HW 9
CHEM 362

Due: November 19, 2019

1. For each of the following a) determine the ground state term symbol and b) determine the state symbol(s) if split by an octahedral field

a. d^1

__|__ _____ _____ _____ _____
+2 +1 0 -1 -2

L=2 → D

2S+1 = 2(0.5)+1 = 2

^{2}D

$\rightarrow {}^2E + {}^2T_2$

b. d^6

__||__ __|__ __|__ __|__ __|__
+2 +1 0 -1 -2

L=2 → D

2S+1 = 2(2)+1 = 5

^{5}D

$\rightarrow {}^5E + {}^5T_2$

c. d^7

__||__ __||__ __|__ __|__ __|__
+2 +1 0 -1 -2

L=3 → F

2S+1 = 2(1.5)+1 = 4

^{4}F

$\rightarrow {}^4A_2 + {}^4T_1 + {}^4T_2$

d. d^8

__||__ __||__ __||__ __|__ __|__
+2 +1 0 -1 -2

L=3 → F

2S+1 = 2(1)+1 = 3

^{3}F

$\rightarrow {}^3A_2 + {}^3T_1 + {}^3T_2$

2. Describe the two selection rules for electronic transitions. Be sure to explain *why* they arise or exist

1) Transitions between states of the same parity are forbidden (Laporte Rule). In other words, orbital in ground state and orbital in excited state must have different signs (g/u) with respect to an inversion center

All d→d ligand field transitions are forbidden in a strict O_h symmetry and are therefore weak because transitions are g→g in O_h

2) Spin multiplicity must be the same.

This is because there is no simple mechanism for a photon to "flip" the spin of an electron

3. Rank the following transitions by their absorbance intensity and give an expected molar absorptivity range for those absorbances:

$^3A_{1g} \rightarrow {}^3T_{2g}$

[2], 0.1-100

$E_g \rightarrow E_u$ (ie. MLCT)

[1(highest intensity)], 100+

$^1T_{1g} \rightarrow {}^3T_{2g}$

[3(lowest intensity)], <0.1

4. Why are d-d transitions from tetrahedral complexes stronger than octahedral complexes?

5.

d-d transitions from tetrahedral complexes are not parity forbidden. (There are no u or g designations for Td geometry)

6. The compounds TiO_2 and ZnO appear as white powders. Explain this phenomenon. *Hint: consider the electron configuration of the metal*

These compounds appear white because there are no transitions that can occur, thus no colour. The reason for this is because the Ti in TiO_2 has an oxidation state of 4+, resulting in an electron count of d^0. There are no d electrons so a d-d transition cannot occur. The Zn has an oxidation state of 2+ resulting in an electron count of d^{10}. The orbitals are full, and a d-d transition cannot happen.

7. Consider the Tanabe-Sugano diagram for a d^3 metal in an octahedral field.

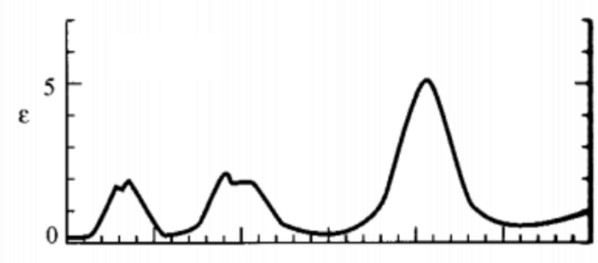
a. From the ground state, which transitions would you expect to see in an absorbance spectrum?

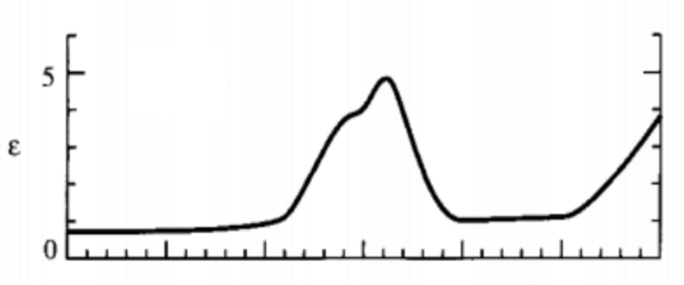
$^4A_2 \rightarrow {}^4T_2$
$^4A_2 \rightarrow {}^4T_1$
$^4A_2 \rightarrow {}^4T_1$ (from P) is also spin allowed, but is probably unlikely to be observed due to the enormous energy gap.

b. The spectra of $[Cr(NH_3)_6]^{3+}$ shows two ligand field transitions at 21 550 cm^{-1} and 28 500 cm^{-1}. Which transition is which?

$^4A_2 \rightarrow {}^4T_2$ is the lower energy
$^4A_2 \rightarrow {}^4T_1$ is the higher energy

8. Consider the UV-vis spectra shown below. One is from an aqueous solution of $[Ni(H_2O)_6]^{2+}$, and the other is from an aqueous solution of $[Ti(H_2O)_6]^{3+}$. Which spectrum belongs to which complex, and why? *Hint: Determine the ground state term symbol for each complex. Consider the Tanabe-Sugano diagram(s) for the respective electron configurations. What are the spin allowed transitions?*





The one on the left is the nickel complex, the one on the right is the titanium complex. A full answer should include a discussion of the number of allowed transitions and their potential assignments.

9. What is the Jahn-Teller theorem? How does it affect the geometry of an octahedral coordination complex?

The Jahn-Teller theorem states that A non-linear molecule in an electronically degenerate state will distort to lower the symmetry, remove the degeneracy, and lower the energy. For an octahedral, this causes axial distortion where the molecule will lengthen or shorten along the z axis

10. List 4 differences between diamond and graphite. Explain these differences based on structural and bonding arguments.

1. Diamond is very hard whereas graphite is soft: In diamond there is a three dimensional network of strong covalent bonds. On the other hand, in graphite there are flat layers of carbon atoms. These layers are held by weak van der Waal's forces and hence can easily slip one over the other.

2. Density of diamond is more than that of graphite: In graphite, there are large spaces between adjacent layers due to weak forces between them. On the other hand, in diamond, atoms are held by strong covalent bonds and relatively more closely packed.

3. Diamond is poor conductor of electricity whereas graphite is a good conductor In diamond, each carbon atom is directly linked to four other carbon atoms through covalent bonds. Thus, in diamond all the four valence electrons carbon are involved in covalent bonds and are not free to conduct electricity. This makes diamond a bad conductor of electricity. On the other hand, in graphite, each carbon atom is directly bonded to only three other carbon atoms. Thus, each carbon atoms utilizes only three valence electrons for forming covalent bonds with other carbon atoms, the fourth valence electron is relatively free, can move from one carbon atom to the other in a layer, and hence is responsible for conducting electricity. Hence, graphite is a good conductor of electricity.

4. The melting point of graphite is slightly higher than the melting point of diamond because in graphite C-C bonds have partial double bond character and hence are stronger and difficult to break. In fact, carbon as graphite has the highest melting point among all the elements.

11. Draw the band structure of a) a conductor or metal b) a semiconductor c) an insulator