

Chemistry 322
Dr. Clark
Spring 2006
Examination I

Name EXAM KEY

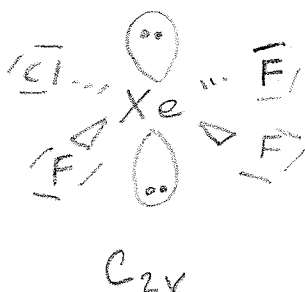
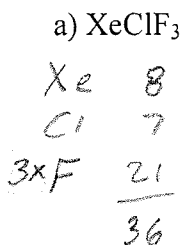
INSTRUCTIONS

1. This exam consists of 8 pages, one sheet of scratch paper, two pages of useful information, and a periodic table. If a page is missing, let me know immediately.
2. PRINT your name NOW at the top of ALL pages.
3. Part A is worth 42 points. Part B is worth 32 points. Part C is worth 25 points.
4. You will have up to 90 minutes to complete this exam. Check your work after completing the exam. **Please show all your work and be certain that all your explanations are given as complete sentences.**
5. **On the grading chart at the bottom of this page, CIRCLE the numbers of the questions you would like to be graded for Parts B and C. BEFORE YOU HAND IN YOUR EXAM, CHECK THAT YOU HAVE CIRCLED THE CORRECT NUMBER OF QUESTIONS FOR PARTS B (2) and C (1).**

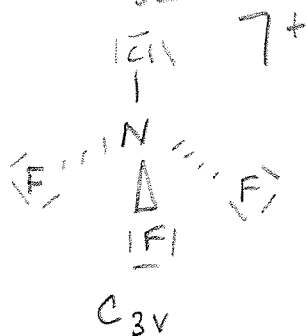
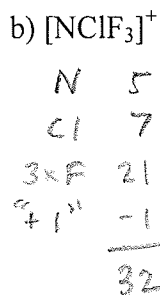
Part A	1	/12 pts.
	2	/08 pts.
	3	/12 pts.
	4	/10 pts.
Part B	5	/16 pts.
	6	/16 pts.
	7	/16 pts.
Part C	8	/26 pts.
	9	/26 pts.
TOTAL		/100 pts.

PART A. (42 points) BASIC QUESTIONS. Answer ALL of the following four questions. Write your answer in the space provided. SHOW YOUR WORK & WRITE EXPLANATIONS IN COMPLETE SENTENCES.

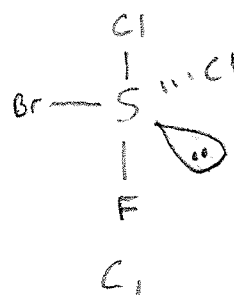
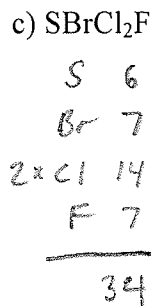
1. For the following molecules, use Lewis dot structures and VSEPR to predict the molecular shape. Assign a point group to each molecule based on the structure you predict, and indicate if the idealized molecule is chiral or not chiral.



NOT CHIRAL



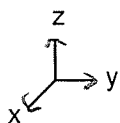
NOT CHIRAL



CHIRAL

VSEPR 2 pts
PTGP 1 pt
CHIRAL 1 pt
(EACH)

2. Generate a transformation matrix for an S_4 operation performed about the z axis using the right handed coordinate system below. Derive the character of the matrix.



$$\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

trace = -1

3x3 matrix 1 pts
7x14 part 3 pts
→ 2 part 2 pts
trace 2 pts

3. For the indicated element in the compounds listed below, determine:

1. the oxidation state of the atom in the compound. *2 pts each*
2. the electron configuration of the neutral atom. *1 pt each*
3. the electron configuration of the element in the oxidation state in which it is found in the compound. *1 pt each*

$$+2 + +4 - 6 = 0$$

a) Ce in Cs_2CeCl_6 1. +4

2. $[\text{Xe}] 6s^2 5d^1 4f^1$ (will also accept $[\text{Xe}] 6s^2 4f^2$)

3. $[\text{Xe}]$

$$+2 + +4 + -6 = 0$$

b) Te in H_2TeO_3 1. +4

2. $[\text{Kr}] 5s^2 4d^{10} 5p^4$

3. $[\text{Kr}] 5s^2 4d^{10}$

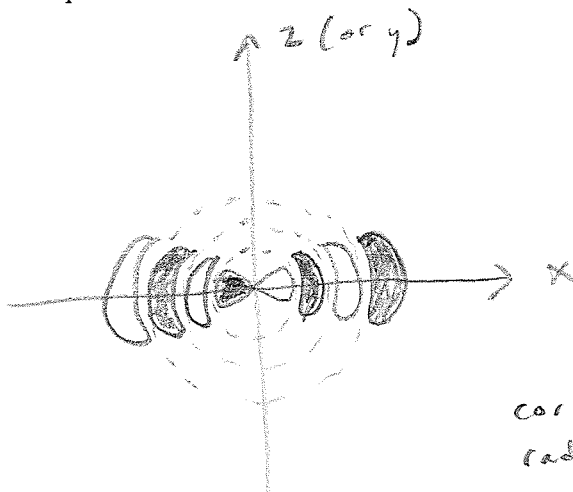
$$+7 + -6 = +1$$

c) I in IF_6^+ 1. +7

2. $[\text{Kr}] 5s^2 4d^{10} 5p^5$

3. $[\text{Kr}] 4d^{10}$

4. Draw an accurate two-dimensional picture of a slice through a $5p_x$ orbital. Your diagram must include a labeled axis system, the correct location and number of radial and angular nodes, and the phases of the wave function.



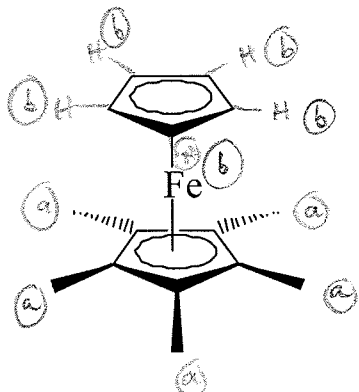
$$\begin{aligned} \text{radial nodes} &= n - l - 1 \\ &= 5 - 1 - 1 \\ &= 3 \end{aligned}$$

$$\text{angular nodes} = l = 1$$

- correct axes - 3 pts
- radial nodes - 3 pts
- angular nodes - 2 pts
- phases - 2 pts

Part B (32 points) **COMPETENCY QUESTIONS.** Answer TWO of the following three questions in the space provided. SHOW YOUR WORK AND WRITE EXPLANATIONS IN FULL SENTENCES.

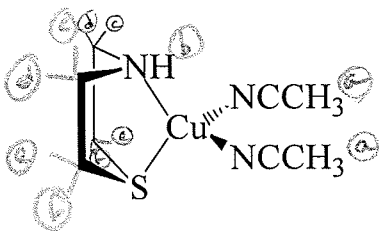
5. For each of the molecules below, determine: a) the point group and b) the number of $^1\text{H-NMR}$ signals you would expect from the protons in the molecule. Briefly explain your choices noting key symmetry elements. (Note: You may assume that all the protons on any one methyl group are equivalent due to free rotation of the methyl group. All other atoms of each of these molecules are assumed to be fixed in space.)



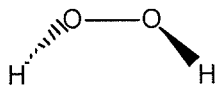
+1 for trying
 +3 for ptgp
 +2 for NMR

 16

a) point group C_{5v}
 b) # NMR signals 2



a) point group C_s
 b) # NMR signals 6

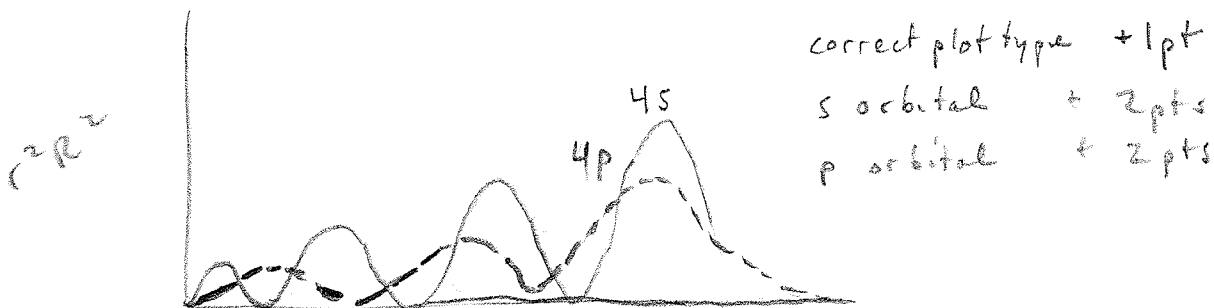


H-O-O-H
 (will accept
 C_{2h})

a) point group C₂
 b) # NMR signals 1

6. Slater's rules provide a useful framework for discussing effective nuclear charge, but the rules rely on simplifications easily seen to be incorrect. To demonstrate this, complete the following questions regarding an atom of bromine (Br).

a) Sketch radial probability functions of a 4s orbital and a 4p orbital for an atom of Br. (Note: Both functions should be plotted on the same set of axes.)



b) Calculate the effective nuclear charge for both a 4s and 4p electron.

$$Z_{4s}^* = 35 - (10 \cdot 1 + 18 \cdot 0.85 + 6 \cdot 0.35)$$

$$= 35 - 27.4 = 7.6$$

$Z^* = 2 - s - 1pt$
 $Z^* \quad 4p - 2pts$
 $Z^* \quad 4s - 2pts$

$$Z_{4p}^* = \quad \quad \quad = 7.6$$

c) Referring to your graph from part a) and your calculations from part b), explain why the use of a single shielding constant, 0.35, for both s and p orbitals within the same shell is not correct.

Part b) suggests both s & p experience the same shielding and thus have the same

Z^* . However, as seen in a) there is greater probability of having s electron density near the nucleus than there is for p; therefore the s electron must experience a greater Z^* and have a lower overall orbital E than for the p electron. Parts, 1) and b) reflect the shortfalls of Slater's R.

6 pts for good discussion

7. In answering this problem, refer to the character table for the D_{4h} point group.

a) What is the order of the D_{4h} point group? Explain briefly with a calculation.

3 pts $\boxed{16} = h$ (add up class #'s : $1+2+1+2+2+1+2+1+2+2 = 16$)

b) What do the designations g and u mean? Make specific reference to the characters of g and u representations. key: positive μ

3 pts $\left(\begin{array}{l} g - \text{gerade, symmetric wrt inversion } \chi(i) = +1, +2 \\ u - \text{ungerade, anti " wrt " } \chi(i) = -1, -2 \end{array} \right.$

c) What irreducible representations describe the transformation properties (symmetry) of the p_x , p_y and p_z orbitals in the D_{4h} point group? Explain briefly. key: negative μ

3 pts $\left(\begin{array}{l} (x, y) \text{ \– } p_x, p_y \text{ fns have the same symmetry as} \\ \text{irreducible reps } E_u \text{ \– } A_{2u}, \text{ respectively} \end{array} \right.$

d) Show that the E_g and B_{2u} irreducible representations are mutually orthogonal.

3 pts $\left(\begin{array}{c} \begin{array}{c|cccccccc} E & 2C_4 & C_2 & 2C_2' & 2C_2'' & i & 2S_4 & \sigma_h & 2\sigma_v & 2\sigma_d \\ \hline E_g & 2 & 0 & -2 & 0 & 0 & 2 & 0 & -2 & 0 & 0 \\ B_{2u} & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \end{array} \\ \hline \text{PRODUCT} & 2 & + & -2 & & + & -2 & + & 2 & & = 0 \end{array} \right. \text{ QED.}$

e) Show, using the coordinate system below, that x and y transform together in D_{4h} symmetry. You will need to make a judicious choice of symmetry operation in answering this question.

4 pts $\left(\begin{array}{l} \text{Coordinate system } (x, y, z) \\ \text{Operation } C_4 \text{ (or } S_4) \\ \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \rightarrow \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \\ \text{Transformation of } \begin{bmatrix} x \\ y \\ z \end{bmatrix} \rightarrow \begin{bmatrix} y \\ -x \\ z \end{bmatrix} \rightarrow \begin{bmatrix} y \\ -x \\ -z \end{bmatrix} \end{array} \right.$

- ptgps 4 total
 - removed 4 total

Part C (25 points) **MASTERY QUESTIONS.** Answer ONE of the following two questions in the space provided. SHOW ALL YOUR WORK AND WRITE EXPLANATIONS IN COMPLETE SENTENCES.

Γ_{vib} 4 pts

8. **XH₃ molecules may be either trigonal planar or trigonal pyramidal in shape.** The IR and Raman spectra of the molecule SbH₃ are identical, with four bands at the same frequencies (1894 cm⁻¹, 1891 cm⁻¹, 831 cm⁻¹, and 782 cm⁻¹). Is this molecule planar or pyramidal? Answer this question by a) determining the symmetry and number of vibrational modes for each shape and b) determining whether these modes are IR or Raman active.

- reduce 8 pts
 - IR/RAMAN 4 pts
 - Q. 2 pts

TRIGONAL PLANAR CASE (D_{3h})



	E	2C ₃	3C ₂	σ _L	2S ₃	3σ _v
$\Gamma_{unmoved}$	4	1	2	4	1	2
Γ_{trans}	3	0	-1	1	-2	1
Γ_{tot}	12	0	-2	4	-2	2
$-\Gamma_{trans}$	3	0	-1	1	-2	1
	9	0	-1	3	0	1
$-\Gamma_{rot}$	3	0	-1	-1	2	-1
Γ_{vib}	6	0	0	4	-2	2

$k=12 \rightarrow$ reduce Γ_{vib}

$$n_{E'} = \frac{1}{12} (1 \cdot 6 \cdot 2 + 1 \cdot 4 \cdot 2 + 2 \cdot 2 \cdot 1)$$

$$= \frac{1}{12} (12 + 8 + 4) = 2$$

$\rightarrow \rightarrow$

$$\Gamma_{vib} = A_1' + 2E' + A_2''$$

↑ ↑ ↑
 Raman only IR/Raman IR only

\rightarrow cant be trig. planar

PYRAMIDAL CASE (C_{3v}) 26 pts



	E	2C ₃	3σ _v
$\Gamma_{unmoved}$	4	1	2
Γ_{trans}	3	0	1
Γ_{tot}	12	0	2
$-\Gamma_{trans}$	3	0	1
	9	0	1
$-\Gamma_{rot}$	3	0	-1
Γ_{vib}	6	0	2

order = 6 \rightarrow reduce Γ_{vib}

$\rightarrow \rightarrow$

$$\Gamma_{vib} = 2A_1 + 2E$$

\rightarrow

BOTH IR/RAMAN ACTIVE
 7 (4 BANDS UNIQUE)

\rightarrow must be pyramidal