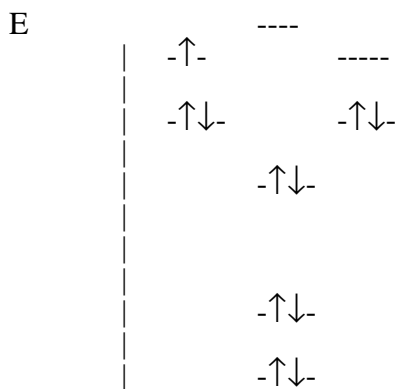


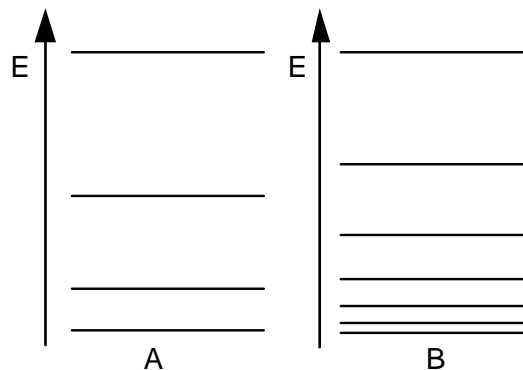
**Part Ia.** Answer 4 (four) of the first 5 (five) questions. If you answer more than 4, cross out the one you wish not to be graded.

1) 8pts) Of absorption or fluorescence spectroscopy, which would you use to determine the vibrational frequency for the ground electronic state of a diatomic molecule? Draw an energy level diagram with the two electronic states and appropriate vibrational states to explain your answer.

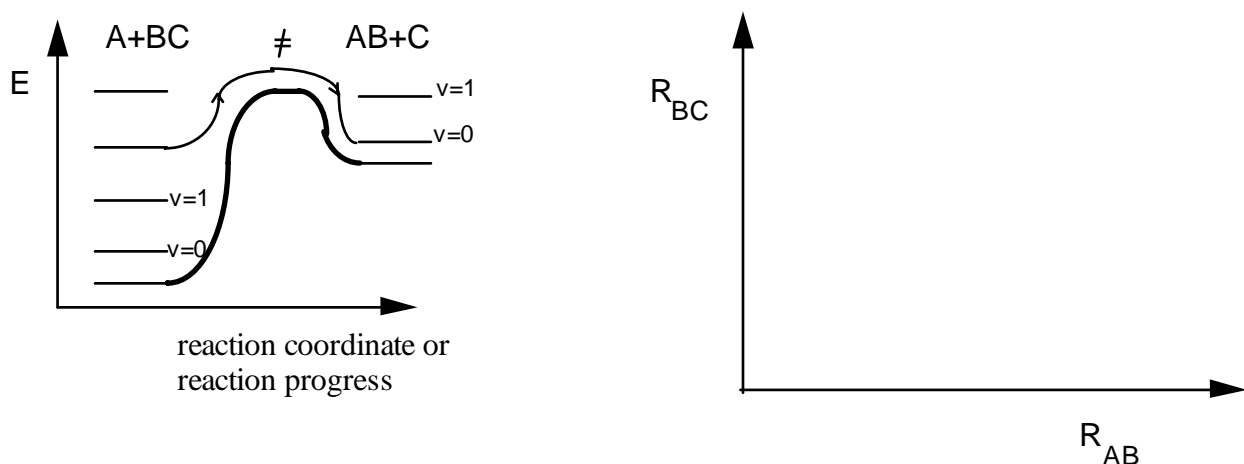
2). 8pts) Find the term symbol for the ground state of  $O_2^+$  diagrammed below. Remember to include the parity ( is it g or u overall?).



3). 8pts) The energy levels for two different systems are shown below. Which would have a larger internal energy? Briefly give your reasoning.



4) 8pts). The potential energy vs. reaction coordinate curve for an atom-diatom collision is shown below including the vibrational levels. Draw a corresponding trajectory for the collision. Label the reactant and product sides.



5) 8pts) (a) Which of the following molecules would give an infrared spectrum?

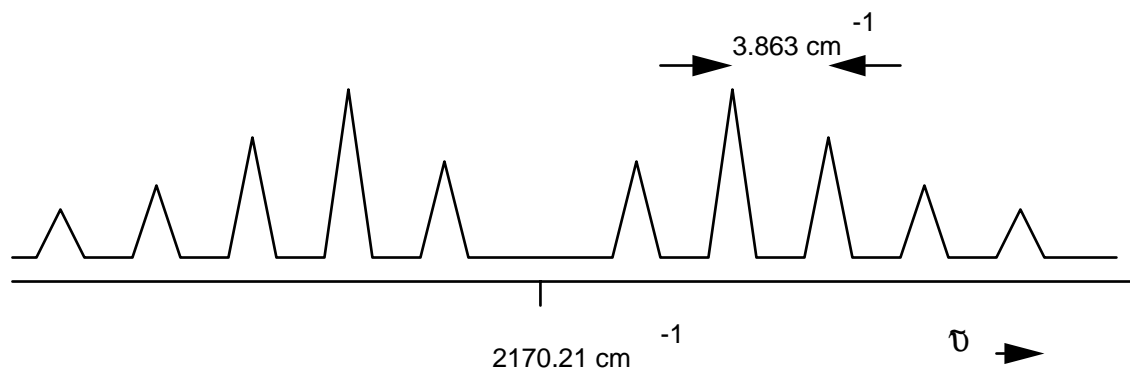
HCl                      O<sub>2</sub>                      H<sub>2</sub>O                      CO<sub>2</sub>

(b) Which of the following molecules would give a pure rotational microwave spectrum?

HCl                      O<sub>2</sub>                      H<sub>2</sub>O                      CO<sub>2</sub>

**Part Ib.** Answer three (3) of the following five questions.

••• The infrared spectrum for <sup>12</sup>C<sup>16</sup>O, carbon monoxide, is given below. Use this information for problems 6 and 7.



6) 14pts) Calculate the force constant for the carbon monoxide bond. (Atomic mass of <sup>16</sup>O = 15.9949 amu).

7) 14pts.) Calculate the bond length of carbon monoxide. (assuming that the rotational constant is the same for the  $v=0$  and the  $v=1$  states).

8) 14pts.) Calculate the vibrational contribution to the Gibbs free energy of the diatomic molecule  $\text{Na}_2$  at 1000K. The fundamental vibration frequency for  $\text{Na}_2$  is  $159 \text{ cm}^{-1}$ . Do the calculation for one mole of gas.

9) 14pts) Consider the reaction  $AB \rightarrow A + B$ , where A and B are atoms. Predict the effect on the equilibrium constant if the following changes are made: (give reasons for credit)

a) the AB molecule was a ground state triplet (like  $O_2$ ) instead of a normal singlet:  $K_p$  would  
a) increase b) decrease c) stay the same

b) the AB bond length is increased:  $K_p$  would a) increase b) decrease c) stay the same

c) the AB force constant is increased:  $K_p$  would a) increase b) decrease c) stay the same

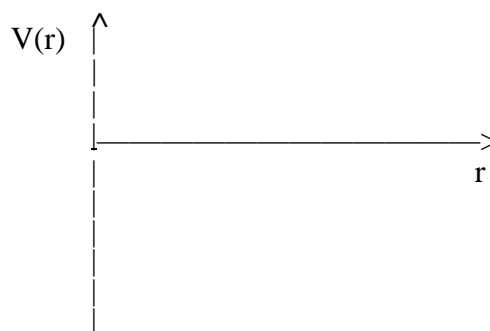
10) 14pts) The translational partition function for a mobile species on a surface is

$$q_t = \frac{2\pi m}{\beta h^2} \sigma$$

where  $\sigma$  is the surface area. Find the translational internal energy,  $U-U(0)$ , from this partition function for this system.

**Part IIa.** Answer four (4) of the following five (5) questions. If you answer more than 4 cross out the one you wish not to be graded.

1. (10pts) Make a rough sketch of the Coulomb potential for the hydrogen atom on the axes at right. Let  $r$  be the distance between the nucleus and the electron.

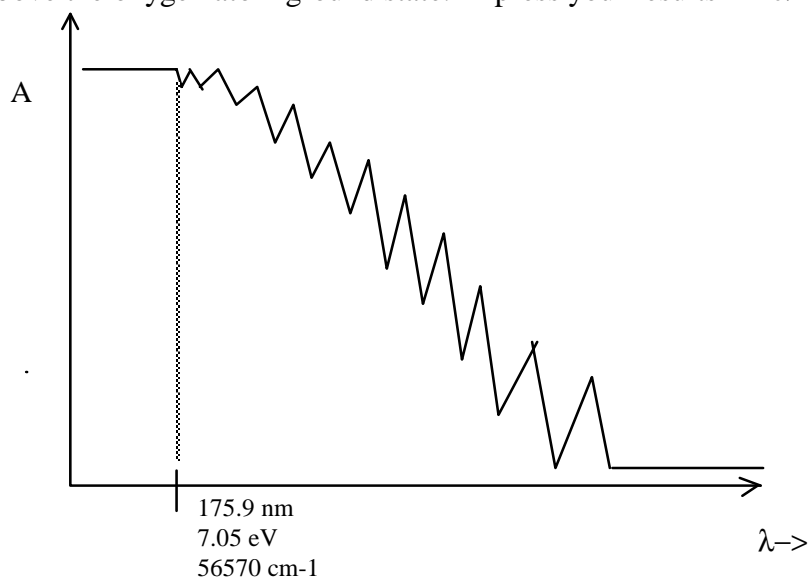


2. (10pts.) Find the  $z$ -component of the angular momentum ( $L_z$ ) using the corresponding operator for the rigid-rotor wavefunction  $\Psi = (3/8\pi)^{1/2} \sin\theta e^{i\phi}$ .

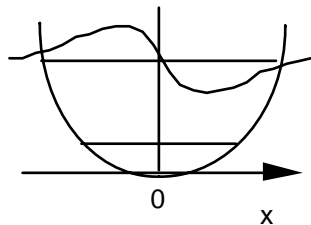
3. (10pts) Which of the following problems show a zero point energy?

- a). Translation ( particle in a box)
- b). Rotation ( rigid rotor)
- c). Vibration ( harmonic oscillator)
- d). Electronic ( e.g. hydrogen atom)

4. (10pts) The UV absorption spectrum of oxygen is shown below. What is the dissociation energy of the ground state oxygen molecule, given that the excited state oxygen atom is at 190 kJ/mol above the oxygen atom ground state. Express your results in kJ/mol.



5) 10pts) The asymptotic form for all the harmonic oscillator wavefunctions is  $\exp(-cx^2)$ , where  $x$  is the displacement and  $c$  is a constant. What is the mathematical form, in terms of  $x$ , of the first excited state of the harmonic oscillator,  $v=1$ . (Don't worry about the value of constants, just call them  $a$ ,  $b$ , etc.)



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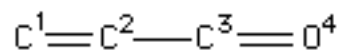
**Part IIb**•• Answer three (3) of the following four questions. If you answer more than 3 cross out the one you wish not to be graded.

6. (20pts). Normalize the wavefunction for the ground state of the hydrogen atom

$$\Psi_{1s} = N e^{-Zr/a_0}$$

7. (20pts)  $\text{XeF}_2$  is a stable compound.  $\text{XeF}_2$  is linear. (a) Give the molecular orbital diagram for this system. (b) Sketch the orbitals for each level. (c) Give the electron occupancy for each level. [Hints: use only p orbitals on each atom as we did for linear ozone (just like linear ozone). The s orbitals will then be core orbitals, each filled with two electrons]

8. The Hückel molecular orbitals for acrolein are shown below.



**Energy Eigenvalues**

$$E_1 = \alpha + 1.8794 \beta$$

$$E_2 = \alpha + 1.0000 \beta$$

$$E_3 = \alpha + -0.3473 \beta$$

$$E_4 = \alpha + -1.5321 \beta$$

**Eigenvectors**

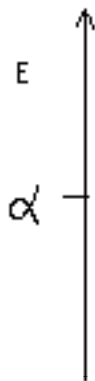
$$\Psi_1 = 0.2280 \phi_1 + 0.4285 \phi_2 + 0.5774 \phi_3 + 0.6565 \phi_4$$

$$\Psi_2 = 0.5774 \phi_1 + 0.5774 \phi_2 + -0.0000 \phi_3 + -0.5774 \phi_4$$

$$\Psi_3 = 0.6565 \phi_1 + -0.2280 \phi_2 + -0.5774 \phi_3 + 0.4285 \phi_4$$

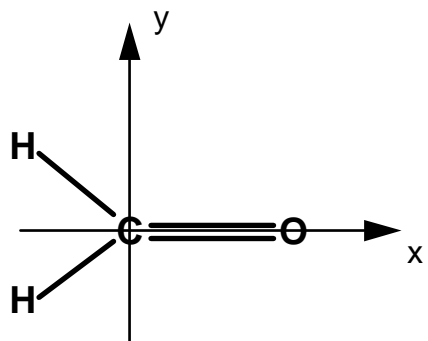
$$\Psi_4 = 0.4285 \phi_1 + -0.6565 \phi_2 + 0.5774 \phi_3 + -0.2280 \phi_4$$

a. (10pts) Draw the energy level diagram and indicate the electron filling.



b. (10pts) Calculate the pi bond order between the carbon and oxygen atoms, atoms 3 and 4.

9. (20pts). The MOPAC calculation for formaldehyde is attached. Answer the following questions on the basis of this printout. The orientation is shown below.



(a.) Calculate the percent S character on the oxygen in orbital 1.

(b.) What is the hybridization of the carbon atom. What did you expect it to be? What is the hybridization of the oxygen atom? What did you expect it to be?

(c.) Which orbitals are the pi bonding and anti-bonding orbitals?

(d.) (extra credit, 10pts) The Lewis dot structure of formaldehyde implies that the non-bonding electrons on oxygen are equivalent. Is this true? Explain your answer. (Hint: Look at the orbital coefficients for carbon and oxygen, while neglecting the hydrogen orbitals. Look for orbitals which are roughly 70% or greater oxygen character for the C=O bond.)

Formaldehyde

FINAL HEAT OF FORMATION = -32.88188 KCAL

TOTAL ENERGY = -478.11917 EV

ELECTRONIC ENERGY = -870.73765 EV

CORE-CORE REPULSION = 392.61847 EV NO. OF FILLED LEVELS = 6

		EIGENVECTORS					
ROOT NO.		1	2	3	4	5	6
Eigenvalue		-42.991	-25.119	-16.955	-16.299	-14.179	-11.041
S H	1	-0.111	0.370	0.383	-0.214	-0.000	-0.396
S C	2	-0.479	0.630	0.000	0.010	0.000	0.000
PX C	2	-0.147	-0.153	-0.525	0.293	0.000	0.184
PY C	2	-0.222	-0.232	0.347	0.443	-0.000	-0.122
PZ C	2	0.000	0.000	-0.000	-0.000	-0.591	0.000
S O	3	-0.787	-0.455	0.000	-0.337	0.000	0.000
PX O	3	0.128	-0.113	-0.463	-0.395	0.000	-0.665
PY O	3	0.194	-0.171	0.307	-0.596	-0.000	0.440
PZ O	3	0.000	0.000	-0.000	-0.000	-0.806	-0.000
S H	4	-0.111	0.370	-0.383	-0.214	0.000	0.396
ROOT NO.		7	8	9	10		
Eigenvalue		0.859	3.676	3.849	7.126		
S H	1	0.000	0.550	-0.441	0.030		
S C	2	-0.000	-0.534	-0.000	0.294		
PX C	2	-0.000	0.167	-0.620	0.381		
PY C	2	0.000	0.251	0.411	0.576		
PZ C	2	0.806	-0.000	-0.000	0.000		
S O	3	0.000	0.028	0.000	-0.240		
PX O	3	0.000	-0.070	0.194	0.338		
PY O	3	-0.000	-0.106	-0.128	0.511		
PZ O	3	-0.591	0.000	0.000	0.000		
S H	4	0.000	0.550	0.442	0.030		

SIGMA-PI BOND-ORDER MATRIX									
		S-SIGMA	S-SIGMA	P-SIGMA	P-PI	S-SIGMA	P-SIGMA	P-PI	S-SIGMA
		H 1	C 2	C 2	C 2	O 3	O 3	O 3	H 4
S-SIGMA	H 1	0.999							
S-SIGMA	C 2	0.325	0.927						
P-SIGMA	C 2	0.571	0.000	1.835					
P-PI	C 2	0.002	0.000	0.000	1.035				
S-SIGMA	O 3	0.000	0.029	0.099	0.000	0.129			
P-SIGMA	O 3	0.034	0.247	0.593	0.000	0.000	0.909		
P-PI	O 3	0.019	0.000	0.000	1.030	0.000	0.000	1.068	
S-SIGMA	H 4	0.047	0.325	0.571	0.002	0.000	0.034	0.019	0.999