Chemistry 2720 Fall 2002 Test 3 Solutions

1. The second ionization energy of helium would be

$$E_I = -E_1 = \frac{2^2 R_H}{1^2} = 4R_H.$$

In electron-volts, Rydberg's constant is therefore $54.416\,\text{eV}/4 = 13.604\,\text{eV}$.

2. (a) $\Delta p \geq \frac{h}{4\pi\Delta x}$. Since the cavity has a radius of 1.14 nm, $\Delta x = 1.14$ nm. (If we guess that the molecule is in the middle of the cavity, we can be wrong by at most 1.14 nm.) Thus,

$$\begin{aligned}
\Delta p &\geq \frac{6.626\,068\,8 \times 10^{-34}\,\text{J/Hz}}{4\pi(1.14 \times 10^{-9}\,\text{m})} = 4.63 \times 10^{-26}\,\text{kg m/s}. \\
m_{\text{CH}_4} &= \frac{16.043 \times 10^{-3}\,\text{kg/mol}}{6.022\,142\,0 \times 10^{23}\,\text{mol}^{-1}} = 2.6640 \times 10^{-26}\,\text{kg}. \\
\therefore \Delta v &= \Delta p/m \geq \frac{4.63 \times 10^{-26}\,\text{kg m/s}}{2.6640 \times 10^{-26}\,\text{kg}} = 1.74\,\text{m/s}.
\end{aligned}$$

(b) If the radius is 1.14 nm, then the length of the box is the diameter, 2.28 nm. (This is of course very crude.) The minimum kinetic energy is

$$\begin{aligned}
K_{\text{min}} &= E_1 = \frac{1^2 h^2}{8mL^2} \\
&= \frac{(6.626\,068\,8 \times 10^{-34}\,\text{J/Hz})^2}{8(2.6640 \times 10^{-26}\,\text{kg})(2.28 \times 10^{-9}\,\text{m})^2} \\
&= 3.9629 \times 10^{-25}\,\text{J}. \\
\therefore v_{\text{min}} &= \sqrt{2K_{\text{min}}/m} \\
&= \sqrt{\frac{2(3.9629 \times 10^{-25}\,\text{J})}{2.6640 \times 10^{-26}\,\text{kg}}} = 5.4545\,\text{m/s}.
\end{aligned}$$

(c) The minimum speed is 5.4545 m/s. Since the velocity vector can be oriented in any direction in the cavity, the uncertainty in any component of the velocity (which is what we get from the uncertainty principle) is 5.4545 m/s. This is considerably larger than the limit imposed by the uncertainty principle.

3. This is a conservation of momentum question. The photon has momentum. When it is created, the atom's momentum must therefore change by an equal and opposite amount.

$$p_{\text{photon}} = \frac{h}{\lambda} = \frac{6.626\,068\,8 \times 10^{-34}\,\text{J/Hz}}{0.4960 \times 10^{-6}\,\text{m}} = 1.336 \times 10^{-27}\,\text{kg m/s}.$$

$$
\begin{aligned}
m_{\mathrm{Hg}} &= \frac{201.970\,617\times10^{-3}\,\mathrm{kg/mol}}{6.022\,142\,0\times10^{23}\,\mathrm{mol}^{-1}} = 3.3538\times10^{-25}\,\mathrm{kg}.\\
\therefore \Delta v &= \frac{\Delta p}{m} = \frac{1.336\times10^{-27}\,\mathrm{kg\,m/s}}{3.3538\times10^{-25}\,\mathrm{kg}} = 3.983\times10^{-3}\,\mathrm{m/s}.
\end{aligned}
$$

This is an insignificant change.

4. The energy of the photon is

$$E_{\mathrm{photon}} = \frac{hc}{\lambda} = \frac{(6.626\,068\,8\times10^{-34}\,\mathrm{J/Hz})(2.997\,924\,58\times10^{8}\,\mathrm{m/s})}{58.4\times10^{-9}\,\mathrm{m}} = 3.40\times10^{-18}\,\mathrm{J}.$$

The kinetic energy of the ejected electrons is

$$K = \frac{1}{2}mv^2 = \frac{1}{2}(9.109\,381\,9\times10^{-31}\,\mathrm{kg})(1.59\times10^{6}\,\mathrm{m/s})^2 = 1.15\times10^{-18}\,\mathrm{J}.$$

The difference between the two is the ionization energy:

$$E_I = E_{\mathrm{photon}} - K = 2.25\times10^{-18}\,\mathrm{J}.$$

5. (a) Because the symmetry is not cubic, the (100), (010) and (001) reflections are all different. It seems highly likely that they will produce the three lowest angles, so I'll start with these. Note that the (010), which corresponds to planes separated by the largest lattice constant, will give the smallest angle.

$$
\begin{aligned}
d_{010} &= b = 784\,\mathrm{pm}.\\
\sin\theta_{010} &= \frac{\lambda}{2d_{010}} = \frac{178.5\,\mathrm{pm}}{2(784\,\mathrm{pm})} = 0.114.\\
\therefore \theta_{010} &= 6.54^\circ.\\
d_{100} &= a = 634\,\mathrm{pm}.\\
\sin\theta_{100} &= \frac{\lambda}{2d_{100}} = \frac{178.5\,\mathrm{pm}}{2(634\,\mathrm{pm})} = 0.141.\\
\therefore \theta_{100} &= 8.09^\circ.\\
d_{001} &= c = 516\,\mathrm{pm}.\\
\sin\theta_{001} &= \frac{\lambda}{2d_{001}} = \frac{178.5\,\mathrm{pm}}{2(516\,\mathrm{pm})} = 0.173.\\
\therefore \theta_{001} &= 9.96^\circ.
\end{aligned}
$$

After that, we're going to have to experiment a little. The smallest angles correspond to the largest distances. Let's just calculate a few distances and pick the smallest two:

$$\frac{1}{d_{110}^2} = \frac{1}{(634\,\mathrm{pm})^2} + \frac{1}{(784\,\mathrm{pm})^2} = 4.11\times10^{-6}\,(\mathrm{pm})^2.$$

$$\begin{aligned}
\therefore d_{110} &= 493\,\text{pm}.\\
\frac{1}{d_{011}^2} &= \frac{1}{(784\,\text{pm})^2} + \frac{1}{(516\,\text{pm})^2} = 5.38\times10^{-6}\,(\text{pm})^2.\\
\therefore d_{011} &= 431\,\text{pm}.\\
\frac{1}{d_{101}^2} &= \frac{1}{(634\,\text{pm})^2} + \frac{1}{(516\,\text{pm})^2} = 6.24\times10^{-6}\,(\text{pm})^2.\\
\therefore d_{101} &= 400\,\text{pm}.\\
d_{020} &= b/2 = 392\,\text{pm}.
\end{aligned}$$

It should be clear by now that we're not going to do better than the (110) and (011). We can now proceed to calculate the corresponding refraction angles:

$$\begin{aligned}
\sin\theta_{110} &= \frac{\lambda}{2d_{110}} = \frac{178.5\,\text{pm}}{2(493\,\text{pm})} = 0.181.\\
\therefore \theta_{110} &= 10.43^\circ.\\
\sin\theta_{011} &= \frac{\lambda}{2d_{011}} = \frac{178.5\,\text{pm}}{2(431\,\text{pm})} = 0.207.\\
\therefore \theta_{011} &= 11.95^\circ.
\end{aligned}$$

(b)

$$\begin{aligned}
p &= \frac{h}{\lambda} = \frac{6.626\,068\,8\times10^{-34}\,\text{J/Hz}}{178.5\times10^{-12}\,\text{m}} = 3.712\times10^{-24}\,\text{kg m/s}.\\
v &= \frac{p}{m} = \frac{3.712\times10^{-24}\,\text{kg m/s}}{1.674\,927\,16\times10^{-27}\,\text{kg}} = 2216\,\text{m/s}.
\end{aligned}$$

6. The longest wavelength line will have the smallest ΔE of the series. This has to be the transition from level n_f+1 to level n_f. The photon energy is

$$\begin{aligned}
E_{\text{photon}} &= \Delta E = \frac{hc}{\lambda}\\
&= \frac{(6.626\,068\,8\times10^{-34}\,\text{J/Hz})(2.997\,924\,58\times10^{8}\,\text{m/s})}{12.368\times10^{-6}\,\text{m}}\\
&= 1.6061\times10^{-20}\,\text{J}.
\end{aligned}$$

The difference in energy between the two levels can be written as

$$\begin{aligned}
\Delta E &= R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)\\
&= R_H\left(\frac{1}{n_f^2} - \frac{1}{(n_f+1)^2}\right).\\
\therefore \frac{1}{n_f^2} - \frac{1}{(n_f+1)^2} &= \frac{\Delta E}{R_H} = 7.3679\times10^{-3}.
\end{aligned}$$

$1/n_f^2$ has to be larger than the quantity on the right of the last equality, which means that $n_f \leq 11$. Let's just try values of n_f, working our way down from 11:

n_f	$\frac{1}{n_f^2} - \frac{1}{(n_f+1)^2}$
11	1.3200×10^{-3}
10	1.7355×10^{-3}
9	2.3457×10^{-3}
8	3.2793×10^{-3}
7	4.7832×10^{-3}
6	7.3696×10^{-3}

This last value is in reasonably close agreement with the experimental value. The difference is almost certainly attributable to experimental error. Accordingly, we conclude that $n_f = 6$.