CHEM-457: Inorganic Chemistry

Midterm I – March 13th, 2014

NAME_____

This exam is comprised of six questions and is ten pages in length. Please be sure that you have a complete exam and place your name on each page.

Answer each question to the best of your ability. Partial credit will be awarded where appropriate. You are not permitted to use any supplemental materials other than what is included in this test booklet. Calculators are not needed and are not permitted to be used. **PLEASE DO NOT REMOVE ANY PAGES FROM THIS EXAM.**

Write all your answers directly in this test booklet and show all work where necessary.

Good Luck!

1. _____ (10 pts)
2. _____ (20 pts)
3. _____ (15 pts)
4. _____ (10 pts)
5. _____ (10 pts)
6. _____ (35 pts)

Total _____

1. (10 total points) Please answer each of the following questions dealing with solutions to the Schrödinger equation, $\Psi(n, l, m_l)$. Please keep your answers succinct – two sentences or less.

(a) What information about an orbital is conveyed by each of the quantum numbers for the three-number solution to the Schrödinger equation? Be sure to make clear which property correlates with each quantum number (3 pts)

(0.5 pts for each QN + property)

n - size + energy

l - shape

m_l - spatial orientation

(b) How does the energy of the $3d_{xy}$ orbital in the hydrogen atom compare to the energy of the $3p_x$ orbital of hydrogen? Please explain your answer. (3 pts)

They are <u>equal</u> to each other. (2) Energy only depends on n when there is only one e^- (no e^-/e^- repulsion). (1)

(c) How does the energy of the 1s orbital of hydrogen compare to the energy of the 1s orbital of carbon? Please explain your answer. (2 pts)

It is higher. Z^*_{1s} increases as Z increases
(2) (1)

Note $Z^* \neq Z$ due to shielding but 1s e^- are very poorly shielded. For H, the 1s e^- is attracted to 1 proton, but for C, the 2 1s electrons are attracted to 6 protons.

(d) Why does fluorine (χ_p = 4.0) have a higher electronegativity than oxygen (χ_p = 3.6)? (2 pts)

Z^*_{2p} increased as Z increases. 2p orbitals are poor at shielding, $\therefore Z^*_{2p}$ for F > Z^*_{2p} for Oxygen.

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2. (20 total points. 4 points each, no partial credit awarded). Write the letter of the most correct answer to each of the following multiple-choice questions on electron configurations and periodic trends in the box to the left of the question. Note: only answers placed in the boxes along the left side of this page will be graded.

[D]

i. Which of the following statements is true about the ionization energy of Mg^+?
   a. It will be equal to the ionization energy of Li.
   b. It will be equal to and opposite in sign to the electron affinity of Mg.
   c. It will be equal to and opposite in sign to the electron affinity of Mg^+.
   d. It will be equal to and opposite in sign to the electron affinity of Mg^{2+}.
   e. none of the above

[A]

ii. An atom of which of the following elements has the largest second ionization energy?
   a. Li
   b. C
   c. F
   d. Be
   e. O

[D]

iii. The statement that the first ionization energy for an oxygen atom is lower than the first ionization energy for a nitrogen atom is
   a. consistent with the general trend relating changes in ionization energy across a period from left to right because it is easier to take an electron from an oxygen atom than from a nitrogen atom.
   b. consistent with the general trend relating changes in ionization energy across a period from left to right because it is harder to take an electron from an oxygen atom than from a nitrogen atom.
   c. inconsistent with the general trend relating changes in ionization energy across a period from left to right and due to the fact that the oxygen atom has two doubly occupied 2p orbitals and nitrogen has only one.
   d. inconsistent with the general trend relating changes in ionization energy across a period from left to right and due to the fact that oxygen has one doubly occupied 2p orbital and nitrogen does not. You eliminate Π_c + maximize Π_e when moving Oxygen.
   e. incorrect.

[E]

iv. The ground-state electron configuration of a gas-phase Cr^{2+} ion is
   a. a singlet.
   b. a doublet.
   c. a triplet.
   d. a quartet.
   e. a quintet.

[C]

v. Which of the following statements is incorrect?
   a. All s-block main-group elements have only one or two valence electrons.
   b. Carbon and silicon have the same number of valence electrons.
   c. All elements in the $n = 4$ period have a partially or completely filled $n = 4$ shell.
   d. All noble gases have completely filled shells.

4d + 4f are not filled

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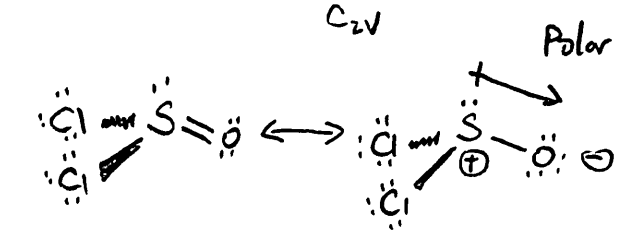
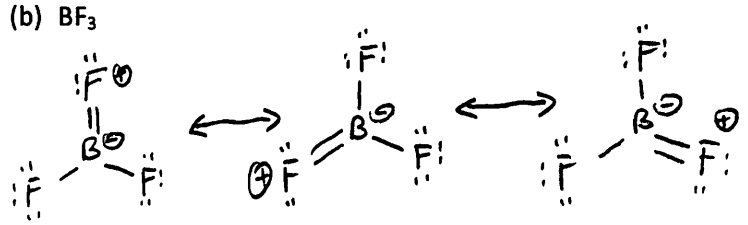
3. Draw the Lewis dot structure for each of the species below. Please show resonance and formal charges where appropriate. In addition, please provide the lowest energy VSEPR structure for each of the following. Indicate whether the species is polar or non-polar and if polar, denote the direction of the dipole moment. Lastly, please indicate the point group to which the molecule belongs. (15 pts)

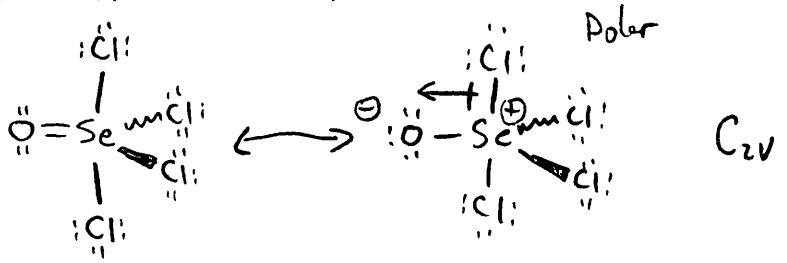
(a) $SOCl_2$



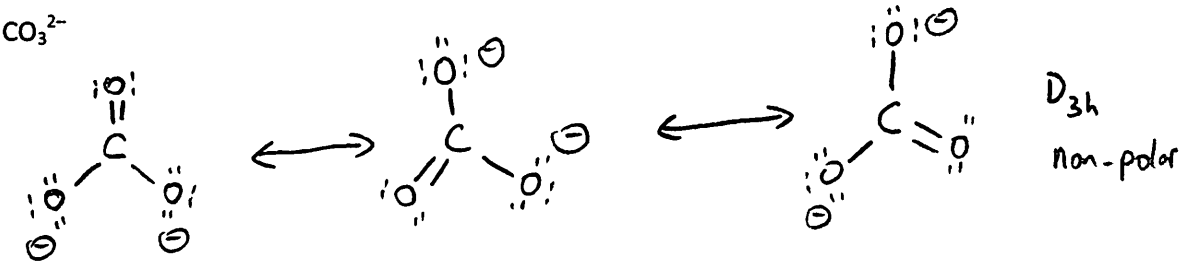
(b) BF_3



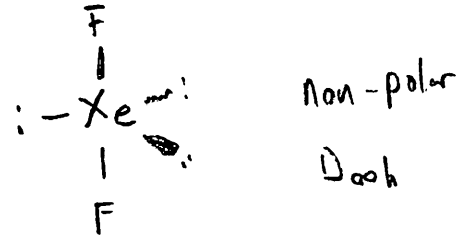
(c) $SeOCl_4$ (Se is central atom)



(d) CO_3^{2-}



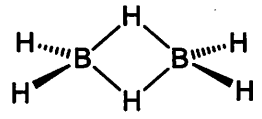
(e) XeF_2



Name: _____

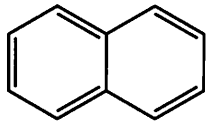
4. (10 total points) Determine the point groups of the following species. Note: only answers placed in the empty boxes will be graded.

(a)



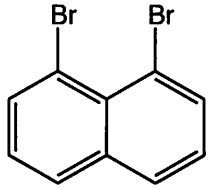
D_{2h}

(b)



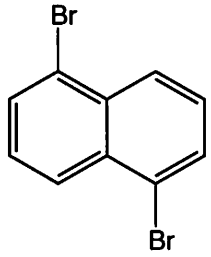
D_{2h}

(c)



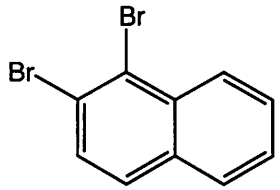
C_{2v}

(d)



C_{2h}

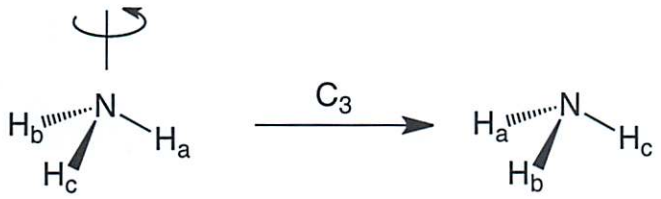
(e)



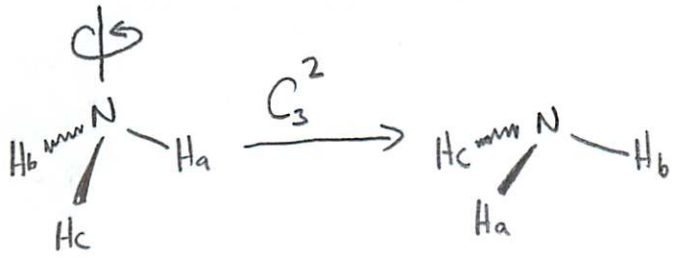
C_s

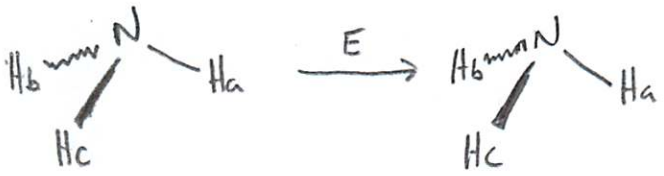
Name: _____

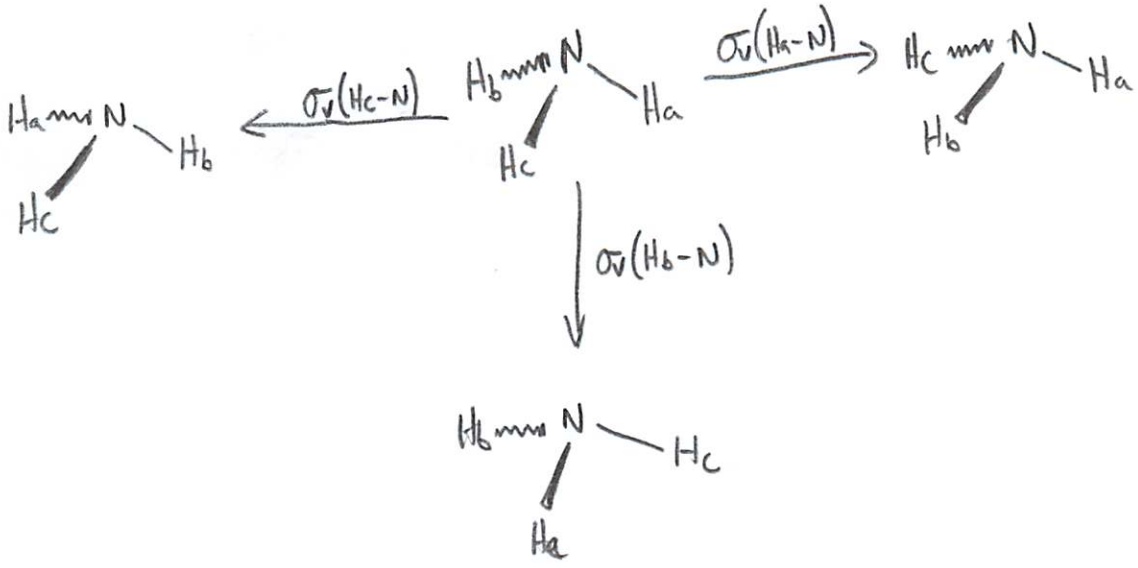
5. (10 total points) The structure of ammonia is illustrated below with the hydrogen atoms labeled. Show how the hydrogen atoms would be labeled after performing each of the 6 symmetry operations of the C_{3v} point group. Be sure to indicate the symmetry element about which you perform each operation. As an example, C_3 is illustrated. The C_{3v} character table also provided for your reference.



C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	−1	R_z
E	2	−1	0	$(x, y), (R_x, R_y)$

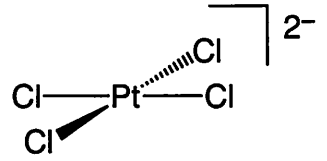




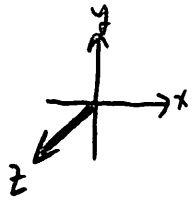


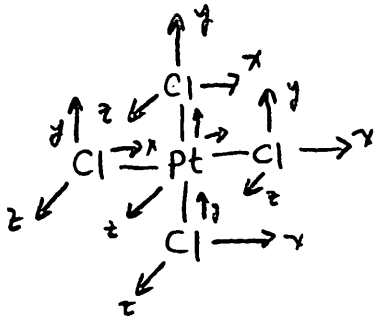
Name: _____

6. (25 total points) Consider the molecule tetrachloroplatinate $[PtCl_4]^{2-}$, the structure of which is shown below. This molecule belongs to the D_{4h} point group. Using the methodology we developed in class please complete the following. Note: a copy of the D_{4h} character table is found at the end of this exam for your reference.



(a) Please determine the reducible representation (Γ) for all translational, rotational and vibrational motions of tetrachloroplatinate. (10 pts)





	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	15	1	−1	−3	−1	−3	−1	5	3	1

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(b) Find all of the irreducible representations that form the Γ you determined in part (a). (10 pts)

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	Σ	$\Sigma/16$
Γ	15	1	−1	−3	−1	−3	−1	5	3	1	—	—
A_{1g}	15	1	−1	−3	−1	−3	−1	5	3	1	16	1
A_{2g}	15	2	−1	6	2	−3	−2	5	−6	−2	16	1
B_{1g}	15	−2	−1	−6	2	−3	2	5	6	−2	16	1
B_{2g}	15	−2	−1	6	−2	−3	2	5	−6	2	16	1
E_g	30	0	2	0	0	−6	0	−10	0	0	16	1
A_{1u}	15	2	−1	−6	−2	3	2	−5	−6	−2	0	0
A_{2u}	15	2	−1	6	2	3	2	−5	6	2	32	2
B_{1u}	15	−2	−1	−6	2	3	−2	−5	−6	2	0	0
B_{2u}	15	−2	−1	6	−2	3	−2	−5	6	−2	16	1
E_u	30	0	2	0	0	6	0	10	0	0	48	3

$$\Gamma = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

Note we found 15 total motion modes

↳ 3N modes

Name: _____

(c) Indicate which of the irreducible representations correspond to translation, rotation and vibration. (10 pts)

Translation

E_u A_{2u}

x, y z

Rotation

E_g A_{2g}

R_x, R_y R_z

Vibration ⇒ 9 modes = 3N-6 modes

$A_{1g}, B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$

(d) Please indicate which of the vibrational modes that you identified in part (c) are infrared active and which of the vibrational modes are Raman active? (5 pts)

IR Active = $A_{2u} + 2E_u$

Raman Active = $A_{1g} + B_{1g} + B_{2g}$