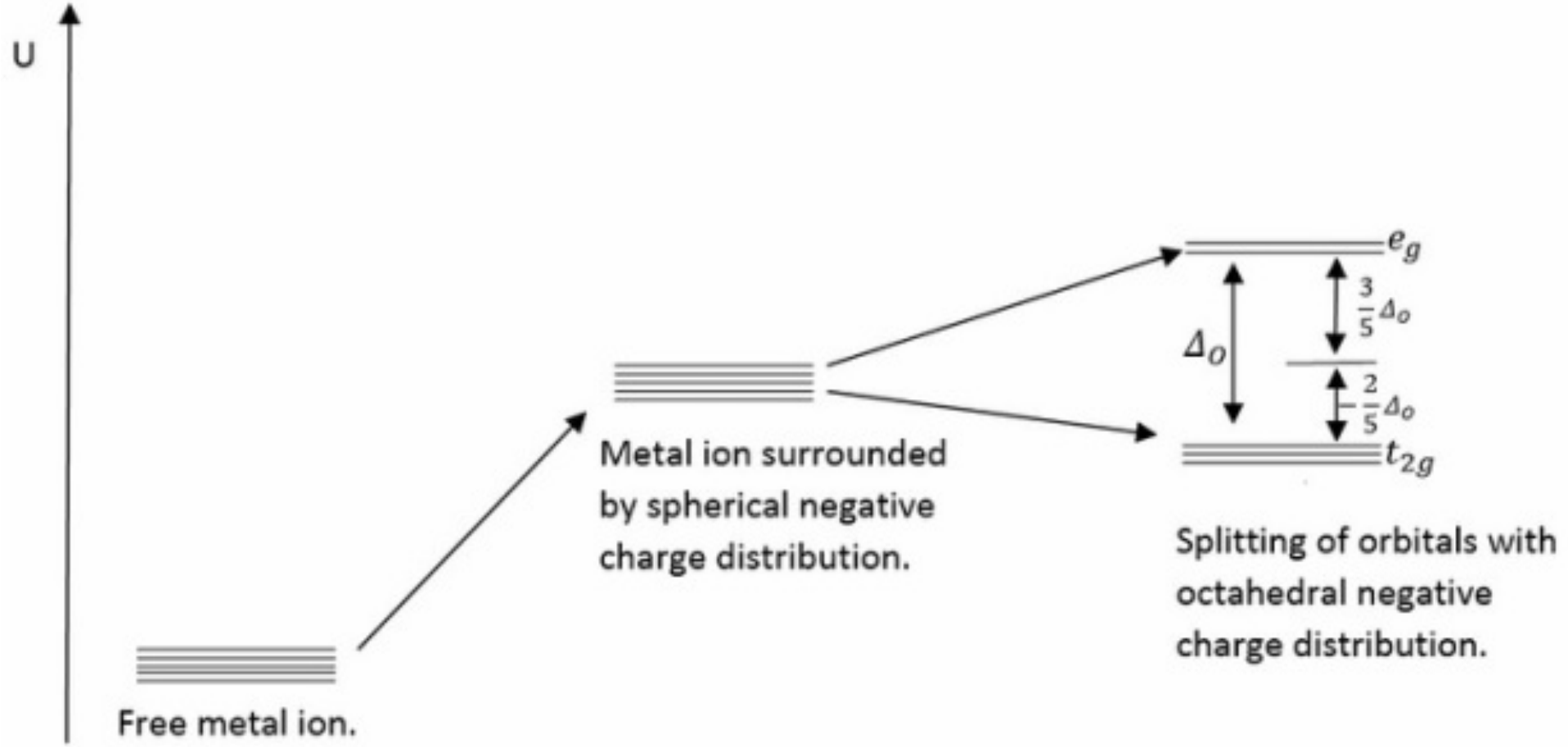
COORDINATION COMPLEXES

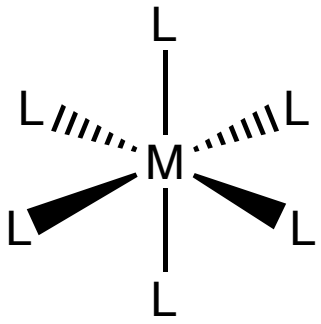
d orbital splitting in octahedral complexes

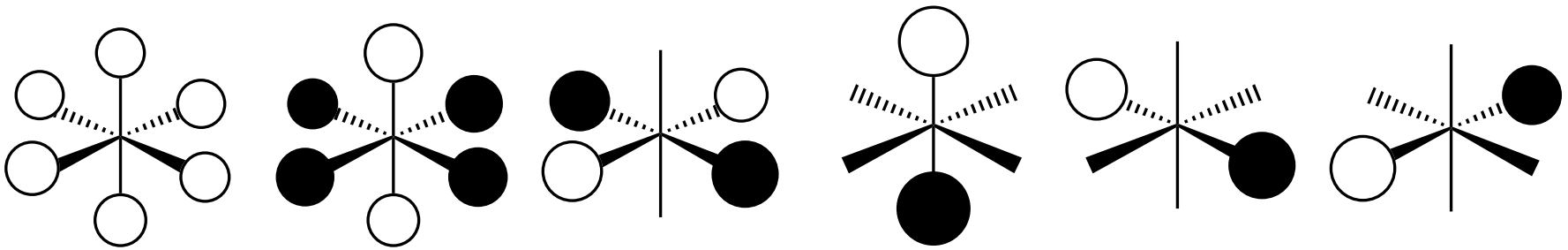
MFT Chapters 6,9,10

Octahedral crystal field splitting



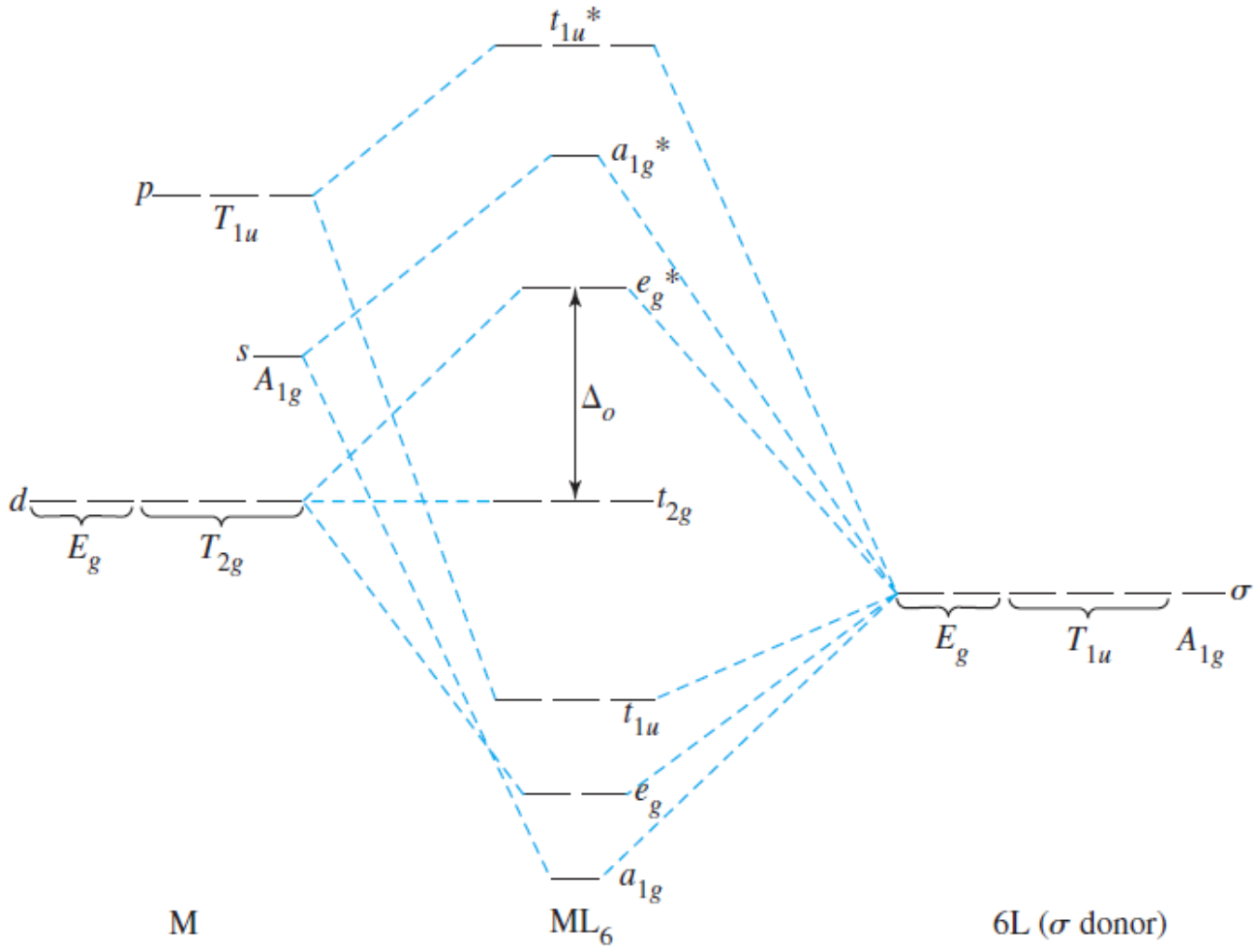
Sigma SALCs for octahedral complexes





4s 3dz2 3dx2-y2 4pz 4px 4py

MO diagram of octahedral metal complex, sigma interactions only



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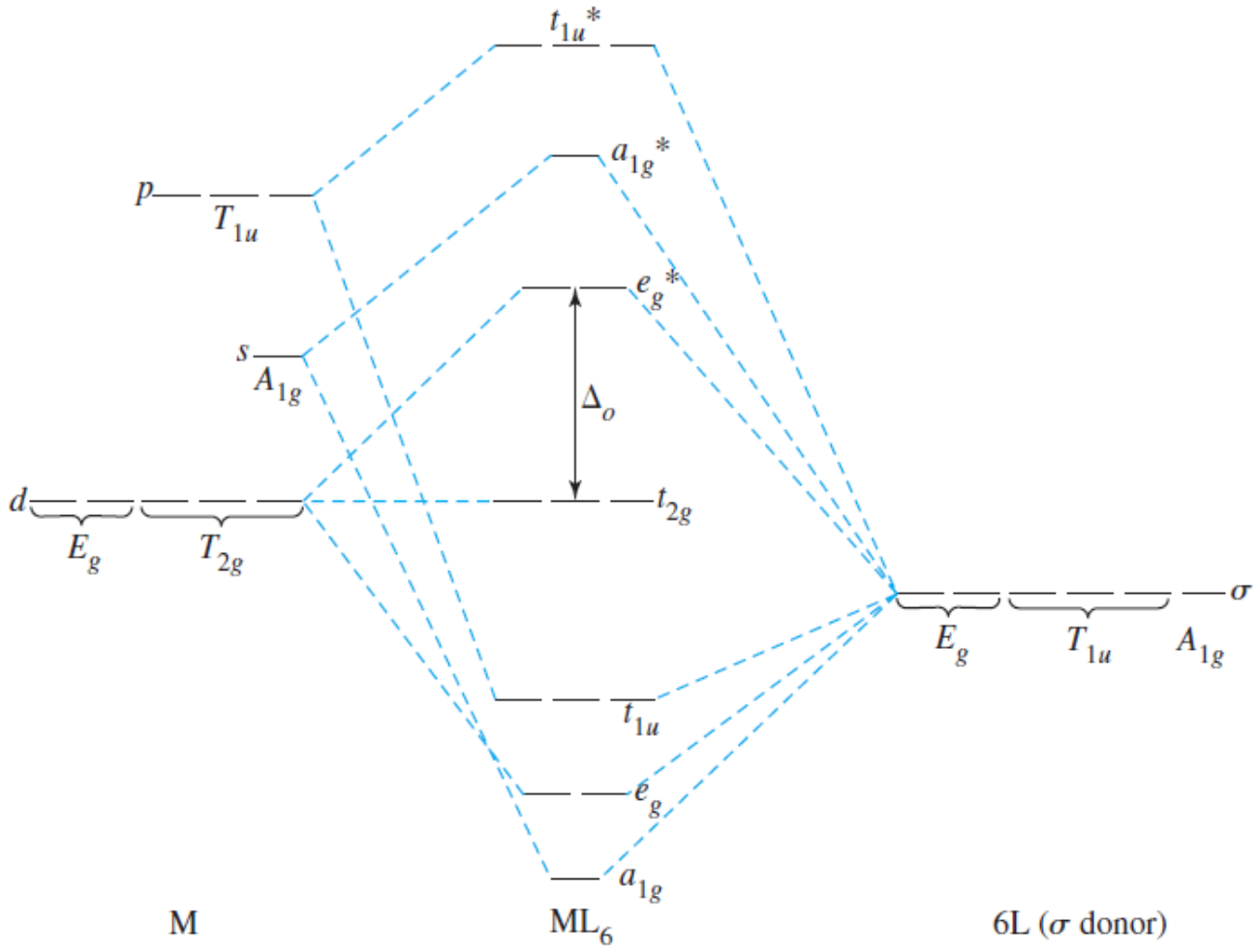
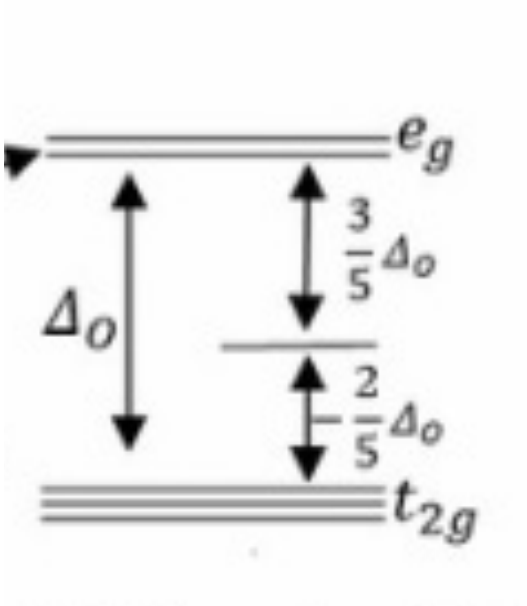
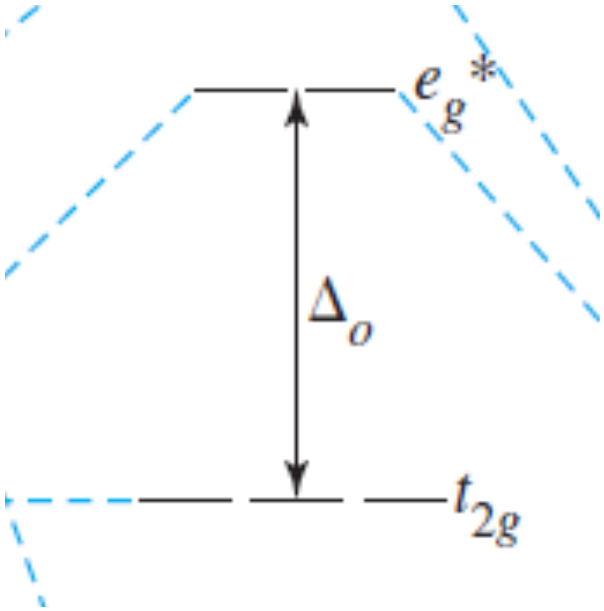


d orbital splitting in octahedral



crystal field theory

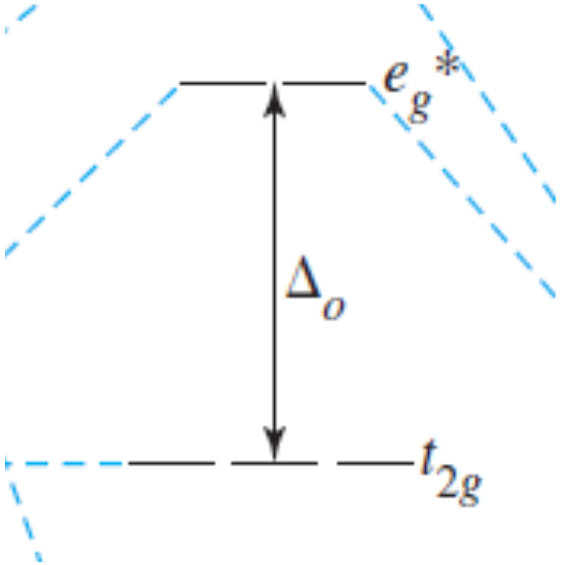


ligand field theory

Δ_o contributes to many different properties of metal complexes

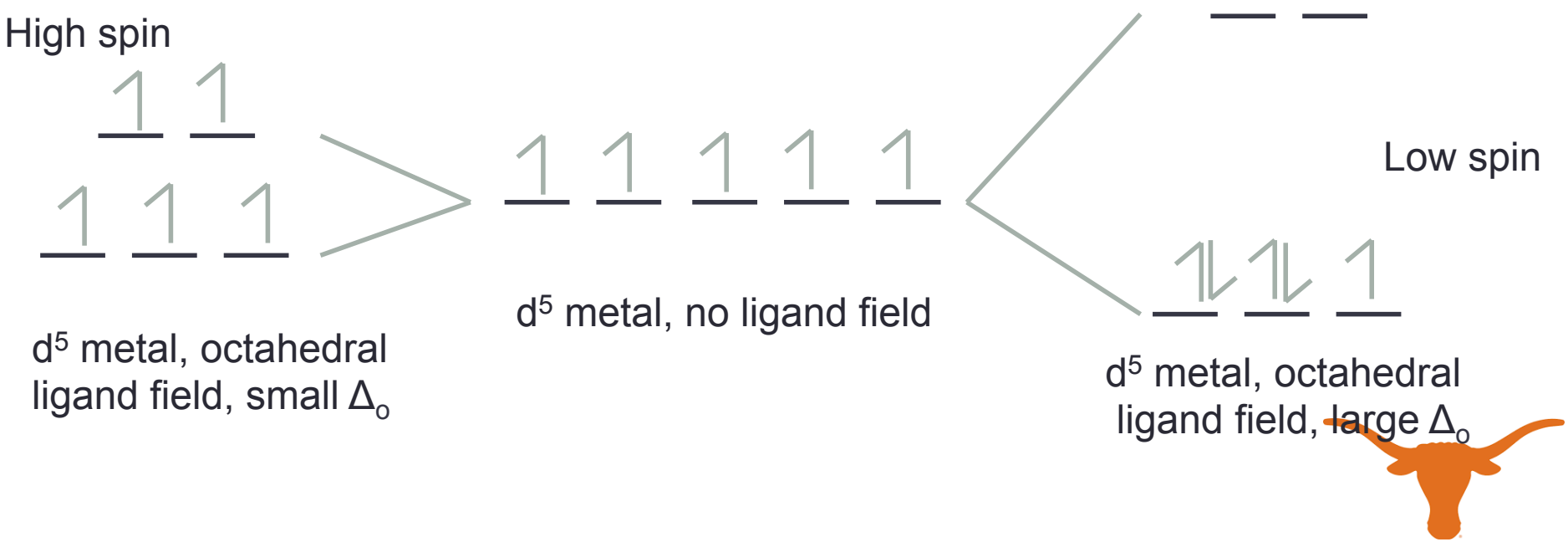
- The magnitude of Δ_o, in other words, the size of the energy gap between the t2g and eg* orbitals, can contribute to many different properties of metal complexes

- **Magnetic moment (high spin vs low spin)**
  - lab this week
- **Electronic spectra (UV-vis)**
  - lab next week
- **Kinetic stability (later lectures…)**

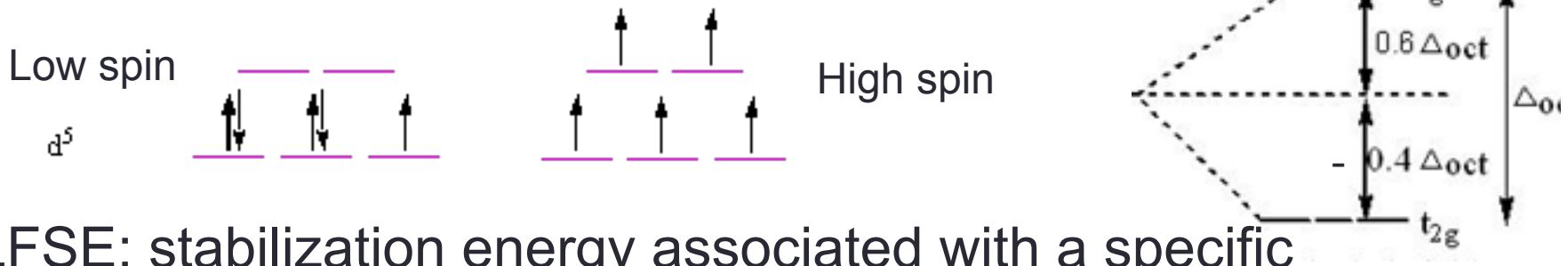


Magnetic moment: High spin vs low spin complexes

- Low spin complexes: electrons fill lower energy d orbitals first (pairing energy < Δ_o)
- High spin complexes: electrons fill into lower and higher energy d orbitals before pairing (pairing energy > Δ_o)



Ligand Field Stabilization Energy (LFSE)



- LFSE: stabilization energy associated with a specific electronic configuration

- LFSE = $(-2/5\Delta_o)$ x (# of t_2g electrons) + $(3/5\Delta_o)$ x (# of e_g electrons)

This is for octahedral geometry! Other geometries will have similar types of calculations but numbers are different

- LFSE for low spin d^5: $(-2/5\Delta_o)*5 = -2\Delta_o$
- LFSE for high spin d^5: $(-2/5\Delta_o)*3 + (3/5\Delta_o)*2 = 0$

- More negative values are more stable, (however if Δ_o is small, so is the LFSE, so h.s. complexes are observed!)

Magnetic susceptibility

- The magnetic properties of a coordination compound help determine number of unpaired electrons in a compound
- Helps us indirectly understand orbital energy levels and how electrons fill the orbitals
- d orbitals are all the same energy in a free atom or ion, BUT once you put them in a coordination environment, the relative energy of the different orbitals can change
- This results in a varied numbers of unpaired electrons depending on metal ion and its coordination environment

Magnetic susceptibility

- **Diamagnetic** compounds contain zero unpaired electrons
  - Diamagnetic compounds are slightly repelled by a magnetic field
- **Paramagnetic** compounds contain one or more unpaired electrons
  - Paramagnetic compounds are attracted into a magnetic field
- Magnetic susceptibility (χ^2) is the measure of this magnetism
- Higher susceptibility = more unpaired electrons

Magnetic moment

Magnetic moment is the quantity that describes the torque a molecule or object will experience in an external magnetic field

$$\mu = 2.828(\chi T)^{1/2}$$

μ: magnetic moment in Bohr magnetons (μ_B)

χ: magnetic susceptibility (cm^3/mol)

T: temperature (in Kelvin)

$1\ \mu_B = 9.27 \times 10^{-24}$ joules/tesla

Magnetic moment

- Electrons (negative charges in motion) behave like tiny magnets, generate a spin magnetic moment
- $\mu_s = -1/2$ 'negative' electron spin
- $\mu_s = +1/2$ 'positive' electron spin
- Total spin magnetic moment = S = sum of μ_s values = spin quantum number

- Orbital angular momentum can also affect magnetism
- Orbital quantum number = L = sum of m_l

Calculating magnetic moment

$$\mu_{S+L} = g\sqrt{[S(S+1)] + \tfrac{1}{4}[L(L+1)]}$$

μ = magnetic moment

g = gyromagnetic ratio (= 2.00023 μ_B/Bohr magnetons)

S = spin quantum number

L = orbital quantum number

Orbital contribution (L) is more important in molecules containing larger orbitals (metals from 4d, 5d…)

Spin only magnetic moment

$\mu_S = g\sqrt{[S(S+1)]}$

You must know this equation!

μ = magnetic moment

g = gyromagnetic ratio (= 2.00023 μ_B/Bohr magnetons)

S = spin quantum number

Orbital contribution (L) is more important in molecules containing larger orbitals (metals from 4d, 5d, 4f…)

TABLE 10.3 Calculated and Experimental Magnetic Moments

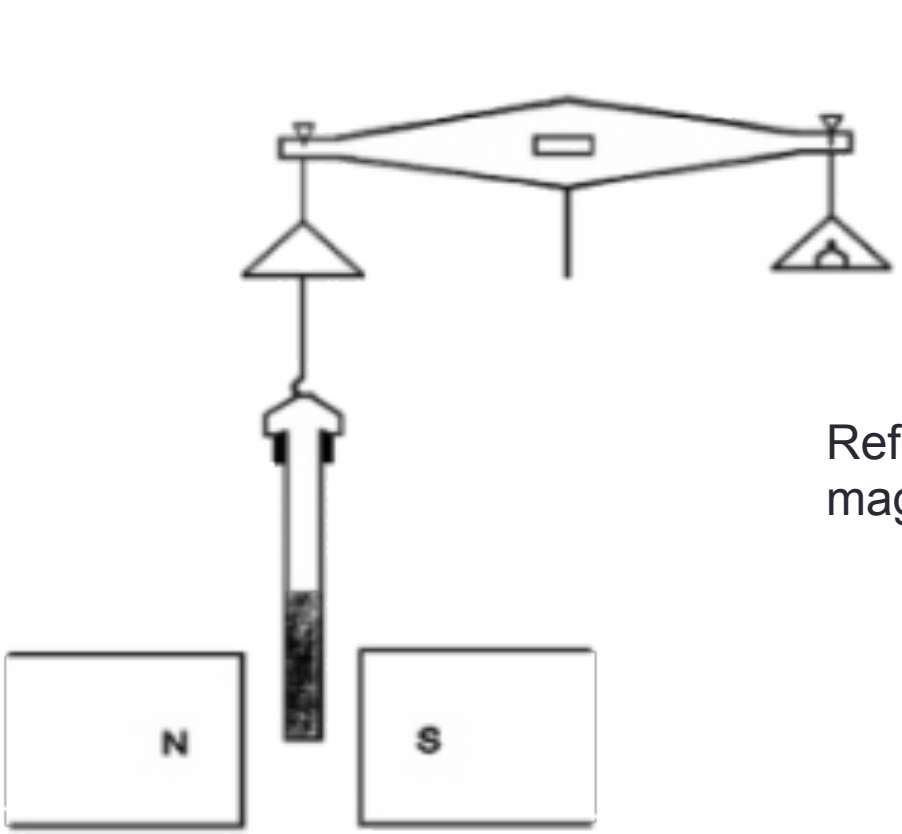
Ion	n	S	L	μ_S	μ_{S+L}	Observed
V^{4+}	1	$\frac{1}{2}$	2	1.73	3.00	1.7–1.8
Cu^{2+}	1	$\frac{1}{2}$	2	1.73	3.00	1.7–2.2
V^{3+}	2	1	3	2.83	4.47	2.6–2.8
Ni^{2+}	2	1	3	2.83	4.47	2.8–4.0
Cr^{3+}	3	$\frac{3}{2}$	3	3.87	5.20	~3.8
Co^{2+}	3	$\frac{3}{2}$	3	3.87	5.20	4.1–5.2
Fe^{2+}	4	2	2	4.90	5.48	5.1–5.5
Co^{3+}	4	2	2	4.90	5.48	~5.4
Mn^{2+}	5	$\frac{5}{2}$	0	5.92	5.92	~5.9
Fe^{3+}	5	$\frac{5}{2}$	0	5.92	5.92	~5.9

Data from F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, 1980, pp. 627–628.

NOTE: All moments are given in Bohr magnetons.

Guoy balance

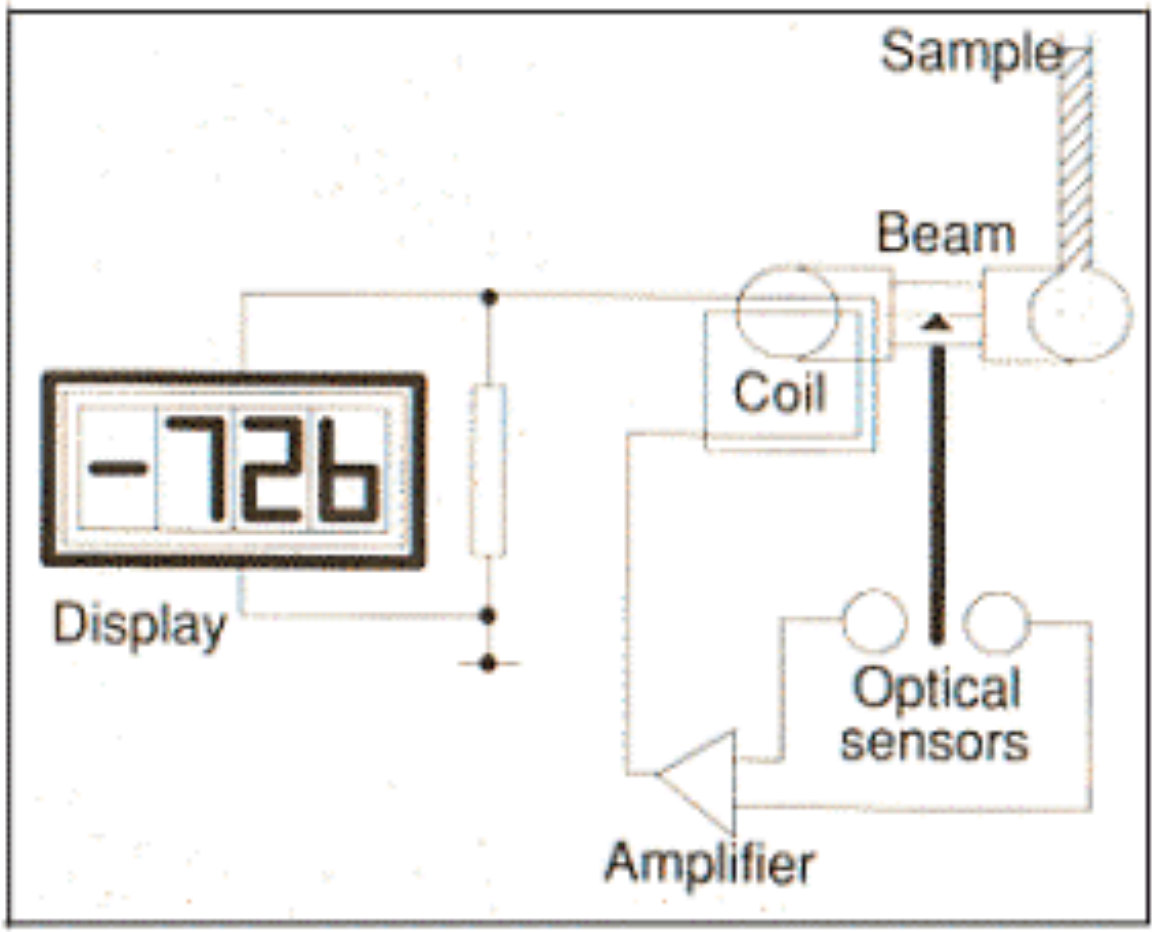
- Old method for measuring μ



Refer to MFT to read up on how magnetic moment is measured

Evans susceptibility balance

- More modern method for measuring μ



Moving Magnetic Field and Null Point Detection

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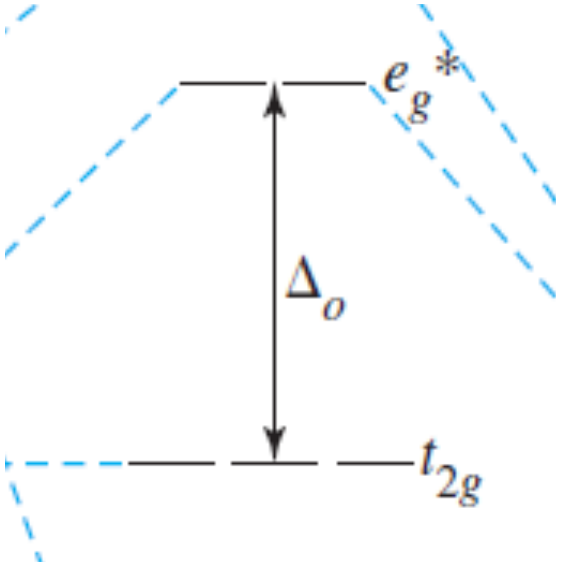
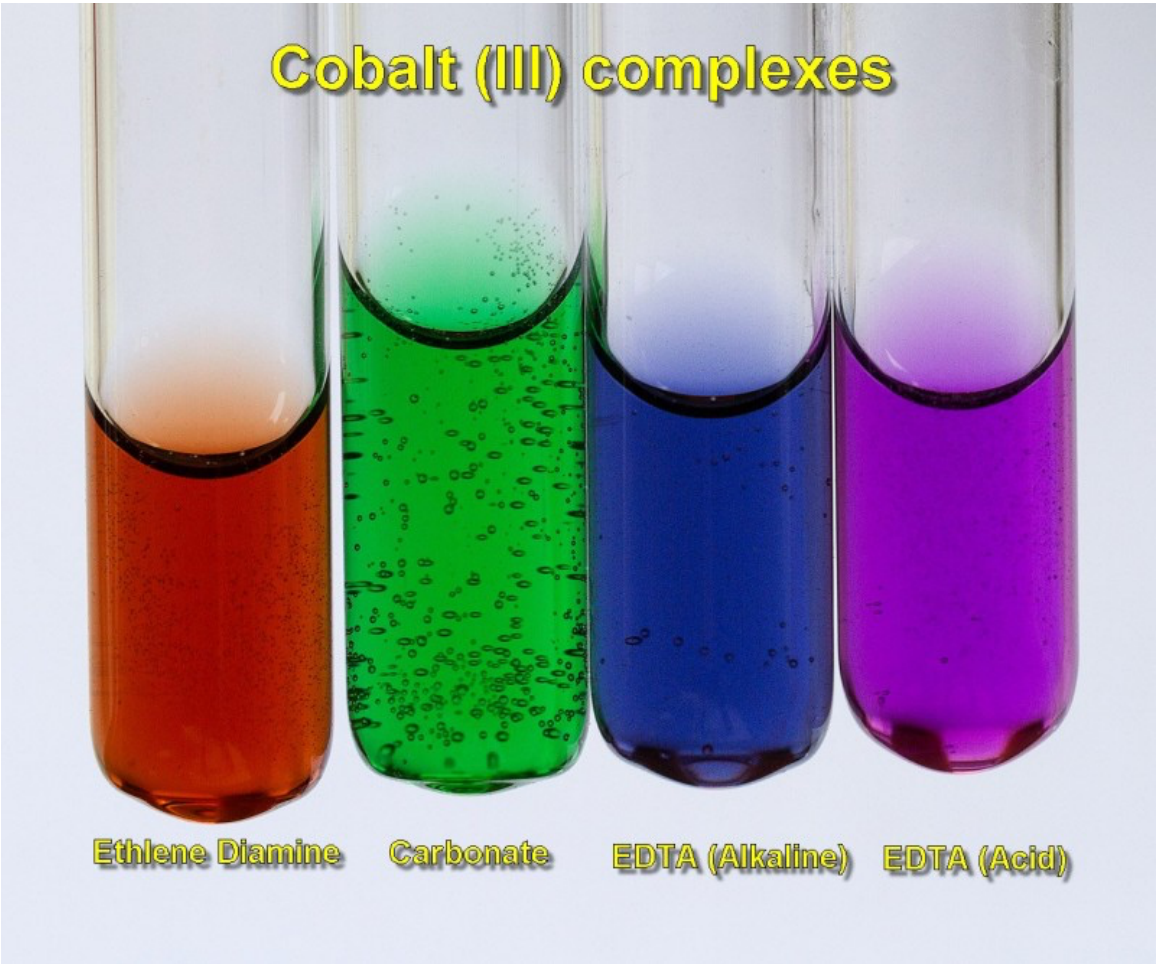


Electronic spectra

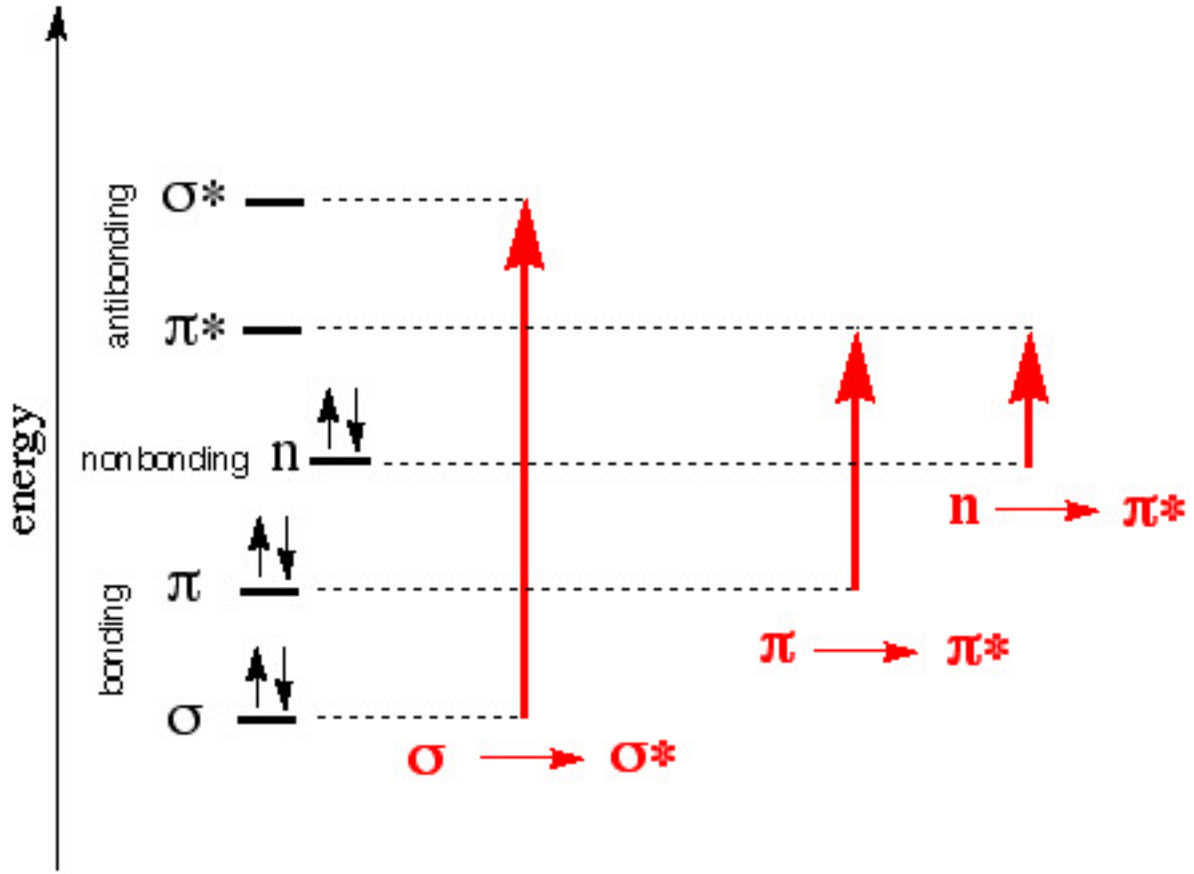
- Electronic spectra (UV-vis) can give you information about the orbital energy levels in a coordination complex

- Different colors are due to different electronic transitions, different structures in complexes



What kind of electronic transitions make up a UV-vis spectrum?

- UV-vis spectra show transitions of electrons from one orbital to another.



What transitions give rise to colors in metal complexes?

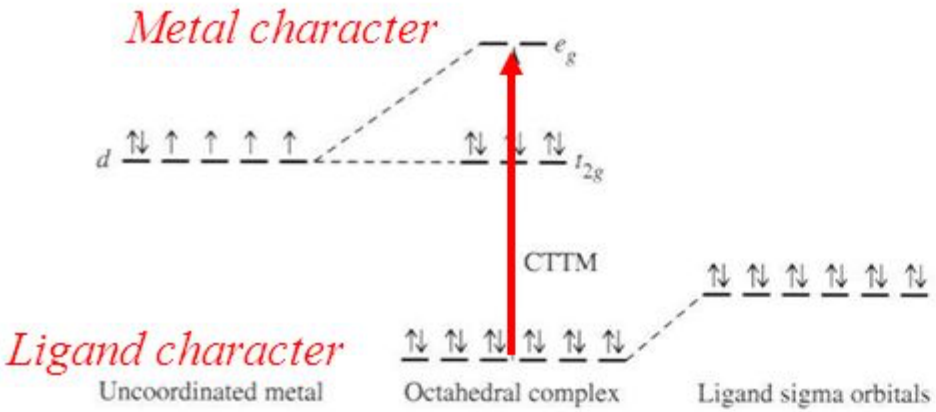
- Ligand to metal charge transfer (LMCT)
- Metal to ligand charge transfer (MLCT)

- Both are transitions between orbitals with more ligand character and orbitals with more metal character

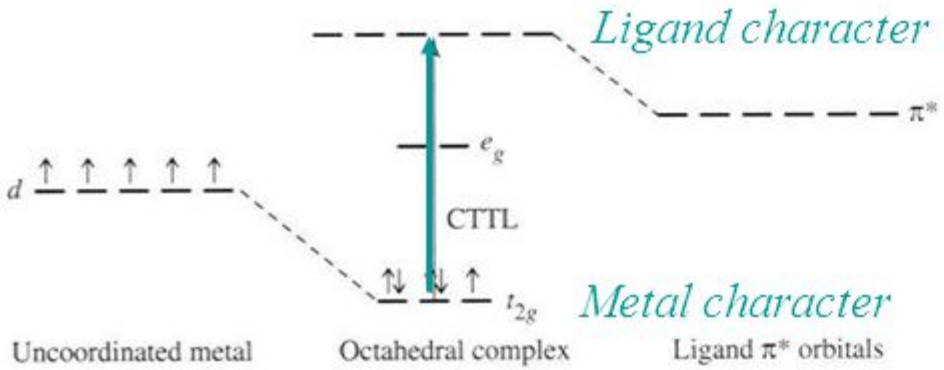
- If they exist in the complex, these tend to be strong absorbances (extinction coefficient is large, ε = 500-10,000 $M^{-1}cm^{-1}$)

- Remember: $A = \varepsilon bc$
- (A is absorbance, b is pathlength, c is concentration)

Charge transfer spectra



LMCT



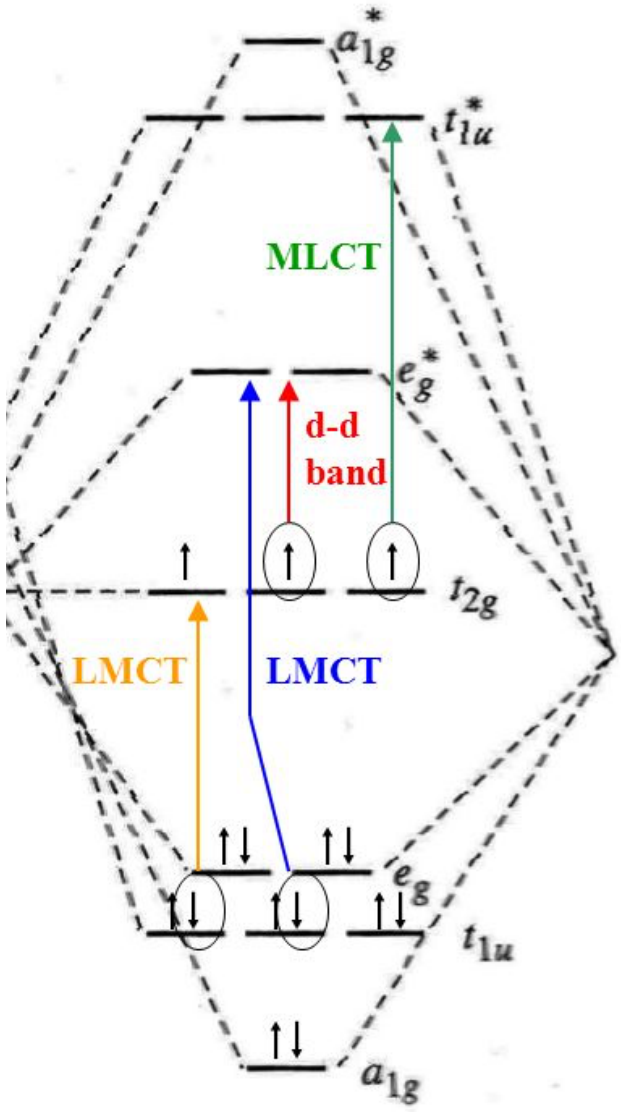
MLCT

Much more intense bands

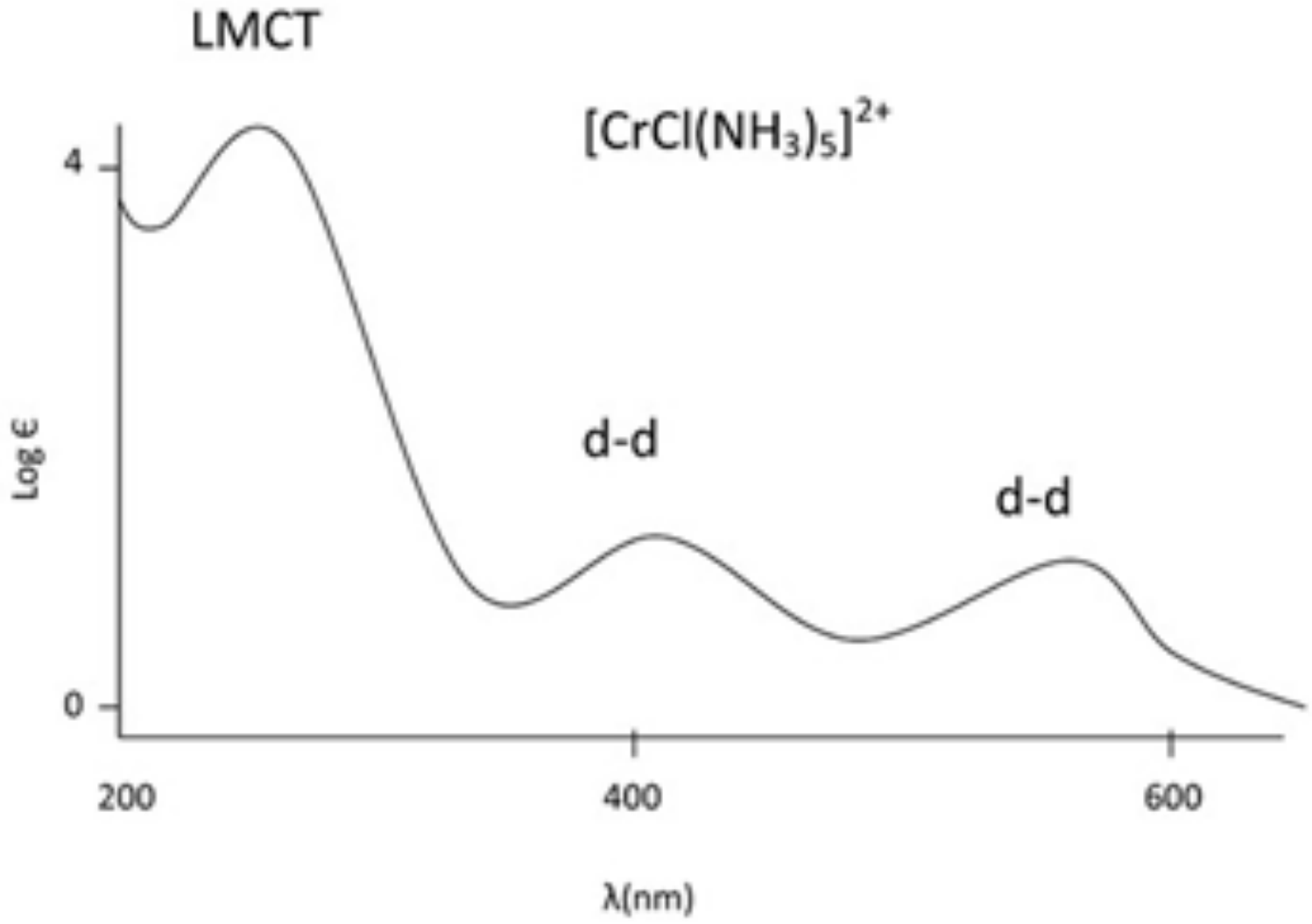
What transitions give rise to colors in metal complexes?

- For this class, we are most interested in **d-d transitions**, which relate to Δ_o
- These transitions are *forbidden* by quantum mechanics because quantum number l does not change

- However, they happen anyway, although their ε values are low (ε ~100 $M^{-1}cm^{-1}$ or lower)

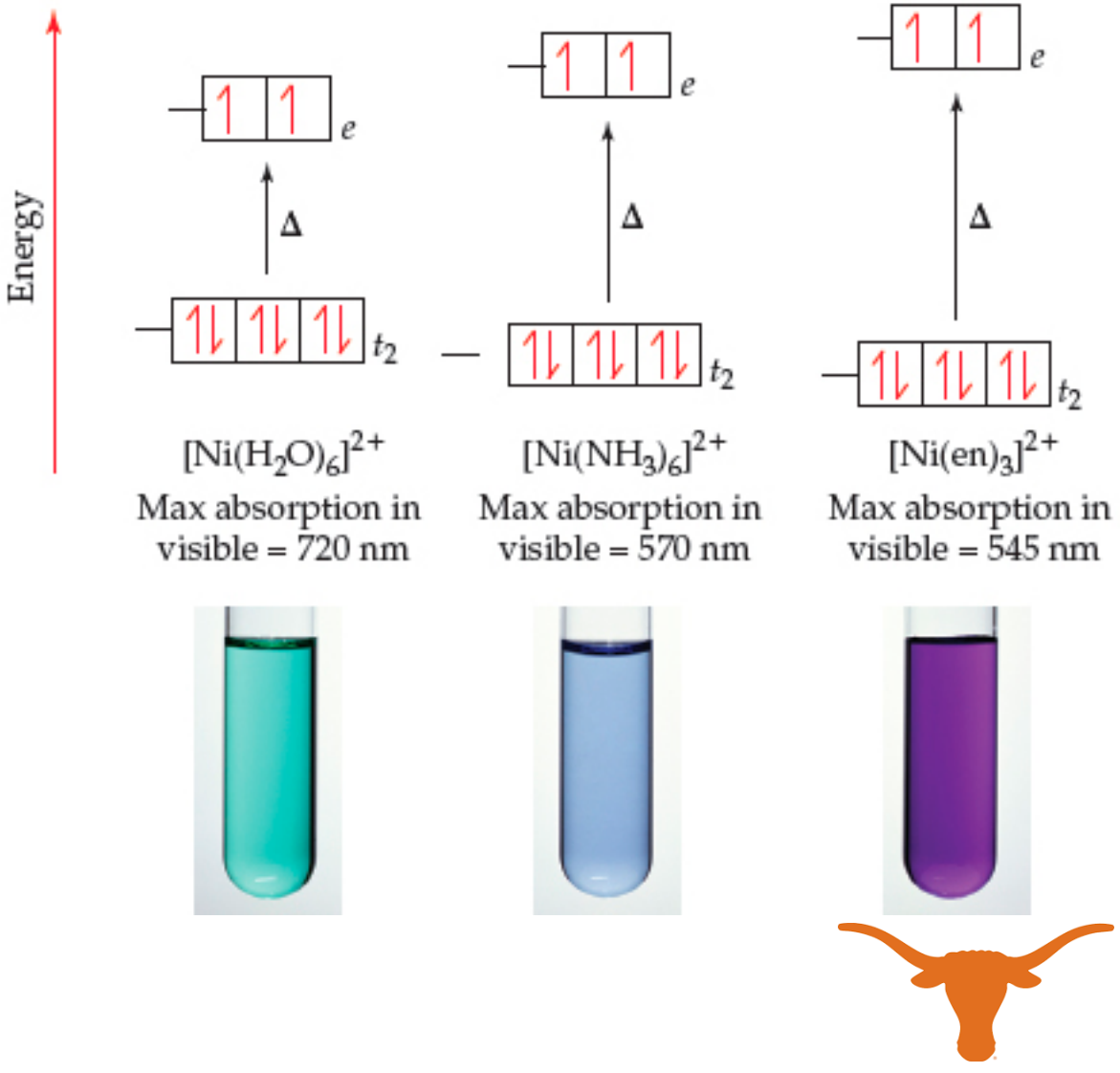


What transitions give rise to colors in metal complexes?



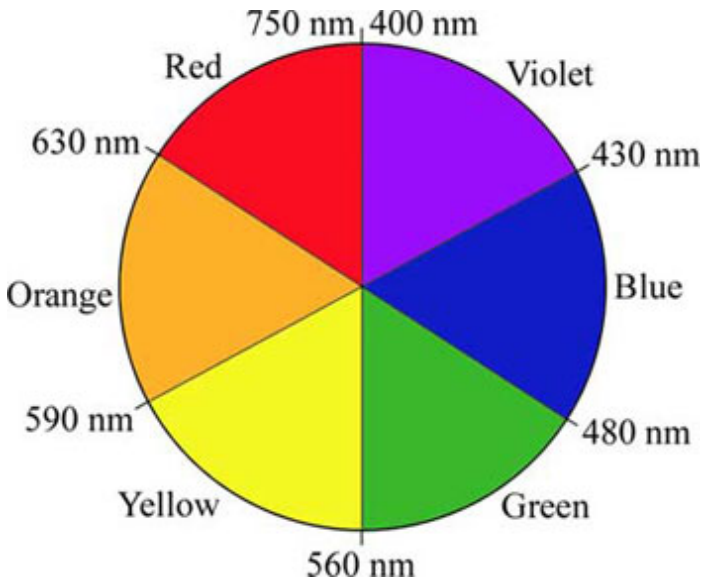
Electronic spectra: UV-vis

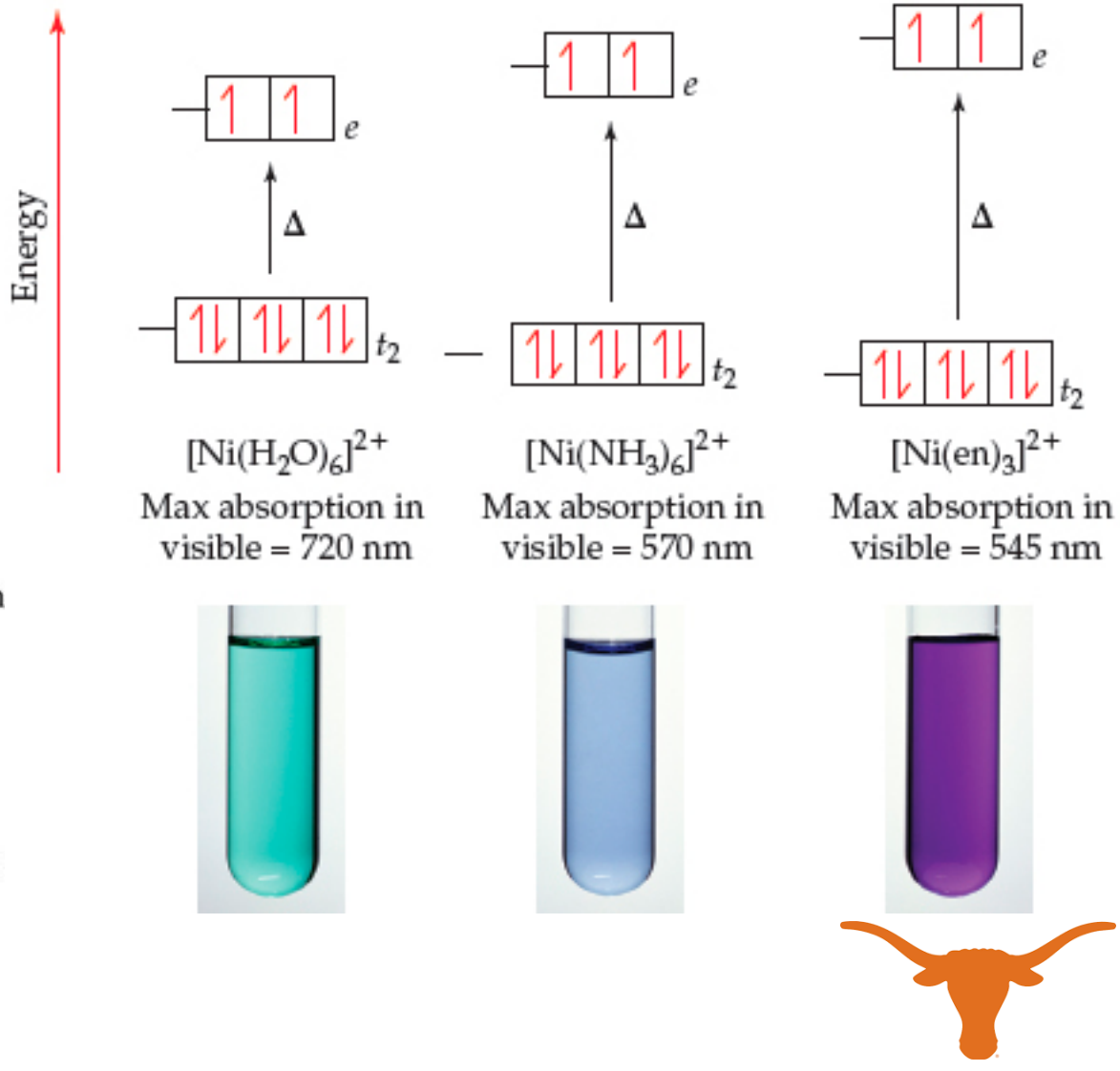
- Observation: three octahedral nickel complexes have three different colors.
- This is due to the fact that each of has a different Δ_o
- As splitting increases, energy difference increases, and the wavelength of light required for the electronic transition from t_{2g} to e_g gets shorter.



Electronic spectra: UV-vis

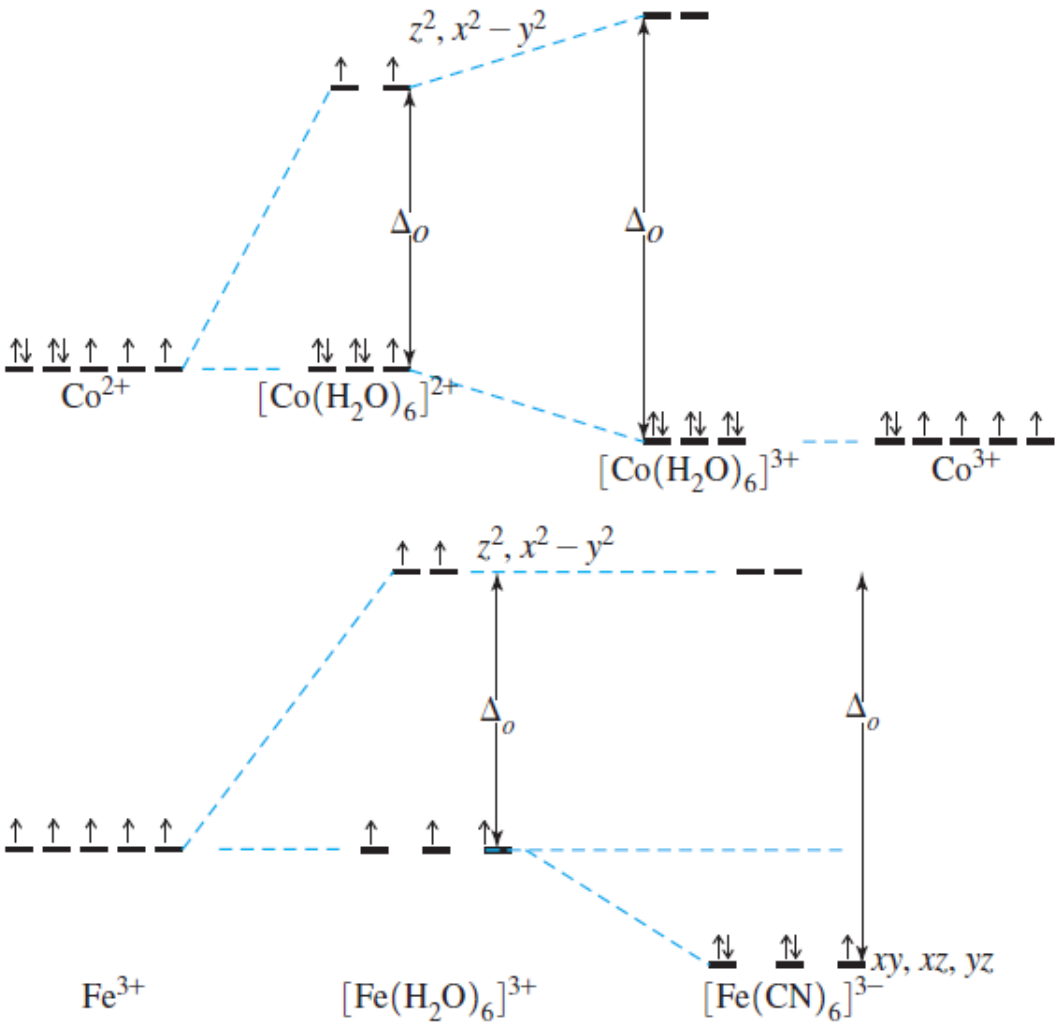
- Remember: color of light absorbed by the compound is complementary to the color it is (see color wheel)





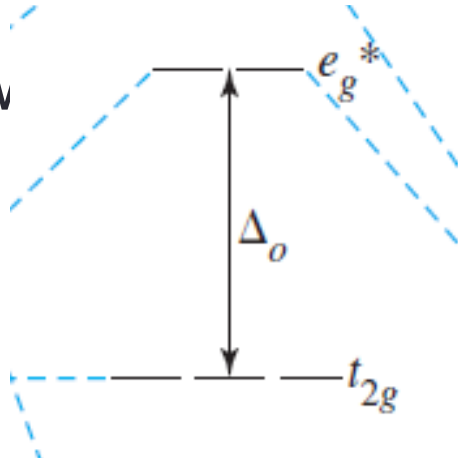
What factors contribute to different Δ_o values?

- Nature of the metal **M**
- Nature of the ligand **L**
- The coordination environment (will discuss soon)



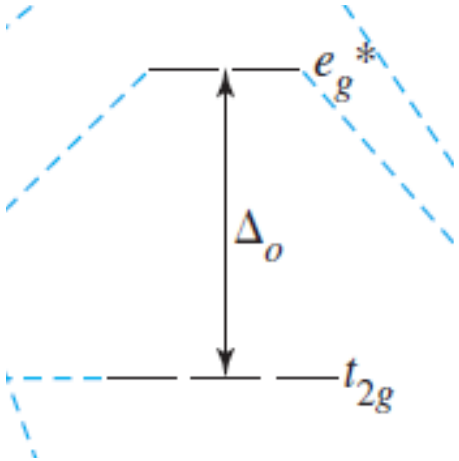
Octahedral d-d splitting

- For **M**:
  - Δ_o increases with increasing charge on metal (shorter, stronger bonds = more interaction = more splitting)
    - Δ_o (Fe^{2+}) < Δ_o (Fe^{3+})
  - Δ_o increases going down a group (larger d orbitals = more interaction with ligands = more splitting)
    - Δ_o (Fe^{2+}) < Δ_o (Ru^{2+})
    - Note: 4d, 5d metals typically have only low configurations because of their large Δ_o



Octahedral d-d splitting

- For **L**:
  - Δ_o will depend on a number of characteristics of the ligand, most importantly, whether it can interact with the metal as a
    - sigma-only donor
    - sigma and pi donor
    - sigma donor and pi acceptor



The spectrochemical series

Next week's lab will explore this!

- The spectrochemical series ranks ligands in the order of their 'field strength'

The complexes of cobalt (III) show the shift in color due to the ligand.

(a) CN^- (b) NO_2^- (c) phen (d) en (e) NH_3

(f) gly (g) H_2O (h) ox^{2-} (i) CO_3^{2-}

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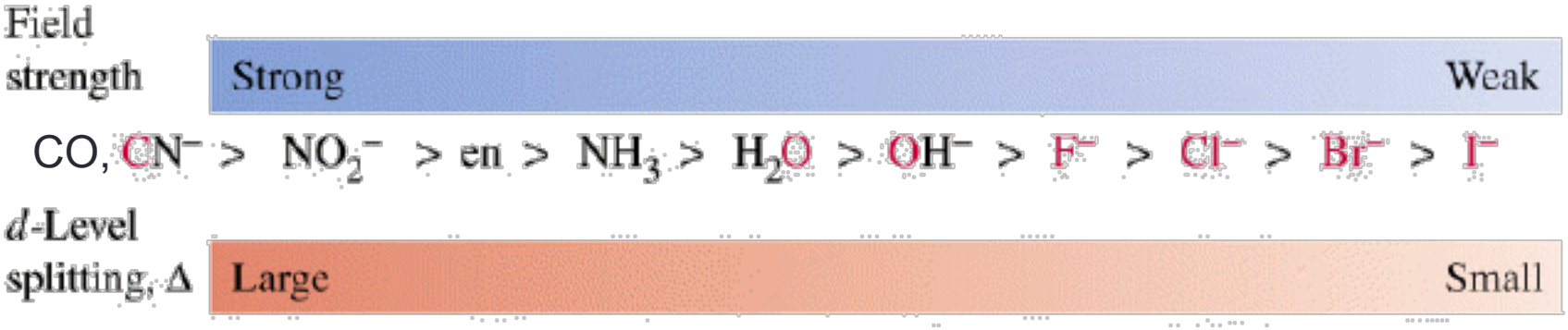

- Strong field ligands produce complexes with a large Δ_o
- Weak field ligands produce complexes with a small Δ_o

- Strong field ligands are pi acceptors, weak field ligands are pi donors