

**CHEM 325**  
**Spring 2009**  
**Take-Home Portion of Exam 2**

Name: \_\_\_\_\_

**Instructions**

Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't assess it and I will assume that you don't know it and will grade your work accordingly.

Show all work for full credit! Use complete sentences. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer. Better yet, write out your answers on scratch paper first and then transfer your final answers to this booklet.

There are **14** pages, **1** blank.

You may use your book to look up any needed physical constants, equations, etc. However, you may not work with anyone else, and you may not ask any other faculty members to help you with the specific questions given here. You may ask any chemistry faculty member for help on the concepts involved, and you may ask me anything you want.

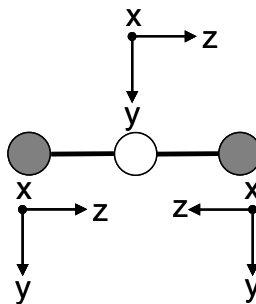
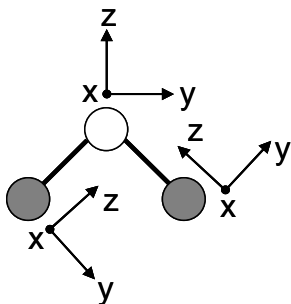
You may use the back of any page as additional workspace. Please indicate that you have done so. You may also use extra pages, but please insert them near the relevant problem.

Problem	Possible Points	Points Received
1	38	
2	23	
3	24	
Free	15	15
Total	100	
	Bonus	
	Grand Total	

1. Nitrogen forms three different chemical species each with a 2:1 O:N stoichiometry,  $\text{NO}_2^+$ ,  $\text{NO}_2^\bullet$  and  $\text{NO}_2^-$ .

a. (9 Points) Draw Lewis dot structures for each of the  $\text{NO}_2$  species. Include resonance and formal charges, as appropriate. Use VSEPR theory to predict the structures and Valence Bond theory to describe the bonding (i. e, hybridization on each atom, etc.).

b. (12 Points) Derive qualitative MO diagrams for a symmetric linear triatomic molecule and for a symmetric bent triatomic molecule using the coordinate system shown below (note that the different colored spheres represent different atoms). You may ignore the oxygen 2s orbitals in this analysis. Show the SALCs and the resulting qualitative MO wavefunctions. Give a rationale for your ordering in each case. Show your work for full credit, but you do not need to re-derive results that we derived in class or on a quiz. You can simply state the result and state where you got your answer. Note that for the linear case there is a central atom. Attach extra pages showing your work between pages 3 and 4 of this packet.



## Symmetric Linear Triatomic Molecule MO Diagram

## Symmetric Bent Triatomic Molecule MO Diagram

c. (4 Points) In your analysis in part *b*, you ignore the effects of the O 2s orbitals. Describe what effects they would have on the MO description of each type of molecule. Be specific.

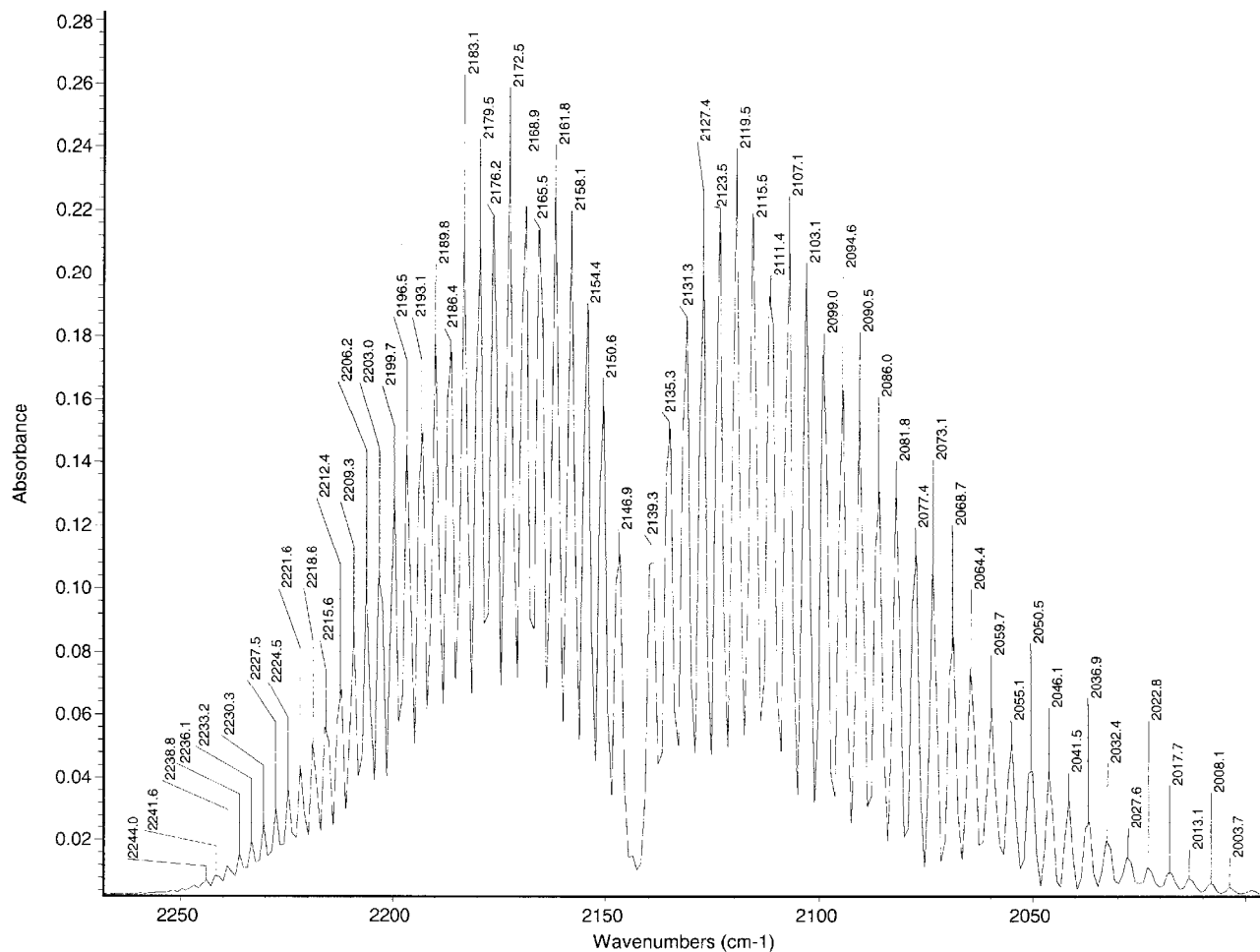
d. (4 Points) Valence Bond and MO theories differ in one major way in their description of  $\text{NO}_2^+$ . What is it? Suggest a way that one might chemically test the models.

e. (9 Points) Draw a qualitative Walsh diagram showing the energy of the molecular orbitals as a function of the O–N–O angle. Use it to explain why  $\text{NO}_2^+$ ,  $\text{NO}_2^\bullet$  and  $\text{NO}_2^-$  adopt the geometries that they do.

2a. (10 Points) The rotational-vibrational spectrum of CO is shown below. From the information given, determine  $\tilde{\nu}_0$ ,  $B$ ,  $\alpha$  and  $D_J$  with their uncertainties at 95% confidence (write your values in the table on page 10). Tape a graph showing you best fit of the data on page 9 (show any work there, too). Use the method described by Garland *et al.* where the equation for the vibrational and rotational terms

$$S(\nu, J) = \left(\nu + \frac{1}{2}\right)\tilde{\nu}_e - \left(\nu + \frac{1}{2}\right)^2 x_e \tilde{\nu}_e + 2BJ(J+1) - D_J J^2(J+1)^2 - \alpha \left(\nu + \frac{1}{2}\right) J(J+1)$$

is simplified to  $\tilde{\nu}(m) = \tilde{\nu}_0 + (2B - 2\alpha)m - \alpha m^2 - 4D_J m^3$ , where  $m$  is an integer that is negative for the P branch and positive for the R branch ( $m = 0$  corresponds to  $\tilde{\nu}_0$ , the wavenumber of the forbidden Q branch). In both equations,  $\tilde{\nu}_e$  is the harmonic oscillator vibrational constant,  $x_e \tilde{\nu}_e$  represents the anharmonicity of the oscillator,  $B$  is the rotational constant,  $D_J$  is the centrifugal distortion constant and  $\alpha$  is the rotational-vibrational coupling constant. In the simplified equation,  $\tilde{\nu}_0$  is defined by  $\tilde{\nu}_0 = \tilde{\nu}_e - \tilde{\nu}_e x_e$ . An Excel file containing the wavenumber of each transition is available from the web page.





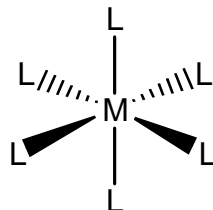
$\tilde{\nu}_0$ (cm <sup>-1</sup> )	
$B$ (cm <sup>-1</sup> )	
$\alpha$ (cm <sup>-1</sup> )	
$D_J$ (cm <sup>-1</sup> )	

b. (5 Points) Assuming a Morse potential for an oscillator, derive a general expression for the maximum vibrational quantum number,  $v_{max}$ .

c. (8 Points) From the parameters calculated in this problem, and data from the book, derive the Morse potential curve (like Fig. 13.30 in the text) for CO and tape it in the space below. Indicate  $D_e$ ,  $D_0$  and  $\nu_{max}$  on your graph and give the actual values. Show (as in Fig. 13.30) the energy of the first four allowed vibrational states. Attach any pages showing your work between pages 11 and 12 of this packet.

3a. (10 Points) Determine all of the terms that arise from the  $d^2$  configuration (you must show the microstates and how you found the terms from the microstates). Place these term symbols in order of increasing energy (lowest to highest). FYI the order you expect is not the order found experimentally. Show all work for full credit and insert any extra pages between pages 12 and 13 of this packet.

b. (6 Points) Many transition metal ions form complexes with octahedral (or nearly octahedral) symmetry, as shown below. Derive the MO diagram for an octahedral metal complex assuming that each ligand (L) forms only a  $\sigma$  bond with the metal ion (M) through its  $p_z$  orbital, that the metal only uses its d orbitals in bonding and that the ligand orbitals are lower in energy than the metal orbitals. Do not determine the SALCs here.



c. (8 Points) If both of the electrons in a  $d^2$  transition metal ion are confined to the  $t_{2g}$  set of orbitals, demonstrate that this electronic configuration (i. e.,  $(t_{2g})^2$ ) gives rise to the following states:  ${}^3T_{1g}$ ,  ${}^1T_{2g}$ ,  ${}^1E_g$ , and  ${}^1A_{1g}$ . You may use the correlation table from my class web page (under the "Help!" button).