

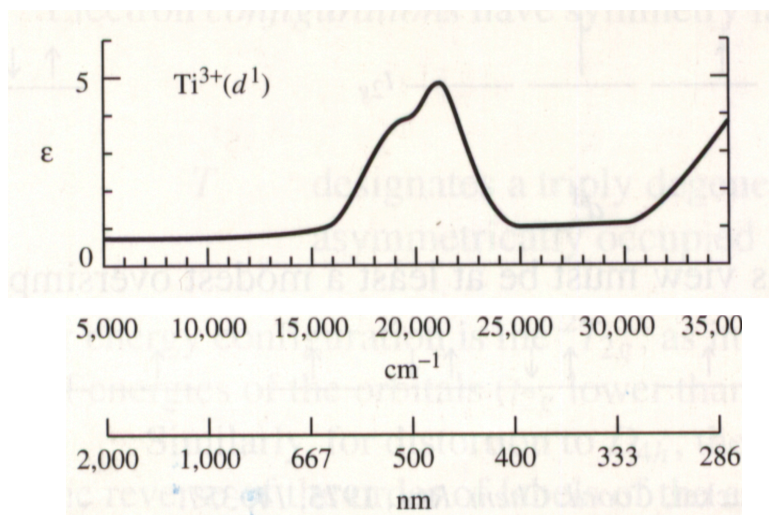
**Inorganic Chemistry with Doc M.
Fall Semester, 2011
Day 19. Transition Metals Complexes IV:
Spectroscopy**

Name(s):

Element:

Topics:

1. The visible spectrum and the d-orbitals
2. Term symbols and the method of microstates
3. Octahedral fields
4. Tanabe-Sugano diagrams

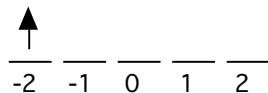


- 1. Visible Spectroscopy.** The spectrum above is that of the d^1 complex $\text{Ti}(\text{H}_2\text{O})_6^{+3}$. Sketch the crystal field energy splitting pattern for the d-orbitals in an octahedral field for (a) the ground state and (b) the excited state. Label Δ_o on at least one of the diagrams

2. Note that the maximum absorbance is at $21,500 \text{ cm}^{-1}$. This corresponds to Δ_o , the difference between the ground and excited states. Convert this to nanometers. Use the color wheel to predict what color the substance should appear.

3. Convert Δ_o to kJ/mol

4. Spectroscopists use term symbols to categorize ground and excited states in various crystal fields and with no ligand field around (free ion). Let's start with the free ion. For the simplest d-electronic configuration, d^1 , the electron can be "spin-up" or "spin down" ($m_s = +$ or $- 1/2$) and it can be in any of the orbitals, $m_l = +2, +1, 0, -1, \text{ or } -2$. We will use these formulas: L and S are associated with the ground state.



$$M_L = \sum m_l \qquad L = \max M_L$$

$$M_S = \sum m_s \qquad S = \max M_S$$

For d^1 , $M_L = +2, +1, 0, -1, -2$, and L is $+2$. Also for d^1 , $M_S = +1/2$ or $-1/2$, and S is $+1/2$.

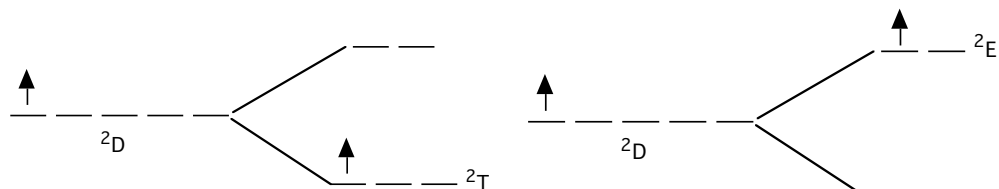
For d^2 , $M_L = +4, +3, +2, +1, 0, -1, -2, -3$ or -4 and L is $+4$. $M_S = +1, 0$ or -1 , and S is $+1$.

The ground state is represented by L and S as follows: This is called a term symbol.

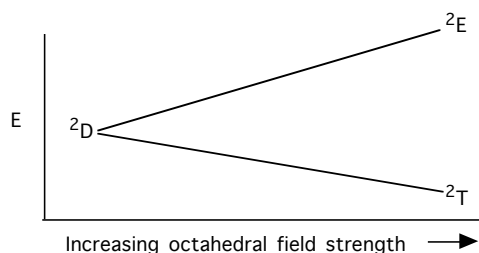
$2S+1 L$ where L is given by a letter "S" for $L = 0$, "P" for $L = 1$, "D" for $L = 2$ and "F" for $L = 3$.

After $L = 3$, the letters are alphabetical ("G" for $L = 4$, etc.). So the ground state term symbol is 2D for the d^1 ion in no field of ligands.

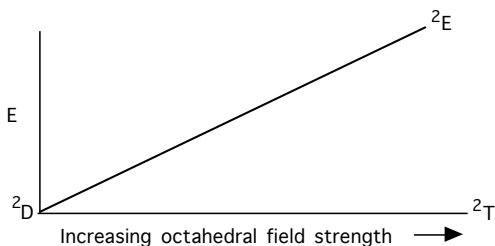
In an octahedral field, the d-orbitals split as you noted on the previous page. The state remains a doublet, but no longer is a 2D because it no longer has 5-fold degeneracy. In fact, there is only 3-fold degeneracy in the ground state (the electron has three orbitals to choose from) and a 2-fold degeneracy in the excited state. The 3-fold degeneracy will always be called a T state. So the 2D becomes a 2T state. The excited state is doubly degenerate and is always an E state. So, to sum, the 2D free ion term becomes ${}^2T + {}^2E$ in an octahedral field:



Collectively, these can be written just in terms of energy with increasing ligand field strength to the right.



It is common to “bend” this drawing so that the ground state is always horizontal (figure below). This is the basis of Tanabe-Sugano diagrams that we will study in the next unit. Sketch the appropriate energy splitting diagram populated with one electron for both the 2T and 2E states.

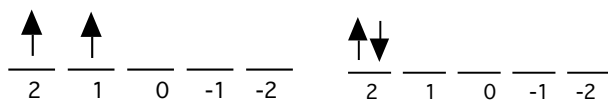


On this diagram, one can imagine water’s position as a vertical line of certain field strength, perhaps in the middle somewhere. The spectrum for $\text{Ti}(\text{H}_2\text{O})_6^{+3}$ has its absorption maxima at $21,500\text{ cm}^{-1}$. Suppose we replaced the waters with better, stronger ligands such as with ammonia molecules. Draw vertical lines on the two diagrams above, one for water as a ligand and the other for ammonia as a ligand.

Use Jorganson’s relationship to calculate Δ_o for $\text{Ti}(\text{NH}_3)_6^{+3}$.

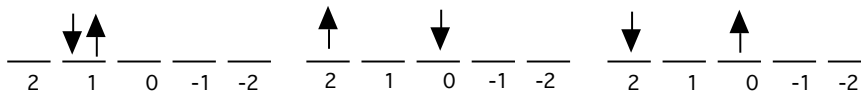
Electron configuration d^2 . When there are two or more electrons, we need to determine all of the ways that they can be arranged. We use a systematic approach called the **method of microstates** where we actually sketch every possible way to fill the d-orbitals. The method of microstates starts with a grid. The columns along the top capture every combination of spin, M_S and the rows are for every combination of orbital angular momentum, M_L . The grid will be different for every d-electron configuration. We will the cells with electron arrangements that correspond to the M_L and M_S for the cell. For example, consider the two **microstates** shown here. The left one would be sketched in the cell for $M_L = 3$ and $M_S = 1$. The right microstate would be sketched in the cell for $M_L = 4$ and $M_S = 0$. In practice, it is easier to start with a cell, say $M_L = 4$ and $M_S = 1$ and try to think of all possible microstates that would give that combination. In fact, there are none, because the only one that would

do it would have to have both electrons in $m_l = 2$ and both would have to have arrows up and that violates the Pauli Exclusion principle.



	M_S		
M_L	+1	0	-1
4		$ \begin{array}{cccccc} \uparrow\downarrow & & & & & \\ \hline 2 & 1 & 0 & -1 & -2 & \\ \end{array} $	
3	$ \begin{array}{cccccc} \uparrow & \uparrow & & & & \\ \hline 2 & 1 & 0 & -1 & -2 & \\ \end{array} $		
2			
1			
0			
-1			
-2			
-3			
-4			

Our objective is to think of all possible microstates that give each M_L and M_S combination. For example, the following three microstates both have $M_L = 2$ and $M_S = 0$. All three would be sketched in the cell for $M_L = 2$ and $M_S = 0$.



It is never necessary to think about more than half of the cells because of the symmetry of the grid. The cells with M_L less than zero will look exactly like the cells with $M_L > 0$ except that the negative m_l orbitals have the electrons. The same with spin. $M_L = -1$ will have the same sorts of combinations as $M_S = +1$ except all of the arrows are facing the opposite way.

In the end, all we want is a tally of how many microstates satisfy each M_L and M_S combination. For the d^2 table above, the results are:

	M_S		
M_L	+1	0	-1
4	0	1	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	0	1	0

From this table of microstates, we will isolate five term symbols. We know there are five because of the value for the central cell, $M_L = 0$ and $M_S = 0$. We start by "removing" a 3×7 matrix with the largest M_S followed by largest M_L . This gives

M_S			
M_L	+1	0	-1
4	0	0	0
3	1	1	1
2	1	1	1
1	1	1	1
0	1	1	1
-1	1	1	1
-2	1	1	1
-3	1	1	1
-4	0	0	0

+

M_L	+1	0	-1
4	0	1	0
3	0	1	0
2	0	2	0
1	1	3	1
0	1	4	1
-1	1	3	1
-2	0	2	0
-3	0	1	0
-4	0	1	0

The set of 21 microstates isolated at the left above have $S = 1$ and $L = 3$ so they collectively are the 3F state. The first state isolated using the maximum M_L and maximum M_S approach is the ground state.

Continuing on with the remaining grid, you should next isolate the 9 microstates that are the 3P state.

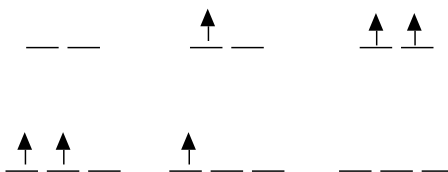
Do so:



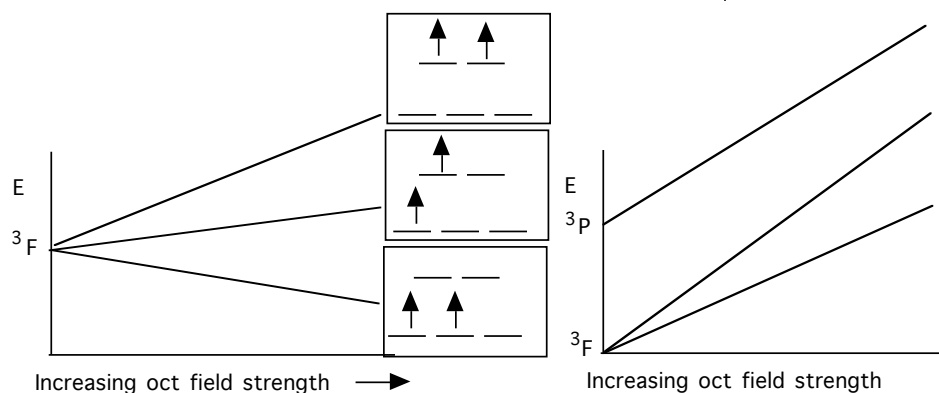
The triplet spin states have both been isolated; there were only two. These are the most important because the 3F state is the ground state and the 3P state is the only one with the same spin-multiplicity. In terms of electron transitions, only transitions between states of the same spin-multiplicity are "allowed." Thus, even though there are three singlet states, electronic transitions from the ground state to them are "spin-forbidden." What are the three singlet states?



d^2 in an octahedral field. There are three distinct possibilities for d^2 in an octahedral field of ligands. Both electrons can be in the t_{2g} orbitals, the ground state; one can be in the t_{2g} and the other in the e_g (singly excited state) and both can be in the e_g orbitals.



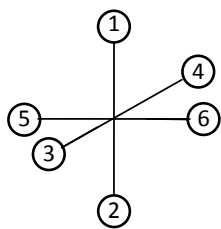
The ground state free ion 3F state will split into these three possibilities in an octahedral field of ligands. The split can be sketched these ways:



We need a way to refer to the new states that arise from the 3F state as the octahedral field is applied. There are “rules” for doing this. Empty, half-filled, and completely filled t_{2g} or e_g orbitals are called “A” states. Thus, the top boxed diagram $(t_{2g})^0(e_g)^2$ is a 3A state. Partially filled t_{2g} situations are called T states and partially filled e_g situations are called E states. Thus, the bottom box contains a T state, labeled 3T . When two different “situations” result, such as with the middle box — containing a “T” and an “E”, priority is given to the one with the largest multiplicity. Thus T trumps E, trumps A. So the middle state is also a “T.” state. Because we have two T states resulting from the 3F state, we call the ground state 3T_1 and the excited T-state, 3T_2 . Label the diagrams above.

Day 18 Answers

1. Step 1:

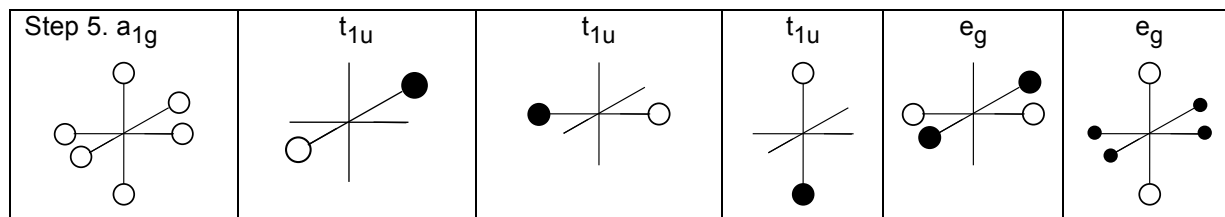


Step 3. (4 pts)

O_h	E	8C ₃	6 C ₂	6 C ₄	3 C ₂	i	6 S ₄	8 S ₆	3 σ _h	6 σ _d
Γ	6	0	0	2	2	0	0	0	4	2

Step 4. (5 pts):

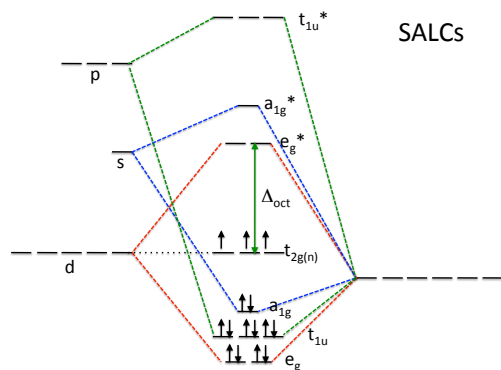
O_h	E	8C ₃	6 C ₂	6 C ₄	3 C ₂	i	6 S ₄	8 S ₆	3 σ _h	6 σ _d
A _{1g}	1	1	1	1	1	1	1	1	1	1
T _{1u}	3	0	-1	1	-1	-3	-1	0	1	1
E _g	2	-1	0	0	2	2	0	-1	2	0



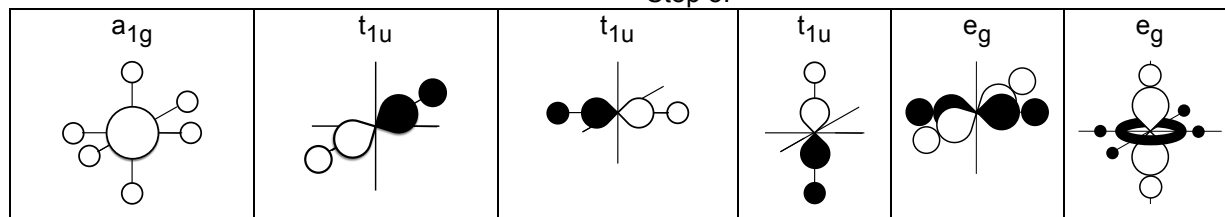
(symmetry)	AO #1	AO #2	AO #3	AO #4	AO #5	AO #6	Total:
SALC (a _{1g})	1/6	1/6	1/6	1/6	1/6	1/6	=1
SALC (t _{1u})	1/2	1/2					=1
SALC (t _{1u})			1/2	1/2			=1
SALC (t _{1u})					1/2	1/2	=1
SALC (e _g)			1/4	1/4	1/4	1/4	=1
SALC (e _g)	1/3	1/3	1/12	1/12	1/12	1/12	=1
Total:	=1	=1	=1	=1	=1	=1	

Step 6. 4s (a_{1g}), 4p_x (t_{1u}), 4p_y (t_{1u}), 4p_z (t_{1u}), 3d_{xz} (t_{2g}), 3d_{yz} (t_{2g}), 3d_{xy} (t_{2g}), 3d_{x²-z²} (e_g), 3d_{z²} (e_g)

Step 7.



Step 8:



B. Using the MO energy diagram. Populate the MO diagram (sketched in Step 7, above) for the complex $\text{Cr}(\text{NH}_3)_6^{+3}$. See above; i. Cr^{+3} : $[\text{Ar}] 3d^3$; ii. $(e_g)^4 (t_{1u})^6 (a_{1g})^2 (t_{2g})^3$; iii. Write electron configurations for these complexes: $\text{Co}(\text{H}_2\text{O})_6^{+2}$: $(e_g)^4 (t_{1u})^6 (a_{1g})^2 (t_{2g})^5 (e_g^*)^2$; VCl_6^{-4} : $(e_g)^4 (t_{1u})^6$

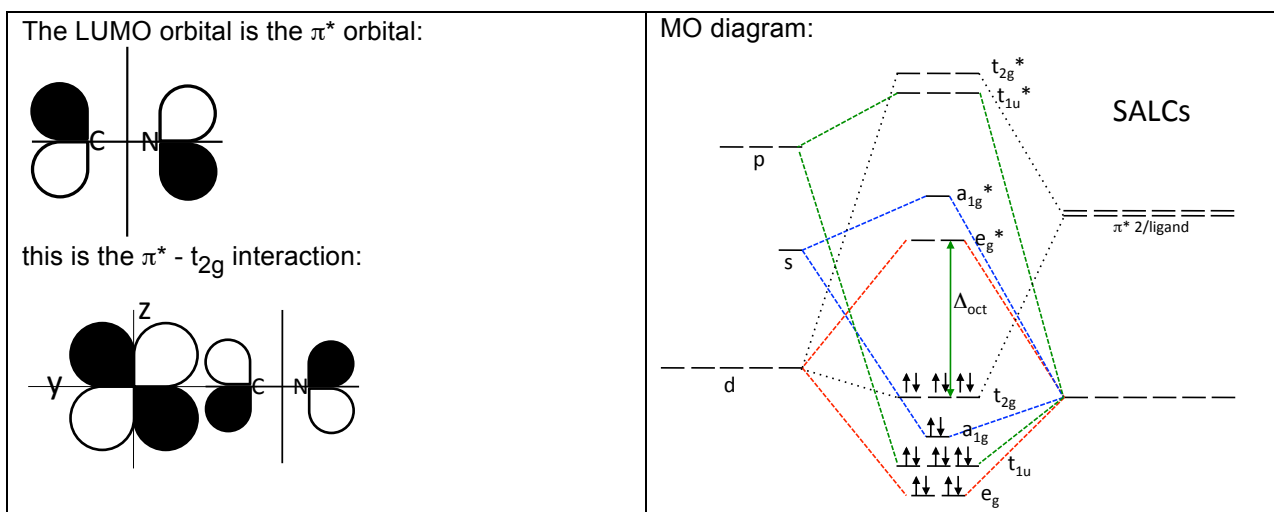
$(a_{1g})^2 (t_{2g})^3$; $Fe(py)_6^{+3}$: $(e_g)^4 (t_{1u})^6 (a_{1g})^2 (t_{2g})^5$ (assuming the +3 charge and nitrogen ligand results in low-spin; iv. Box should be around the HOMO, t_{2g} , and LUMO, e_g^* . Add the arrow for Δ_O).

C. The three scenarios for the MO energy diagram. Scenario #1. Weak field ligands.

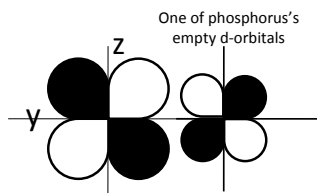
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
12 e^-	13 e^-	14 e^-	15 e^-	16 e^-	17 e^-	18 e^-	19 e^-	20 e^-	21 e^-	22 e^-
Sc ⁺³	Ti ⁺³	Ti ⁺²	V ⁺²	Cr ⁺²	Mn ⁺²	Fe ⁺²	Co ⁺²	Ni ⁺²	Cu ⁺²	Zn ⁺²
Ti ⁺⁴	V ⁺⁴	V ⁺³	Cr ⁺³	Mn ⁺³	Fe ⁺³	Co ⁺³	Ni ⁺³		Cu ⁺	

Scenario #2. Strong field ligands. Strong; 0 – 6 electrons; 12 – 18 electrons

Scenario 3. π -back bonding. MO for cyanide: see earlier homework packet; The sp-hybrid orbital residing on carbon would be used for σ -bonding from cyanide to the metal; Oxygen is transported through the blood by an octahedral Fe⁺² in hemoglobin. The sp²-hybrid orbital on oxygen would be used for σ -donation by a coordinated O₂ ligand



One of phosphine's empty d-orbitals has the right symmetry to overlap with the metal's t_{2g} orbital



CO is much better at π -back bonding than cyanide because CO has no negative charge. If the metal is in a low oxidation state, π -back bonding is more significant because a metal in a low oxidation state is less electronegative, and more able to donate electrons to the π -back-bonding ligand.