Coordination Chemistry III: Tanabe-Sugano Diagrams and Charge Transfer

Chapter 11

extra material (to finish Chapter 11)

Symmetry Labels for Configurations

Free ion terms split into states in the ligand field, according to symmetry:

TABLE 11.6 Splitting of Free-Ion Terms in Octahedral Symmetry

Term	Irreducible Representations
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

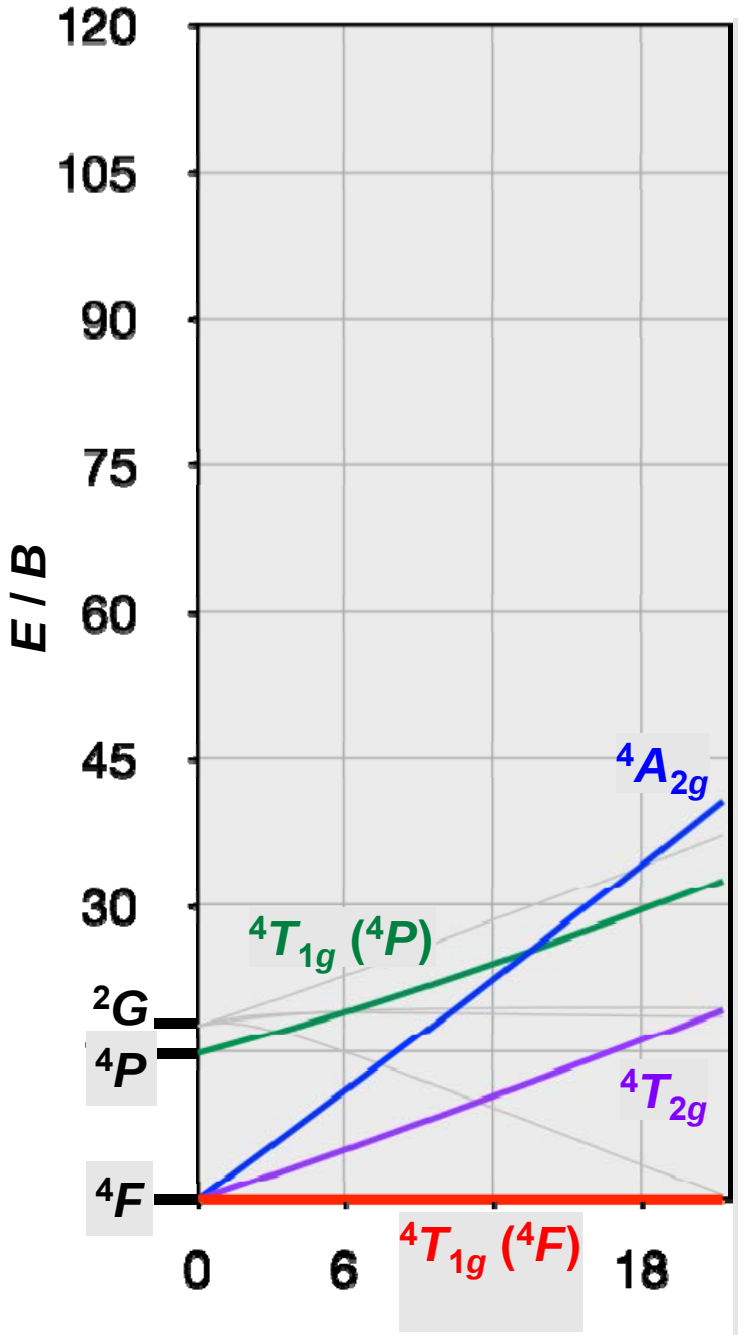
The state labels also indicate the degeneracy of the electron configuration:

		Examples
T	Designates a triply degenerate asymmetrically occupied state.	
E	Designates a doubly degenerate asymmetrically occupied state.	
A or B	Designate a nondegenerate state. Each set of levels in an A or B state is symmetrically occupied.	

d^7 Tanabe-Sugano Diagram

Complexes with d^4-d^7 electron counts are special

- at small values of Δ_o/B the diagram looks similar to the d^2 diagram
- at larger values of Δ_o/B, there is a break in the diagram leading to a new ground state electron configuration



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Complexes with d^4-d^7 electron counts are special

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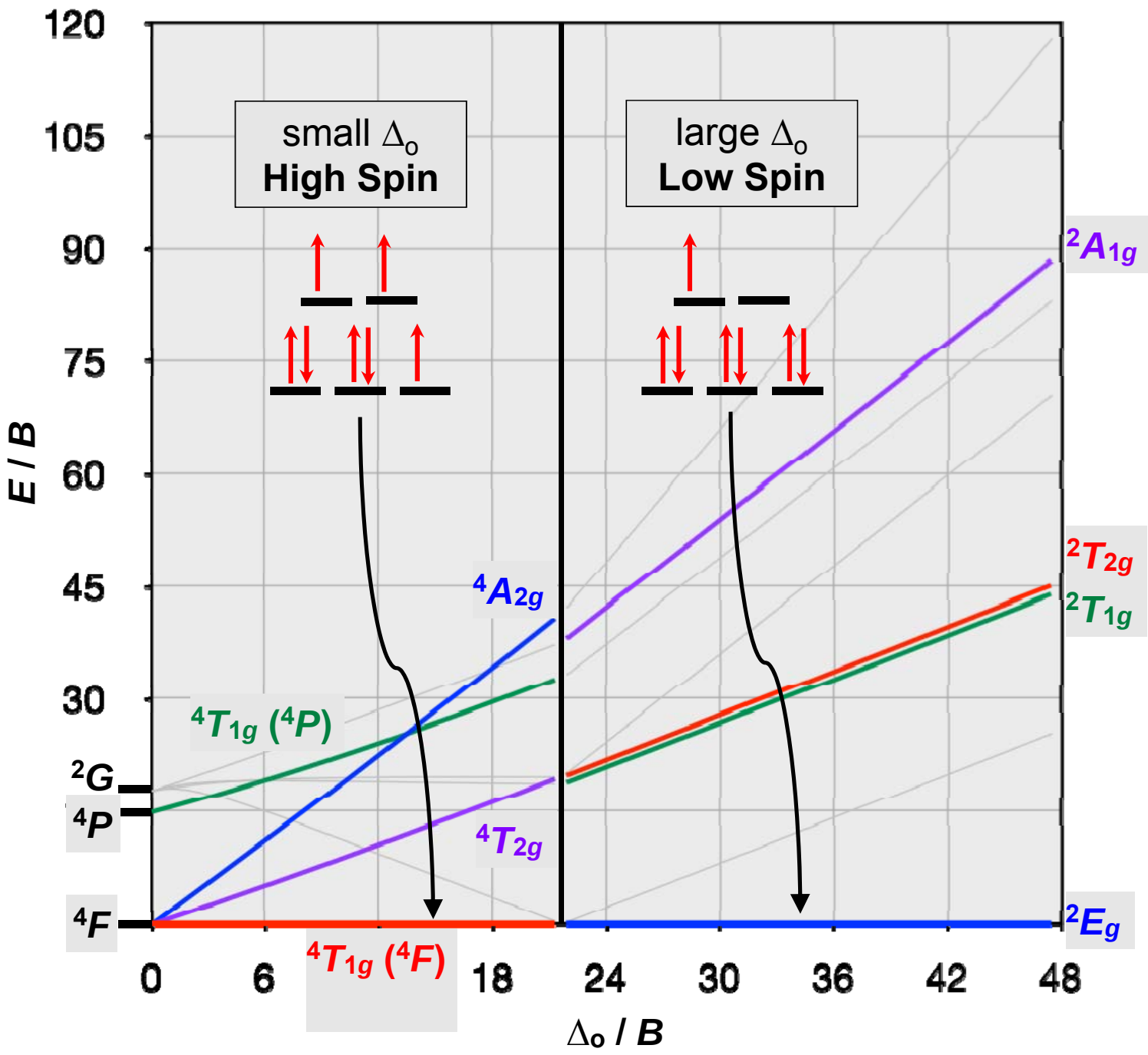


Sample Problem, $[Co(NH_3)_6]^{2+}$

$[Co(NH_3)_6]^{2+}$ has Δ_o = 10,100 cm^{-1} and *B* = 920 cm^{-1}. How many electronic absorptions do you expect for the complex and at what energies?

To solve this problem we first need to determine the *d*-electron count for the $[Co(NH_3)_6]^{2+}$ complex.

$$\left[Co\left(NH_3\right)_6\right]^{2+} \xrightarrow{-6\,NH_3} \left[Co\right]^{2+}$$

So we have cobalt(II). Since cobalt is in the ninth column of the Periodic Table, it must be a d^7 complex so we can use the d^7 Tanabe-Sugano diagram from the last slide.

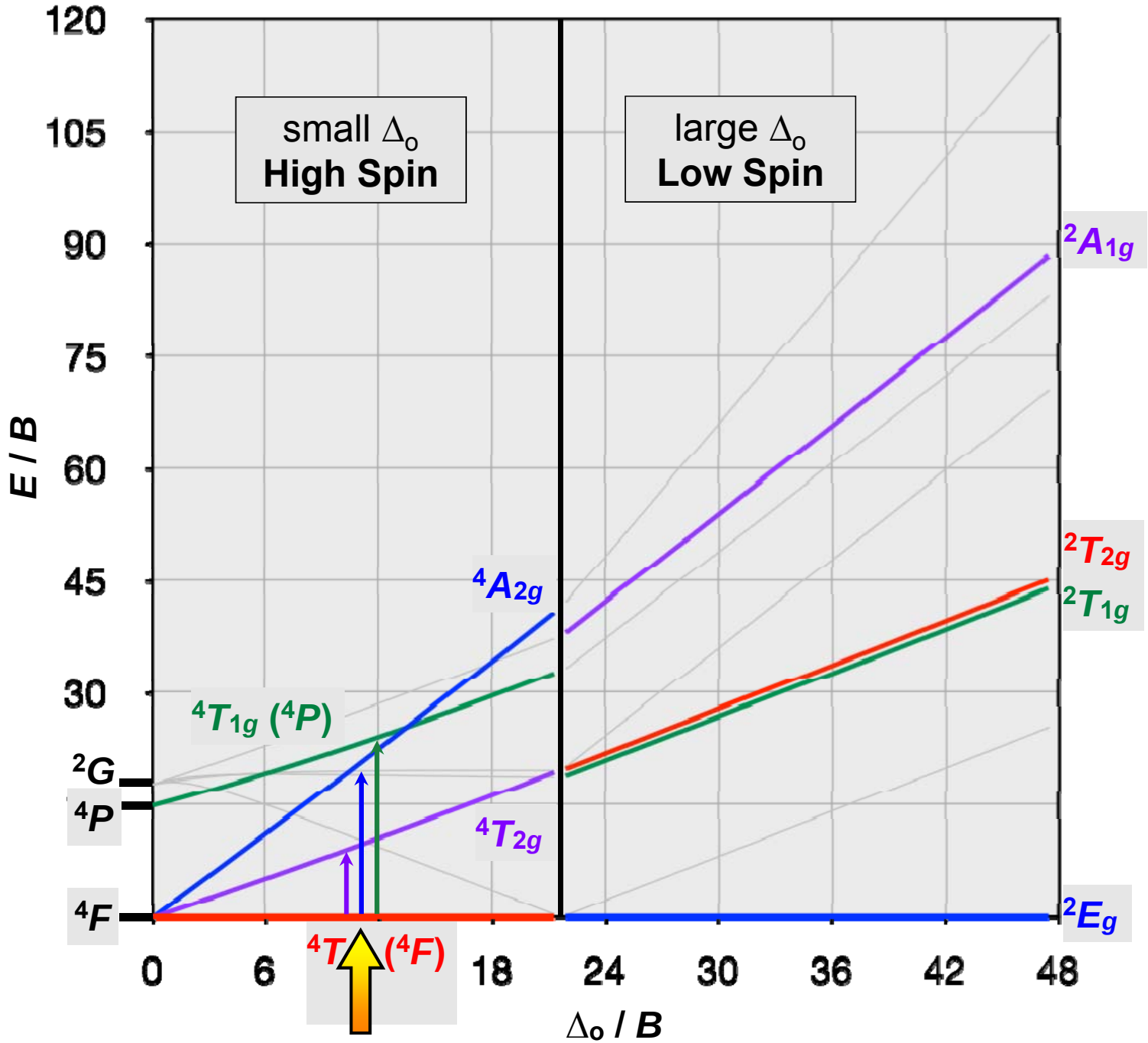
Next we need to find Δ_o/B:

$$\frac{\Delta_O}{B} = \frac{10{,}100 \cdot cm^{-1}}{920 \cdot cm^{-1}} \cong 11$$

Sample Problem, $[Co(NH_3)_6]^{2+}$

We have d^7 $[Co(NH_3)_6]^{2+}$ with $\Delta_o/B \cong 11$

So we expect three absorptions in the UV-vis spectrum.

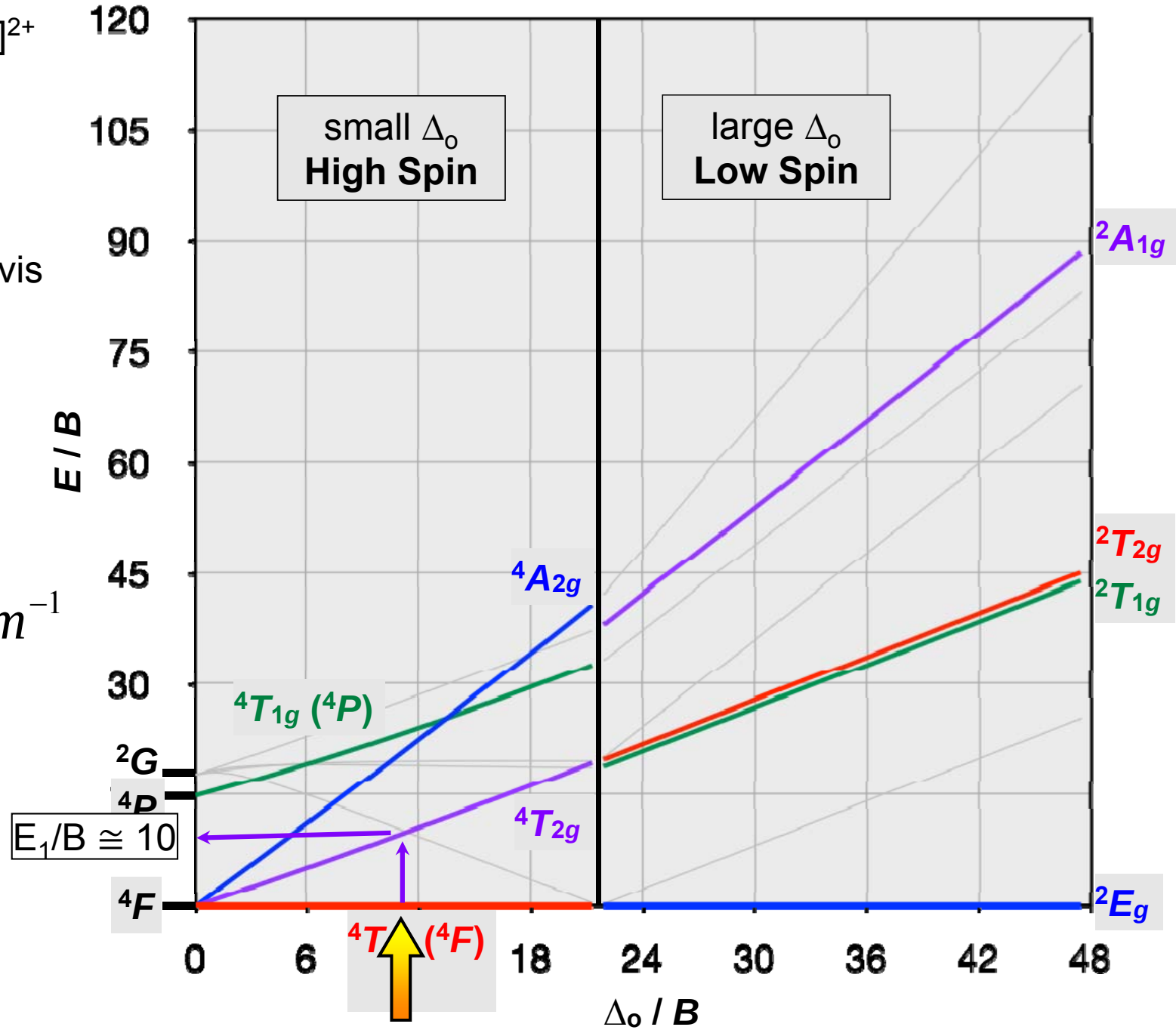


Sample Problem, $[Co(NH_3)_6]^{2+}$

We have d^7 $[Co(NH_3)_6]^{2+}$ with $\Delta_o/B \cong 11$

So we expect three absorptions in the UV-vis spectrum.

$$E_1 \cong 10B$$
$$= 10 \times 920 \cdot cm^{-1}$$
$$= 9200 \cdot cm^{-1}$$

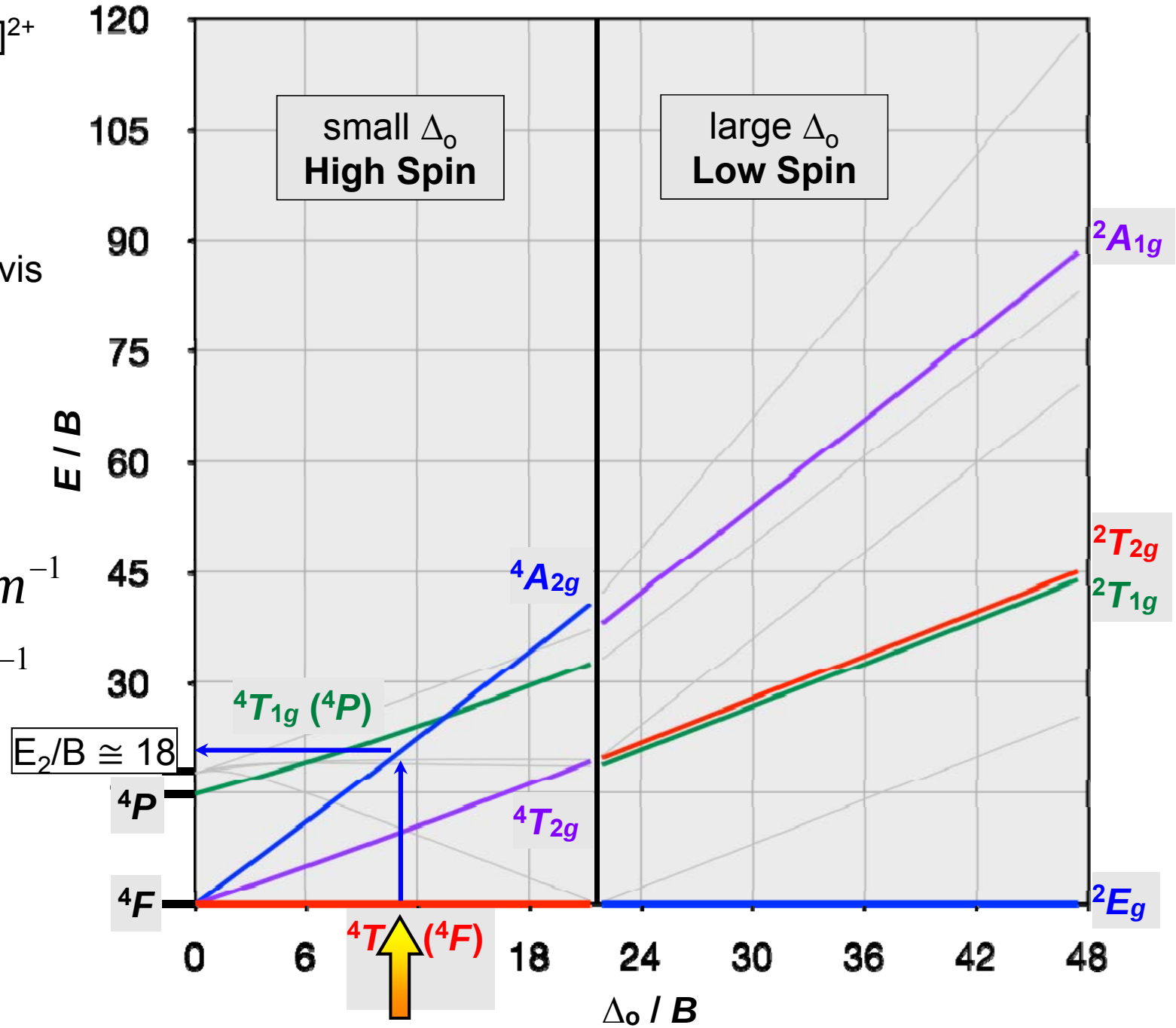


Sample Problem, $[Co(NH_3)_6]^{2+}$

We have d^7 $[Co(NH_3)_6]^{2+}$ with $\Delta_o/B \cong 11$

So we expect three absorptions in the UV-vis spectrum.

$$E_1 \cong 18B$$
$$= 18 \times 920 \cdot cm^{-1}$$
$$= 16,500 \cdot cm^{-1}$$



Sample Problem, $[Co(NH_3)_6]^{2+}$

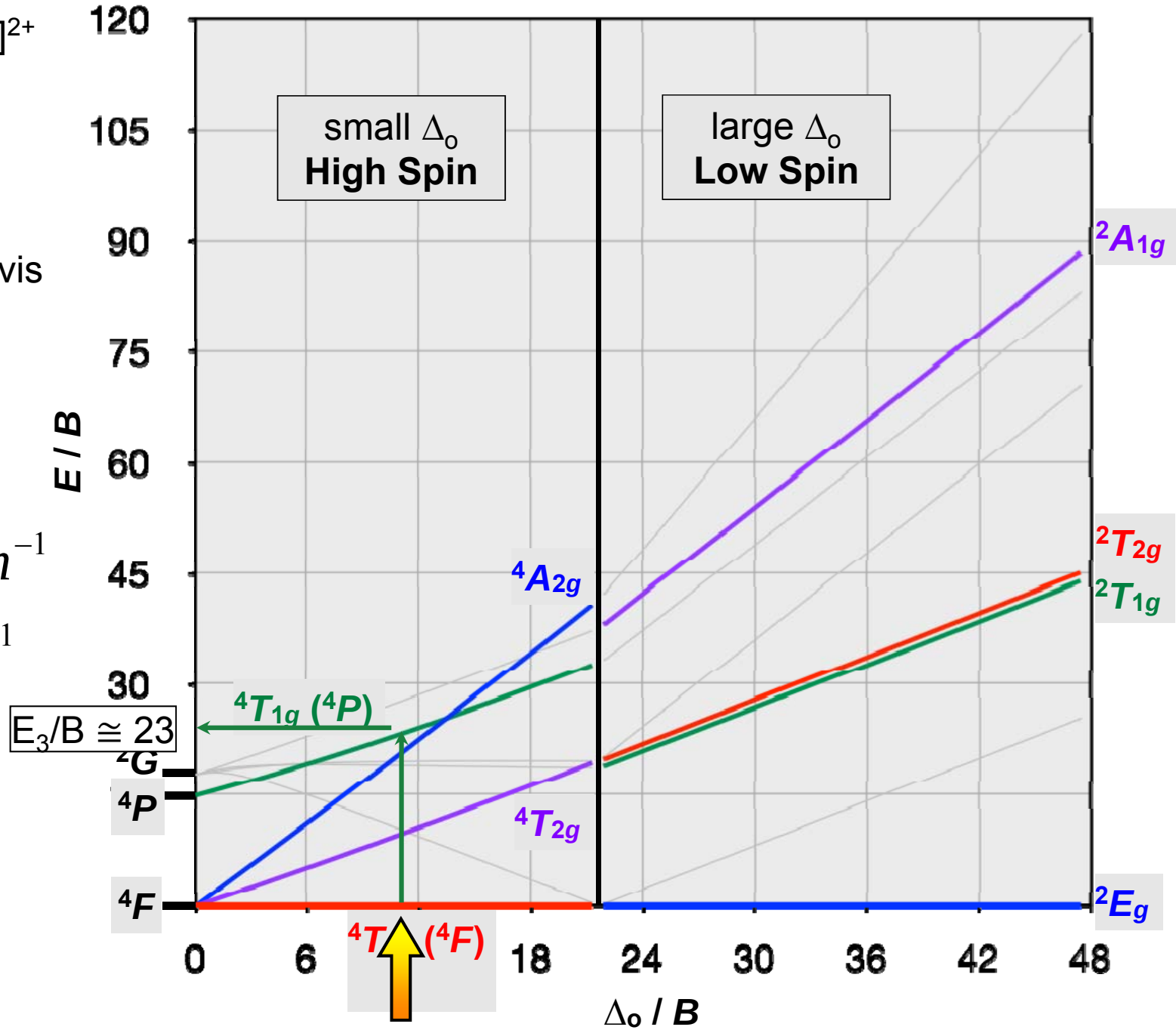
We have d^7 $[Co(NH_3)_6]^{2+}$ with $\Delta_o/B \cong 11$

So we expect three absorptions in the UV-vis spectrum.

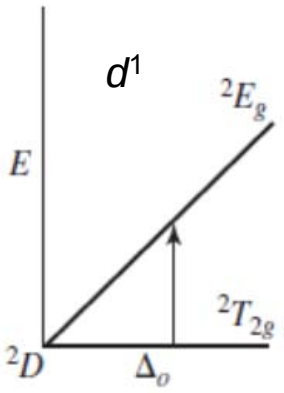
$$E_3 \cong 23B$$

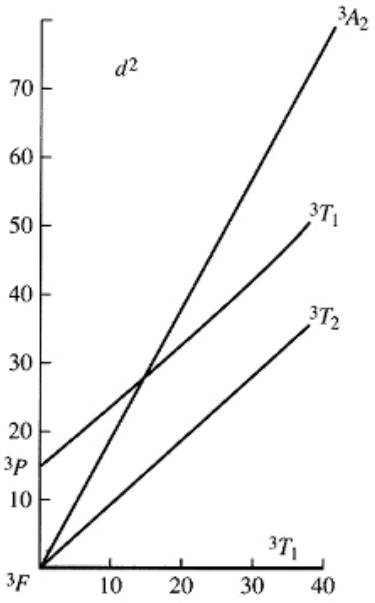
$$= 23 \times 920 \cdot cm^{-1}$$

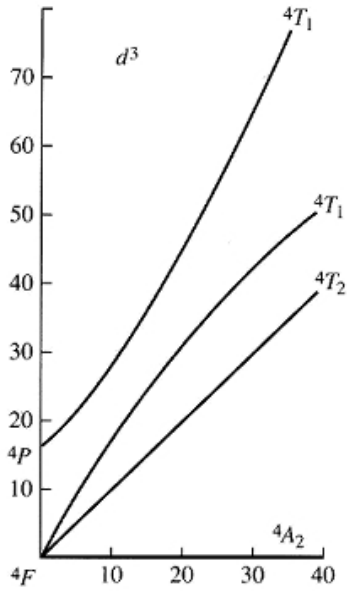
$$= 21,200 \cdot cm^{-1}$$

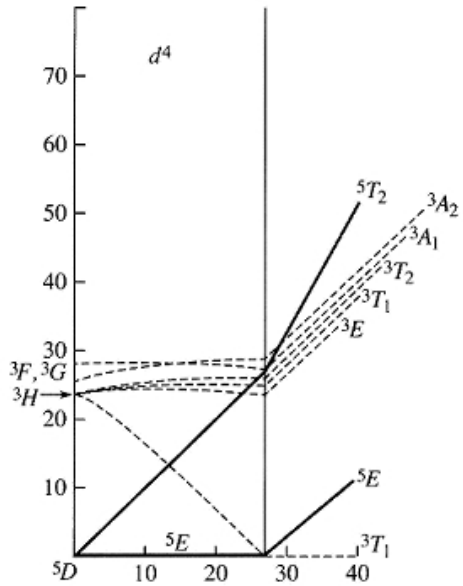


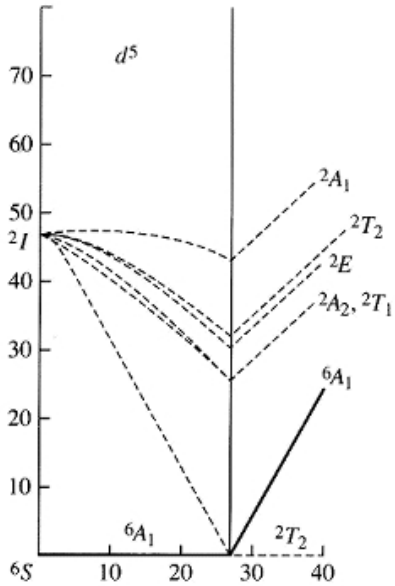
Simplified Tanabe-Sugano Diagrams

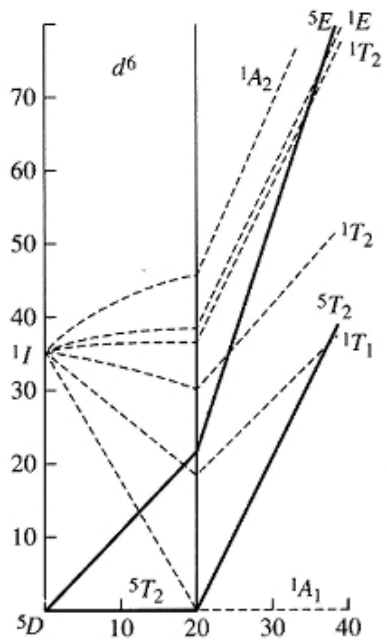


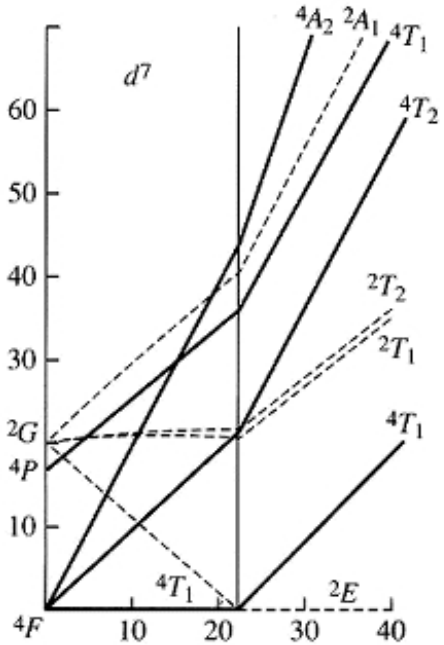


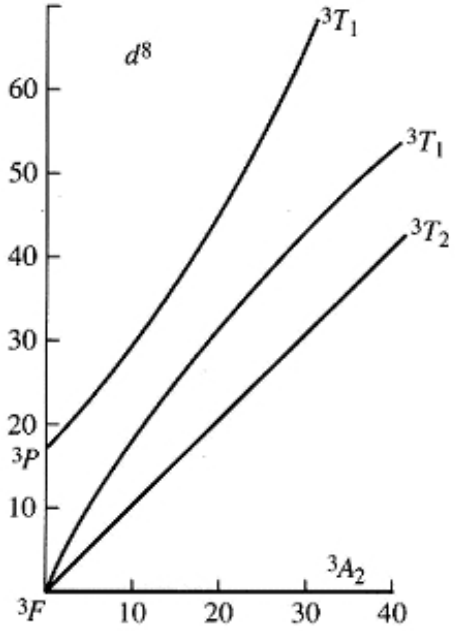


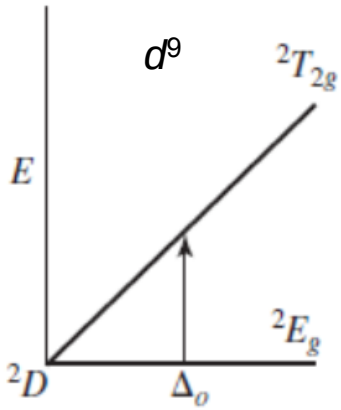




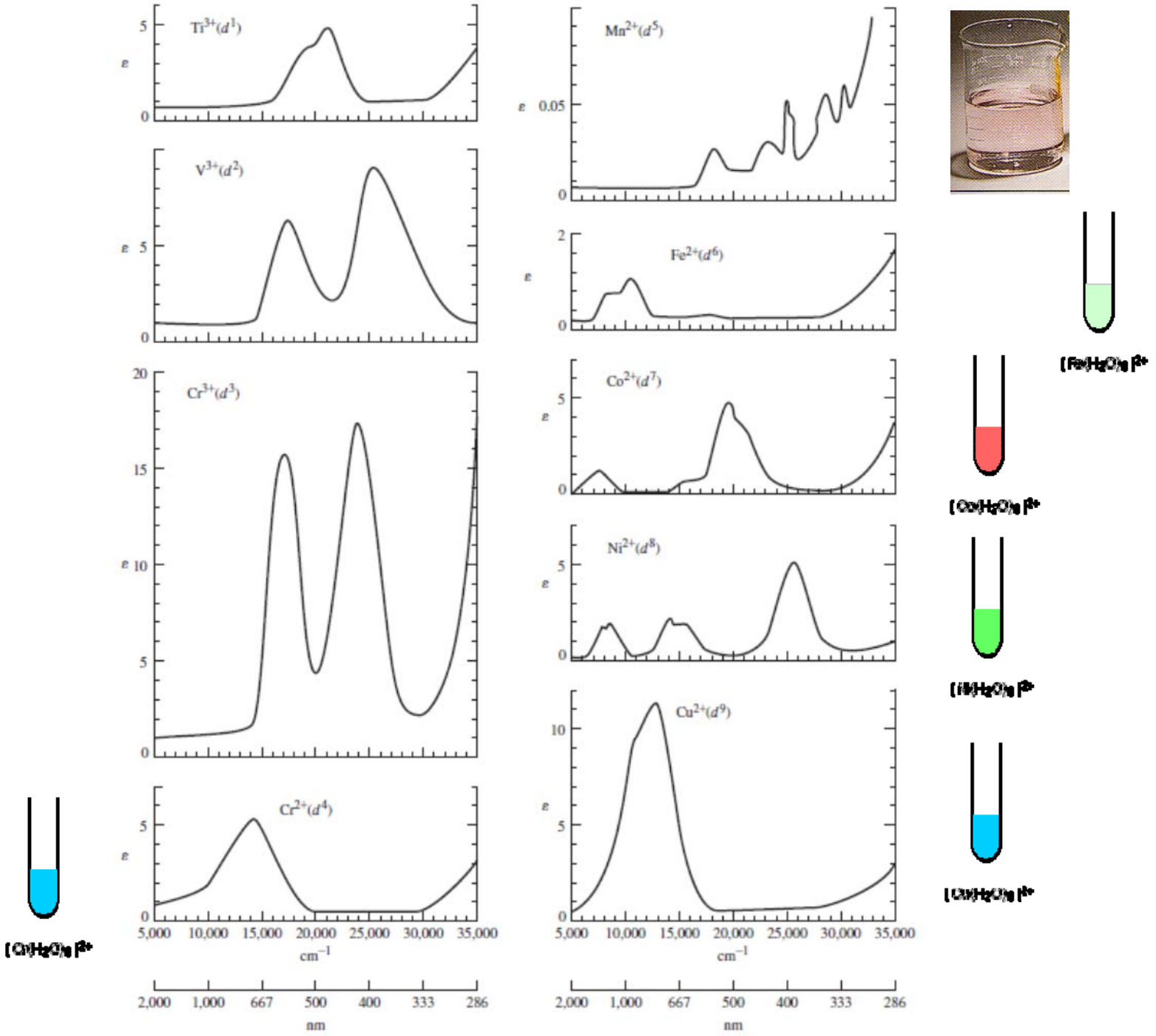




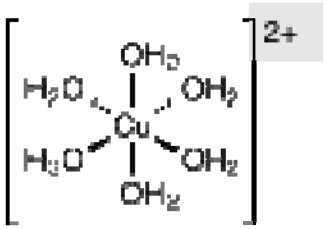




Spectra of First-Row HS $[M(H_2O)_6]^{n+}$ Complexes

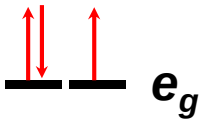


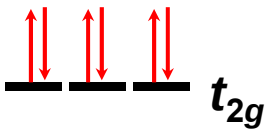
Jahn-Teller Effect in Spectroscopy

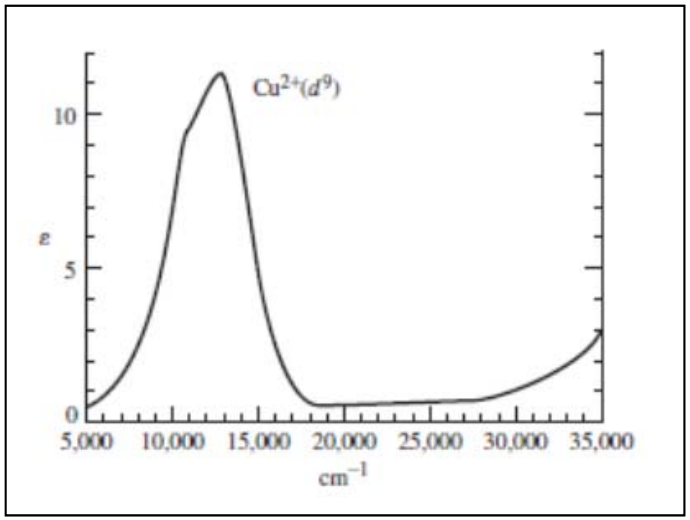


Cu^{II}, d^9

Frontier MO diagram



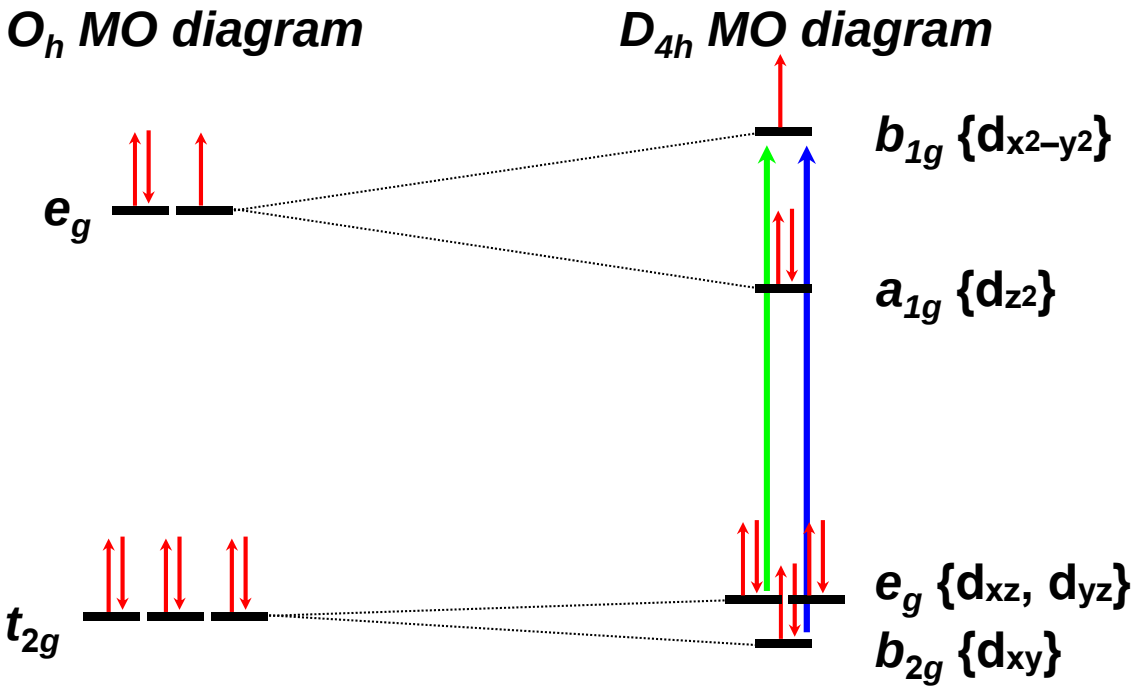


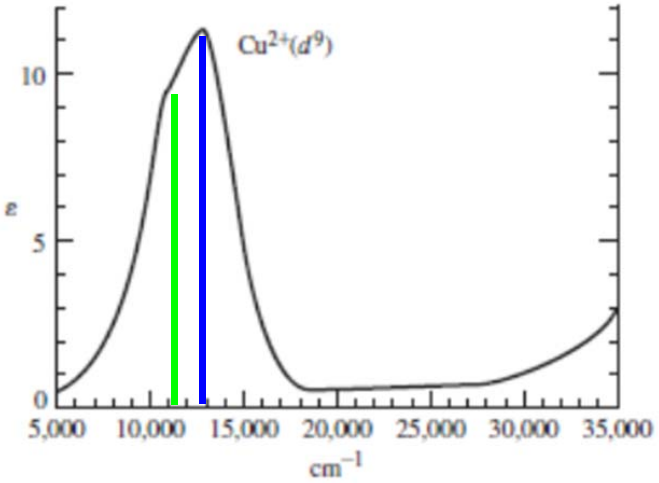


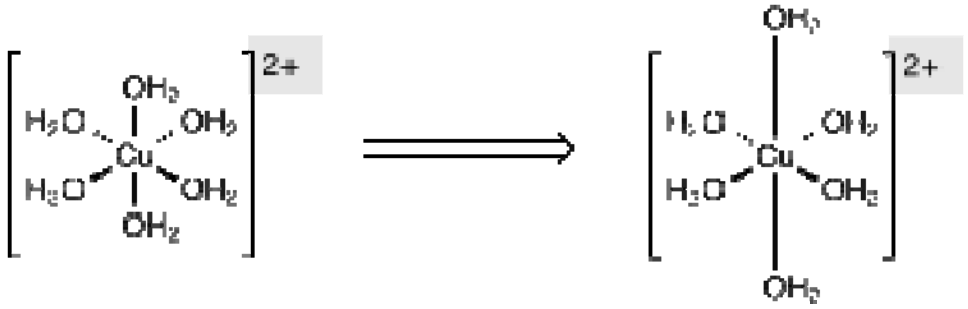
There should only be one *d–d* transition, why is there a split in the absorption band at 900 nm?

- **Jahn-Teller Theorem: complexes with unequal occupation of degenerate orbitals will distort to lower their energy**
  - degenerate electronic states occur when a degenerate orbital set (t_{2g} or e_g) is partially filled with electrons (not half-filled)
  - partially occupied e_g orbitals (M–L σ*) lead to more pronounced distortions than partially-occupied t_{2g} orbitals (non-bonding)
  - the most common distortion is tetragonal, but trigonal distortions are also possible

Jahn-Teller Effect in Spectroscopy



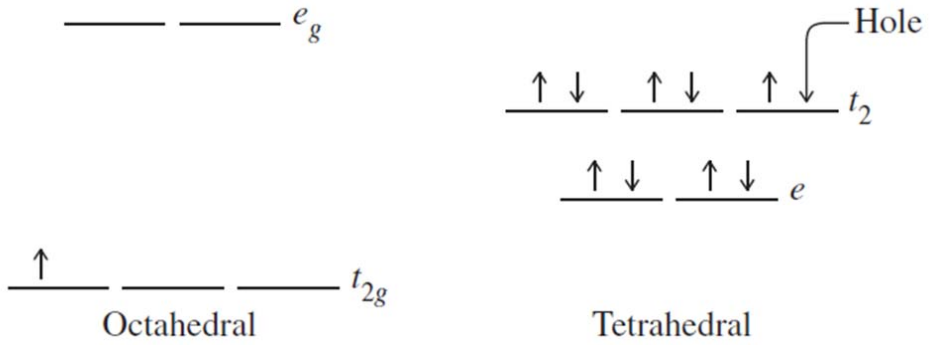




Tetrahedral Complexes

No inversion center → Laporte selection rule does not apply → more intense absorptions than in octahedral complexes

***Hole Formalism*: since the splitting of the *d*-orbitals is opposite in tetrahedral and octahedral complexes, tetrahedral configurations with *n* empty orbitals (*n* "holes") have the same symmetry as d^n octahedral configurations:**



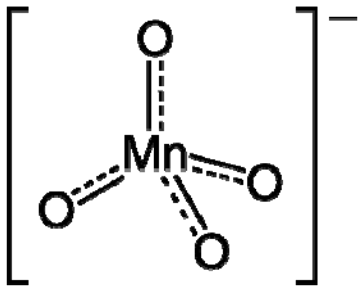
As a result, we can use octahedral d^{10-n} T-S diagrams to describe d^n tetrahedral complexes. For example, d^8 looks like d^2 octahedral, d^7 looks like d^3, etc.

Charge Transfer Transitions

In addition to transitions between *d*-orbitals, transitions between ligand-based orbitals and metal *d*-orbitals are possible.

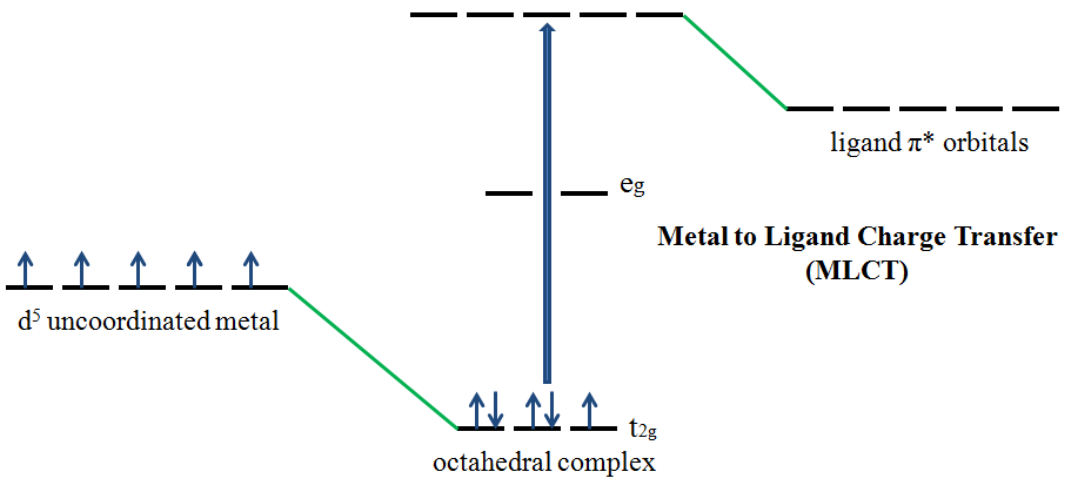
- **called *charge transfer* transitions since an electron is transferred from the metal to the ligand or vice versa**
- **very intense transitions since they are Laporte and spin allowed (ε ~50,000 compared to <20 L mol^{-1} cm^{-1} for *d-d* transitions)**
- **energies often depends strongly on solvent (*solvatochromic*) since the charge transfer changes the dipole moment of the complex**
  - **this can be used to distinguish between charge transfer bands and *d-d* transitions**

permanganate is intensely purple due to CT from O 2*p* to Mn^{7+} *d*-orbital



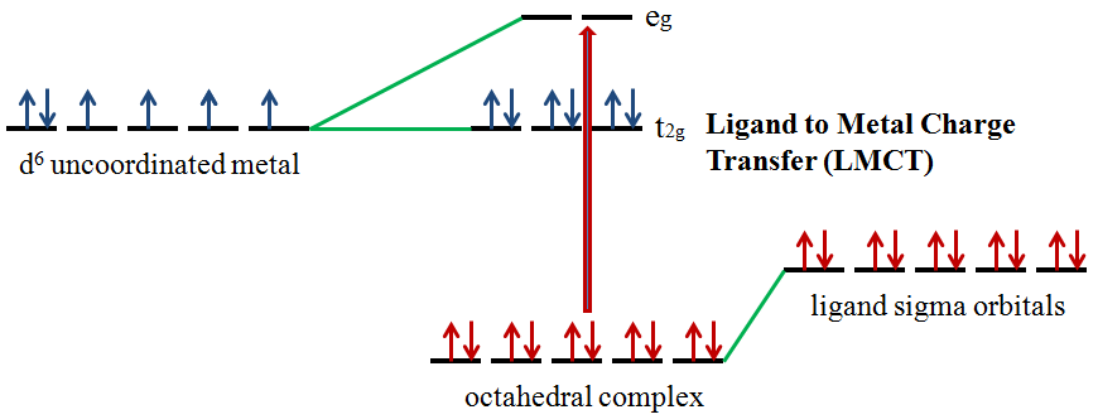
Charge Transfer Transitions

1. metal to ligand CT (MLCT)



- higher energy
- ligand reduced
- metal oxidized

2. ligand to metal CT (LMCT)

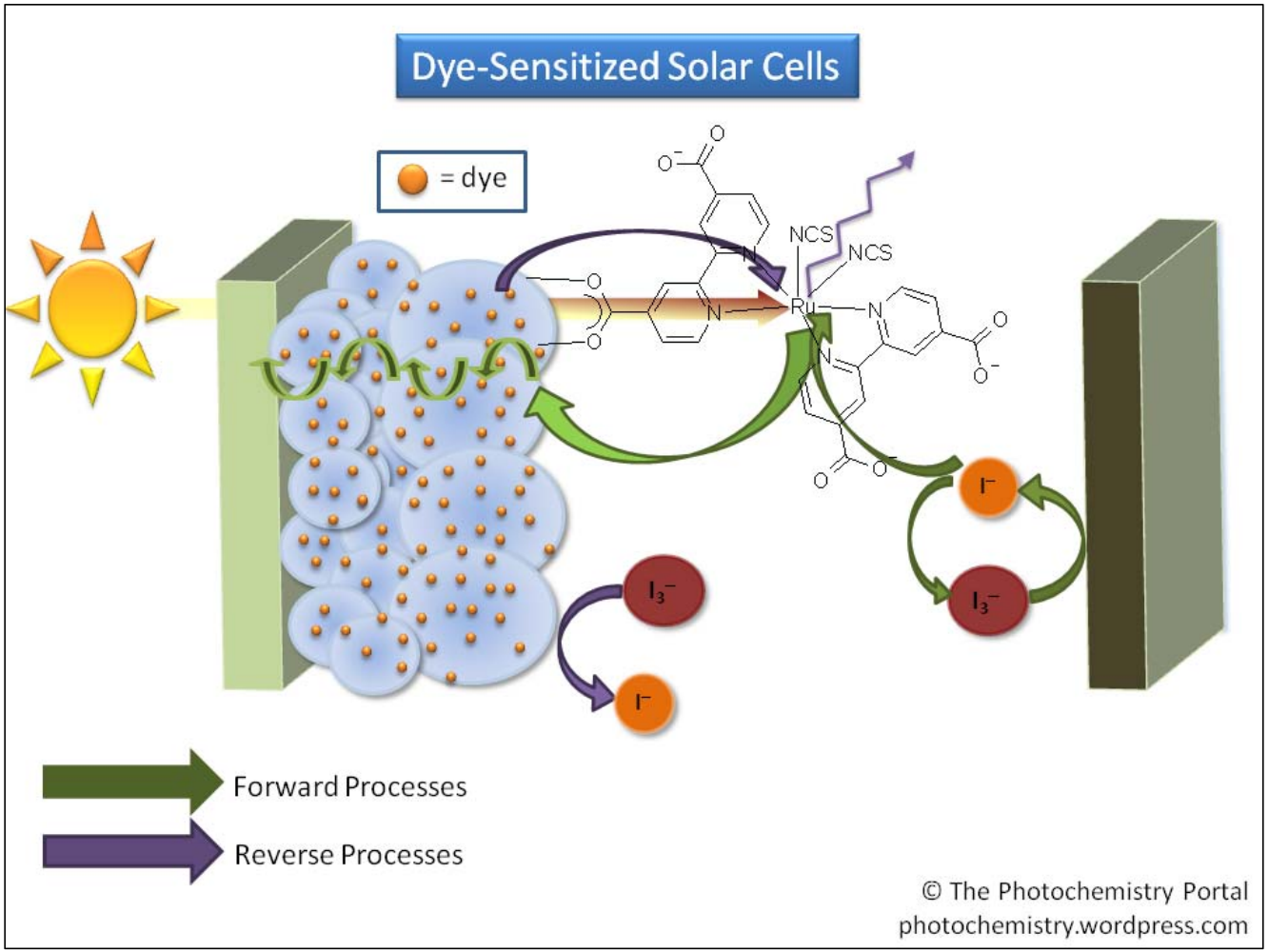


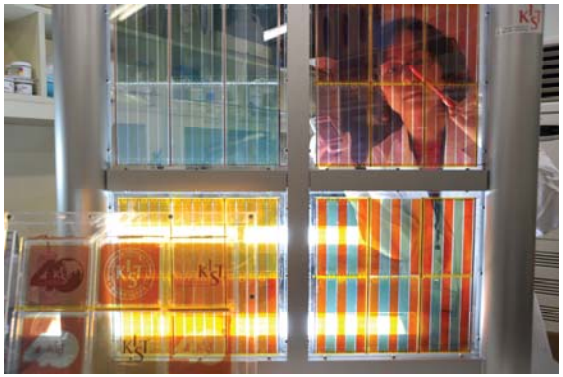
- higher energy
- ligand oxidized
- metal reduced

3. intraligand CT: involves electron transfer within a ligand or between ligands; any energy.

Application of CT: Dye-Sensitized Solar Cells

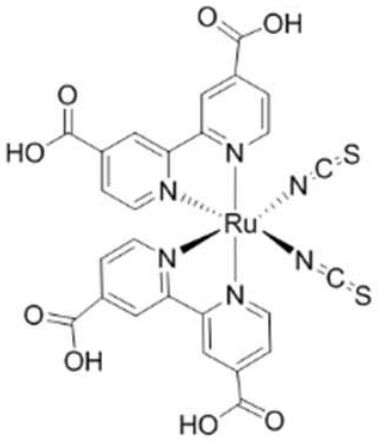
A dye-sensitized solar cell uses an MLCT dye adsorbed on a high surface area TiO_2 nanoparticle film to absorb sunlight and produce electricity.





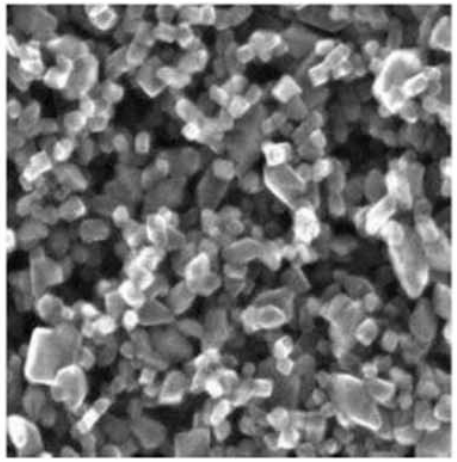
Application of CT: Dye-Sensitized Solar Cells

Sensitizing Dye



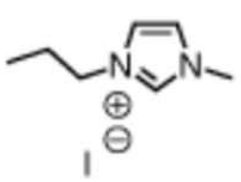
Chemical Structure of N3 Dye

Titania Nanoparticles



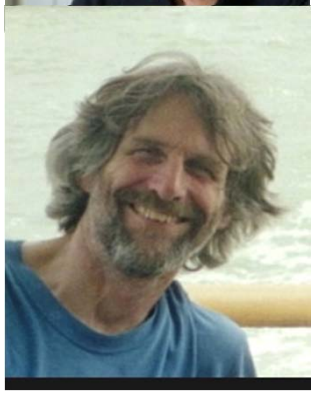
20 nm Titania nanoparticles

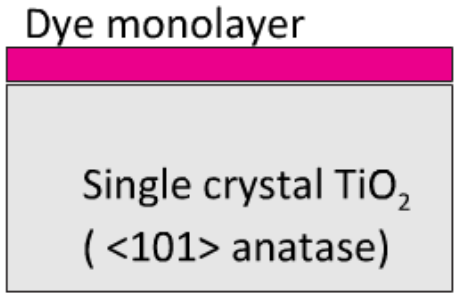
Electrolyte

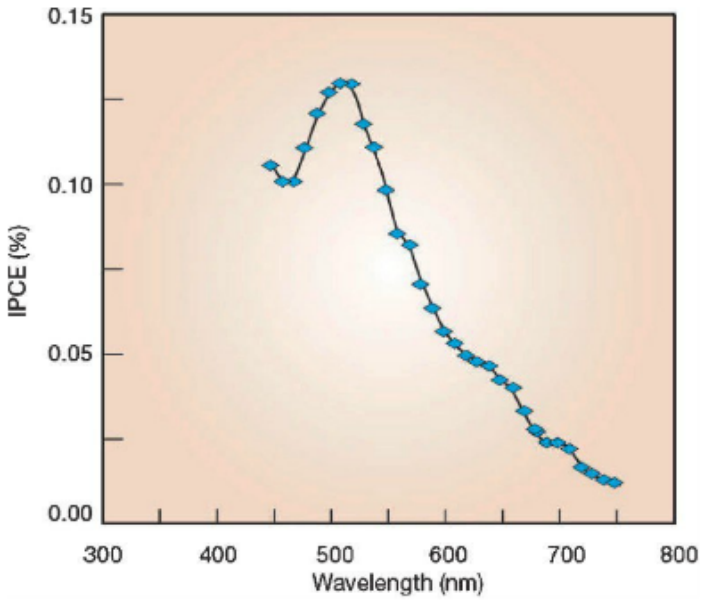


Iodide/Tri-iodide
Redox Couple

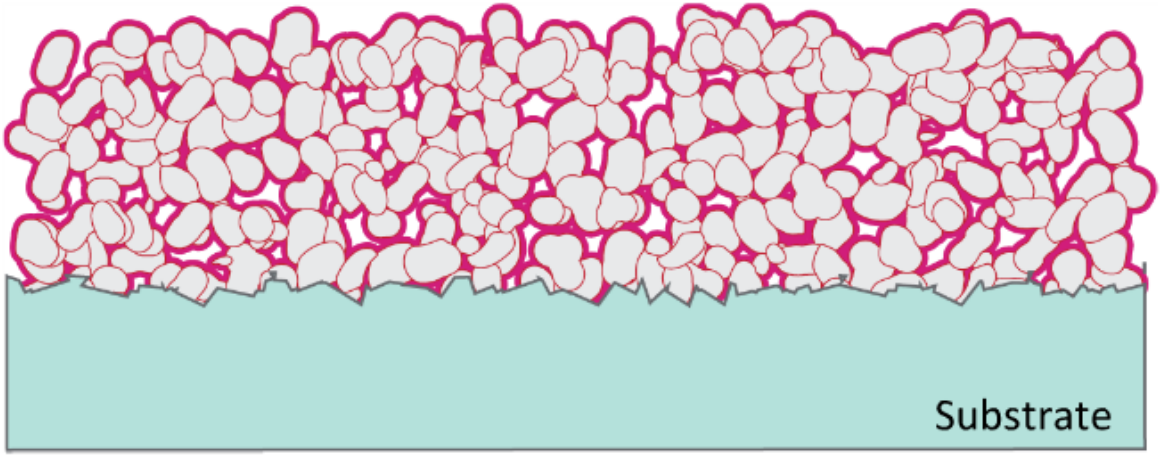
Application of CT: Dye-Sensitized Solar Cells

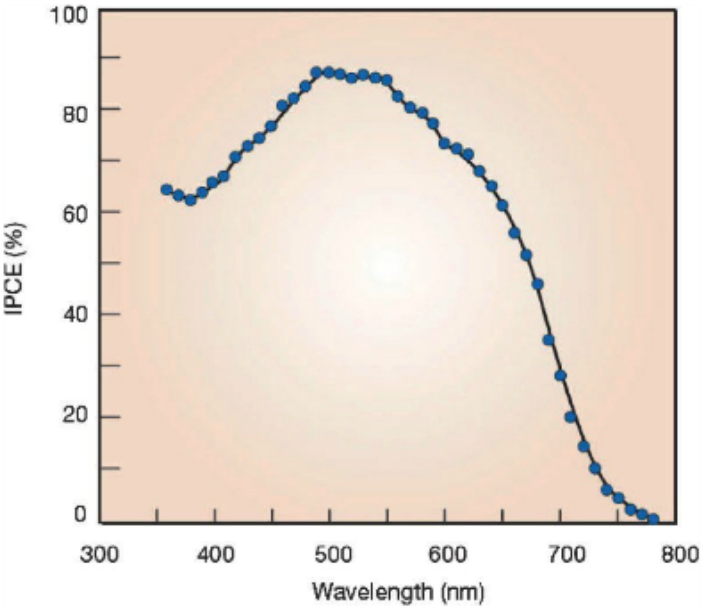






Dye Sensitized Mesoporous anatase TiO_2

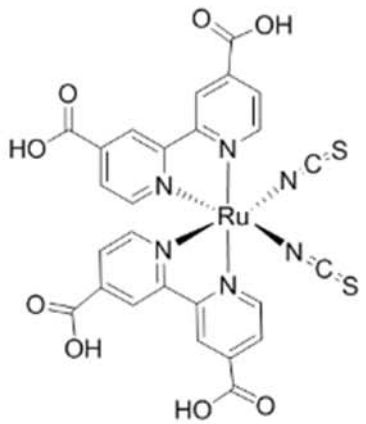




O'Regan and M. Gratzel, Nature ***1991***

Brian E. Hardin, Stanford.

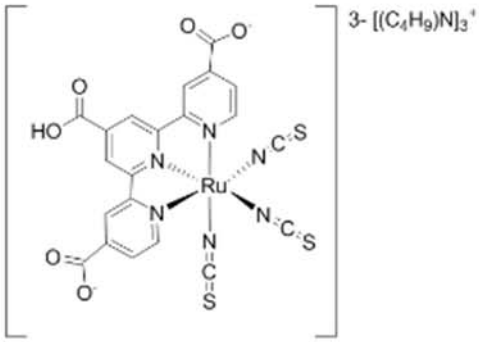
Application of CT: Dye-Sensitized Solar Cells



N3

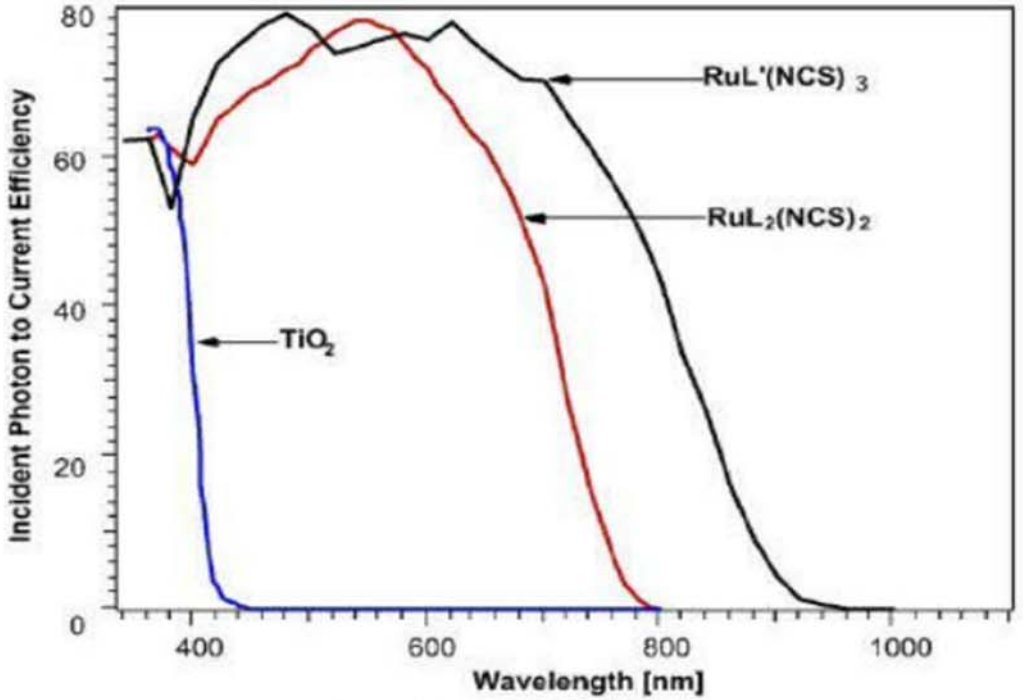
cis-$Ru(SCN)_2L_2$

(L = 2,2-bipyridyl-4,4-dicarboxylate)



N749

tri(cyanato)-2.22-terpyridyl-4,44-tricarboxylate)Ru(II)

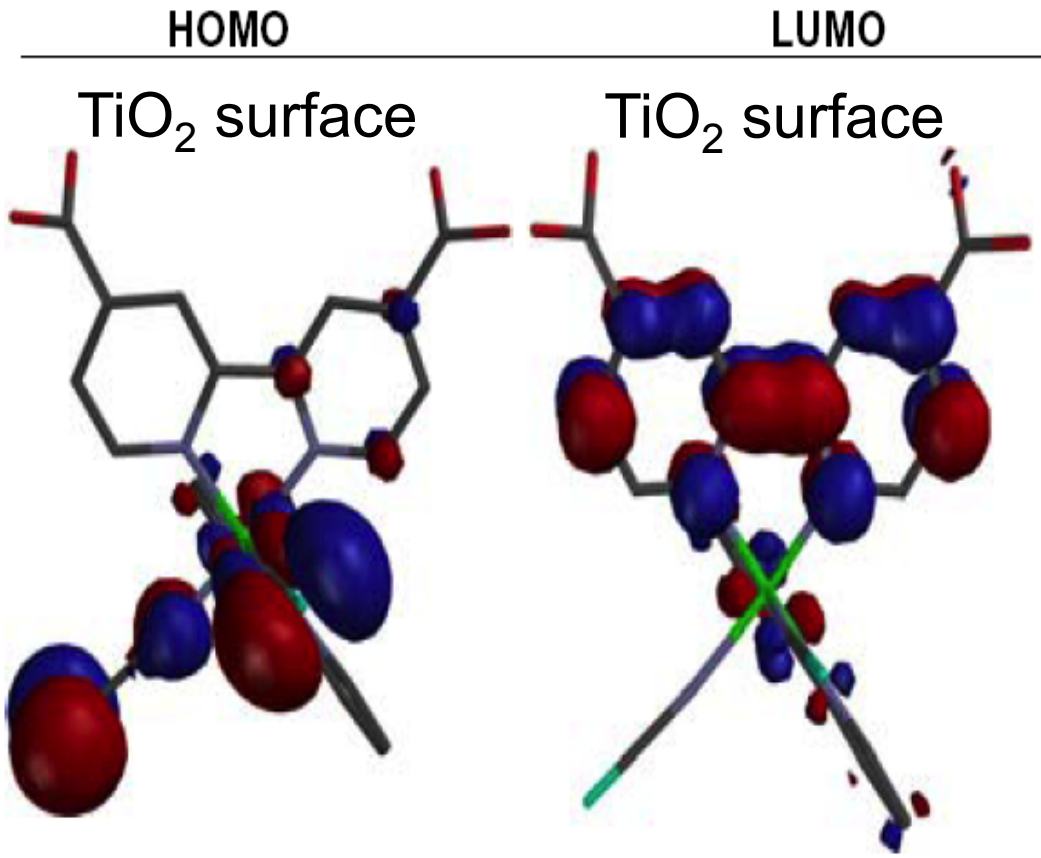


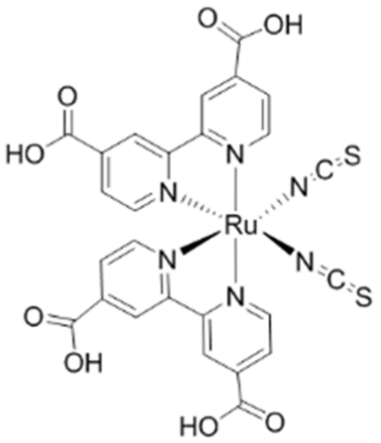
L = 4,4'-COOH-2,2'-bipyridine

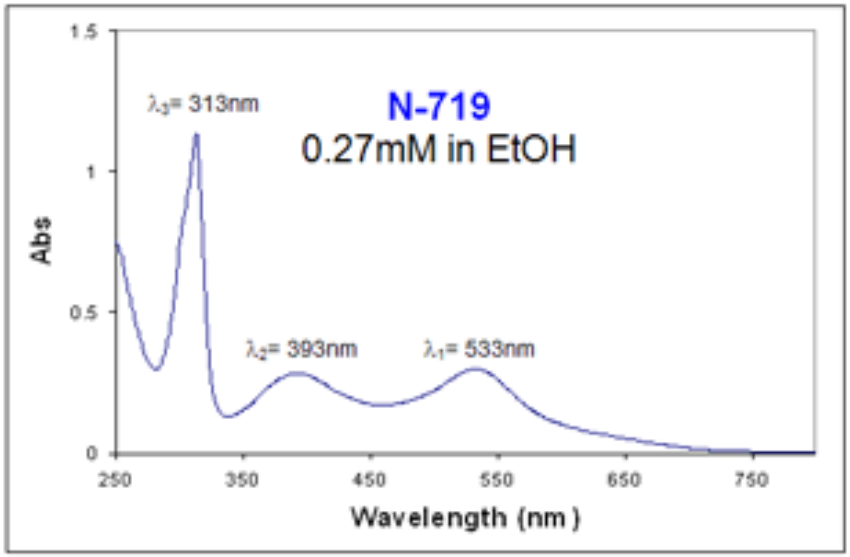
L' = 4,4',4"-COOH-2,2':6',2"-terpyridine

M.K. Nazeeruddin et al., *J. Am. Chem.Soc.* 123, 1613, (2001)

Application of CT: Dye-Sensitized Solar Cells







A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 2000, 33, 2679−27

HOMO localized on electrolyte side, far from TiO_2 surface.
LUMO localized on anchoring ligands, next to TiO_2 surface.
→ rapid electron transfer into TiO_2

Fin

Good luck on the final, have a great break, and see you around campus!