Chem 332: Problem Set #7

Due in class: Wednesday, March 27th

(1) A diatomic molecule is determined to be in a state with n = 1, J=1, and M=1.

(a) in the harmonic oscillator-rigid rotor approximation, what is the explicit form of the rotational-vibrational wavefunction?

(b) what are the expected values of J^2 (square of the total rotational angular momentum) and J_z (the projection of the angular momentum on the molecular z-axis) in this state?

(2) Assume that vibrational force constants are independent of isotopic species. Ignoring rotation and using the harmonic oscillator approximation, calculate the frequency (in cm^{-1}) of the fundamental vibrational transition (n=0-1) of $H^{35}Cl$ and $D^{35}Cl$, where D is a deuterium atom. Please use accurate masses. Take the force constant of HCl to be 516 N/m.

(3) Consider the first overtone vibrational band ($n = 0 \rightarrow 2$) of the $^{11}B^{19}F$ molecule within the harmonic oscillator, rigid-rotor approximation. The harmonic frequency and rotational constant of this isotopomer are equal to 1402.13 cm^{-1} and 1.50724 cm^{-1}, respectively.

(a) Determine the frequency (in cm^{-1}) of the $J = 5 \rightarrow 6$ R-branch transition in the 1st overtone.

(b) The ^{10}B isotope has a natural abundance of nearly 20%. Predict the frequency (in cm^{-1}) of the same transition as part (a) for the $^{10}B^{19}F$ isotopomer.

(c) Predict the equilibrium bond length (in Å) of BF.

(4) Show that the following are true for hydrogen-like atoms.

(a) The average value of r for the ground state is $\frac{3a_0}{2Z}$.

(b) The most probable value of r for the ground state is $\frac{a_0}{Z}$. Explain why this result differs from part (a) by a drawing.

(c) For a 2p state, $\langle r \rangle = \frac{5a_0}{Z}$.