2018 Ch112 – problem set 5
Due: Thursday, Nov. 29

Problem 1 (2 points)

Part A

Consider a free ion with a d^3 electronic configuration.

a) By inspection, obtain the term symbol (^{2S+1}L) for the ground state.

^4F

b) For this ground state, obtain all possible *J* values and order them from lowest to highest in energy.

L = 3 S = 3/2

J = {9/2, 7/2, 5/2, 3/2}

3/2 < 5/2 < 7/2 < 9/2

c) The first excited state for the d^3 ion is the ^4P state. How many microstates does the ^4P state contain?

4·3 = 12 microstates

Splitting of terms and orbitals in a chemical environment:

Consider an octahedral ligand field on a set of atomic wave functions. The full symmetry of the octahedron is O_h but we can work with the rotational subgroup O. An atomic orbital can be represented as follows (radial, angular (θ, φ), and spin wavefunctions):

$$\Psi = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi) \cdot \psi_s$$

We can ignore ψ_s assuming negligible spin-orbit coupling. The radial function R has no directionality, so it can also be ignored. The angular function Θ is invariant with respect to rotation in the z axis (principal rotation axis), so it can be ignored as well. Working only with Φ, we show without derivation that the character of the reducible representation under C_α for a basis set in which the orbital angular momentum is l is given by:

$$\chi(\alpha) = \frac{\sin[\left(l + \frac{1}{2}\right)\alpha]}{\sin(\alpha/2)}$$

For example, for the set of *f* orbitals ($l = 3$) :

$$\chi(C_3) = \frac{\sin[\left(3+\frac{1}{2}\right)\left(\frac{2\pi}{3}\right)]}{\sin(\pi/3)} = \frac{\sin(7\pi/3)}{\sin(\pi/3)} = 1$$

In the limit where $\alpha = 0$, $\chi(E) = 2l+1$.

These characters belong to irreducible representations of the spherical point group of atoms (K). The table below allows conversion to the lower symmetry point group, *O*.

a) By applying the formula, complete the table below.

	E	6 C_4	3 C_2 (= C_4^2)	8 C_3	6 C_2'
S ($l = 0$)	1	1	1	1	1
P ($l = 1$)	3	1	-1	0	−1
D ($l = 2$)	5	-1	1	-1	1
F ($l = 3$)	7	-1	-1	1	−1
G ($l = 4$)	9	1	1	0	1
H ($l = 5$)	11	1	-1	-1	−1
I ($l = 6$)	13	-1	1	1	1

b) Each row is a reducible representation in the *O* point group. Represent each row as a sum of irreducible representations.

S: A_1
P: T_1
D: $E + T_2$
F: $A_2 + T_1 + T_2$
G: $A_1 + E + T_1 + T_2$
H: $E + 2\ T_1 + T_2$
I: $A_1 + A_2 + E + T_1 + 2\ T_2$

2018 Ch112 – problem set 5
Due: Thursday, Nov. 29

Part B

In class, we derived the electronic states for a carbon atom ($1s^2 2s^2 2p^2$). They are, in ascending order, ^3P, ^1D, and ^1S. Below is a more complete table of the energy states of carbon (with total angular momentum, J, left out):

Electron configuration	Term Symbol	Rel. Energy (cm^{-1})
$2s^2 2p^2$	^3P	0
$2s^2 2p^2$	^1D	10,193
$2s^2 2p^2$	^1S	21,648
$2s^1 2p^3$	^5S	33,735
$2s^2 2p^1 3s^1$	^3P	60,333
$2s^2 2p^1 3s^1$	^1P	61,982
$2s^1 2p^3$	^3D	64,087
$2s^2 2p^1 3p^1$	^1P	68,856
$2s^2 2p^1 3p^1$	^3D	69,689
$2s^2 2p^1 3p^1$	^3S	70,744

a) For each of the excited state electron configurations in the table, fill in the electronic ground state with the appropriate term symbol. Note, the ground state of the $2s^2 2p^1 3p^1$ electron configuration for carbon is not what you would predict with Hund's rules, instead the first excited state of this configuration matches the prediction using the shortcut presented in class.

b) Give the two lowest energy electronic transitions that are spin allowed (high intensity).

^3P ($2s^2 2p^2$) → ^3P ($2s^2 2p^1 3s^1$)

^3P ($2s^2 2p^2$) → ^3D ($2s^1 2p^3$)

Problem 2 (1 point)

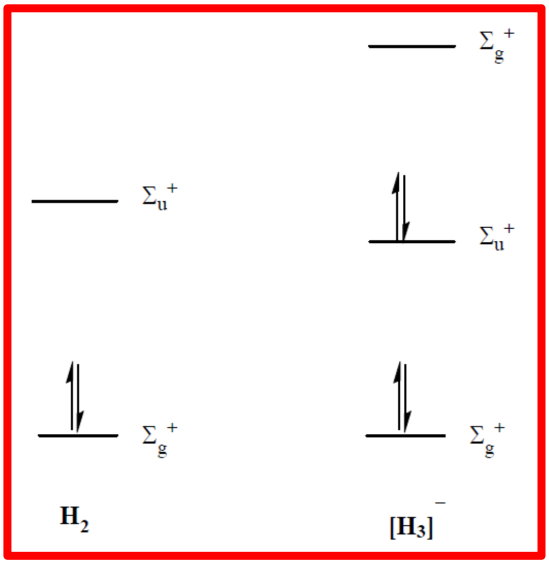
Three center four electron (3c/4e) bonds were introduced in class. John F. Berry (*Dalton Trans.* **2012**, *41*, 700-713) discusses the effect of the larger density of states for the 3c/4e interaction than for the 2c/2e case. The 3c/4e system is expected to be not only more reactive than the 2c/2e system, but also more diverse in reactivity.

To illustrate this concept, consider H_2 and $[H_3]^-$.

1. Sketch the MO diagram of H_2 and assign Mulliken symbols for all molecular orbitals. Write down all possible electronic configurations of H_2. Obtain all electronic states clearly indicating the configuration they correspond to and predict their relative energy.

$(\Sigma_u^+)^2$: $^1\Sigma_g^+$
$(\Sigma_g^+)^1(\Sigma_u^+)^1$: $^1\Sigma_u^+ + {}^3\Sigma_u^+$
$(\Sigma_g^+)^2$: $^1\Sigma$g+
Total: $2(^1\Sigma_g^+) + {}^1\Sigma_u^+ + {}^3\Sigma_u^+$

2. Sketch the MO diagram of $[H_3]^-$ and assign Mulliken symbols for all molecular orbitals. Write down all possible electronic configurations of $[H_3]^-$. Obtain all electronic states clearly indicating the configuration they correspond to and predict their relative energy.



(highest energy) $(nb)^2(\sigma^*)^2$: $^1\Sigma_g^+$
$(\sigma)^1(nb)^1(\sigma^*)^2$: $^1\Sigma_u^+ + {}^3\Sigma_u^+$
$(\sigma)^2(\sigma^*)^2$: $^1\Sigma_g^+$
$(\sigma)^1(nb)^2(\sigma^*)^1$: $^1\Sigma_g^+ + {}^3\Sigma_g^+$
$(\sigma)^2(nb)^1(\sigma^*)^1$: $^1\Sigma_u^+ + {}^3\Sigma_u^+$
(lowest energy) $(\sigma)^2(nb)^2$: $^1\Sigma_g^+$
Total: $4(^1\Sigma_g^+) + (^3\Sigma_g^+) + 2(^1\Sigma_u^+) + 2(^3\Sigma_u^+)$

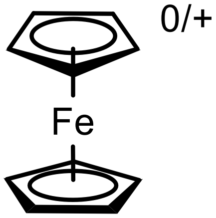
3. Indicate the lowest energy spin allowed transition from the ground state to an excited state for $[H_3]^-$. Indicate the lowest energy spin forbidden transition from the ground state to an excited state for $[H_3]^-$.

Spin allowed: $((\sigma)^2(nb)^2\,)^1\Sigma_g^+ \rightarrow ((\sigma)^1(nb)^2(\sigma^*)^1)^1\Sigma_u^+$

Spin forbidden: $((\sigma)^2(nb)^2\,)^1\Sigma_g^+ \rightarrow ((\sigma)^1(nb)^2(\sigma^*)^1)^3\Sigma_u^+$

Problem 3 (1 point)

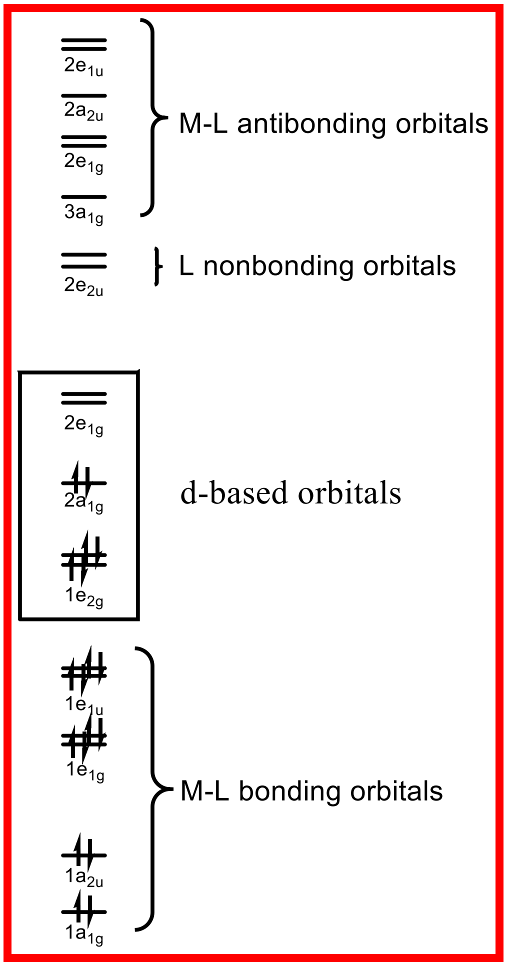
The electronic spectroscopy of metallocenes has been studied extensively. For this problem, you will analyze, in part, the electronic spectrum of ferrocene and its one electron analogue, ferricenium.



We've already derived an MO diagram for ferrocene in lecture, however that was in the D_{5h} point group.

a) Provide the MO diagram of ferrocene in D_{5d} point group. Metal-ligand interactions do not change, just the Mulliken symbol of the MOs. Occupy the MO with electrons and provide the lowest energy electronic configuration. What is the term symbol for this electronic state?

Lowest energy configuration: $(1e_{2g})^4(2a_{1g})^2$
Term Symbol: $^1A_{1g}$



b) What are the two lowest d-d electron configuration transitions expected, based on your MO diagram? What are the term symbols of these excited states? (Assume symmetry of $(1e_{2g})^3 = (1e_{2g})^1$)

$(1e_{2g})^4(2a_{1g})^2 \rightarrow (1e_{2g})^4(2a_{1g})^1(2e_{1g})^1$: $^1E_{1g}$, $^3E_{1g}$
$(1e_{2g})^4(2a_{1g})^2 \rightarrow (1e_{2g})^3(2a_{1g})^2(2e_{1g})^1$: $^1E_{1g}$, $^3E_{1g}$, $^1E_{2g}$, $^3E_{2g}$

c) Based on selection rules, what are the highest intensity d-d transitions you expect to observe for ferrocene?

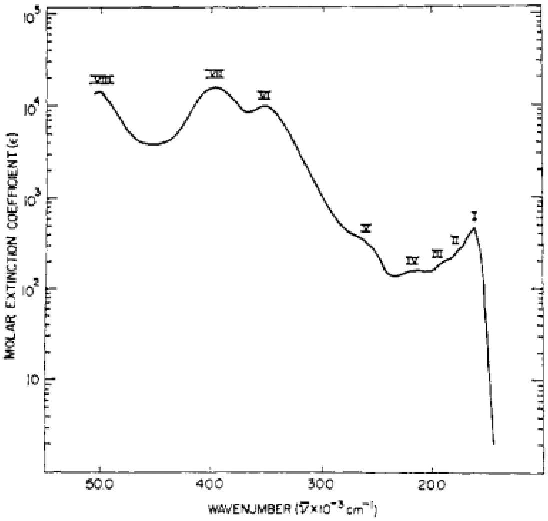
$^1A_{1g} \rightarrow {}^1E_{1g}$ $[(1e_{2g})^4(2a_{1g})^1(2e_{1g})^1]$
$^1A_{1g} \rightarrow {}^1E_{1g}$ $[(1e_{2g})^3(2a_{1g})^2(2e_{1g})^1]$
$^1A_{1g} \rightarrow {}^1E_{2g}$ $[(1e_{2g})^3(2a_{1g})^2(2e_{1g})^1]$

The ferricenium cation is considered to have a $(1e_{2g})^3(2a_{1g})^2$ ground state.

d) What is the term symbol for the ground state configuration?
$^2E_{2g}$

e) Give the term symbols for the excited states of: $(1e_{2g})^3(2a_{1g})^2 \rightarrow (1e_{2g})^4(2a_{1g})^1$ d-d transition, LMCT from $1e_{1u}$ MO to $1e_{2g}$.

$(1e_{2g})^3(2a_{1g})^2 \rightarrow (1e_{2g})^4(2a_{1g})^1$ d-d transition: $^2A_{1g}$
LMCT: $^2E_{1u}$



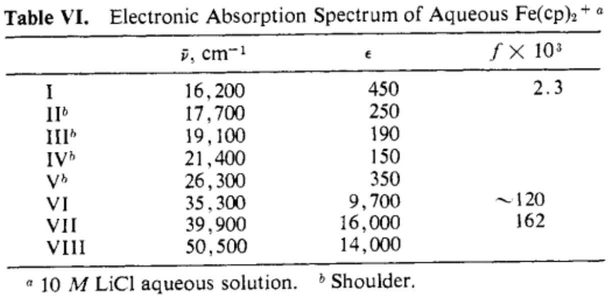


Table VI. Electronic Absorption Spectrum of Aqueous $Fe(cp)_2^+$ [a]

	$\bar{\nu}$, cm^{-1}	ε	$f \times 10^3$
I	16,200	450	2.3
II[b]	17,700	250	
III[b]	19,100	190	
IV[b]	21,400	150	
V[b]	26,300	350	
VI	35,300	9,700	~120
VII	39,900	16,000	162
VIII	50,500	14,000	

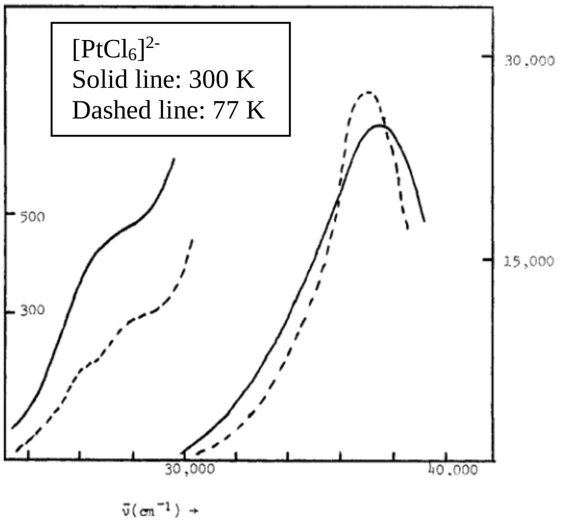
[a] 10 *M* LiCl aqueous solution. [b] Shoulder.

f) Based on the absorption spectrum of ferricenium above, which bands do you attribute to d-d transitions, and which do you attribute to charge transfer?

Bands I-V consistent with d-d transitions ($\varepsilon < 10^3$ [d-d transitions inherently orbitally forbidden), lower energy transitions)
Bands VI-VIII consistent with LMCT ($\varepsilon > 10^3$, higher energy transitions)

Problem 4 (3 Points)

Consider the following electronic spectrum of $[PtCl_6]^{2-}$. For this question, consider only the spectrum collected at 77 K (dashed line). Vertical scales are different for the left and right sides (in $M^{-1}cm^{-1}$).



a. Based on intensity, assign the three features as spin forbidden, spin allowed – orbitally forbidden, or fully allowed. What is the origin of these transitions? (d-d, MLCT, LMCT)

26,400 cm^{-1}: spin allowed-orbitally forbidden (d-d)
28,300 cm^{-1}: spin allowed-orbitally forbidden (d-d)
36,900 cm^{-1}: fully allowed (LMCT)

b. Determine the Pt oxidation state and d-electron count of this ion. List the first four (if applicable) spin-allowed d-d transitions that you expect for this ion in the correct field strength limit (using the appropriate Tanabe-Sugano diagram).

Pt^{4+}, d^6, five d-d transitions (low spin).
$^1A_1 \rightarrow {}^1T_1$
$^1A_1 \rightarrow {}^1T_2$
$^1A_1 \rightarrow {}^1E$
$^1A_1 \rightarrow {}^1T_2$

c. What is the lowest-energy d-d transition (represented in state symbols) that you might see if the spin-selection rule is ignored?

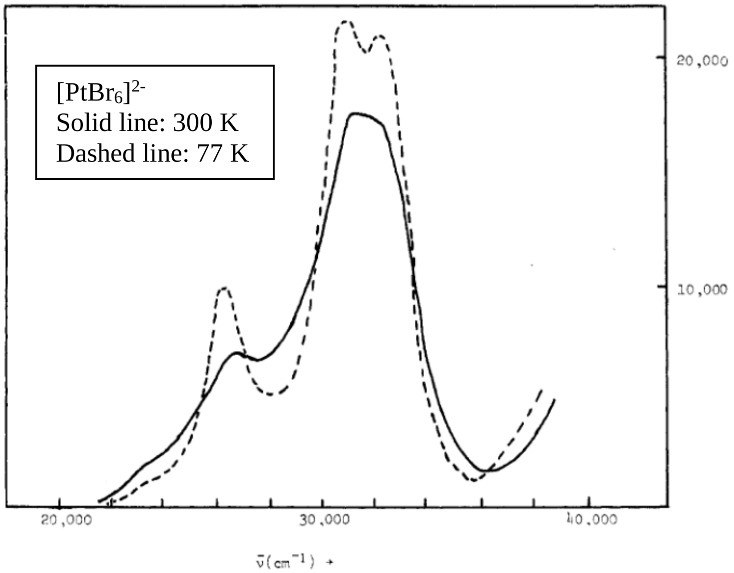
$^1A_1 \rightarrow {}^3T_1$.

d. To explain the high intensity band do the following. Consider that the highest occupied ligand-based orbitals are of T_{1u} and T_{2g} symmetry. Determine the electron configuration for the lowest energy transition that is orbitally allowed. Identify the ground and excited states for this transition.

Electron configuration: $(t_{1u})^6(t_{2g})^6(e_g)^0 \rightarrow (t_{1u})^5(t_{2g})^6(e_g)^1$
Ground state: $^1A_{1g}$
Possible excited states: $E_g \times T_{1u} = T_{1u} + T_{2u}$ (both singlet and triplet)
Spin-allowed: $^1T_{1u} + {}^1T_{2u}$

e. The spectrum of $[PtBr_6]^{2-}$ is shown below. Propose an explanation for the energy difference compared to $[PtCl_6]^{2-}$ of the highest intensity bands based on the properties of the ligands.

Cl^- (1.36 V reduction potential for Cl_2) is less reducing than Br^- (1.07 V reduction potential for Br_2). Chlorine's high-energy p-orbitals are lower energy than bromine's high-energy p-orbitals, so the LMCT band is higher in energy (Pt d-based orbitals roughly the same in energy).

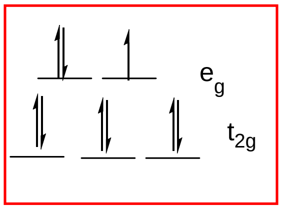


f. Using the appropriate Tanabe-Sugano diagram, list the first four (if applicable) spin allowed d-d transitions for the following two ions:

i. $[Mn(CN)_6]^{3-}$	ii. $[MnF_6]^{3-}$
$^3T_1 \rightarrow {}^3E$ $^3T_1 \rightarrow {}^3T_1$ $^3T_1 \rightarrow {}^3T_2$ $^3T_1 \rightarrow {}^3A_1$	$^5E \rightarrow {}^5T_2$

g. Consider octahedral $[Cu(H_2O)_6]^{2+}$. Draw the d-orbital splitting diagram, label with Mulliken symbols, and populate with electrons. How many spin-allowed d-d transitions do you expect for this ion?

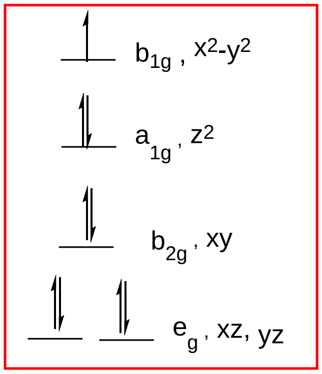
One



h. Three features attributable to d-d transitions can be resolved in the electronic spectrum for $[Cu(H_2O)_6]^{2+}$. Propose a structural distortion that lowers the symmetry of this ion, and assign the new point group.

Elongation along the z axis. D_{4h}.

i. Draw the new d-orbital splitting diagram corresponding to this new structure (consider aquo ligands as σ-donors and very weak π-donors).



2018 Ch112 – problem set 5
Due: Thursday, Nov. 29

Problem 5 (3 points)

Consider the vanadyl ion $[VO(H_2O)_5]^{2+}$

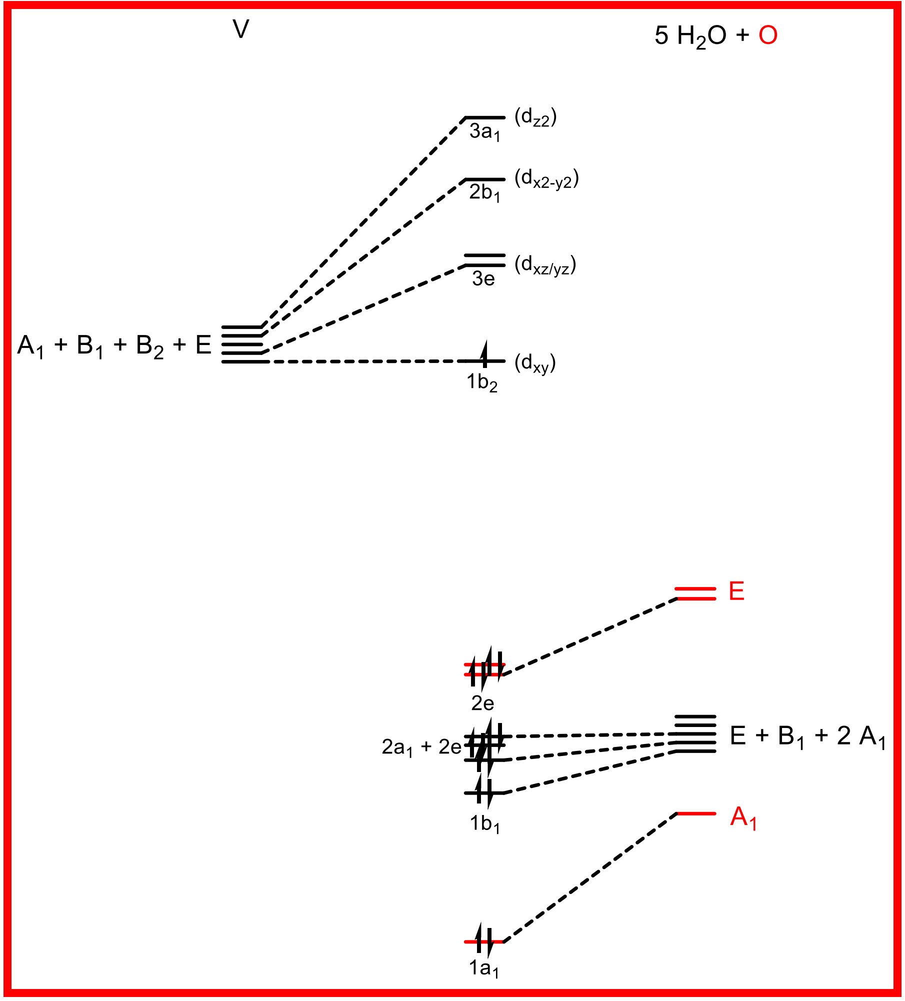
a) Assign the point group of this ion and the oxidation state and d-electron count of vanadium.

C_{4v}, V^{IV}, d^1

b) Draw the complete d-orbital splitting diagram from the following basis set:

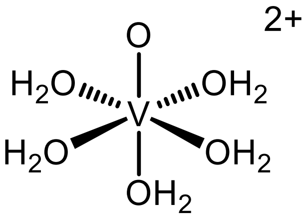
- Five d-orbitals on vanadium.
- Three p orbitals on the oxo ligand.

A single σ-donor orbital for each aquo ligand



c) Populate the diagram with electrons. Assign the ground state symbol of this ion. Assign the V-oxo bond order.

Ground state: $^2B_2$ V-O BO: 3



d) The four features observed in the electronic spectra for $[VO(H_2O)_5]^{2+}$ are listed in the table below. They correspond to the two lowest energy d-d transitions and the two lowest energy ligand to metal charge transfers. The charge transfer bands, which are also the most intense, correspond to the highest energy transitions observed. Fill in the chart corresponding to the following information.

i. Assign the electron configuration (using Mulliken symbols) corresponding to the excited states for these transitions. Assume that charge transfer transitions involving ligands only take place with the oxo ligand.
ii. Assign the symbols for the excited states.
iii. Indicate the transitions that are orbitally allowed with z and (x,y) polarized light, respectively.

	υ (cm^{-1})	i. Excited state configuration	ii. Excited state symbol	iii. Orbitally allowed? z	iii. Orbitally allowed? (x,y)
1.	13,060	..$(1b_2)^0(3e)^1$	^2E	N	Y
2.	16,000	…$(1b_2)^0$…$(2b_1)^1$	$^2B_1$	N	N
3.	41,700	…$(2e)^3$…$(1b_2)^2$	^2E	N	Y
4.	50,000	$(2e)^3$…$(1b_2)^1(3e)^1$ *	$^2B_1$**	Y	N

***Did not go through in lecture how to assign state symbols to this configuration. The transition going to the $(1a_1)^1$…$(1b_2)^2$ excited state configuration was accepted. However, based on the MO diagram, this transition will be much higher in energy and is actually orbitally forbidden (so will not be an intense band in the spectrum as this band is described to be)**

**** Possible Mulliken symbols would be $(E)(B_2)(E) = B_2 + B_1 + A_1 + A_2$ with multiplicities 4, 3, 2. Transition to $^2B_1$ will be spin- and orbitally allowed.**