrac{(12.0111u)(15.9994u)}{12.0111u + 15.9994u} = 6.8607u$

(d) For HCl: $\mu = \dfrac{(1.0078u)(35.453u)}{1.0078u + 35.453u} = 0.980u$

9-25. (a) $\mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{(39.1u)(35.45u)}{39.1u + 35.45u} = 18.6u$

(b) $E_v = \dfrac{\hbar^2}{2I}$ (Equation 9-14) $\quad I = \mu r_0^2$

$$E_v = \frac{\hbar^2}{2\mu r_0^2} = \frac{(\hbar c)^2}{2\mu c^2 r_0^2} \rightarrow r_0^2 = \frac{(\hbar c)^2}{2\mu c^2 E_v}$$

$$\therefore \; r_o = \frac{\hbar c}{(2\mu c^2 E_v)^{1/2}} = \frac{197.3\ eV\cdot nm}{[2(10.6uc^2)(931.5\times 10^6 eV/uc^2)(1.43\times 10^{-5} eV)]^{1/2}}$$

$$= 0.280\ nm$$

9-26. $f = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$ (Equation 9-21)

(a) For $H^{35}Cl : \mu = 0.980u$ (see solution to Problem 9-22) and $f = 8.97 \times 10^{13}\ Hz$

$$K = (2\pi f)^2 \mu = (2\pi)^2 (8.97 \times 10^{13} Hz)^2 (0.980u)(1.66 \times 10^{-27} kg/u) = 517 N/m$$

(b) For $K^{79}Br : \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(39.102u)(78.918u)}{39.102u + 78.918u} = 26.147u$ and $f = 6.93 \times 10^{12}\ Hz$

$$K = (2\pi f)^2 \mu = (2\pi)^2 (6.93 \times 10^{12} Hz)^2 (26.147u)(1.66 \times 10^{-27} kg/u) = 82.3 N/m$$

9-27. $E_{0r} = \hbar^2 / 2I$ Treating the *Br* atom as fixed,

$$I = m_H r_0^2 = (1.0078u)(1.66 \times 10^{-27} kg/u)(0.141 nm)^2$$

$$E_{0r} = \frac{(1.055 \times 10^{-34} J \cdot s)^2}{2(1.0078u)(1.66 \times 10^{-27} kg/u)(0.141 nm)^2 (10^{-9} m/nm)^2}$$

$$= 1.67 \times 10^{-22} J = 1.04 \times 10^{-3} eV$$

$E_\ell = \ell(\ell + 1)E_{or}$ for $\ell = 0, 1, 2, \cdots$ (Equation 9-13)

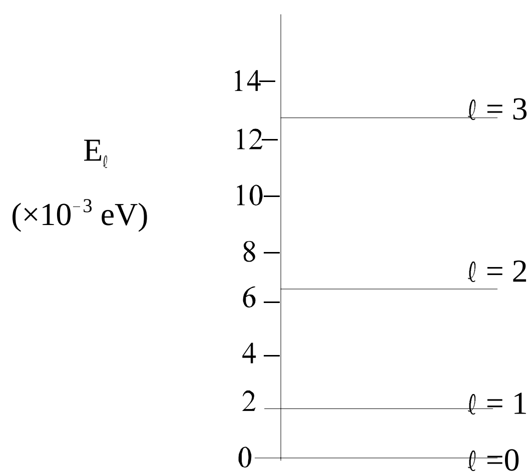
The four lowest states have energies:

$E_0 = 0$

$E_1 = 2E_{0r} = 2.08 \times 10^{-3}\ eV$

$E_2 = 6E_{0r} = 6.27 \times 10^{-3}\ eV$

$E_3 = 12E_{0r} = 12.5 \times 10^{-3}\ eV$



9-28. $\Delta E = hf$ where $f = 1.05\times 10^{13}\,Hz$ for Li_2. Approximating the potential (near the bottom) with a square well,

$$\Delta E(2\rightarrow 1) = (2^2-1)\left(\frac{\pi^2}{2}\right)\frac{\hbar^2}{mr_0^2} = hf$$

For Li_2: $r_0^2 = \dfrac{3\pi^2}{2}\dfrac{\hbar}{2\pi}\dfrac{1}{f\mu} = \dfrac{3\pi}{4}\dfrac{\hbar}{f\mu}$

$$r = \left[\left(\frac{3\pi}{4}\right)\frac{1.055\times 10^{-34}\,J\cdot s}{(1.05\times 10^{13}\,Hz)(6.939\,u)(1.66\times 10^{-27}\,kg/u)}\right]^{1/2}$$

$$= 4.53\times 10^{-11}\,m = 0.045\,nm$$

9-29. $E_{0r} = \dfrac{\hbar^2}{2I}$ where $I = \mu r_0^2$ (Equation 9-14)

For $K^{35}Cl$: $\mu = \dfrac{(39.102\,u)(34.969\,u)}{39.102\,u + 34.969\,u} = 18.46\,u$

For $K^{37}Cl$: $\mu = \dfrac{(39.102\,u)(34.966\,u)}{39.102\,u + 34.966\,u} = 19.00\,u$

$r_0 = 0.267\,nm$ for KCl.

$$E_{0r}(K^{35}Cl) = \frac{(1.055\times 10^{-34}\,J\cdot s)^2}{2(18.46\,u)(1.66\times 10^{-27}\,kg/u)(0.267\times 10^{-9}\,m)^2}$$

$$= 2.55\times 10^{-24}\,J = 1.59\times 10^{-5}\,eV$$

$$E_{0r}(K^{37}Cl) = \frac{(1.055\times 10^{-34}\,J\cdot s)^2}{2(19.00\,u)(1.66\times 10^{-27}\,kg/u)(0.267\times 10^{-9}\,m)^2}$$

$$= 2.48\times 10^{-24}\,J = 1.55\times 10^{-5}\,eV$$

$$\Delta E_{or} = 0.04\times 10^{-5}\,eV$$

9-30. (a) NaF – ionic (b) KBr – ionic
(c) N_2 – covalent (d) Ne – dipole-dipole

9-31. (a) $\lambda = 2400\,nm \rightarrow E = hc/2400\,nm = \dfrac{1240\,eV\cdot nm}{2400\,nm} = 0.517\,eV$

$E_2 - E_1 = 3.80\,eV \quad E_3 - E_2 = 0.500\,eV \quad E_4 - E_3 = 2.9\,eV \quad E_5 - E_4 = 0.30\,eV$

The $E_3 - E_2$ and the $E_5 - E_4$ transitions can occur.

(b) None of these can occur, as a minimum of 3.80 eV is needed to excite higher states.

(c) $\lambda = 250\,nm \rightarrow E = 1240\,eV\cdot nm/250\,nm = 4.96\,eV$. All transitions noted in (a) can occur.

If the temperature is low so only E_1 is occupied, states up to E_3 can be reached, so the $E_2 - E_1$ and the $E_3 - E_2$ transitions will occur, as well as $E_3 - E_1$.

(d) $E_4 - E_3 = 2.9\,eV = hc/\lambda$ or $\lambda = 1240\,eV\cdot nm/2.9\,eV = 428\,nm$

$E_4 - E_2 = 3.4\,eV = hc/\lambda$ or $\lambda = 1240\,eV\cdot nm/3.4\,eV = 365\,nm$

$E_4 - E_1 = 7.2\,eV = hc/\lambda$ or $\lambda = 1240\,eV\cdot nm/7.2\,eV = 172\,nm$

9-32. $\dfrac{A_{21}}{B_{21}u(f)} = e^{hf/kT} - 1$ (Equation 9-39)

For the Hα line $\lambda = 656.1\,nm$

At T = 300 K, $\dfrac{hf}{kT} = \dfrac{hc}{\lambda kT} = \dfrac{1240\,eV\cdot nm}{(656.1\,nm)(8.62\times10^{-5}\,eV/K)(300\,K)} = 73.1$

$e^{hf/\lambda kT} - 1 = e^{73.1} - 1 \approx 5.5\times10^{31}$

Spontaneous emission is more probable by a very large factor!

9-33. $\dfrac{n(E_1)}{n(E_0)} = \dfrac{e^{-E_1/kT}}{e^{-E_0/kT}}$ i.e., the ratio of the Boltzmann factors.

For O_2 : $f = 4.74\times10^{13}\,Hz$ and

$E_0 = hf/2 = (4.14\times10^{-15}\,eV\cdot s)(4.74\times10^{13}\,Hz)/2 = 0.0981\,eV$

$E_1 = 3hf/2 = 0.294\,eV$

At 273 K, $kT = (8.62\times10^{-5}\,eV/K)(273\,K) = 0.0235\,eV$

(Problem 9-33 continued)

$$\frac{n(E_1)}{n(E_0)} = \frac{e^{-0.294/0.0235}}{e^{-0.0981/0.0235}} = \frac{e^{-12.5}}{e^{-4.17}} = 2.4\times10^{-4}$$

Thus, about 2 of every 10,000 molecules are in the E_1 state.

Similarly, at 77K, $\frac{n(E_1)}{n(E_0)} = 1.4\times10^{-13}$

9-34. $E = \ell(\ell+1)E_{0r}$ for $\ell = 0, 1, 2, \cdots$ (Equation 9-13)

Where $E_{0r} = \frac{\hbar^2}{2I}$ and $I = \mu r_0^2$ with $\mu = m/2$

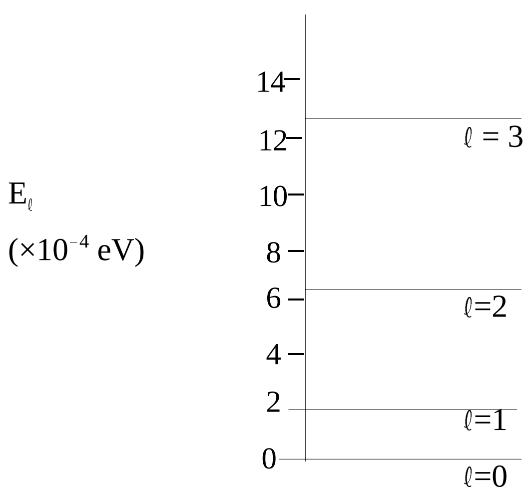
$$E_{0r} = \frac{(1.055\times10^{-34}J\cdot s)^2}{2(18.99u/2)(1.66\times10^{-27}kg/u)(0.14\times10^{-9}m)^2} = 1.80\times10^{-23}J = 1.12\times10^{-4}eV$$

(a) $E_0 = 0$

$E_1 = 2E_{0r} = 2.24\times10^{-4}\,eV \quad E_1 - E_0 = 2.24\times10^{-4}\,eV$

$E_2 = 6E_{0r} = 6.72\times10^{-4}\,eV \quad E_2 - E_1 = 4.48\times10^{-4}\,eV$

$E_3 = 12E_{0r} = 13.4\times10^{-4}\,eV \quad E_3 - E_2 = 6.72\times10^{-4}\,eV$



(Problem 9-34 continued)

(b) $\Delta\ell = \pm 1 \quad \Delta E = hc/\lambda \rightarrow \lambda = hc/\Delta E$

For $E_1 - E_0$: $\lambda = \dfrac{1240\,eV\cdot nm}{2.24\times 10^4 eV} = 5.54\times 10^6 nm = 5.54\ nm$

For $E_2 - E_1$: $\lambda = \dfrac{1240\,eV\cdot nm}{4.48\times 10^4 eV} = 2.77\times 10^6 nm = 2.77\ nm$

For $E_3 - E_2$: $\lambda = \dfrac{1240\,eV\cdot nm}{6.72\times 10^4 eV} = 1.85\times 10^6 nm = 1.85\ nm$

9-35. (a) $10\,MW = 10^7 J/s \rightarrow E = (10^7 J/s)(1.5\times 10^{-9} s) = 1.5\times 10^{-2} J$

(b) For ruby laser: $\lambda = 694.3\ nm$, so the energy/photon is:

$E = hc/\lambda = 1240\,eV\cdot nm/694.3\ nm = 1.786\ eV$

Number of photons = $\dfrac{(1.5\times 10^{-2} J)}{(1.786\,eV)(1.60\times 10^{-19} J/eV)} = 5.23\times 10^6$

9-36. $4\,mW = 4\times 10^{-3}\ J/s$

$E = hc/\lambda = \dfrac{1240\,eV\cdot nm}{632.8\ nm} = 1.960\ eV\ per\ photon$

Number of photons = $\dfrac{4\times 10^{-3} J/s}{(1.960\,eV)(1.60\times 10^{-19} J/eV)} = 1.28\times 10^{16}/s$

9-37. $\sin\theta = 1.22\lambda/D = 1.22(600\times 10^{-9} m)/(10\times 10^{-2} m) = 7.32\times 10^{-6}$

$\approx \theta \approx 7.32\times 10^{-6}\ radians$

$\theta = S/R$ where S = diameter of the beam on the moon and R = distance to the moon.

$S = R\theta = (3.84\times 10^8 m)(7.32\times 10^{-6}\ radians) = 2.81\times 10^3\ m = 2.81\ km$

9-38. (a) $\dfrac{n(E_2)}{n(E_1)} = \dfrac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{-(E_2-E_1)/kT}$ $\quad E_2 - E_1 = hc/\lambda = 1240\,eV\cdot nm/420\,nm = 2.95\,eV$

At T = 297 K, $kT = (8.61\times10^{-5}\,eV/K)(297\,K) = 0.0256\,eV$

$n(E_2) = n(E_1)\,e^{-2.95/0.0256} = 2.5\times10^{21}\,e^{-115} = 2\times10^{-29} \approx 0$

(b) Energy emitted = $(1.8\times10^{21})(2.95\,eV/photon) = 5.31\times10^{21}\,eV = 850\,J$

9-39. (a) Total potential energy: $U(r) = -\dfrac{ke^2}{r} + E_{ex} + E_{ion}$

the electrostatic part of $U(r)$ at r_0 is $-\dfrac{ke^2}{r_0} = -\dfrac{1.44\,eV\cdot nm}{0.24\,nm} = -6.00\,eV$

(b) The net ionization energy is:

$$E_{ion} = (ionization\ energy\ of\ Na) - (electron\ affinity\ of\ Cl)$$

$$= 5.14\,eV - 3.62\,eV = 1.52\,eV$$

dissociation energy of NaCl = 4.27 eV (from Table 9-2)

$$4.27\,eV = -U(r_0) = 6.00\,eV - 1.52\,eV = 4.67\,eV - E_{ex}$$

$$E_{ex} = 6.00\,eV - 4.27\,eV - 1.52\,eV = 0.21\,eV$$

(c) $E_{ex} = \dfrac{A}{r^n}$ (Equation 9-2)

At $r_0 = 0.24\,nm, E_{ex} = 0.21\,eV.$

At $r = 0.14\,nm, U(r) = 0$ and $E_{ex} = \dfrac{ke^2}{r} - E_{ion} = 8.77\,eV$

At $r_0 : E_{ex} = 0.21\,eV = \dfrac{A}{(0.24\,nm)^n} \rightarrow A = (0.21\,eV)(0.24\,nm)^n$

(Problem 9-39 continued)

At $r = 0.14\,nm: E_{ex} = 8.77\,eV = \dfrac{A}{(0.14\,nm)^2} \quad \rightarrow \quad A = (8.77\,eV)(0.14\,nm)^n$

Setting the two equations for A equal to each other:

$$\frac{(0.24\,nm)^2}{(0.14\,nm)^n} = \left(\frac{0.24}{0.14}\right)^2 = \left(\frac{8.77\,eV}{0.21\,eV}\right) \quad \rightarrow \quad (1.71)^n = 41.76$$

$$n \log 1.71 = \log 41.76$$

$$n = (\log 41.76)/(\log 1.71) = 6.96$$

$$A = 0.21\,eV(0.24\,nm)^n = 0.21\,eV(0.24\,nm)^{6.96} = 1.02 \times 10^{-5}\,eV{\cdot}nm^{6.96}$$

9-40. (a) $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ (Equation 9-17). Subtracting m_1 from both sides of the equation,

$$\mu - m_1 = \frac{m_1 m_2}{m_1 + m_2} - m_1 = \frac{m_1 m_2 - m_1^2 - m_1 m_2}{m_1 + m_2} = -\frac{m_1^2}{m_1 + m_2}$$

Because m_1^2 and $m_1 + m_2$ are always positive, $-m_1^2/(m_1 + m_2)$ is always negative, thus $\mu - m_1$ is always negative; therefore, μ is always smaller than m_1. Subtracting m_2 from both sides of Equation 9-17 leads to $\mu - m_2$ always being negative, hence μ is also always smaller than m_2.

(b) $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ Because we expect a very small difference between the two reduced masses, we must use the best available atomic masses in the calculations.

$$\mu(35) = \frac{(1.007825\,u)(34.968851\,u)}{1.007825\,u + 34.968851\,u} = 0.979593\,u$$

$$\mu(37) = \frac{(1.007825\,u)(36.965898\,u)}{1.007825\,u + 36.965898\,u} = 0.981077\,u$$

$\dfrac{\Delta\mu}{\mu(35)} = 1.52 \times 10^{-3}$, a difference of 0.15%.

9-41. (a) $U_{att} = -\dfrac{ke^2}{r} = \dfrac{1.440\,eV\cdot nm}{0.267\,nm} = 5.39\,eV$

(b) To form K^+ and Cl^- requires $E_{ion} = 4.34\,eV - 3.61\,eV = 0.73\,eV$

$$E_d = -U_C = -\left(-\frac{ke^2}{r} + E_{ion}\right) = 5.39\,eV - 0.73\,eV = 4.66\,eV$$

(c) $E_{ex} = 4.66\,eV - 4.43\,eV = 0.23\,eV$ at r_0

9-42. $E_{0r} = \dfrac{\hbar^2}{2I}$ where $I = \mu r_0^2$ with $r_0 = 0.267\,nm$ and

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(39.102\,u)(35.453\,u)}{39.102\,u + 35.453} = 18.594\,u$$

$$E_{0r} = \frac{(1.055\times10^{-34}J\cdot s)^2}{2(18.594\,u)(1.66\times10^{-27}kg/u)(0.267\times10^{-9}m)^2} = 2.53\times10^{-24}J = 1.58\times10^{-5}\,eV$$

9-43. (a) $E_d = \dfrac{kp_1}{x^3}$ where $p_1 = qa$, being the separation of the charges $+q$ and $-q$ of the dipole.

(b) $U = -\boldsymbol{p}\cdot\boldsymbol{E}$ and $\boldsymbol{p} \propto \boldsymbol{E} \rightarrow \boldsymbol{p} = \alpha\boldsymbol{E}$

So the individual dipole moment of a nonpolar molecule in the field produced by p_1 is

$p_2 = \alpha E_d = \alpha kp_1/x^3$ and $U = -\boldsymbol{p_2}\cdot\boldsymbol{E_d} = \alpha(kp_1)^2/x^6$

$$F_x = -\frac{dU}{dx} = -\frac{d}{dx}[\alpha(k^2p_1^2)/x^6] = 6\alpha k^2 p_1^2/x^7$$

9-44. (a) $E_3 = hc/\lambda = 1240\,eV\cdot nm/(0.86\,mm)(10^6\,nm/mm) = 1.44\times10^{-3}\,eV$

$E_2 = 1240\,eV\cdot nm/(1.29\,mm)(10^6\,nm/mm) = 9.61\times10^{-4}\,eV$

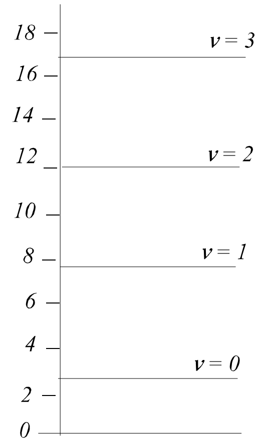
$E_1 = 1240\,eV\cdot nm/(2.59\,mm)(10^6\,nm/mm) = 4.79\times10^{-4}\,eV$

(Problem 9-44 continued)

These are vibrational states, Because they are equally spaced. Note the $\nu = 0$ state at ½ the level spacing.

E_ν

($\times\ 10^{-4}$ eV)



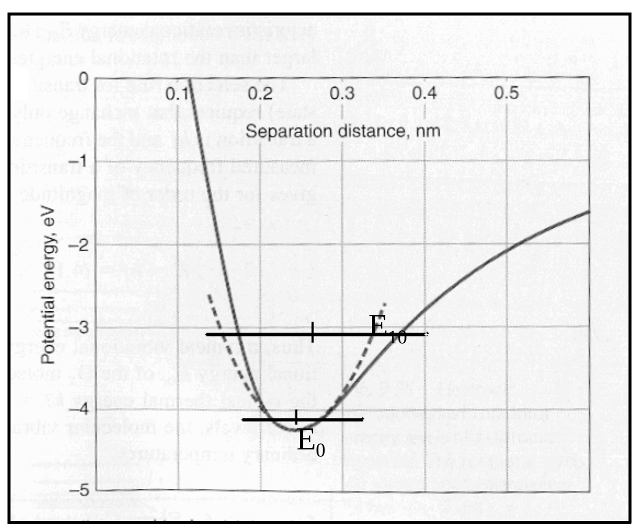
(b) Approximating the potential with a square well (at the bottom),

$$E_1 = 4.79\times10^{-4}eV = n^2\frac{\pi^2}{2}\frac{\hbar^2}{mr_0^2}$$

$$r_0 = \left[\frac{(2^2-1^2)\pi^2(1.055\times10^{-34}J\cdot s)^2}{2(28.01\,u)(1.66\times10^{-27}kg/u)(4.79\times10^{-4}eV)(1.60\times10^{-19}J/eV)}\right]^{1/2}$$

$$= 2.15\times10^{-10}m = 0.215\ nm$$

9-45. Using the NaCl potential energy vs separation graph in Figure 9-23(b) as an example (or you can plot one using Equation 9-1):



(Problem 9-45 continued)

The vibrational frequency for NaCl is 1.14×10^{13} Hz (from Table 9-7) and two vibrational levels, for example $\nu = 0$ and $\nu = 10$ yield (from Equation 9-20)

$$E_0 = 1/2\,hf = 0.0236\,eV$$

$$E_{10} = 11/2\,hf = 0.496\,eV$$

above the bottom of the well. Clearly, the average separation for $\nu_{10} > \nu_0$.

9-46. (a) $E_{0r} = \dfrac{\hbar^2}{2\mu r_0^2}$ where $r_0 = 0.128\,nm$ for HCl and

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.0079u)(35.453u)}{1.0079u + 35.453} = 0.980u$$

$$E_{0r} = \frac{(1.055\times10^{-34}J\cdot s)^2}{2(0.980u)(1.66\times10^{-27}kg/u)(0.128\times10^{-9}m)^2} = 2.089\times10^{-22}J = 1.303\times10^{-3}\,eV$$

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

$$E_0 = 0 \qquad E_1 = 2E_{0r} = 2.606\times10^{-3}eV \qquad E_2 = 6E_{0r} = 7.82\times10^{-3}\,eV$$

$$\Delta E_{01} = E_1 - E_0 = 2.606\times10^{-3}\,eV \qquad \Delta E_{12} = E_2 - E_1 = 5.214\times10^{-3}\,eV$$

$$\Delta f_{01} = \Delta E_{01}/h = \frac{2.606\times10^{-3}eV}{4.136\times10^{-15}eV\cdot s} = 0.630\times10^{12}\,Hz$$

$$\Delta f_{12} = \Delta E_{12}/h = \frac{5.214\times10^{-3}eV}{4.136\times10^{-15}eV\cdot s} = 1.26\times10^{12}\,Hz$$

$$f'_{01} = f \pm \Delta f_{01} = 6.884\times10^{14} \pm 0.63\times10^{12} = 6.890\times10^{14}\,Hz\,;\, 6.878\times10^{14}\,Hz$$

$$\lambda'_{01} = c/f'_{01} = 435.5\,nm\,;\,436.2\,nm$$

$$f'_{02} = f \pm \Delta f_{02} = 6.884\times10^{14} \pm 1.26\times10^{12} = 6.897\times10^{14}\,Hz\,;\, 6.871\times10^{14}\,Hz$$

$$\lambda'_{02} = c/f'_{02} = 435.0\,nm\,;\,436.6\,nm$$

(Problem 9-46 continued)

(b) From Figure 9-29: $\Delta f_{01} = 0.6\times10^{12}\,Hz$ and $f_{02} = 1.2\times10^{12}\,Hz$

The agreement is very good!

9-47. (a) $Li_2 : E_\nu = (\nu + 1/2)hf$

$$E_1 = (3/2)(4.14\times10^{-15}\,eV\cdot s)(1.05\times10^{13}\,Hz) = 0.0652\,eV = 6.52\times10^{-2}\,eV$$

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

$$E_1 = 2(8.39\times10^{-5}\,eV) = 1.68\times10^{-4}\,eV$$

(b) $K^{79}Br$: $E_\nu = (\nu + 1/2)hf$

$$E_1 = (3/2)(4.14\times10^{-15}\,eV\cdot s)(6.93\times10^{12}\,Hz) = 4.30\times10^{-2}\,eV$$

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

$$E_1 = 2(9.1\times10^{-6}\,eV) = 1.8\times10^{-5}\,eV$$

9-48. $\mu(HCl) = 0.980\,u$ (See solution to Problem 9-46)

From Figure 9-29, the center of the gap is the characteristic oscillation frequency f:

$$f = 8.65\times10^{13}\,Hz \rightarrow E = 0.36\,eV \quad \text{Thus, } f = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \text{ or } K = (2\pi f)^2\mu$$

$$K = (2\pi)^2(8.65\times10^{13}\,Hz)^2(0.980\,u)(1.66\times10^{-27}\,kg/u) = 480\,N/m$$

9-49. $n(E_n) = g(E_n)\,e^{-E_n/kT}$

$$\lambda_{21} = 694.3\,nm \rightarrow E_2 - E_1 = hc/\lambda_{21} = \frac{1240\,eV\cdot nm}{694.3\,nm} = 1.7860\,eV$$

$$E_2' - E_1 = 1.7860\,eV + 0.0036\,eV = 1.7896\,eV$$

(Problem 9-49 continued)

Where E_2 is the lower energy level of the doublet and $E_2^{/}$ is the upper.

Let T = 300 K, so $kT = 0.0259\,eV$

(a) $$\frac{n(E_2^{/})}{n(E_1)} = \frac{g(E_2)}{g(E_1)}e^{-(E_2-E_1)/kT} = \frac{2}{4}e^{-1.7896/0.0259} = \frac{1}{2}e^{-69} = 4.91\times10^{-31}$$

$$\frac{n(E_2)}{n(E_1)} = \frac{1}{2}e^{-1.7896/0.0259} = 5.64\times10^{-31}$$

(b) If only $E_2 \rightarrow E_1$ transitions produce lasing, but E_2 and $E_2^{/}$ are essentially equally populated, in order for population inversion between levels E_2 and E_1, at least 2/3 (rather than 1/2) of the atoms must be pumped. The required power density (see Example 9-8) is:

$$p \approx \frac{2N}{3}\left(\frac{hf}{t_s}\right) \approx \frac{2(2\times10^{19}\,cm^3)(6.63\times10^{-34}J\cdot s)(4.32\times10^{14}Hz)}{3(3\times10^{-3}s)} \approx 1273\;W/cm^3$$

9-50. (a) $E_\nu = (\nu + 1/2)hf \quad$ (Equation 9 – 20)

For ν = 0, $E_0 = hf/2 = (6.63\times10^{-34}J\cdot s)(8.66\times10^{13}Hz)/2 = 0.179\,eV$

(b) For Δℓ = ±1, $\Delta E_\ell = \ell^2\hbar/I = \ell h\Delta f$

so $$I = h/(4\pi^2\Delta f) = \frac{6.63\times10^{-34}J\cdot s}{4\pi^2(6\times10^{11}Hz)} = 2.8\times10^{-47}\,kg\cdot m^2$$

(c) $I = \mu r^2$, where μ is given by Equation 9-17.

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = 0.973\,u \;\Rightarrow r = 0.132\,nm$$

9-51. (a) $\dfrac{dU}{dr} = U_0[-12a^{12}r^{-13} - 2(-6a^6)r^{-7}]$

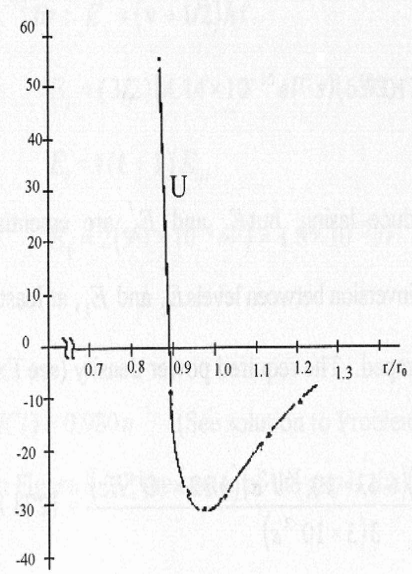
For U_{min}, $dU/dr = 0$, so $-12a^{12}r^{-6} + 12a^6 = 0 \rightarrow r^{-6} = a^{-6} \rightarrow r = a$

(b) For $U = U_{min}$, $r = a$ then $U_{min} = U_0\left[\left(\dfrac{a}{a}\right)^{12} - 2\left(\dfrac{a}{a}\right)^6\right] = (1-2)U_0 = -U_0$

(c) From Figure 9-8b: $r_0 = 0.074\,nm$ $(= a)$ $U_0 = 32.8\,eV$

(d)

r/r_0	$(r_0/r)^{12}$	$-2(r_0/r)^6$	U
0.85	7.03	– 5.30	+56.7
0.90	3.5	– 3.8	– 9.8
0.95	1.85	– 2.72	– 28.5
1.00	1	– 2.0	– 32.8
1.05	0.56	– 1.5	– 30.8
1.10	0.32	– 1.12	– 26.2
1.15	0.19	– 0.86	– 22.0
1.20	0.11	– 0.66	– 18.0



9-52. (a) $U(r) = -\frac{ke^2}{r} + E_{ex} + E_{ion}$ (Equation 9-1)

For NaCl, E_d = 4.27 eV and r_o = 0.236 nm (Table 9-1).

$E_{ion} = E_{ion}$ (Na) + E_{aff} (Cl) = 5.14 – 3.62 = 1.52 eV and $U(r_o) = -E_d = -4.27$ eV

$$E_{ex} = -4.27 + \frac{ke^2}{0.236} - 1.52 = 0.31\,eV$$

(b) $E_{ex} = Ar^{-n} = 0.31\,eV$ (Equation 9-2)

Following Example 9-2,

$$\frac{ke^2}{r_0^2} = 25.85\,eV/nm = \frac{n}{r_0}\frac{A}{r_0^n} = \frac{n}{r_0}(0.31\,eV)$$

Solving for *n*

$$n = (25.85\,eV/nm)(0.236\,nm)/0.31\,eV = 19.7 \approx 20$$

$$A = (0.31\,eV)(0.236\,nm)^{20} = 8.9\times10^{-14}\,eV\cdot nm^{20}$$

9-53. For $H^+ - H^-$ system, $U(r) = -\frac{ke^2}{r} + E_{ion}$

There is no E_{ex} term, the two electrons of H^- are in the n = 1 shell with opposite spins.

E_{ion} = ionization energy for H^+ – electron affinity for H^- = $13.6\,eV - 0.75\,eV = 12.85\,eV$.

$$U(r) = -\frac{1.440\,eV\cdot nm}{r} + 12.85\,eV \qquad \frac{dU(r)}{dr} = \frac{1.440}{r^2}$$

For *U(r)* to have a minimum and the ionic $H^+ - H^-$ molecule to be bound, $dU/dr = 0$. As we see from the derivative, there is no non-zero or finite value of *r* for which this occurs.

9-54. (a) 1.52×10^{-3}. See Problem 9-40(b).

(b) The energy of a transition from one rotational state to another is

$$\Delta E_{\ell,\ell+1} = (\ell + 1)\hbar^2/I = hf \quad \text{(Equation 9-15)}$$

$$f = \frac{(\ell+1)\hbar^2}{hI} = \frac{(\ell+1)h^2}{4\pi^2 h\mu r_0^2} = \frac{(\ell+1)h}{4\pi^2 \mu r_0^2}$$

$$\Delta f \approx \frac{df}{d\mu}\Delta\mu = \left[\frac{(\ell+1)h}{4\pi^2 r_0^2}\right]\left(-\frac{1}{\mu^2}\right)\Delta\mu$$

$$\frac{\Delta f}{f} = \left[\frac{(\ell+1)h}{4\pi^2\mu r_0^2}\right]\left(-\frac{\Delta\mu}{\mu}\right)\left[\frac{(\ell+1)h}{4\pi^2\mu r_0^2}\right]^{-1} = -\frac{\Delta\mu}{\mu}$$

(c) $\dfrac{\Delta f}{f} = -\dfrac{\Delta\mu}{\mu} = -1.53\times10^{-3}$ from part (b). In Figure 9-29 the Δf between the ^{35}Cl lines (the taller ones) and the ^{37}Cl lines is of the order of $0.01\times10^{13}\,Hz$, so $\Delta f/f \approx 0.0012$, about 20% smaller than $\Delta\mu/\mu$.

9-55. (a) For CO: $r_0 = 0.113$ $\quad \mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{(12.0112u)(15.994u)}{12.0112u + 15.9994u} = 6.861u$

$$I = \mu r_0^2 = (6.861u)(1.66\times10^{-27}kg/u)(0.113\times10^{-9})^2 = 1.454\times10^{-46}\,kg\cdot m^2$$

$$E_{0r} = \frac{\hbar^2}{2I} = \frac{(1.055\times10^{-34}J\cdot s)^2}{2(1.454\times10^{-46}kg\cdot m^2)} = 3.827\times10^{-23}J = 2.39\times10^{-4}\,eV$$

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

$E_0 = 0$

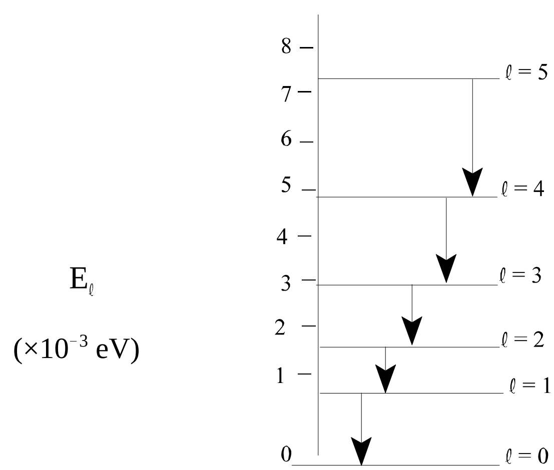
$E_1 = 2E_{0r} = 4.78\times10^{-4}\,eV$

$E_2 = 6E_{0r} = 1.43\times10^{-3}\,eV$

$E_3 = 12E_{0r} = 2.87\times10^{-3}\,eV$

$E_4 = 20E_{0r} = 4.78\times10^{-3}\,eV$

$E_5 = 30E_{0r} = 7.17\times10^{-3}\,eV$



(Problem 9-55 continued)

(c) (See diagram)

$$E_{54} = (7.17 - 4.78) \times 10^{-3}\, eV = 2.39 \times 10^{-3}\, eV$$

$$E_{43} = (4.78 - 2.87) \times 10^{-3}\, eV = 1.91 \times 10^{-3}\, eV$$

$$E_{32} = (2.87 - 1.43) \times 10^{-3}\, eV = 1.44 \times 10^{-3}\, eV$$

$$E_{21} = (1.43 - 0.48) \times 10^{-3}\, eV = 0.95 \times 10^{-3}\, eV$$

$$E_{10} = 4.78 \times 10^{-4}\, eV$$

(d) $\lambda = hc/E$

$$\lambda_{54} = \frac{1240\, eV \cdot nm}{2.39 \times 10^{-3}\, eV} = 5.19 \times 10^{5}\, nm = 0.519\, mm$$

$$\lambda_{43} = \frac{1240\, eV \cdot nm}{1.91 \times 10^{-3}\, eV} = 6.49 \times 10^{5}\, nm = 0.649\, mm$$

$$\lambda_{32} = \frac{1240\, eV \cdot nm}{1.44 \times 10^{-3}\, eV} = 8.61 \times 10^{5}\, nm = 0.861\, mm$$

$$\lambda_{21} = \frac{1240\, eV \cdot nm}{0.95 \times 10^{-3}\, eV} = 13.05 \times 10^{5}\, nm = 1.31\, mm$$

$$\lambda_{10} = \frac{1240\, eV \cdot nm}{4.78 \times 10^{-4}\, eV} = 25.9 \times 10^{5}\, nm = 2.59\, mm$$

All of these are in the microwave region of the electromagnetic spectrum.