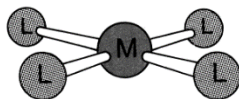
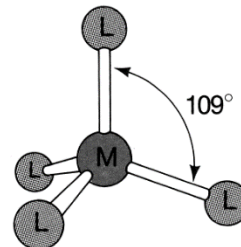


Geometric and Electronic Structures of Complexes

Coordination number 4

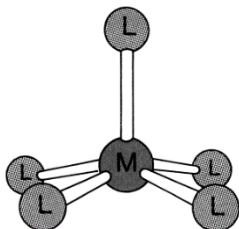


Square planar

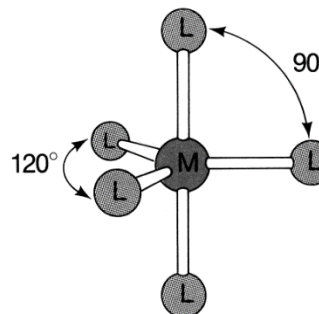


Tetrahedral

Coordination number 5

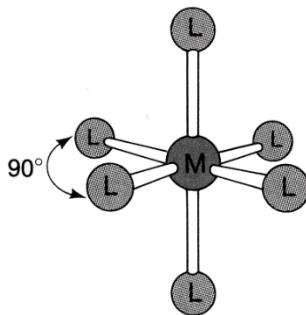


Square pyramidal



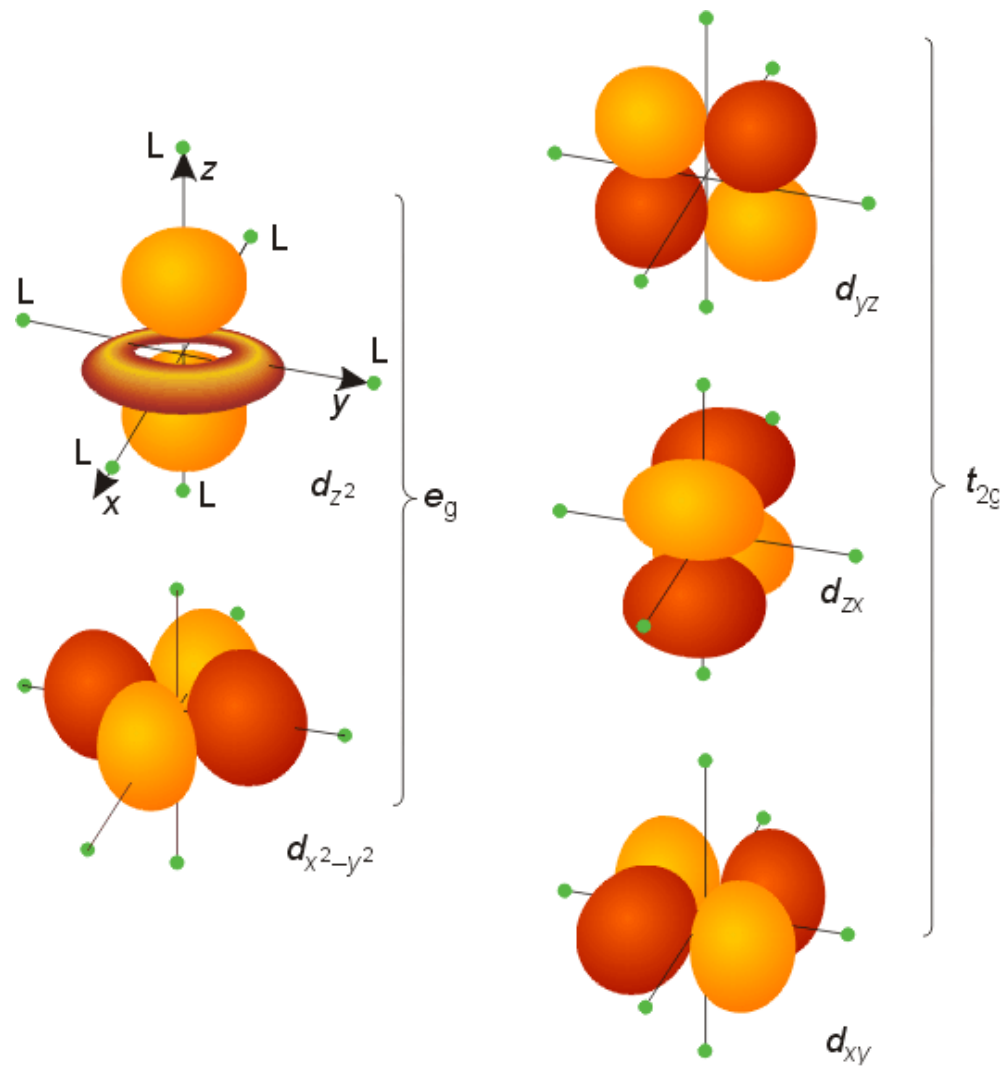
Trigonal bipyramidal

Coordination number 6



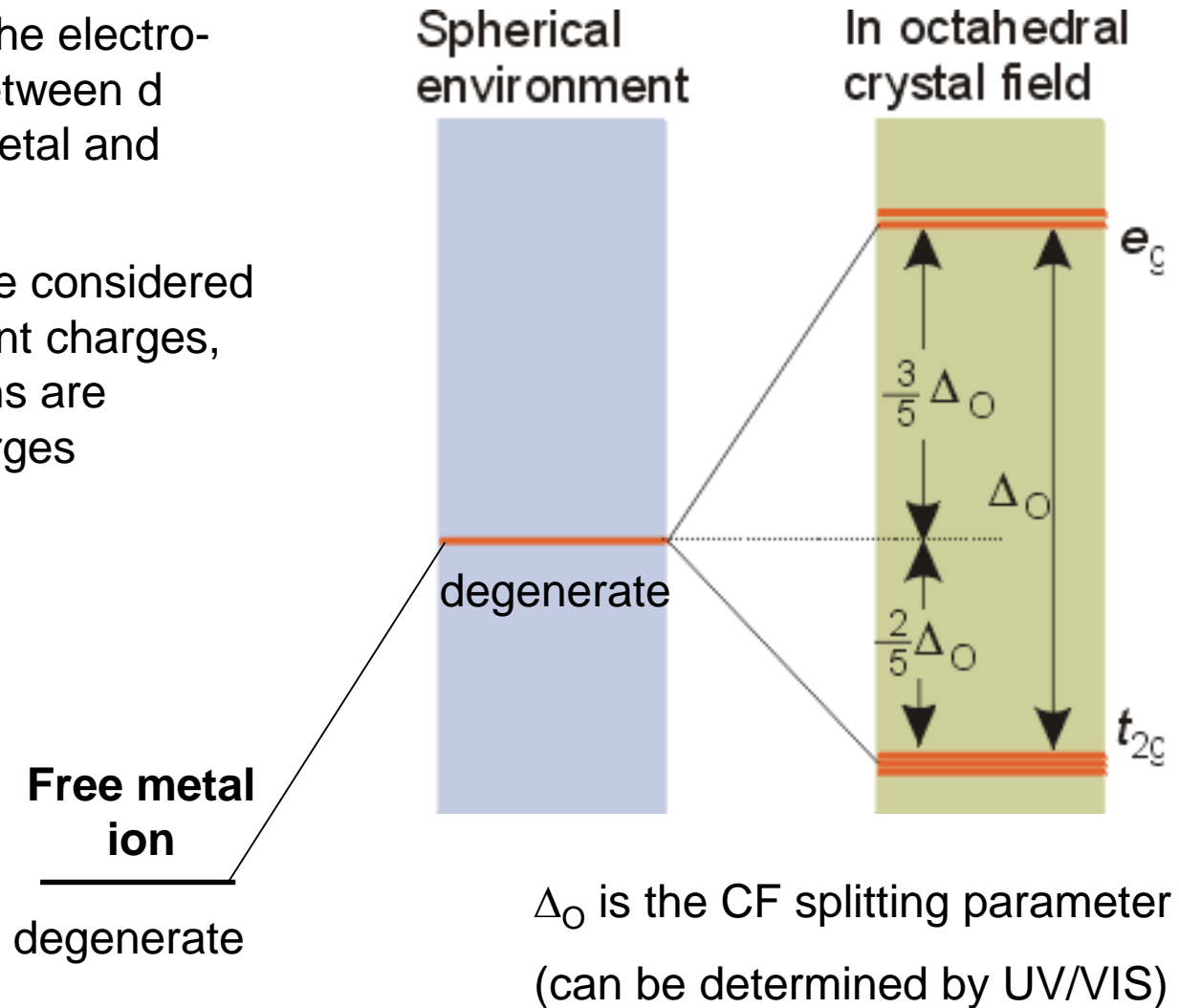
Octahedral

The Five d-Orbitals



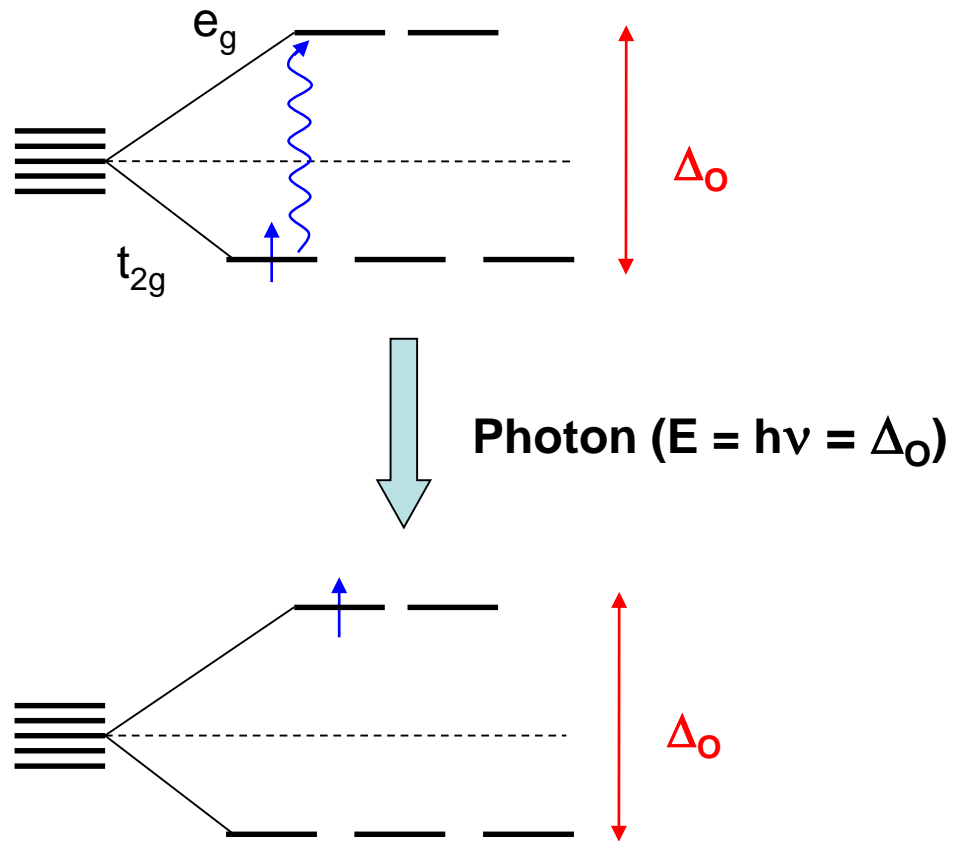
Crystal Field Theory (CFT)

- CFT is based on the electrostatic repulsion between d electrons of the metal and ligand electrons
- In CFT, ligands are considered to be negative point charges, whereas metal ions are positive point charges

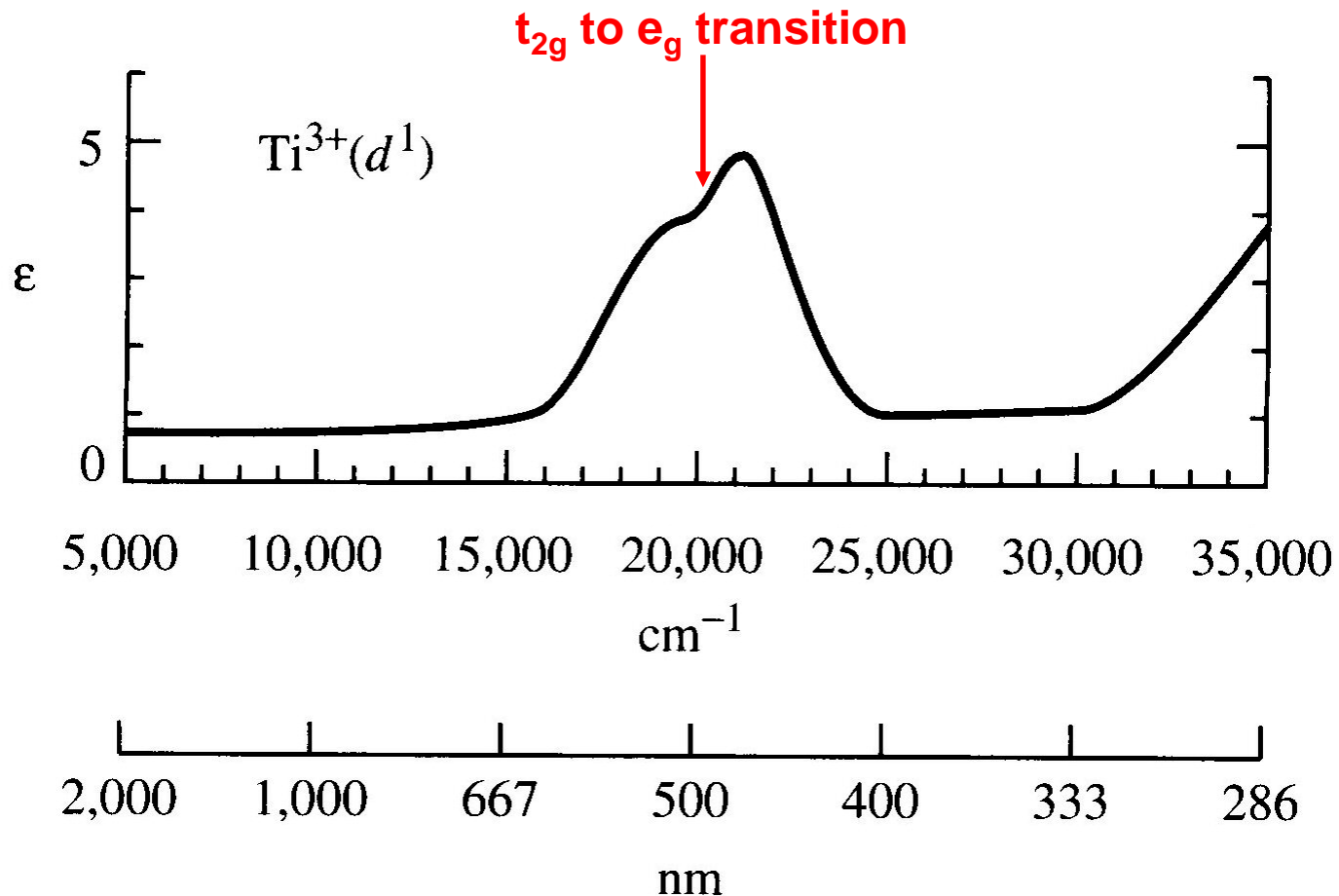


d-d Transitions and UV/VIS Spectra

For Ti^{3+}

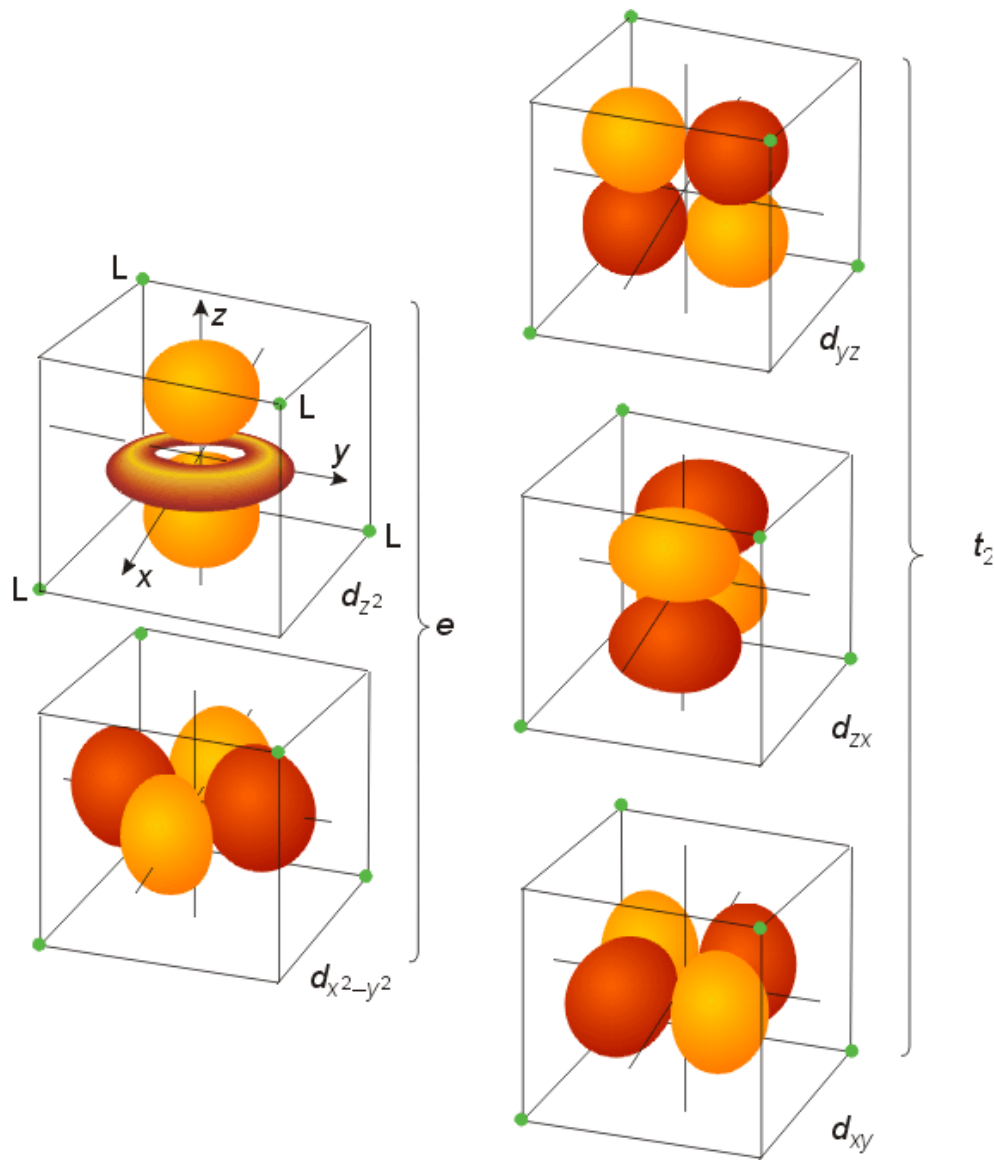


UV/VIS Spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



Note that the spectrum is not as simple as previously described! The shoulder in the spectrum is due to the Jahn-Teller effect (described later)

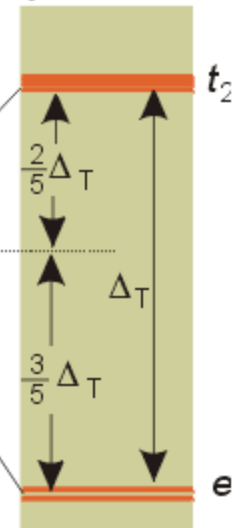
Tetrahedral geometry



Spherical environment

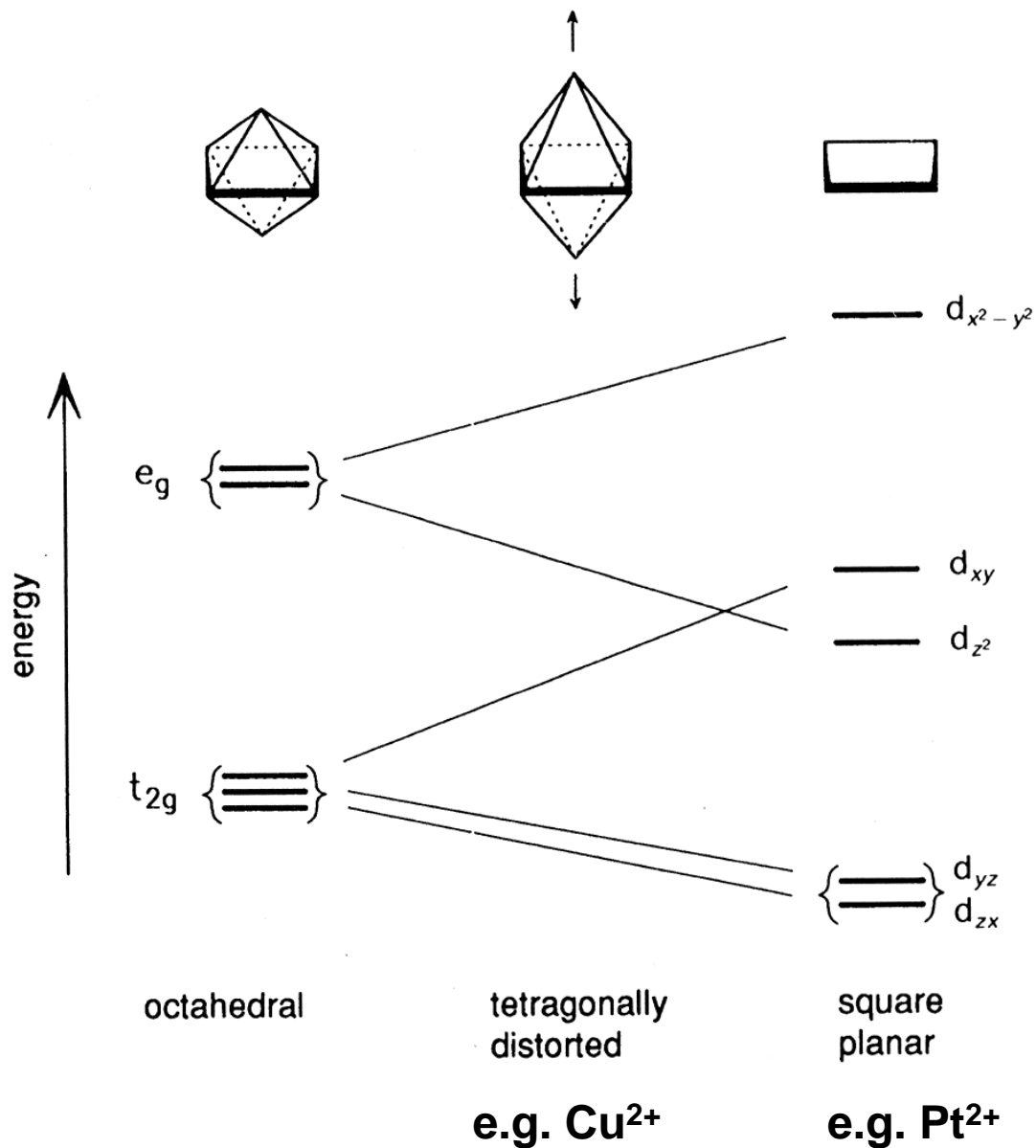


In tetrahedral crystal field



$$\Delta_T = \frac{4}{9} \Delta_O$$

Tetragonal Distortions



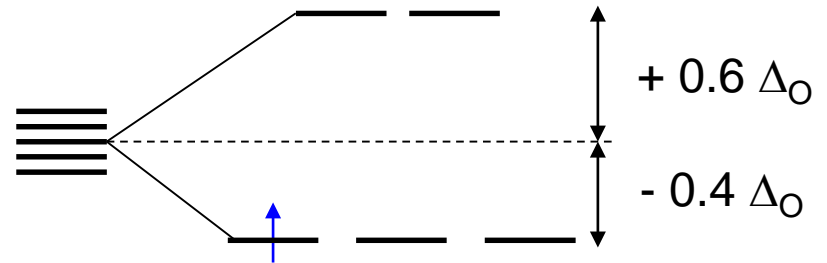
Crystal Field Stabilization Energies

CFSE = Energy released when a complex rearranges from the (hypothetical) spherical field to its final geometry

Examples for octahedral ions:

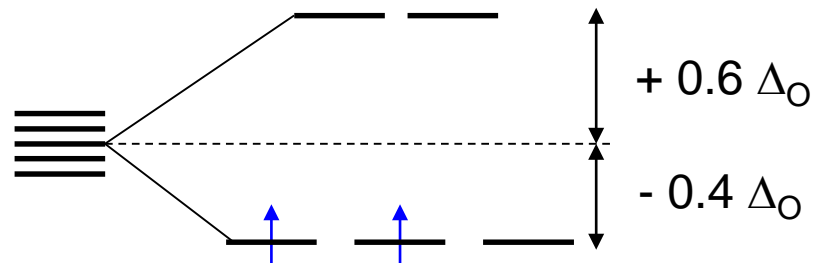
d¹ (Ti³⁺)

$$\text{CFSE} = -0.4 \Delta_{\text{O}}$$



d² (V³⁺)

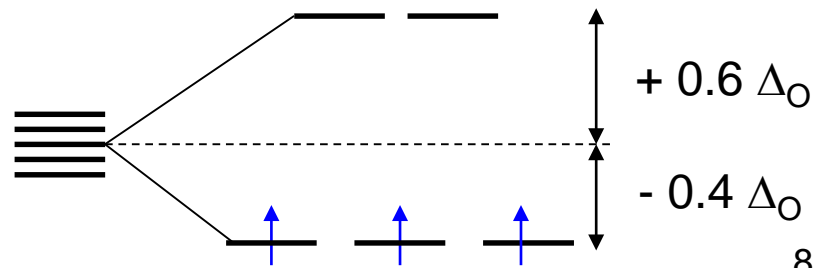
$$\text{CFSE} = -0.8 \Delta_{\text{O}}$$



d³ (Cr³⁺)

$$\text{CFSE} = -1.2 \Delta_{\text{O}}$$

High CFSE – strong preference for octahedral geometry

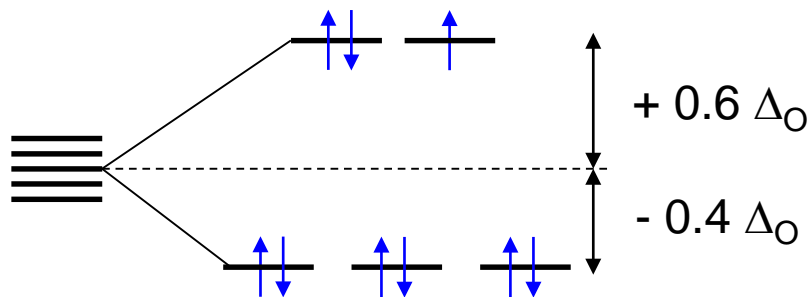


All species are paramagnetic

Examples:

d⁹ (Cu²⁺)

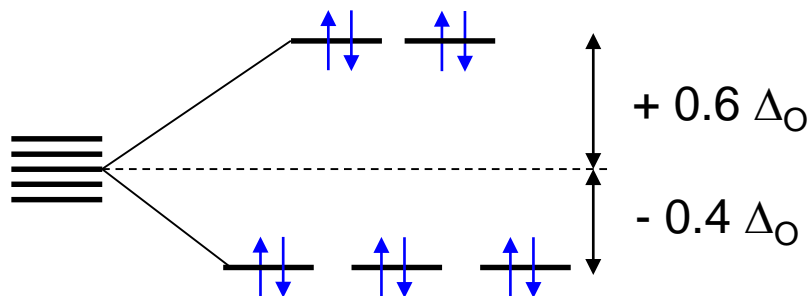
$$\text{CFSE} = (6 \times -0.4) + (3 \times 0.6) \Delta_{\text{O}} = -0.6 \Delta_{\text{O}}$$



Paramagnetic

d¹⁰ (Zn²⁺)

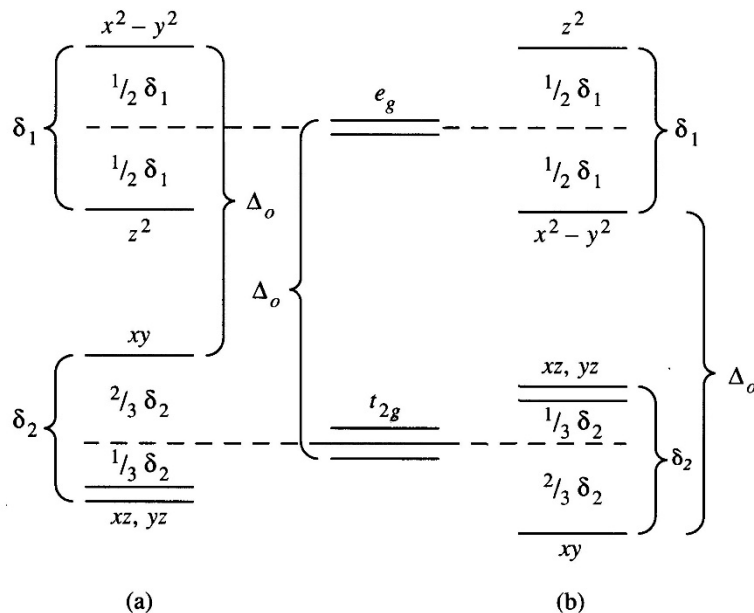
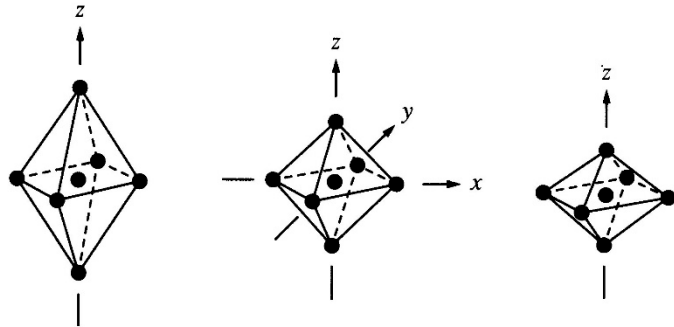
$$\text{CFSE} = (6 \times -0.4) + (4 \times 0.6) \Delta_{\text{O}} = 0 \Delta_{\text{O}}$$



Diamagnetic

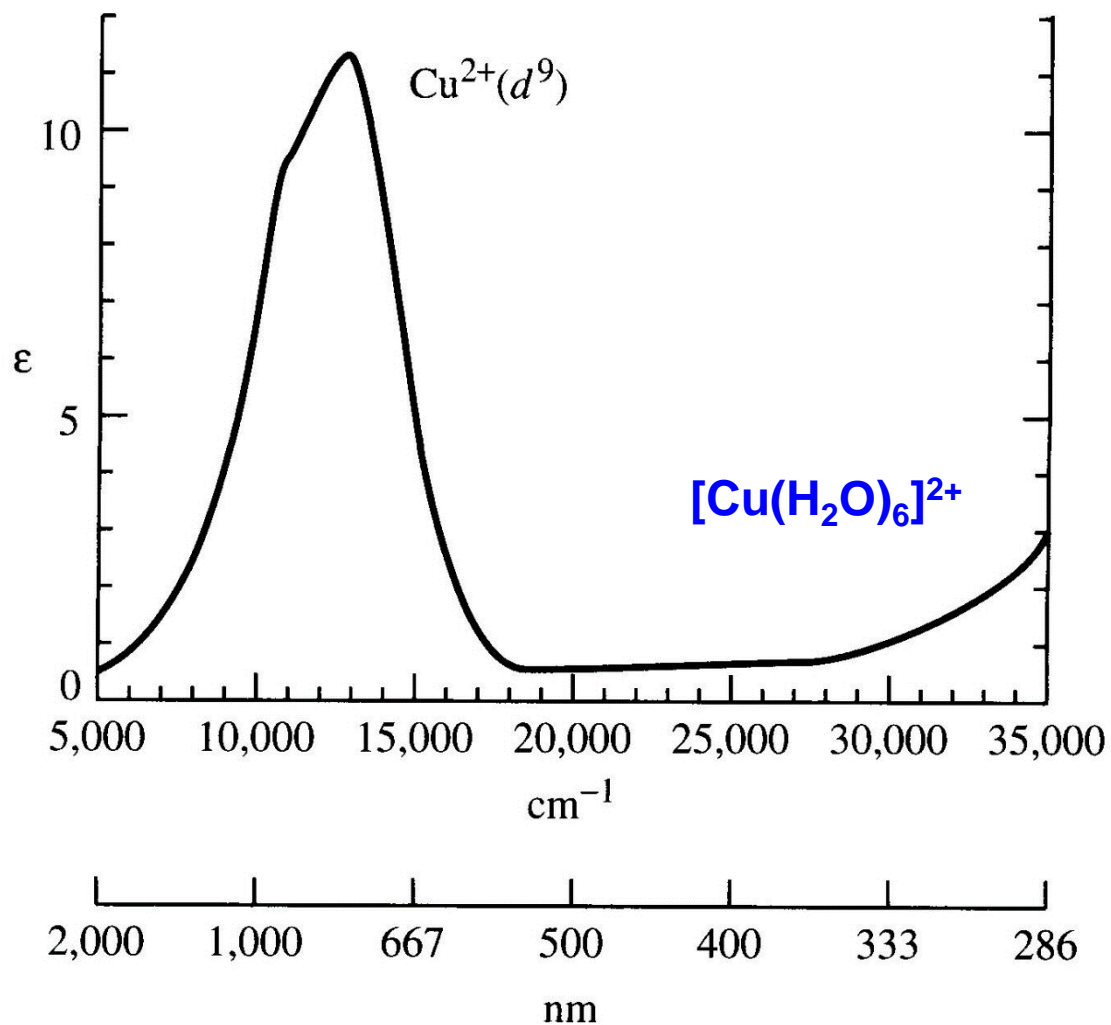
Cu(II) – d⁹ and the Jahn-Teller Effect

Jahn-Teller Theorem (1937): *For a non-linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy, and lower the energy.*



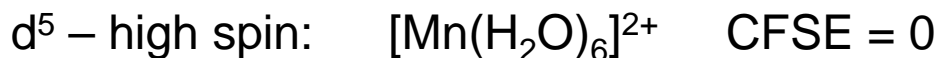
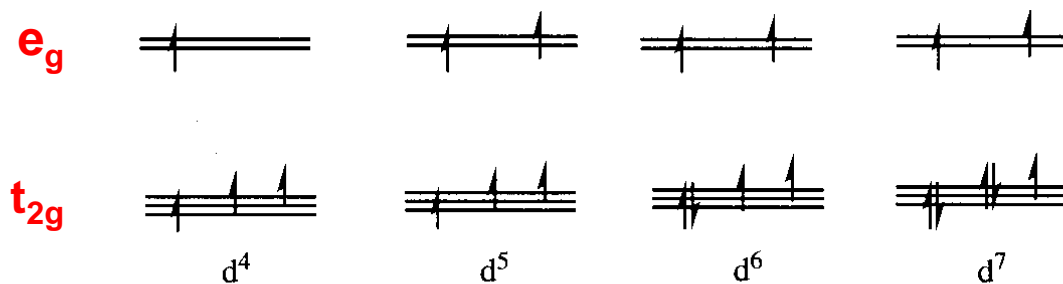
- The electronic ground state of octahedral Cu(II) is degenerate (the electron “hole” can be in either of the two e_g orbitals)
- Therefore, a tetragonal distortion of octahedral Cu(II) complexes should occur
- Such distortion (along the z axis) removes the degeneracy and leads to a higher CFSE
- **The gain in CFSE is what drives this process!**

The Jahn-Teller effect is visible in the UV/VIS spectra of Cu(II) and Ti(III)* complexes in form of a shoulder in the absorption peak



* See page 5

High-spin and low-spin configurations (octahedral field)



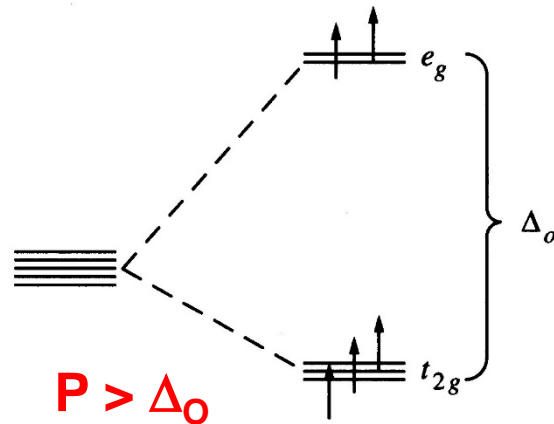
Diamagnetic !

P = Pairing energy

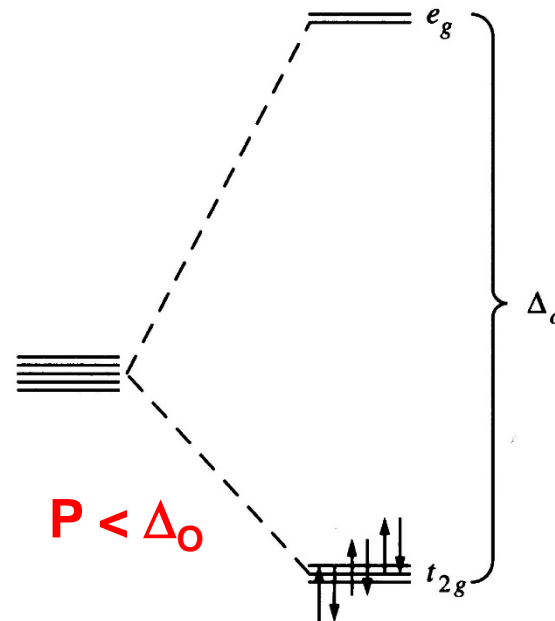
High-spin versus Low-spin

(a) d^5 ion in a weak octahedral field (small Δ_o) results in a high-spin complex (e.g. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$)

(b) d^6 ion in a strong octahedral field (large Δ_o) results in a low-spin complex (e.g. $[\text{Fe}(\text{CN})_6]^{4-}$)



(a)



(b)

Factors Governing the Magnitude of Δ

1. Oxidation state of the metal ion:

Δ increases with increasing ionic charge of the central metal ion

2. Nature of the metal ion:

Δ increases for analogous complexes within a given group in the order $3d < 4d < 5d$ (Rule of thumb: $3d \rightarrow 4d$: $\leq 50\%$ increase in Δ)

3. Number and geometry of ligands:

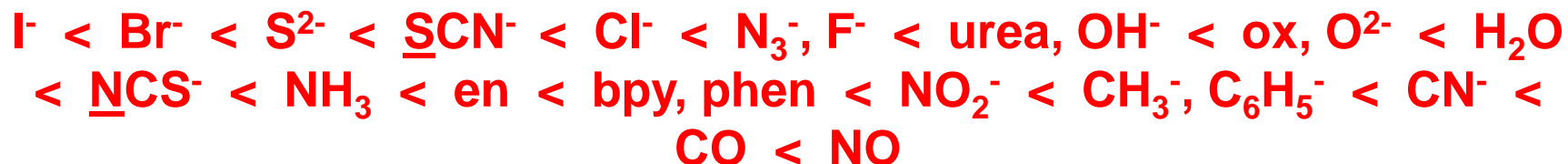
Δ for tetrahedral complexes is $\sim 50\%$ as large as for octahedral complexes

4. Nature of the ligands:

Based on absorption spectra (d-d transitions) of a variety of complexes with different types of ligands and central metal ions, one can order the ligands according to their 'field strength'. The order is known as the **Spectrochemical Series**.

The Spectrochemical Series

The field strength (and thus Δ) increases in the following order:



(ox = oxalate, en=ethylenediamine, bpy=2,2'-bipyridine, phen=1,10-phenanthroline; for the thiocyanato ligand: underlined atoms are bound to the metal centre)

- **Important note:** The spectrochemical series of ligands cannot be explained by the CFT! **WHY?**
- The series can be explained, however, with the help of the Ligand Field Theory (extension of CFT which includes MO theoretical considerations)

Applications of CFT

■ Hydration energies:

■ the smaller the cation, the larger its hydration energy (which is closely related to the enthalpy of formation of $[M(H_2O)_6]^{2+}$, for instance.)

■ cations possessing CFSE show higher hydration energies than otherwise expected. CFSE therefore adds to the stabilization of the aqua complexes.

■ V^{2+} and Ni^{2+} have the highest CFSE values. This is reflected in the so-called “double-humped” curve of hydration energies.

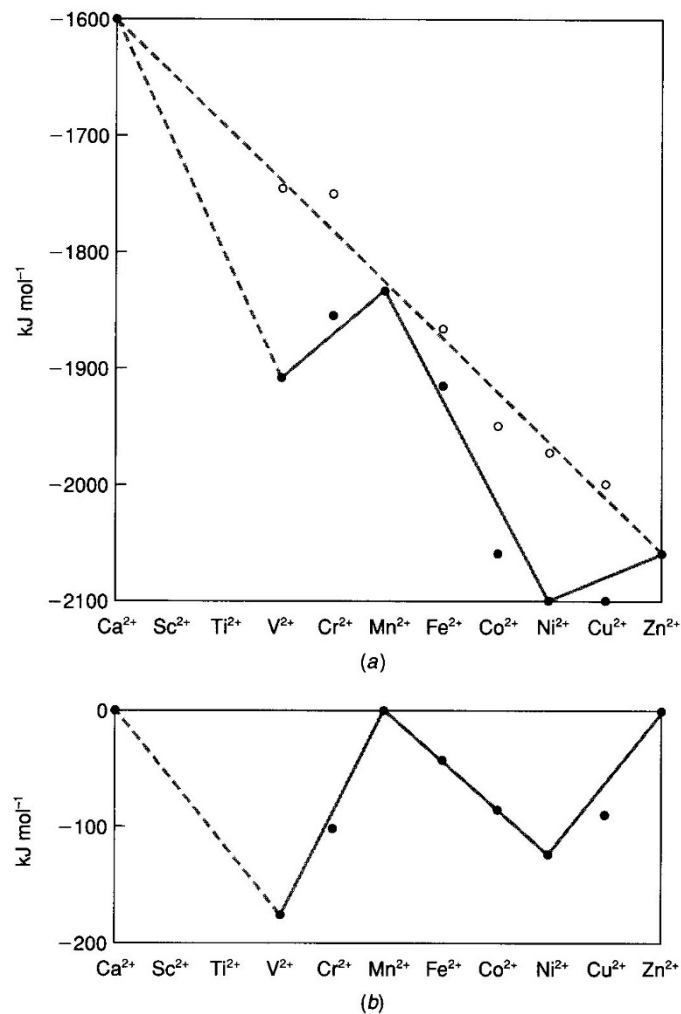


Figure 8.9

(a) Hydration energies of the +2-charged $3d^n$ ions (solid circles); (b) Crystal field stabilization energies of these ions; (a, open circles) hydration energies with the CFSEs subtracted.

■ Enthalpy of complex formation

- same considerations as with the hydration energies (i.e., same type of double-humped curve is observed), since hydration energies are only a specific case of complex formation enthalpies
- Looking back at the previous figure, one can order the metals according to their magnitude of complex formation enthalpies: This is the IRVING-WILLIAMS series of metal ions

Irving-Williams series for divalent 3d metal ions



Cu(II) is the most acidic metal ion, Zn(II) is next (although it is the hardest ion in the series)

■ Radius of metal ions:

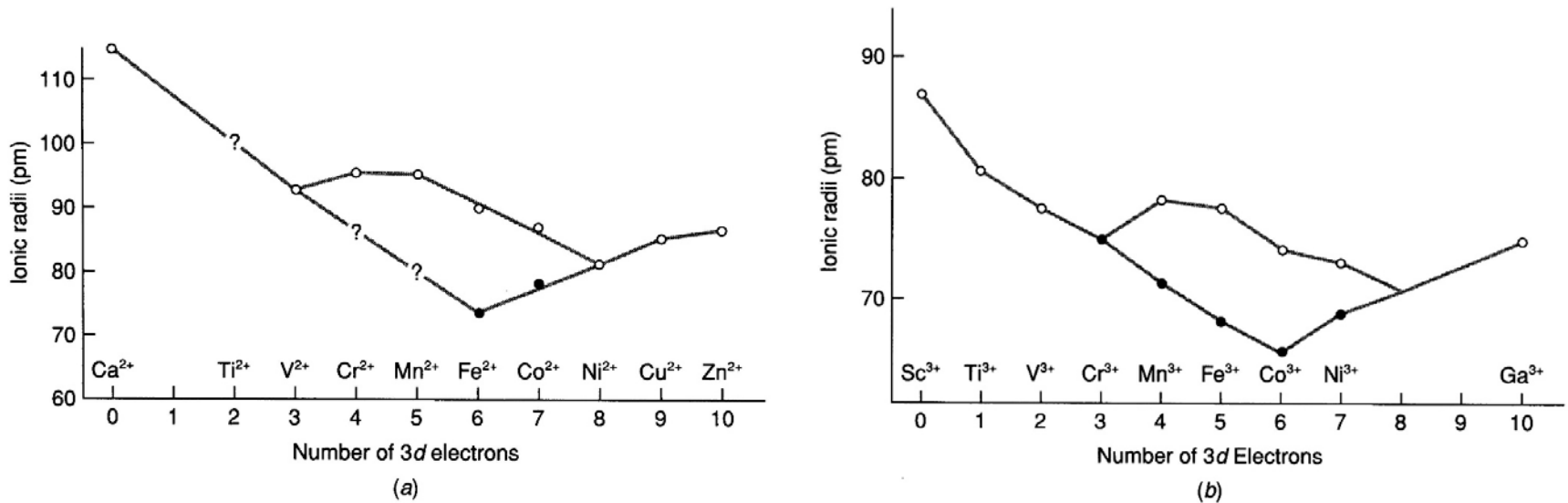


Figure 8.12

Radii of the +2 ions (a) and the +3 ions (b) as a function of the 3dⁿ electron configuration. Open circles represent high-spin (weak-field) ions; closed circles represent low-spin (strong-field) ions.

[Adapted from R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B*, **26**, 1076 (1970).]

- For low-spin complexes: minimum of the curve is at Fe(II) – d⁶ (because all electrons are in the t_{2g} orbitals → maximal CFSE)
- For high-spin complexes: an increase in radius occurs after V(II) – d³ (because a fourth electron would occupy the e_g orbital, which directly points towards the ligands → repulsion → effective increase in radius)