Chemistry 362 Mini-Exam V
Fall 2019

Tuesday November 25, 2019

Professor Kim R. Dunbar

NAME: ____

ID: ____

Total Points on Exam is 50 points

1. (9 pts)

Other than electronic transitions between d orbitals in an octahedral metal compound (d-d transitions), there are two other possible types

a) What are they?

MLCT – Metal to ligand charge transfer
LMCT – Ligand to metal charge transfer

b) What types of orbitals are involved in the ground state and excited state for each type

M→L : d→p
L→M : p→d

c) Which one would be favored with high oxidation state metals and which one would be favored for low oxidation state metals?

MLCT would be favoured with low oxidation state metals, while LMCT would be favoured with high oxidation state metals.

2. (10 pts)

There are two main selection rules that govern the intensities of electronic transitions between the Ground state (g.s.) and the Excited state (e.s.) in molecules.

a) What are they?

- **spin multiplicity must be the same between the ground state and the excited state**
- **orbital in the ground state and orbital in the excited state must have different signs with respect to an inversion center**

b) How do they apply to (and affect) the electronic spectra of octahedral transition metal complexes? *BE AS COMPLETE WITH YOUR ANSWER AS POSSIBLE.*

Spin allowed transitions are moderate-to-weak in octahedral complexes, but if the transition is spin forbidden (different multiplicities between the ground state and the excited state) then the intensity of the d-d transition would be very weak and often not observed

All d-d transitions in octahedral transition metal complexes are orbitally (or Laporte forbidden) because any potential d-d transition always will involve a g→g transition. As such, d-d transitions will be weak.

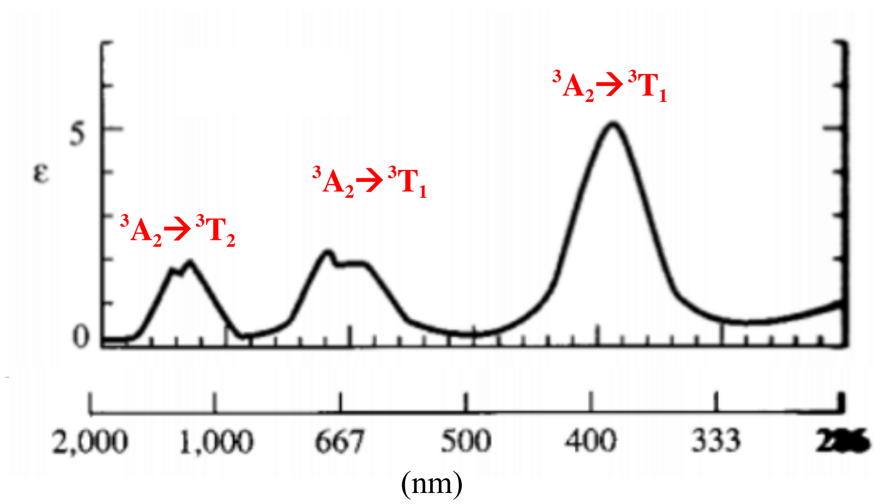
3. (10 points)

The Tanabe Sugano diagram for a d^8 octahedral compound is attached to the exam.

a) What are the possible *allowed* transitions from the ground state that can be deduced from the diagram?

$^3A_2 \rightarrow {}^3T_2$
$^3A_2 \rightarrow {}^3T_1$
$^3A_2 \rightarrow {}^3T_1$ (P)

b) The absorbance spectrum for a d^8 octahedral compound is shown below. Assign the transitions directly onto the figure. **Ignore the little spikes on the side of the major peaks**



4. (6 points)

Why is there no Tanabe-Sugano diagram for d^0, d^1, d^9, or d^{10} octahedral compounds?

d^0: with no d electrons, there cannot be any d-d transitions.

d^{10}: with completely filled d orbitals, there cannot be any d-d transitions

d^1: there is only one potential transition for the electron to be excited to, and so it is irrelevant to construct a Tanabe Sugano diagram for that

d^9: with 9 electrons, there can only be one potential transition that can occur, as there is only one "place" for that electron to be excited to. A T.S diagram is irrelevant for describing that one transition

5. (8 points)

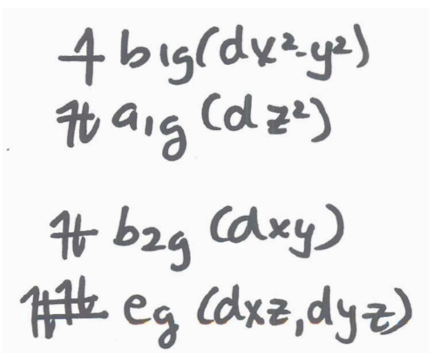
a) State the Jahn-Teller theorem.

Jahn-Teller Theorem states that for a non-linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, i.e. to remove the degeneracy and lower the energy

b) What does this theorem tell us about a molecule that has a d^9 configuration ($t_{2g}^6 e_g^3$ configuration in an octahedral geometry?

The molecule would undergo distortion to lower the symmetry and remove the degeneracy of the electronically degenerate state it currently is in. This would result in an axial elongation or compression

c) Draw the orbital splitting diagram for the molecule discussed in 6 b)



5. (7 pts)
Is it possible to observe more transitions than what the Tanabe Sugano diagram would predict? Provide reasoning for your answer

Yes:
You may observe spin forbidden transitions

You can also observe transitions that arise from Jahn-Teller distortion, which would not be predicted by the Tanabe Sugano Diagram