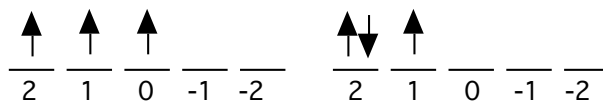**Inorganic Chemistry with Doc M.**
Day 20. Transition Metals Complexes V: Spectroscopy II

Topics:

1. d^3 term symbols

2. Octahedral d^3 complexes and Δ_O

3. Octahedral d^2 complexes and Δ_O

4. Relationships between octahedral d^n configurations

5. Relationships between octahedral and tetrahedral terms

6. High-spin and low-spin complexes

7. Jahn-Teller distortions

A. d^3. Chromium(III) is the most important oxidation state for chromium and is a very common first row d^3 ion. Other d^3 metal ions include V^{+2} and Mn^{+4}. Starting with the free ion, we can sketch the microstate with the maximum spin multiplicity as shown above, left. This microstate has 3 unpaired electrons, so that $S = \max M_S = 3/2$. In fact, the microstate at left in the figure above allows us to determine the ground-state free-ion term. Not only have we maximized the spin, but we have secondarily maximized the orbital angular momentum for all states with this maximum spin (Basically, we put all the electrons spin-up in the largest numbered m_l valued orbitals.) Thus, the ground state is a ^4F:

$$S = \max M_S = 3/2$$

… and for this value of S, $L = \max M_L = 3$ which is an "F" state.

The term symbol is ^{2S+1}L or ^4F

1. Use the method of microstates to determine the term symbols for d^3. Note that only the positive M_L values and positive M_S values are shown (next page) because of the symmetry we first noticed when we did d^2. Numbers in () represent how many microstates I got trying it. Let me know if I goofed!

|	M_S	
M_L	+3/2	+1/2
5	(0)	(1)
4	(0)	(2)
3	(1)	(4)
2	(1)	(6)
1	(2)	(8)
0	(2)	(8)

2. Term symbols for the d^3 free ion. In the previous worksheet, we reduced the table of microstates for d^2 to a set of five term symbols for the free ion (^3F, ^3P, ^1G, ^1D, and ^1S). 2a. Do the same for the set of microstates above. You should end up with eight terms.

3. Review from previous worksheet: the d¹ and d² ions in an octahedral field.

3a. As we saw in the previous worksheet, the ground state free ion term changes in a predictable way in an octahedral field. For example, the free ion term for d^1 is ^{2}D which converts to a ^{2}T and ^{2}E state in an octahedral field. Review again what each state looks like in terms of a typical microstate. Fill in the representative microstate diagrams next to the term symbols.

E ^{2}D ^{2}E

^{2}T

Increasing octahedral field strength →
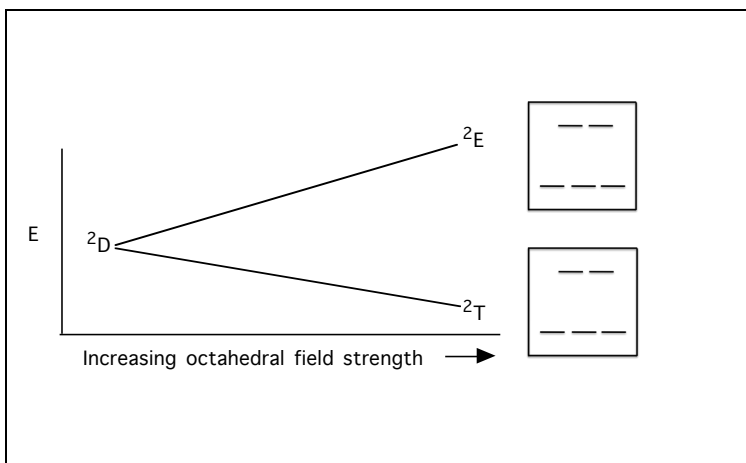
3b. Repeat for d^2 (also originally done in previous worksheet). In each case, sketch a typical microstate one for each of the three terms for d^2 in an octahedral field.
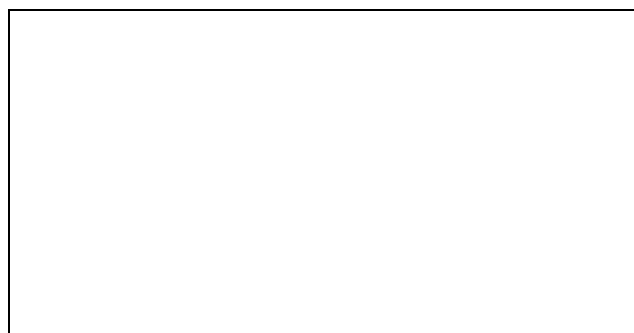
4. The d³ ion in an octahedral field. Do the same for d^3. 4a. Start by sketching the possible configurations for three electrons, all unpaired using the "octahedral representative microstates" as shown at right. 4b. Knowing the three possible notations are A, T, and E, provide labels for the microstates you drew. From this exercise, you should discover that the ground free ion state, ^{4}F splits into an A, a T$_1$ and a T$_2$ state.
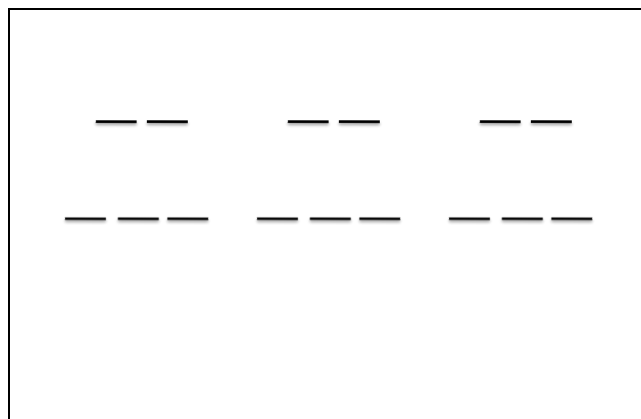
4c. Add the above microstates and terms to the diagram at right. Unlike d^2, the ground state is different.

E
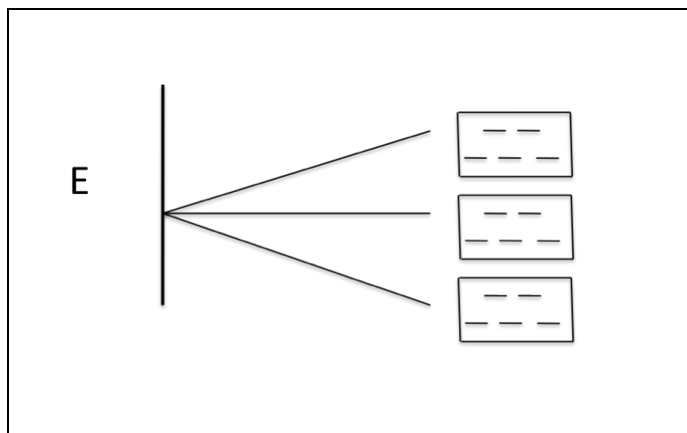
5. When the energy diagram for d^3 gets turned into a Tanabe-Sugano diagram at right. Sketch a typical microstate next to each line at the right. Also note that the $^4T_1(F)$ and $^4T_1(P)$ lines curve away from each other. This is just a curiosity for d^3 but is a problem with d^2 as we will see soon.
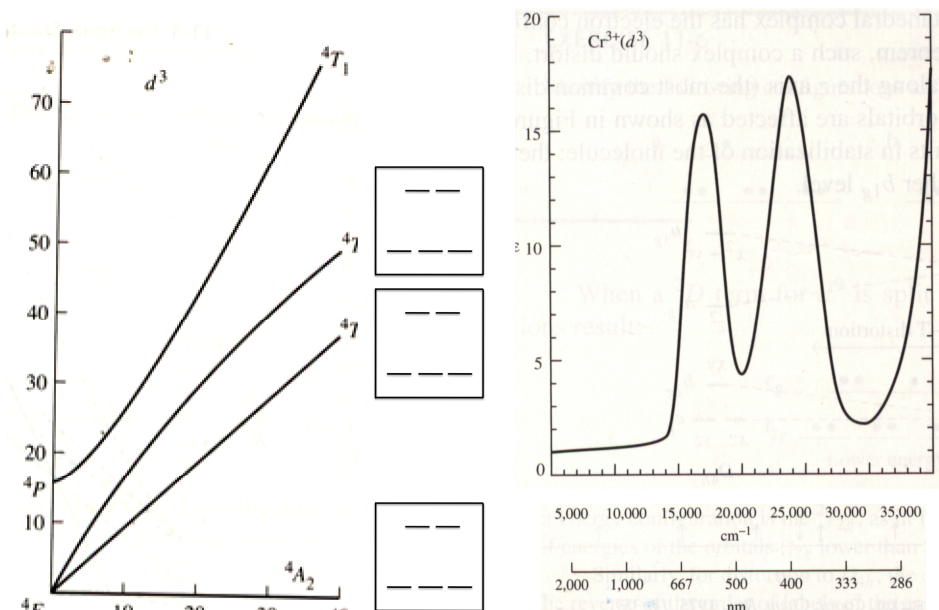
Estimate values for the three spin-allowed transitions expected and the first one corresponds to Δ_o:

$^4A \rightarrow {}^4T_2 \qquad \omega_1 = ($_____$)$ or $\lambda_1 = ($_____$) = \Delta_o$

$^4A \rightarrow {}^4T_1(F) \qquad \omega_2 = ($_____$)$ or $\lambda_2 = ($_____$)$

$^4A \rightarrow {}^4T_1(P) \qquad \omega_3 = ($_____$)$ or $\lambda_3 = ($_____$)$

5. The transition $^4T_2 \rightarrow {}^4T_1(F)$ also represents Δ_o. Show this is true using the microstate diagrams.

6. Use Jorgenson's relationship to estimate Δ_o.

7. What mathematical relationship between ω values would give us Δ_o?

8. $Cr(H_2O)_6^{+3}$ is green-blue. Is this consistent with the spectrum shown? Use the color wheel.

B. Back to d^2 complexes.

With d^3 complexes, we were able to determine Δ_o without using the curvy $^4T_1(F)$ and $^4T_1(P)$ lines. The curvy nature of these lines is due to "mixing" that occurs between the spin and orbital angular momentum components between the two states. Details are not necessary for us to understand; we just need to know that the $^3T_1(F)$ and $^3T_2(F)$ lines cannot be used to get a good measure of Δ_o.
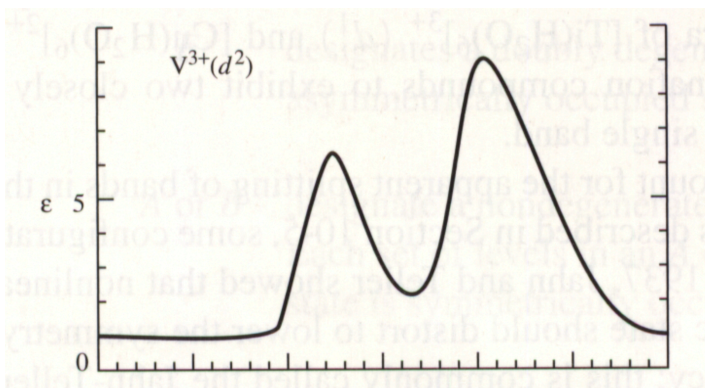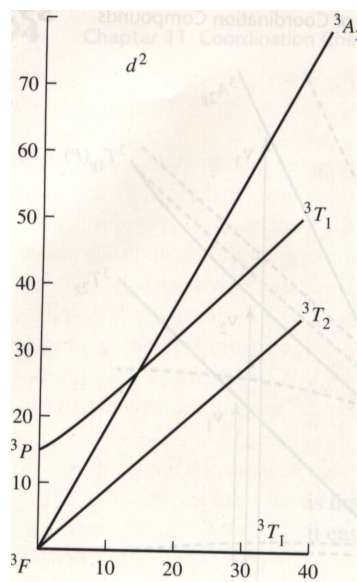
1. Looking at the Tanabe-Sugano diagram above, one notices there is ambiguity as to the correct assignment of ω_2 and ω_3. In the case of d^3, we had the same ambiguity, but it was of no consequence because Δ_o was equal to ω_1. With d^2, Δ_o is still equal to $^3T_2(F) \rightarrow {}^3A_2$. However, this transition does not correspond to any of the observed absorbances.

        (a) Why is Δ_o equal to $^3T_2(F) \rightarrow {}^3A_2$? Use microstates (like you did on previous page for d^3)

        (b) Complete the transitions below by inspecting the Tanabe-Sugano diagram:

             $\omega_1 = 17{,}800$ cm^{-1} $^3T_1(F) \rightarrow$ _____

             $\omega_2 = 25{,}700$ cm^{-1} $^3T_1(F) \rightarrow$ _____   or $^3T_1(F) \rightarrow$ _____

             $\omega_3 = 38{,}000$ cm^{-1} $^3T_1(F) \rightarrow$ _____   or $^3T_1(F) \rightarrow$ _____

2. The curvy $^3T_1(F)$ becomes the flat baseline so all the lines should have a slight curve except $^3T_1(P)$ which should have a larger curve. As with d^3, the best, truest representation of Δ_o is the energy between T_2 and A_2. In theory, we could subtract two of the observed bands and obtain the energy associated with the energy between T_2 and A_2. Because $E = hc/\lambda = hc\omega$, we can directly subtract the wavenumbers to estimate Δ_o. Which two will you subtract? Is there more than one possibility?

While the above discussion seems reasonable, there are complications that are best solved with a more elaborate explanation, that we do not have time to develop. We have learned how Δ_o for d^1 and d^3 are straight-forward, and we shall leave d^2 with the general understanding of how it might be done, but knowing that it isn't as simple as d^1 and d^3.
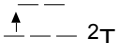
C. Other d-configurations.
1. Determine the ground state free ion term symbols for $d^1 - d^{10}$:

	Ground State Term:
d^1	$\underset{2\quad1\quad0\ -1\ -2}{\uparrow\ —\ —\ —\ —}$ ^2D
d^2	$\underset{2\quad1\quad0\ -1\ -2}{\uparrow\ \uparrow\ —\ —\ —}$ ^3F
d^3	$\underset{2\quad1\quad0\ -1\ -2}{\uparrow\ \uparrow\ \uparrow\ —\ —}$ ^4F
d^4	
d^5	
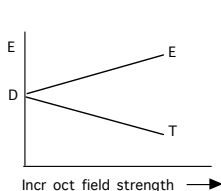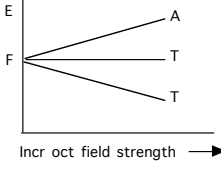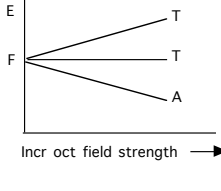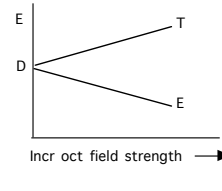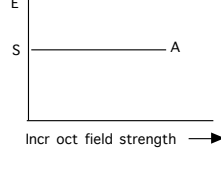
	Ground State Term:
d^6	
d^7	
d^8	
d^9	
d^{10}	

2. Notice a pattern emerging between d^1 and d^6, d^2 and d^7, d^3 and d^8, and so on? What is it?

3. The same pattern occurs between these "pairs of states" such as d^1 and d^6 when the ion is placed in an octahedral field of ligands. Designate each electron configuration as A, E, or T once it is in an octahedral field of ligands. In each case, we will assume the complex is high-spin for now. Add the spin multiplicity. Under "Comments" you should note things like: For d^6: "Same as d^1."

|	Ground state	First excited state	Second excited state	Comments:
d^1	⬆ — — — ⁣ ^2T		N/A	
d^2				
d^3				
d^4				
d^5				
d^6				Same as d^1
d^7				
d^8				
d^9				
d^{10}				

4. Ignoring spin multiplicity which reflects the number of unpaired electrons, and focusing on the orbital angular momentum terms, there are only five unique energy patterns for the d-orbitals in an octahedral field of ligands. While that sounds like a lot, the same patterns will be encountered for the tetrahedron. The patterns are:

Oct d^1 and d^6	Oct d^2 and d^7	Oct d^3 and d^8	Oct d^4 and d^9	Oct d^5 and d^{10}
Tetr d— and d—	Tetr d— and d—	Tetr d— and d—	Tetr d— and d—	Tetr d— and d—

D. Tetrahedral complexes use the same five splitting patterns, only the order is not the same. For the configuration shown below, the ground state for d^1 is an E state and the excited state would be a T state. So tetrahedral d^1 has the same energy diagram as octahedral d^4. Sketch the rest of the tetrahedral configurations and complete the bottom row of the table above. Remember, tetrahedral complexes are always high spin.
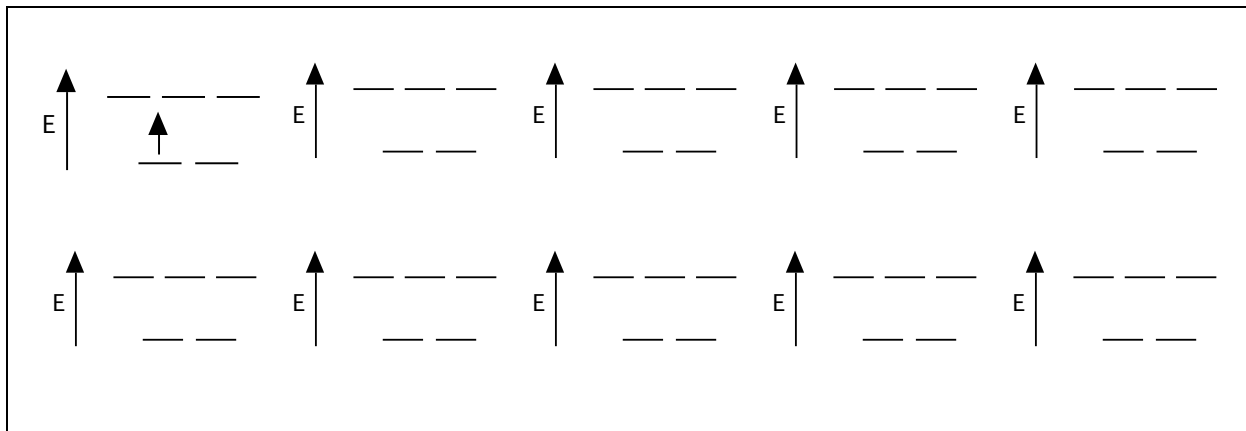
E. Low spin octahedral complexes. For octahedral complexes with electron configurations $d^4 – d^7$, high-spin and low-spin electron configurations are possible. We see this when we look at the Tanabe-Sugano diagrams for these configurations. For example, with d^4, the ground state does from ^5E to ^3T:
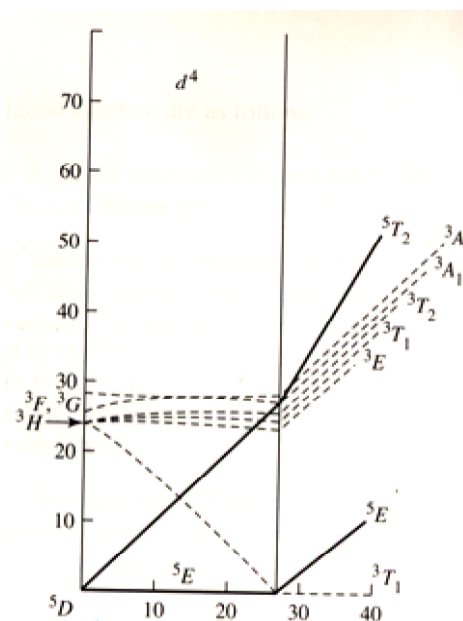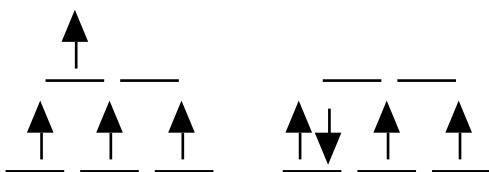
F. Jahn-Teller distortion.

1. Now that everything is starting to make some sense, it's time to shake things up a bit. Remember the shoulder on the single absorption band we saw for d^1 ($Ti(H_2O)_6^{+3}$)? Jahn-Teller distortion explains the shoulder. We will limit our discussion to octahedral complexes, but the same is true for tetrahedral complexes. We can expect JTD when the t_{2g} orbitals or e_g orbitals are unevenly filled. For the octahedron, that includes d^1, d^2, d^4(hs), d^4(ls), d^5(ls), d^6(hs), d^7(hs). d^7(ls), and d^9. Omitted from the list are the configurations that are symmetrically filled (A terms) and are not affected by JTD: d^3, d^5(hs), d^6(ls), d^8, and d^{10}. Start by showing how these five configurations are symmetrically filled.

2. With d^1, a JTD is expected. This occurs because the t_{2g} orbitals are unevenly filled. One of them has one electron and two have none for d^1. This creates a slight split in energy within the t_{2g} orbitals — only a small fraction of Δ_o. One t_{2g} orbital, the one with the electron in it, drops in energy by some tiny amount, and the other two empty t_{2g} orbitals go up by half that amount — in order to conserve energy. If the amount that the two go up is x, then the amount of energy that the one goes down is 2x. The amount is so small that it is not usually measurable. The same sort of energy split occurs within the e_g orbitals only it is more pronounced because these orbitals are directed towards the ligands. The physical significance of JTD is that either an elongation or compression along the z-axis takes place. Predict the sort of distortions expected for the configurations d^1, d^2, d^4(hs), d^4(ls), d^5(ls), d^6(hs), d^7(hs). d^7(ls), and d^9.
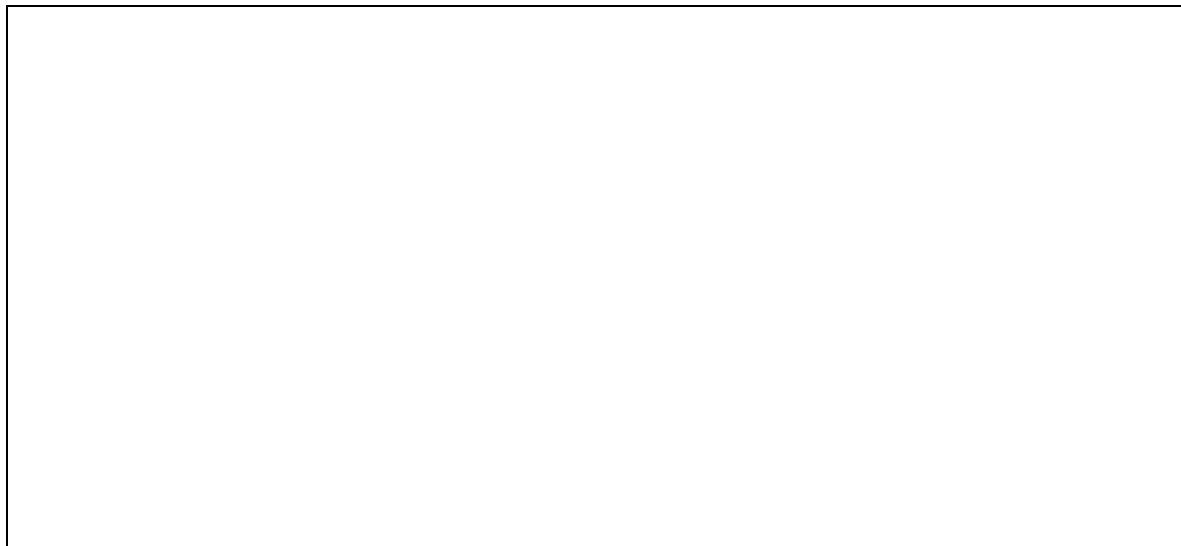
G. Charge Transfer.

1. These are the rogues of electronic spectra. Watch out for them in the UV especially. They do not abide by spin selection rules and have enormous molar absorptivity. Here is a generic MO diagram for a first row transition metal ion in an octahedral field of ligands.
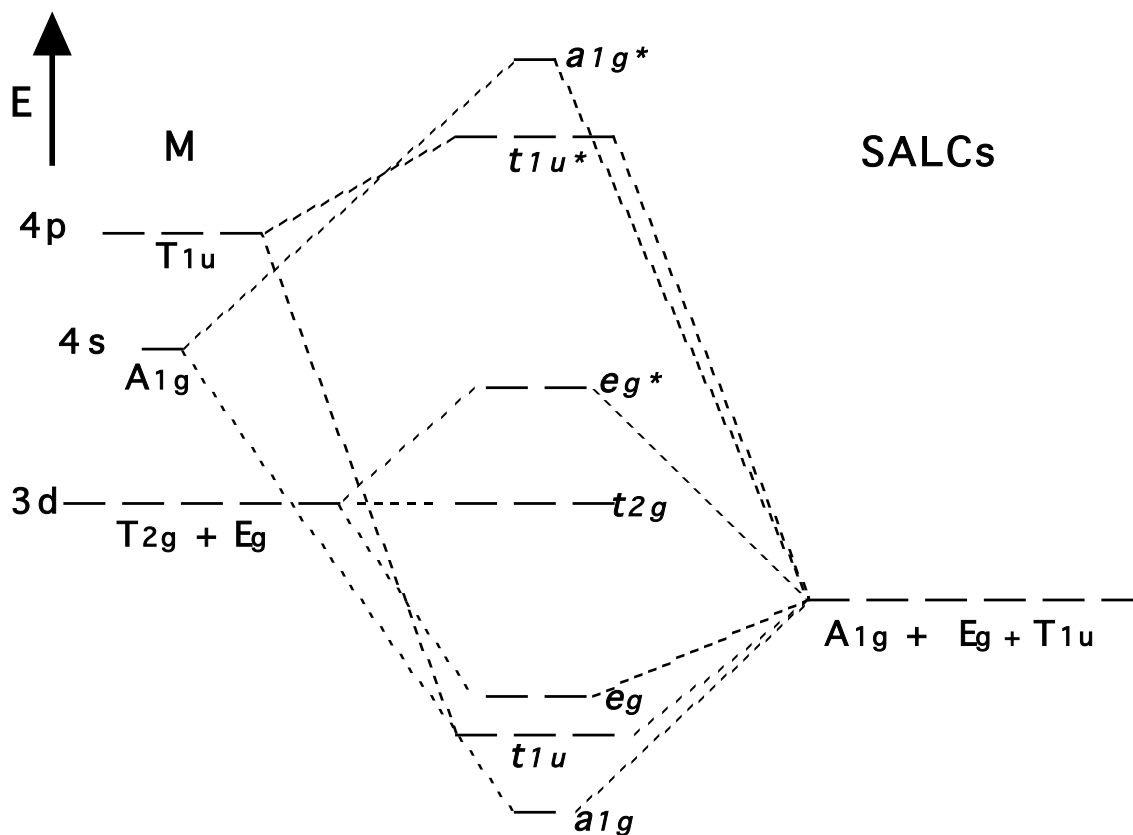
2. Fill the diagram with enough electrons to make d^6(ls), although, any d-configuration works the same way.

3. There are two types of charge-transfer bands: L → M and M → L. In the first case, an electron moves from the lower, filled orbitals (a_{1g}, t_{1u}, and e_g) to the empty e_g* orbital. This represents a much larger energy jump than Δ_0 and so has a large ω, usually in the ultraviolet. This transition is called LMCT which stands for ligand to metal charge transfer. Draw an arrow on the diagram above that shows a possible LMCT and label it.

4. Metal-to-ligand charge transfer is less common but can occur when a t_{2g} electron is excited past the e_g* and up to the a_{1g}*, t_{1u}* orbitals. This is called MLCT.
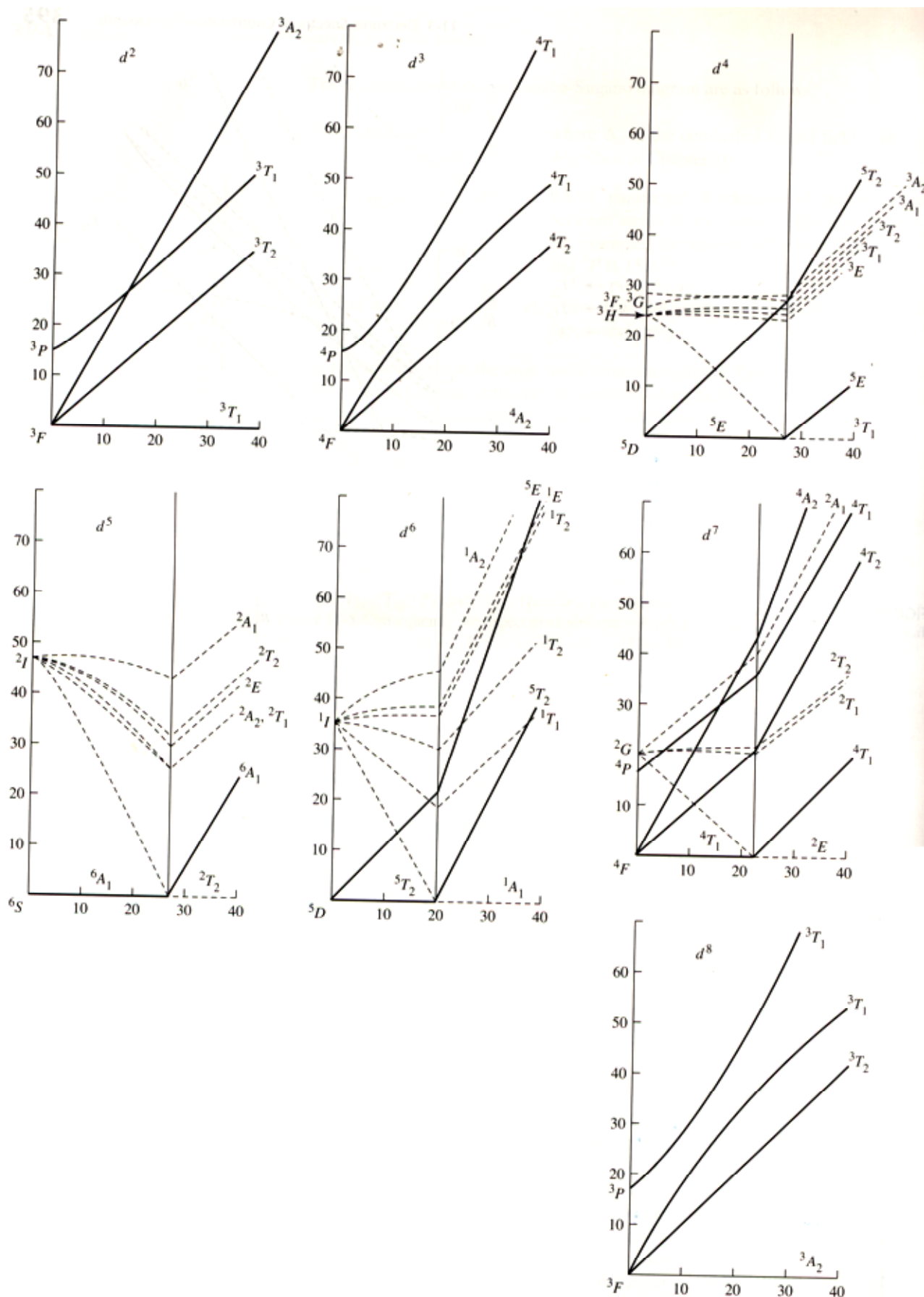
Review for ACS final exam

1. What is the ground state term symbol of d^4?

   (a) ^4D

   (b) ^5D

   (c) ^4F

   (d) ^5F

   (e) ^5P

2. Which of the following is *not* an allowed electron transition?

   (a) $^3T \rightarrow ^3A$

   (b) $^3A \rightarrow ^3T$

   (c) $^3T \rightarrow ^1E$

   (d) $^4T(F) \rightarrow ^4T(P)$

   (e) $^2D \rightarrow ^2E$

3. The Jahn-Teller distortion is greatest in

   (a) $Fe(CN)_6^{-4}$

   (b) $Cr(CN)_6^{-3}$

   (c) $Cu(F)_6^{-4}$

   (d) $V(NH_3)_6^{+2}$

   (e) $Mn(H_2O)_6^{+2}$

Answers B, C, C

Answers to Day 19

1. Visible Spectroscopy. Crystal field energy splitting pattern for octahedral d^1 complex $Ti(H_2O)_6^{+3}$:

Δ_o
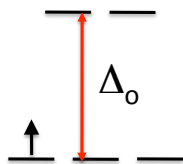
2. 465 nm nanometers – is in the violet region of the spectrum – opposite yellow in the color wheel.

3. E = 257 kJ/mol

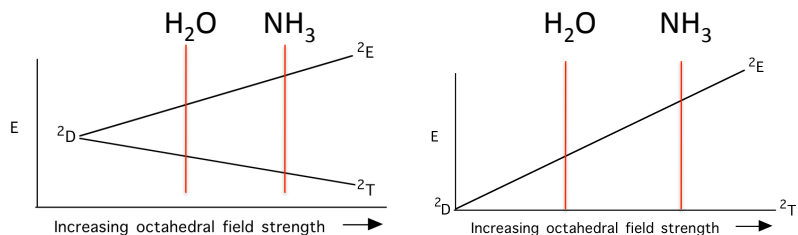4. see figure at right

Given: Δ_o = 21,500 cm^{-1} for $Ti(H_2O)_6^{+3}$, and the Jorganson's relationship, Δ_o = f x g. The f-factor for water is 1.00. Therefore, g = 21.5 for Ti^{+3}. The f-factor is 1.25 for NH_3, therefore the calculated Δ_o = f x g = 26,900 cm^{-1} for $Ti(NH_3)_6^{+3}$.

Electron configuration d^2.

M_L	M_S		
	+1	**0**	**-1**
4	none	↑↓ _ _ _ _ 2 1 0 -1 -2 m_l	none
3	↑ ↑ _ _ _ 2 1 0 -1 -2 m_l	↑ ↓ _ _ _ 2 1 0 -1 -2 m_l ↓ ↑ _ _ _	Similar to M_S = +1, only with both arrows pointing down
2	↑ _ ↑ _ _ 2 1 0 -1 -2 m_l	↑ _ ↓ _ _ 2 1 0 -1 -2 m_l ↓ _ ↑ _ _ 2 1 0 -1 -2 m_l _ ↑↓ _ _ _ 2 1 0 -1 -2 m_l	
1	↑ _ _ ↑ _ 2 1 0 -1 -2 m_l _ ↑ ↑ _ _ 2 1 0 -1 -2 m_l	_ ↑ ↓ _ _ 2 1 0 -1 -2 m_l _ ↓ ↑ _ _ 2 1 0 -1 -2 m_l ↓ _ _ ↑ _ 2 1 0 -1 -2 m_l ↑ _ _ ↓ _ 2 1 0 -1 -2 m_l	

| 0 | $\uparrow$ __ __ $\uparrow$
2 1 0 -1 -2
m_l

__ $\uparrow$ __ $\uparrow$ __
2 1 0 -1 -2
m_l | $\uparrow$ __ __ $\downarrow$
2 1 0 -1 -2
m_l

__ $\uparrow$ __ $\downarrow$ __
2 1 0 -1 -2
m_l

__ __ $\uparrow\downarrow$ __ __
2 1 0 -1 -2
m_l

__ $\downarrow$ __ $\uparrow$ __
2 1 0 -1 -2
m_l

$\downarrow$ __ __ $\uparrow$
2 1 0 -1 -2
m_l | |
| **-1 to -4** | Similar to above | | |

Isolating the 9 microstates that are the ^3P state:

M_S **M_S**

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

+

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

The three singlet states are, in order as they are isolated from the remaining grid, above: ^1G state, ^1P state, and the ^1S state.

Increasing oct field strength ⟶

Increasing oct field strength ⟶

$^3T_1(P)$
^3A
$^3T_2$
$^3T_1$