PHYSICAL CHEMISTRY 3520
EXAM 4
April 21, 2006

Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep explanations brief and to the point.

Your name: SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

\( N_A \) or \( L = 6.022 \times 10^{23} \text{ mol}^{-1} \)
\( h = 6.626 \times 10^{-34} \text{ J s} \)

\( k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \)
\( c = 2.998 \times 10^8 \text{ m s}^{-1} \)

H atom mass = \( 1.66 \times 10^{-27} \text{ kg} \)
Electron mass = \( 9.11 \times 10^{-31} \text{ kg} \)

\( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)

Planck: \( E = hv \)
Schroedinger: \( \hat{H}\psi = E\psi \)
de Broglie: \( \lambda = h/p \)

\( \hat{x} \) operator is multiply by \( x \)
\( \hat{p} \) operator is \( h/(2\pi) \text{ d/dx} \)

\( \hat{E}_k \) operator is \(-h^2/(8\pi^2m) \text{ d}^2/\text{dx}^2\)
\( \hat{V} \) operator is multiply by \( V \)

\( E_v = (v + 1/2) \text{ hv} \)
\( v = (k/\mu)^{1/2}/(2\pi) \)

\( g_j = 2J + 1 \)
\( B = h/(8\pi^2l) \text{ in Hz} \)
\( E_J = BhJ(J+1) \)

\( \sin^2x = (1 - \cos 2x)/2 \)
\( \cos^2x = (1 + \cos 2x)/2 \)

\( \int_0^\infty x^n \exp(-ax) = \frac{n!}{a^{n+1}} \)

I.P. of one-electron atom proportional to \( Z^2/n^2 \). I.P. of H = 13.6 eV = \( 2.18 \times 10^{-18} \text{ J} \).

\( |L^2| = l(l+1) \text{ h}^2/(4\pi^2) \)
\( L_z = m_l \text{ h}/(2\pi) \)
1. **50 points**
Consider the electronic spectroscopy of $^1\text{H}^{19}\text{F}$. The longest wavelength band in the X to A spectrum is measured to be at $1.5 \times 10^4 \text{ cm}^{-1}$, and originates from the $v''=0$ vibrational level of the X state. The gaps between successive bands for transitions to $v'$ levels in the A state are found to decrease. The plot shown is of the gap $\Delta$ between transitions to $v'$ and to $v'+1$ against $v'+1/2$, where $v'$ is the vibrational quantum number for the upper (A) state. This state dissociates to a ground state F atom plus a ground state H atom, and so does the X state. The vibrational frequency of X state HF in $v''=0$ is 3300 cm$^{-1}$.

![Graph showing vibrational frequencies](image)

The sum of $\Delta$s is the area under this
Birge-Sponer plot,

$$\frac{1}{2} \times 2100 \times 10.5 \text{ cm}^{-1} = 11025 \text{ cm}^{-1}$$

i) Use the information provided to deduce the bond dissociation energy $D_0$ for ground (X) state HF, in kJ mol$^{-1}$.

ii) Do you expect $D_0$ for ground state DF (i.e. $^2\text{H}^{19}\text{F}$) to be larger or smaller than that for HF, and by how many kJ mol$^{-1}$? *Show work.*
1. contd.

DF is heavier than HF so the frequency will be less, so the zpe will be less, so Do will be greater.

\[ \text{zpe for HF is } \frac{1}{2}h\nu = \frac{3300 \text{ cm}^{-1}}{2} = 1650 \text{ cm}^{-1}. \]

\[ \nu \propto \frac{1}{M} \]

\[ M \text{ for HF is } \frac{19}{20} = 0.95 \text{ amu}, \]

\[ M \text{ for DF is } \frac{24}{21} = 1.19 \text{ amu} \]

\[ \nu \text{ for DF } = 3300 \text{ cm}^{-1} \times \sqrt{\frac{0.95}{1.19}} = 2891 \text{ cm}^{-1}. \]

So zpe for DF is \[ \frac{2891 \text{ cm}^{-1}}{2} = 1445 \text{ cm}^{-1}. \]

This is 455 cm\(^{-1}\) less than for HF, \( \nu \)

Do for DF is increased by 455 cm\(^{-1}\) or 5.4 kJ mol\(^{-1}\).
Here is part of the microwave spectrum of the mixture of gases in the Orion nebula.

a) Read off the transition for CO (i.e. $^{12}$C$^{16}$O) at about 230 GHz, and use it to predict where the same transition would occur for $^{13}$CO (i.e. $^{13}$C$^{16}$O). Do you confirm the assignment of the line at roughly 220 GHz?

b) The next line for CO ($^{12}$C$^{16}$O) occurs at 360 GHz (not shown). Determine the bond length of CO.

\[
\begin{align*}
\text{a) } & \quad M_{\text{CO}} = \frac{12\times16}{12+16} = 6.86 \text{ amu}, \quad M_{^{13}\text{CO}} = \frac{13\times16}{13+16} = 7.17 \text{ amu}, \\
& \quad B \propto 1/2 \times \frac{\mu}{\sqrt{m}} \quad (\text{bond length unchanged}) \\
& \quad \text{Thus line for } ^{13}\text{CO will be at } 230.5 \frac{\text{GHz}}{7.17} = 229.5 \text{ GHz} \\
\text{b) } & \quad \text{Line spacing therefore } 360 - 229.5 = 129.5 \text{ GHz} = 28 \\
& \quad B = 6.475 \times 10^{-10} \text{ m/s} \quad \text{so } I = \frac{h}{8\pi^2 B} = 1.296 \times 10^{-26} \text{ kg m}^2 \\
& \quad = \frac{\mu r^2}{m} \quad \text{so } r = \sqrt{\frac{I}{\mu}} = 1.07 \times 10^{-10} \text{ m}.
\end{align*}
\]
3. 10 points
A spectral line at $2 \times 10^4 \text{cm}^{-1}$ has a width of 0.01 cm$^{-1}$. If this width is attributed to lifetime broadening, what approximate lifetime do you estimate for the upper state? Show work and briefly justify your answer in terms of the Heisenberg Uncertainty principle.

Energy and time are complementary variables so

$$\Delta E \cdot \Delta t \approx \frac{\hbar}{2\pi}.$$  

$$\Delta E = 0.01 \text{ cm}^{-1} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 6.626 \times 10^{-34} \text{ Js}$$

$$= 1.99 \times 10^{-25} \text{ J}$$

$$\implies \Delta t = \frac{6.626 \times 10^{-34} \text{ Js}}{1.99 \times 10^{-25} \text{ J}} = 3.3 \times 10^{-9} \text{ s}.$$  

Thus, the approximate lifetime is about 0.15 ns
(typical for fluorescence).

Phosphorescence lifetime can typically orders of magnitude longer.