Inorganic Exam 1 **Name:**
Chm 451
28 October 2010

Instructions. Always show your work where required for full credit.

1. In the molecule CO_2, the first step in the construction of the MO diagram was to consider σ-bonding only. We can assume that the 2s orbitals on oxygen are too low in energy to participate, so that the σ-bonding that occurs is between carbon's 2s and 2p orbitals and the SALCs created from oxygen's p-orbitals.

a. (6 pts) Starting with the oxygen atomic orbitals as shown at right, and the D_{2h} character table, determine the reducible representation and irreducible components for the σ-bonding SALCs.

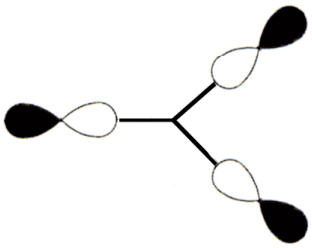
D_{2h} Character Table

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

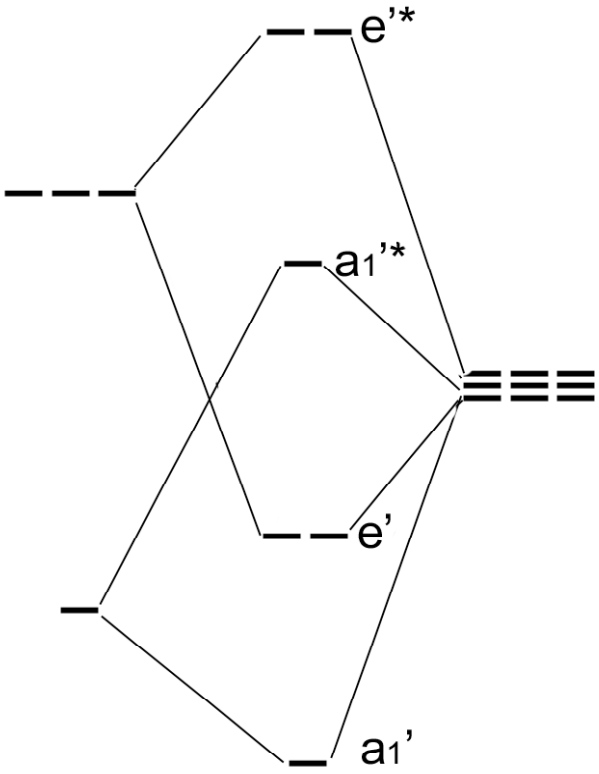
	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)
Γ								

b. (6 pts) Sketch the MO diagram that we would obtain if we considered only σ-bonding, ignoring π-bonding, which is added in a later step. Label every MO with symmetry labels. You do not need to populate the MOs.

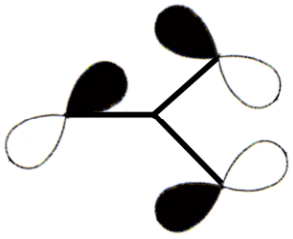
2. In BF_3, the σ–only bonding MO diagram is shown below. The 2s orbitals on fluorine are too low in energy to participate, so that the σ-bonding that occurs is between boron's 2s and 2p orbitals and the SALCs created from fluorine's p-orbitals. The atomic orbital set used to create the SALC set for σ-bonding is shown at right.

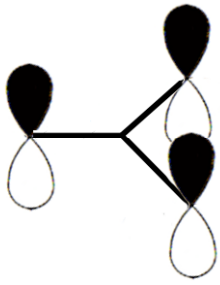


a. (6 pts) Sketch an orbital drawing for each MO adjacent to each MO.



b. (6 pts) So, one p-orbital from each fluorine is involved in σ-bonding. That leaves two more p-orbitals on each fluorine. These can be sorted into two types: those in the xy-plane and those parallel to the principle rotation axis, z:





The former three are non-bonding with any of the s and p-orbitals on boron. The latter three potentially could form a MO with boron's $2p_z$ orbital. Starting with the atomic orbitals on the

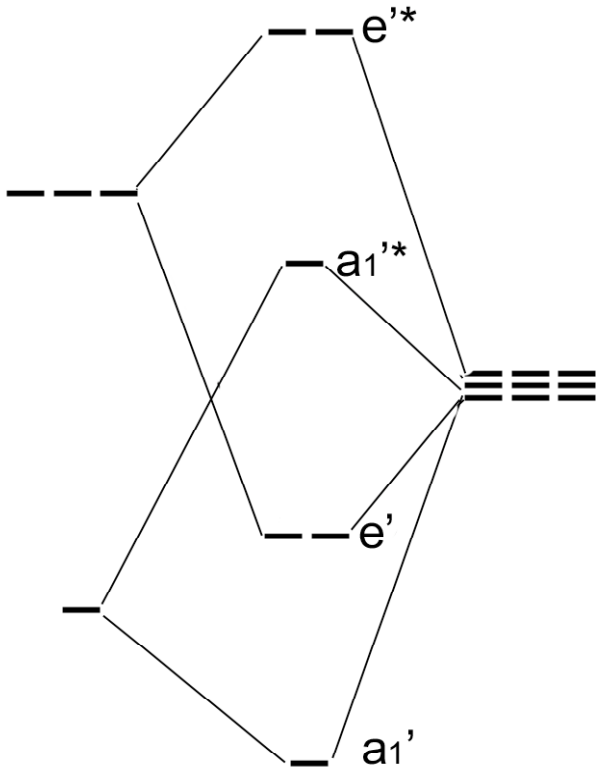
right and the D_{3h} character table, determine the reducible representation for these three p-orbitals and then the irreducible components. (You can ignore S_3 and still get the answer.)

D_{3h} Character Table

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$		
A'_1	1	1	1	1	1	1		x^2+y^2, z^2
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
Γ						

c. (6 pts) Of those you obtained, one of them has the same symmetry as boron's $2p_z$ orbital. The other two are non-bonding because they do not have the proper symmetry to form MOs with boron's 2s or 2p orbitals. Sketch the resulting MO starting from the σ-only MO diagram (copied from above) and adding this new π–bonding. Include symmetry labels.



d. (2 pts) Sketch an orbital drawing for the π–MOs.

3. (3 pts) Cyanide is a Lewis base. Sketch its Lewis dot structure. Use formal charges to decide if carbon or nitrogen is the more basic end of the ion.

4a. (3 pts) Sulfur tetrafluoride could function as a Lewis base. Sketch the Lewis dot structure for SF_4.

b. (3 pts) Show how the sulfur of SF_4 might be a Lewis base towards the Lewis acid Al^{+3}.

c. (3 pts) SF_4 could also function as a Lewis acid. Show with a Lewis dot structure, how SF_4 would accept an electron pair from CN^-.

5a. (2 pts) Antimony forms two acids, H_3SbO_3 and H_3SbO_4. Which of these two would you expect to have the larger pK_{a1}? [Note: $pK_a = 4$ is greater than $pK_a = 3$]

b. (2 pts) Considering H_3SbO_4, which pK_a is the largest? pK_{a1}, pK_{a2}, pK_{a3}

6. (2 pts) For each pair, use hard-soft acid-base chemistry to predict the more water soluble of the two.

A. AgF or AgCl B. CaS or CaF_2

7. Xenon forms a fluoride with a body-centered tetragonal sub-lattice of xenon cations. The fluorides occupy two types of positions: (a) two fluorides are located along each of four parallel edges (while the other eight edges contain no fluorides) and (b) two fluorides are fully contained within the unit cell and located above and below the body-centered xenon ion.

a. (4 pts) Sketch the xenon sublattice (no fluorides) and indicate what you know for sure about bond angles and distances.

7 b – d (3 pts)

b. How many xenon cations are in each unit cell?	c. How many fluoride anions are in each unit cell?	d. What is the formula of this fluoride of xenon?

8. (4 pts) A mineral crystallizes in a cubic close-packed array of sulfur ions with aluminum ions in one-half of the octahedral holes and zinc ions in one-eighth of the tetrahedral holes. What is the formula of the mineral?

9a. (2 pts) Calcium metal exhibits hcp lattice. How many calcium atoms are present per unit cell?

b. (2 pts) How would the density of calcium differ if the metal exhibited ccp rather than hcp?

A. it would be the same B. it would be larger
C. it would be smaller D. probably larger or smaller, but not possible to predict

c. (2 pts) One cubic lattice type (simple, bcc, fcc) is identical to either hcp or ccp. Which two are identical?

10. (3 pts) Suppose the large ions form a face-centered cubic unit cell. The smaller ions would occupy vacant positions within the unit cell. Where are these positions? Check all that are possible locations for the smaller ions.

A. cubic holes B. tetrahedral holes C. octahedral holes

11. (3 pts) Is it thermodynamically favored for the small ions to be somewhat bigger than the holes they occupy within the large ions? Explain.

12. (5 pts) If one were to calculate the volume of a cubic unit cell from the density of an ionic substance, one would need to know which other facts? Circle all that apply.

A. The type of unit cell (simple, body-centered, face-centered)
B. The ionic radius of the large ion
C. The ionic radius of the smaller ion (if large than the hole)
D. Avogadro's number
E. The molar mass of the substance

13. (3 pts) What does the rhombohedron and the simple cubic unit cell have in common in terms of cell dimensions and/or angles?

14. (3 pts) The salt silver iodide, AgI, forms a hexagonal close-packed lattice of iodide ions. The silver ions occupy tetrahedral holes. What fraction of the tetrahedral holes are occupied by silver ions?

15a. (3 pts) Cesium chloride forms a lattice that you studied in the reading guides. To refresh your memory, the larger ions form a simple cubic unit cell and the smaller ions occupy the body-centered positions. Why isn't this structure called body-centered cubic?

b. (3 pts) Continuing on with the cesium chloride structure, what is the coordination number of the smaller ion at the body-centered position?

c. (3 pts) How does the body-centered hole (often called a cubic hole) compare in size to a tetrahedral and octahedral holes? Rank them in size from largest to smallest: cubic, octahedral and tetrahedral holes.

16a. (3 pts) Both MgO and NaF have the same lattice structure, namely NaCl. Write the equation for the lattice energy for MgO.

b. (3 pts) Would you expect MgO to have a larger lattice energy than NaF? Explain.

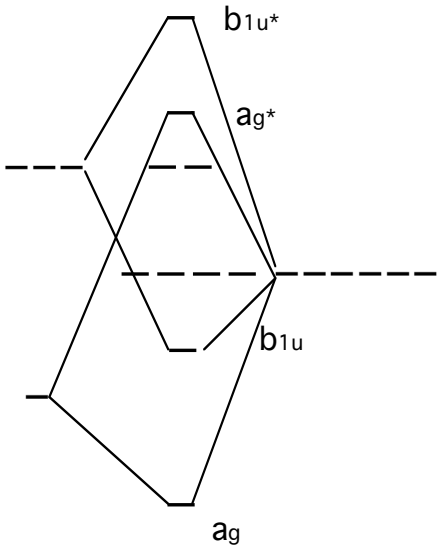
BONUS. (4 pts) A silicate anion has the formula $Si_3O_{10}^{-8}$. Could you describe the silicon part of its structure as being in "a ring of silicons" or as "bent linear"? Explain for credit.

Answers

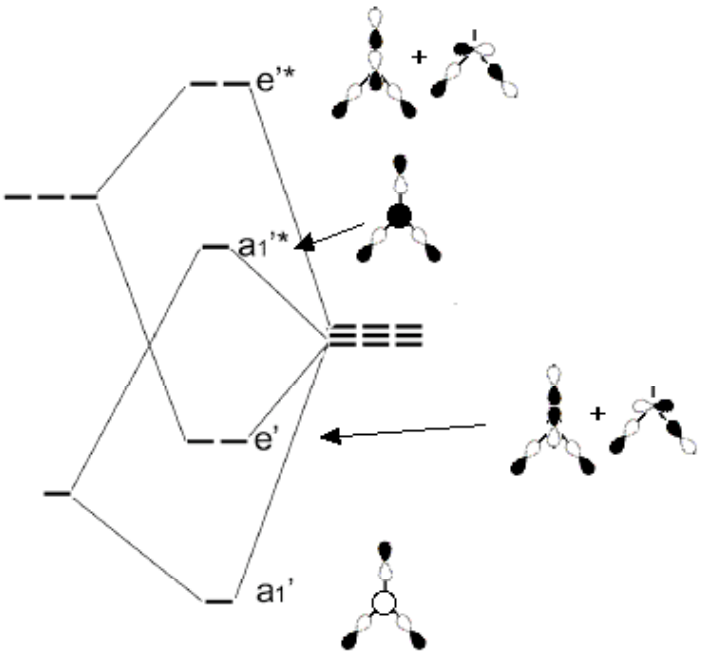
1a.

	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)
Γ	2	2	0	0	0	0	2	2
A_g	1	1	1	1	1	1	1	1
B_{1u}	1	1	-1	-1	-1	-1	1	1

b. (6 pts) Sketch the MO diagram that we would obtain if we considered only σ-bonding, ignoring π-bonding, which is added in a later step. Label every MO with symmetry labels. You do not need to populate the MOs.



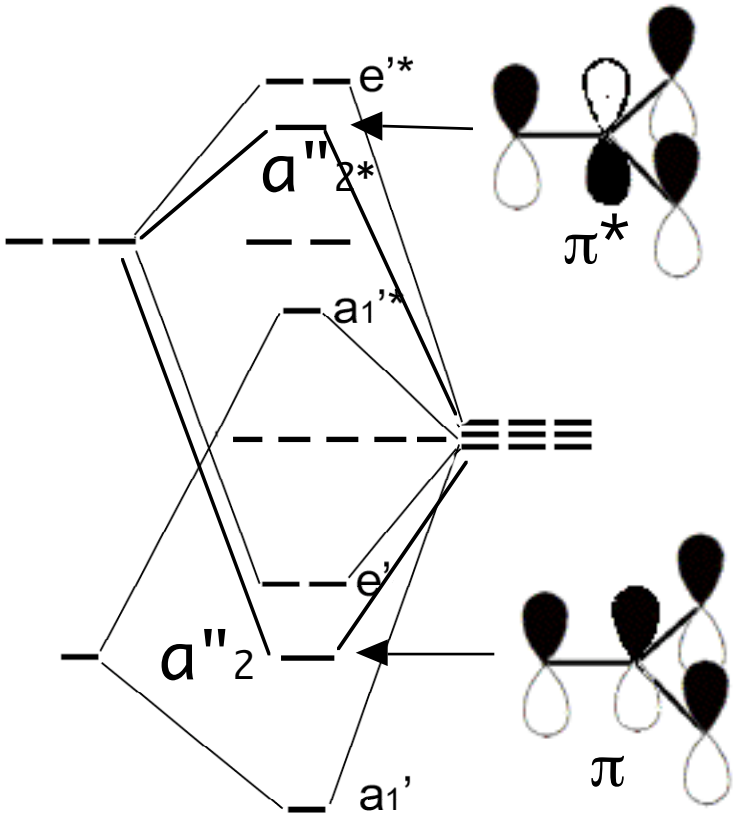
2a.



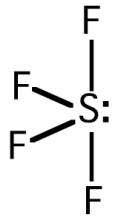
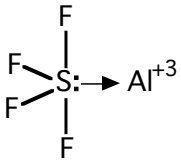
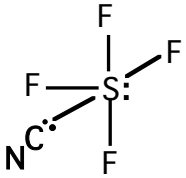
b.

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	3	0	-1	-3	0	1
E"	2	-1	0	-2	1	0
$A"_2$	1	1	-1	-1	-1	1

c and d.



3. :C:::N: $FC_C = -1$ and $FC_N = +1$

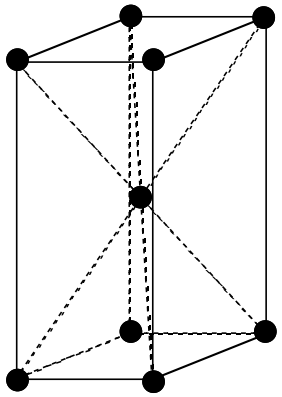
4a.	4b.	4c.
		

5a. H_3SbO_3

b. pK_{a3}

6. A. AgF B. CaS

7a. all angles are 90^{o}; two sides have equal lengths and one side is different



7b. 2; c. 8 x ¼ + 2 = 4; d. XeF_2

8. Al_2ZnS_4

9a. 2

b. a

c. fcc = ccp

10. B and C

11. If they are slightly larger, the contacting is between ions of opposite charge.

12. A, D, E

13. Both have a = b = c and both have all 3 angles the same. In the rhomohedron, the angles are not 90^{o}.

14. 1/2

15a. A body-centered lattice has the same atom or ion at the corners and body-centered position.

b. 8

c. cubic hole > octahedral hole > tetrahedral hole

16a. $Mg^{+2}(g) + O^{-2}(g) \rightarrow MgO$.

b. Yes, because of the larger charges of the ions (+2 and -2 vs. +1 and -1)

BONUS. (4 pts) It's linear, because the ring would have a formula $Si_3O_9^{-6}$.