Chemistry 562 **Spring 2012**

Problem Set 9

Due Wednesday, March 28

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

Note: Keep a copy for of your homework because the graded homework will not be returned before your exam.

1. *Self-test 10.9. Be sure to read Example 10.3*

   Expand the 3 X 3 determinant by hand and find the energies (Use the 3 x 3 analogue of Eqn. 10.42. There is also a good discussion at the bottom of page 396.). Use the energies in the secular equation along with normalization to determine the coefficients for each energy. (Use Eqn 10.44 as a guide, but with $S_{AA}=S_{BB}=1$ and $S_{AB}=S_{BA}=0$. In matrix notation, $(\mathbf{H}-E_i)\mathbf{c}_i=0$. This is Eqn 10.47 with **S** equal to the identity matrix.)

2. The table below gives some spectroscopic constants (in cm^{-1}) for the OH radical in its two lowest electronic states

	$X^2\Pi$	$A^2\Sigma^+$
$V(R_e)$	0	32682
$\tilde{\nu}$	3735.2	3180.6
$x_e\tilde{\nu}$	82.81	94.93
B	18.87	17.36

(a) Calculate the force constant and the equilibrium bond distance for both electronic states. Which is larger in each case?

(b) Predict the wavenumber of the vibrational overtone transition (v=2 ← v=0) *in the ground electronic state* ($X^2\Pi$).

(c) Predict the wavenumber of the electronic transition $A^2\Sigma^+$(v=5, J=5) ← $X^2\Pi$ (v=1, J=5).

(d) Plot the ground and exited electronic states and draw or plot the ground vibrational level on $X^2\Pi$ and the lowest five vibrational levels on $A^2\Sigma^+$. For plotting the electronic states, you should use the Morse potential equation, and determine a and D_e from:

$$x_e = \frac{a^2\hbar}{2\mu\omega} = \frac{\tilde{\nu}}{4D_e}$$

Be sure to use the correct equilibrium bond distances and to offset the excited electronic excited state by *$V(R_e)$.*

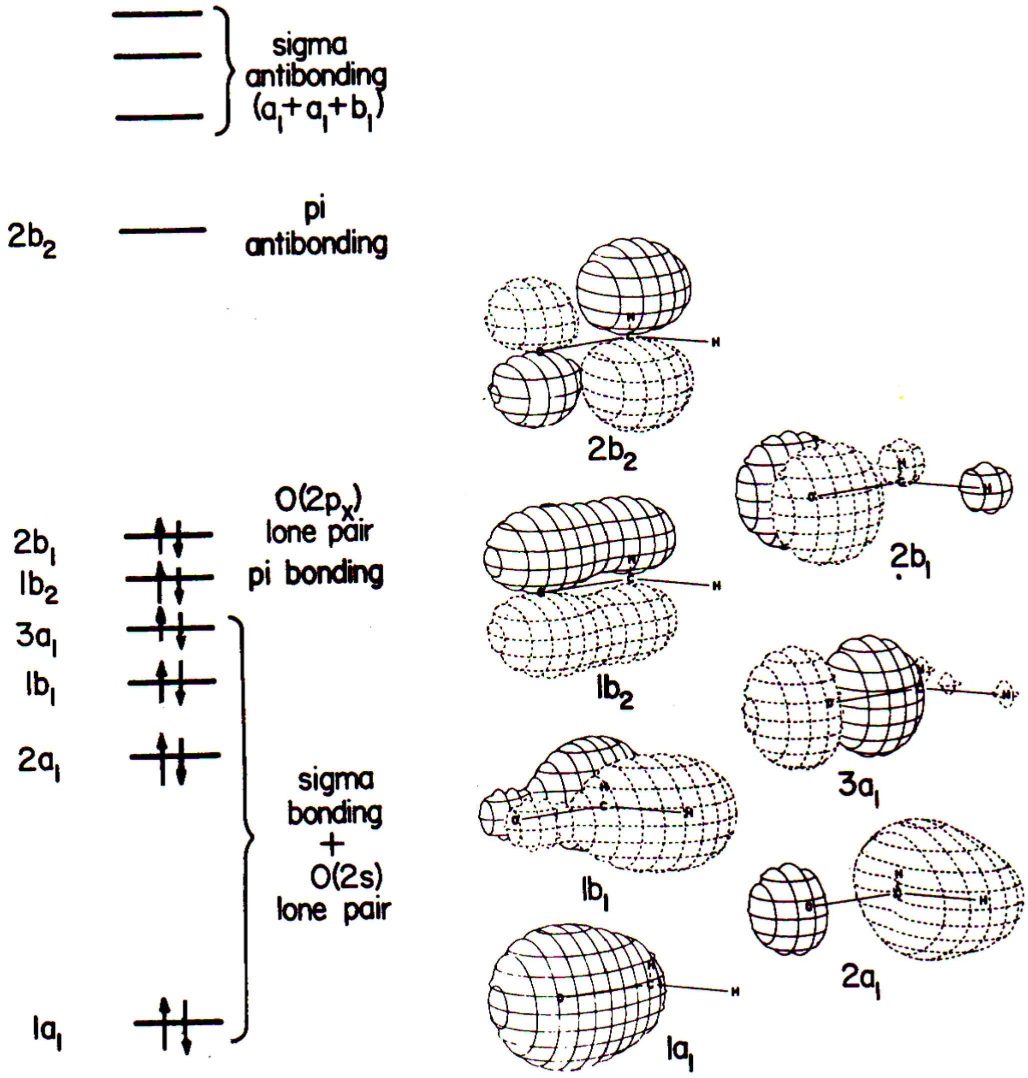
(e) Will v_2=0, 2, or 4 give the largest transition probability from $X^2\Pi$ (v=0, J=0) to $A^2\Sigma^+$ (v_2, J=0)? Why? (*Hint: Consider Franck-Condon Factors*)

(f) Draw the MO energy level diagram of OH radical. (The ionization energy of oxygen atom is the same as the H atom, 13.6 eV). What type of transition is $A^2\Sigma^+ \leftarrow X^2\Pi$ ($\pi^* \leftarrow \pi$)?

(g) Sketch the absorption spectrum for $A^2\Sigma^+(v_2, J=0) \leftarrow X^2\Pi$ $(v=0, J=0)$ for the range $v_2=0$ to $v_2=4$. (These are the Q-branches.)

3.) (a) The drawing below gives the molecular orbital diagram of formaldehyde along with drawings of the orbitals. (The symmetry designations are the same as in water since both are C_{2v} molecules.) There is one high energy orbital that is non-bonding. *Label it and its energy level with an n*. There is an antibonding orbital that is π^* in its local symmetry. *Label it*. (There is another non-bonding orbital. We will call it $3a_1$ even though the situation is actually more complicated because of the strong mixing of the atomic orbitals to make the three lowest a_1 orbitals. Each of them is partially bonding and nonbonding.)

Place electrons on the level diagram and work out the bond order for H_2CO. Is your result consistent with the Lewis dot structure?



(b) What will happen to the length of the C=O bond upon excitation of the π*←*n* transition? The origin transition, 0←0, between the lowest vibrational levels in the ground and electronically excited state has a wavenumber of 28,200 cm^{-1}. Explain how the intensity of this transition compares to the intensity of other transitions.

Draw one-dimensional potential energy curves to illustrate your argument. Indicate the energy of the origin transition on your diagram.