

PLTL Worksheet #10: Electronic Spectroscopy

1. Review of Term Symbols

a. Determine the *ground state* term symbols for the following:

i. d^1

$2D$

ii. d^8

$3F$

b. Given the following term symbols, determine the appropriate orbital electron occupancy (does not need to be ground state)

i. $4F$

$\overline{+2} \quad \overline{+1} \quad \overline{0} \quad \overline{-1} \quad \overline{-2}$

ii. $3D$

$\overline{+2} \quad \overline{+1} \quad \overline{0} \quad \overline{-1} \quad \overline{-2}$

iii. $6S$

$\overline{+2} \quad \overline{+1} \quad \overline{0} \quad \overline{-1} \quad \overline{-2}$

iv. $2P$

$\overline{+2} \quad \overline{+1} \quad \overline{0} \quad \overline{-1} \quad \overline{-2}$

example.
if F, then
 $L=3$
 $m_L \text{ total} = 3$
multiplicity = 4
 $\therefore 2S+1=4$
 $2S=3$
 $S=3/2$

may possible
correct
ensures.

→ This question is just
to see if they
can write

backwards and
not simply memorize
ground state
term
symbols

- c. While you do not need to know how they are derived, you should know what state symbols correspond to which free ion symbols. This can be found on page 340 and page 346.

- i. For a free ion in an octahedral field with a ground state term symbol of 2D , what are the state(s)?

$^2E, ^2T_2$

* multiplicity comes through

- ii. For a free ion in an octahedral field with a ground state term symbol of 6S , what are the state(s)?

6A_1

2. Selection Rules

- a. Why are d-d ligand field transitions weak?

→ parity forbidden. otherwise known as Laporte forbidden or orbitally forbidden.

d orbitals transitions all involve g type orbitals, and $g \rightarrow g$ is forbidden (as is $u \rightarrow u$)

- b. Can you have a transition between states of different multiplicities? Why or why not?

NO. they are spin-forbidden. It is not simple to flip the spin of an electron when it is excited by a photon.

- c. Why are charge transfer transitions so intense?

They are both spin-allowed and orbitally allowed (if the orbital of the ligand is "u")

→ not metal → ligand charge transfer and also ligand → metal.

(MLCT or LMCT)

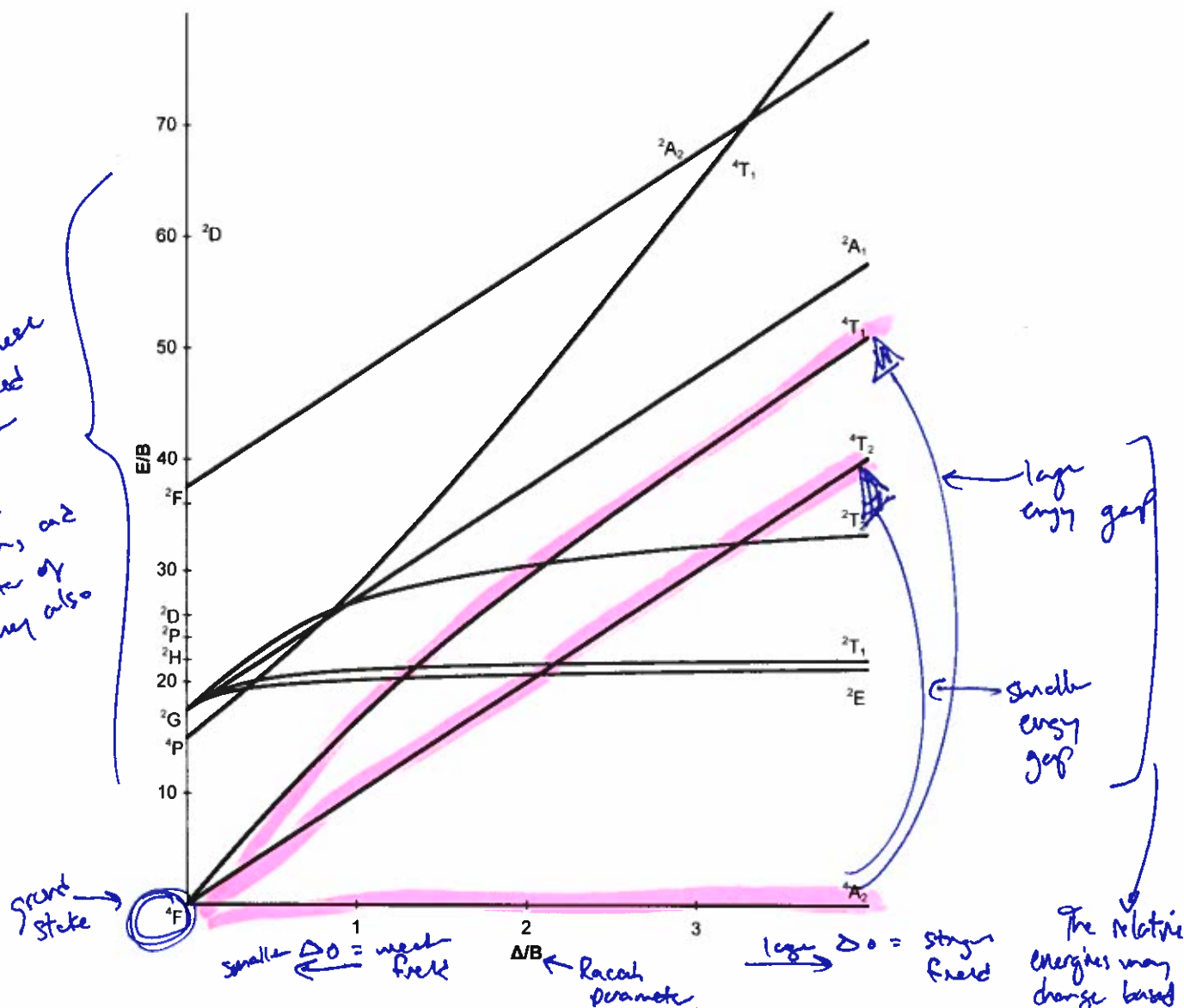
for octahedral.
in tetrahedral, there
is no "g" or
"u" for the
d orbitals, so
they are much stronger.

wavenumber to wavelength conversion:

$$\lambda \text{ nm} = 10\,000\,000 / \lambda \text{ cm}^{-1}$$

Correlation diagram that shows the energy of a state as a function of the ligand field.

3. Tanabe Sugano Diagrams

a. Consider the Tanabe Sugano Diagram for a d^3 metal

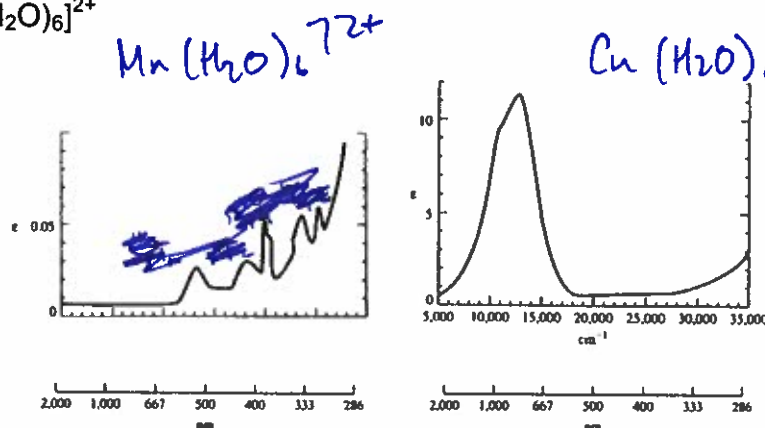
- Trace the states that arise from the $4F$ ground state
- Mark with arrows which transitions from the ground state would be allowed
- The spectra of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ shows two ligand field transitions at $21\,550 \text{ cm}^{-1}$ and $28\,500 \text{ cm}^{-1}$. Which transition is which?

Lower energy is $4A_2 \rightarrow 4T_2 \rightarrow 21\,550 \text{ cm}^{-1}$

high energy is $4A_2 \rightarrow 4T_1 \rightarrow 28\,500 \text{ cm}^{-1}$

look for what other states have the same multiplicity as the ground state.

- b. Consider the UV-vis spectra shown below. One is from an aqueous solution of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, and the other is from an aqueous solution of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$



- i. Which spectrum belongs to which complex, and why?

Hint:

1. Determine the ground state term symbol for each complex



2. Consider the Tanabe-Sugano diagram(s) for the respective electron configurations. What are the spin allowed transitions?

- There is no Tanabe-Sugano diagram for d^1 or d^9 because there is only one transition



- for d^5 , see S1

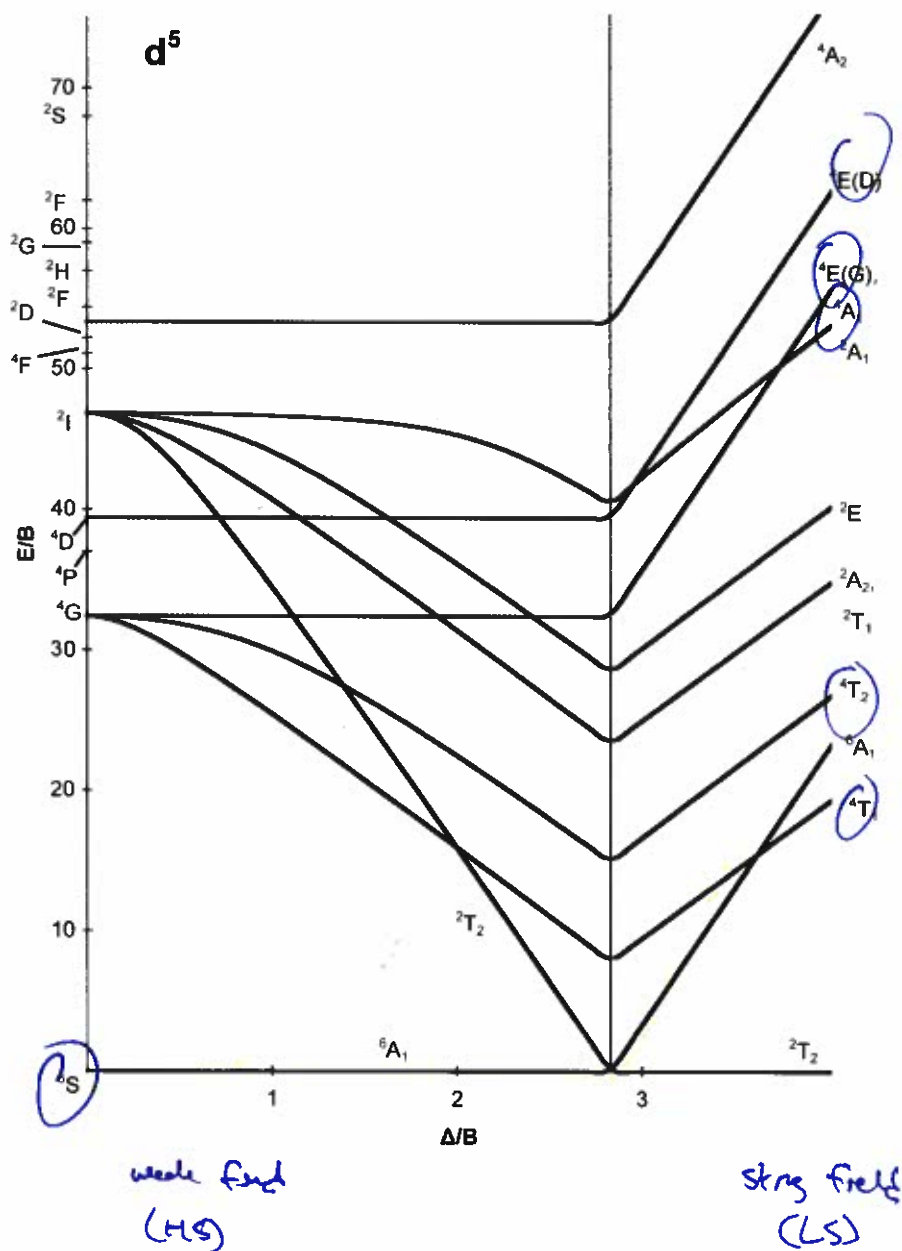
They don't need to know that. The take away is there is only one transition

3. Can you assign the spin-allowed transitions to the given spectra?

$\rightarrow$ take what you see in part 2 and use that in energy.

note ~~transitions~~ how the manganese transitions are all spin forbidden. That is why ϵ is so low.

supplementary info:



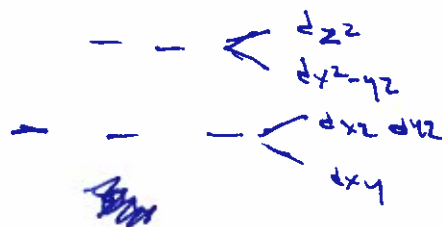
→ → →
 → → → any transition will result in spin flipping.

note that the transitions you see will be $6 \rightarrow 4$

4. Jahn-Teller Effect

a. Briefly describe the Jahn-Teller effect

theorem: for a non-linear molecule in electronically degenerate state, distortion will occur to lower the symmetry.



b. For which electron configurations would you most expect to see a Jahn-Teller distortion?

config of d^9
 LS d^7 → all have doubly degenerate electronic ground states.
 HS d^4

→ They have an e ground state
 (do not need to know how to derive that)

c. How does the Jahn-Teller effect give rise to the shoulder that is observed in the spectrum on the right (from the previous question).

superposition of two transitions. You are seeing an overlap of two peaks. These peaks arise from the Jahn-Teller distortion.