Chem 224 Final Exam
December 11, 2003 8 Questions - 10 Pages (+group theory, periodic tables and Tanabe-Sugano diagrams)
300 points

Name:____________________________ Exam:______ Course:_______

(30 pts) 1) Which of the following low-spin octahedral complexes should undergo a Jahn Teller distortion? Give a reason (state symmetry) for each answer.
$Co(NH_3)_6^{3+}$, $Co(CNC_6H_5)_6^{2+}$, $V(CO)_6$, $Ti(OH_2)_6^{3+}$, and $Zn(S_2CNMe_2)_3^-$.

(40 pts) 2) In $Re_2Cl_8^{2-}$ the □ -> □* transition promotes an electron from the filled □ (b_{2g}) orbital to the empty □* (e_g) orbitals.

a) What is the symmetry of the excited electronic state(s)?

b) What symmetry vibrations could aid and induce vibronic intensity into the spin-allowed dipole-forbidden electronic transition? Specify the polarization expected for the various vibronic components.

(20 pts) 3) If two electrons lie in a degenerate orbital the spin and orbital symmetry problems cannot be considered separately and the direct product has an antisymmetric piece and a symmetric piece. For example, the $t_{2g}{}^2$ configuration for an octahedral d^2 complex gives t_{1g} as the antisymmetric direct product and e_g, a_{1g}, and t_{2g} as the symmetric direct product. Given the fact that the total wavefunction must be antisymmetric with respect to electron interchange list the possible electronic states (spin included) derived from a $e_{2g}{}^2$ electronic configuration.

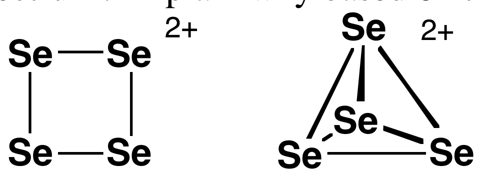
(40 pts) 4) The vibrations of tetrahedral $CoCl_4^{2-}$ ion belong to a_1, e, and $2t_2$ representations. Explain whether or not the $^4A_2$ ----> $^4T_2$ and $^4A_2$ ----> $^4T_1$ d-d electronic transitions can gain intensity by vibronic coupling and what the vibronic polarizations would be for each transition.

(40 pts) 5) The tetrahedral compound $SnCl(CH_3)_3$ exhibits two IR active Sn-C stretching vibrations at 545 cm^{-1} and at 514 cm^{-1}. On addition of pyridine 5-coordinate a monoadduct $[SnCl(CH_3)_3{\cdot}py]$ forms, which shows a single Sn-C stretch at 550 cm^{-1} in the infra red spectrum. What is the probable structure (square pyramidal or trigonal bipyramidal about Sn) of the monoadduct? Explain your answer by giving specific irreducible representations and selection rules for the two structures.

(60 pts) 6) Consider the square planar d^8 complex $Pt(CN)_4^{2=}$. Construct a MO diagram (large and clearly labeled) for this complex ion that includes only metal d orbitals, CN^- lone pair and □□ orbitals.

b) The lowest electronic absorption is a very intense transition at 38,020 cm^{-1}. To what transition do you assign it? Give the symmetry representations of the orbitals involved as well as the specific electronic states and their irreducible representations.

(40 pts) 7) The Raman spectrum of $Se_4\,[AlCl_4]_2$ (shown below) exhibits two absorptions at 301 and 317 cm^{-1} attributable to Se-Se stretching modes. The 317 cm^{-1} absorption exhibits a depolarization ratio of 0.1 and the 301 cm^{-1} absorption exhibits a depolarization ratio of 0.7. Given this information answer the following:
a) Is a square planar or tetrahedral structure more consistent with the observed spectrum? Explain why based on the data.

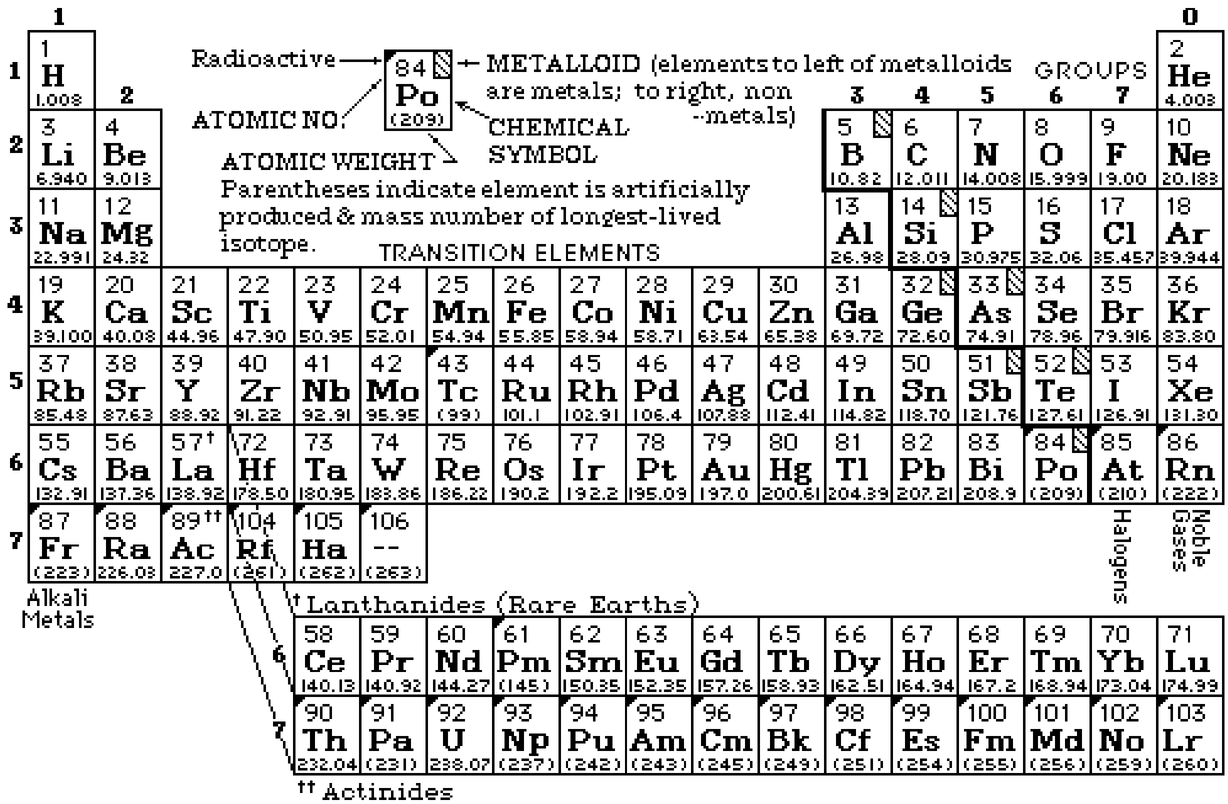


square planar tetrahedral

b) Assign the two absorptions in the Raman spectrum.

c) Sketch the nuclear motions involved for the non-degenerate vibration or vibrations belonging to the Se_4^{2+} cluster ion.

(30 pts) 8) What differences would you expect for the g factors of Co^{2+} in O_h vs. T_d coordination environments and in the ability to obtain a spectrum at room temperature?



Radioactive
84 Po (209)
METALLOID (elements to left of metalloids are metals; to right, non--metals)
ATOMIC NO.
CHEMICAL SYMBOL
ATOMIC WEIGHT
Parentheses indicate element is artificially produced & mass number of longest-lived isotope.
GROUPS
1 2 3 4 5 6 7 0
TRANSITION ELEMENTS
1 H 1.008
2 He 4.003
3 Li 6.940
4 Be 9.013
5 B 10.82
6 C 12.011
7 N 14.008
8 O 15.999
9 F 19.00
10 Ne 20.183
11 Na 22.991
12 Mg 24.32
13 Al 26.98
14 Si 28.09
15 P 30.975
16 S 32.06
17 Cl 35.457
18 Ar 39.944
19 K 39.100
20 Ca 40.08
21 Sc 44.96
22 Ti 47.90
23 V 50.95
24 Cr 52.01
25 Mn 54.94
26 Fe 55.85
27 Co 58.94
28 Ni 58.71
29 Cu 63.54
30 Zn 65.38
31 Ga 69.72
32 Ge 72.60
33 As 74.91
34 Se 78.96
35 Br 79.916
36 Kr 83.80
37 Rb 85.48
38 Sr 87.63
39 Y 88.92
40 Zr 91.22
41 Nb 92.91
42 Mo 95.95
43 Tc (99)
44 Ru 101.1
45 Rh 102.91
46 Pd 106.4
47 Ag 107.88
48 Cd 112.41
49 In 114.82
50 Sn 118.70
51 Sb 121.76
52 Te 127.61
53 I 126.91
54 Xe 131.30
55 Cs 132.91
56 Ba 137.36
57† La 138.92
72 Hf 178.50
73 Ta 180.95
74 W 183.86
75 Re 186.22
76 Os 190.2
77 Ir 192.2
78 Pt 195.09
79 Au 197.0
80 Hg 200.61
81 Tl 204.39
82 Pb 207.21
83 Bi 208.9
84 Po (209)
85 At (210)
86 Rn (222)
87 Fr (223)
88 Ra 226.03
89†† Ac 227.0
104 Rf (261)
105 Ha (262)
106 -- (263)
Alkali Metals
Halogens
Noble Gases
† Lanthanides (Rare Earths)
58 Ce 140.13
59 Pr 140.92
60 Nd 144.27
61 Pm (145)
62 Sm 150.35
63 Eu 152.35
64 Gd 157.26
65 Tb 158.93
66 Dy 162.51
67 Ho 164.94
68 Er 167.2
69 Tm 168.94
70 Yb 173.04
71 Lu 174.99
90 Th 232.04
91 Pa (231)
92 U 238.07
93 Np (237)
94 Pu (242)
95 Am (243)
96 Cm (245)
97 Bk (249)
98 Cf (251)
99 Es (254)
100 Fm (255)
101 Md (256)
102 No (259)
103 Lr (260)
†† Actinides