Crystal Field Theory (CFT) In Detail

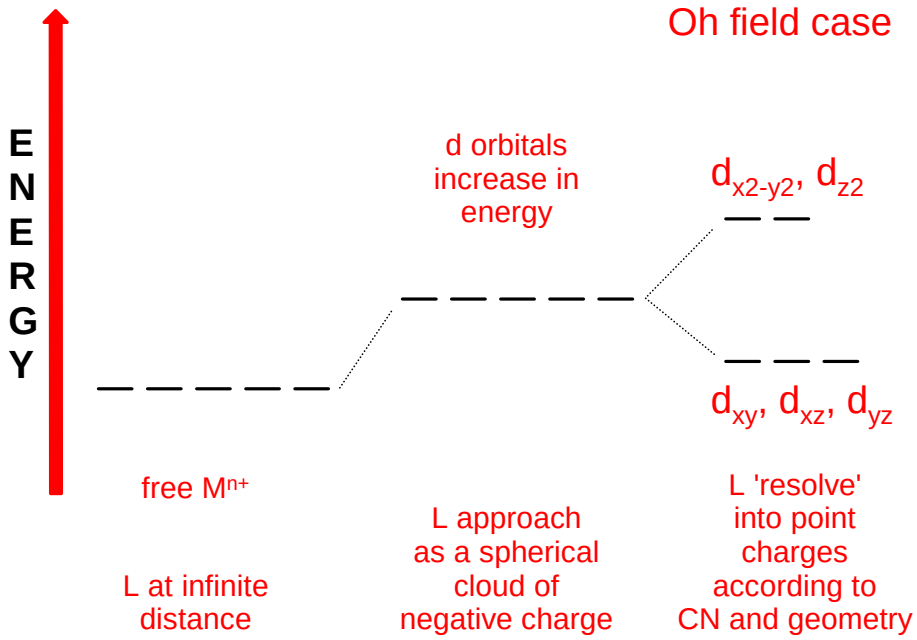
(H&S 3rd Ed. Chpt. 21.3)

CFT provides a simple model for d orbital splitting:

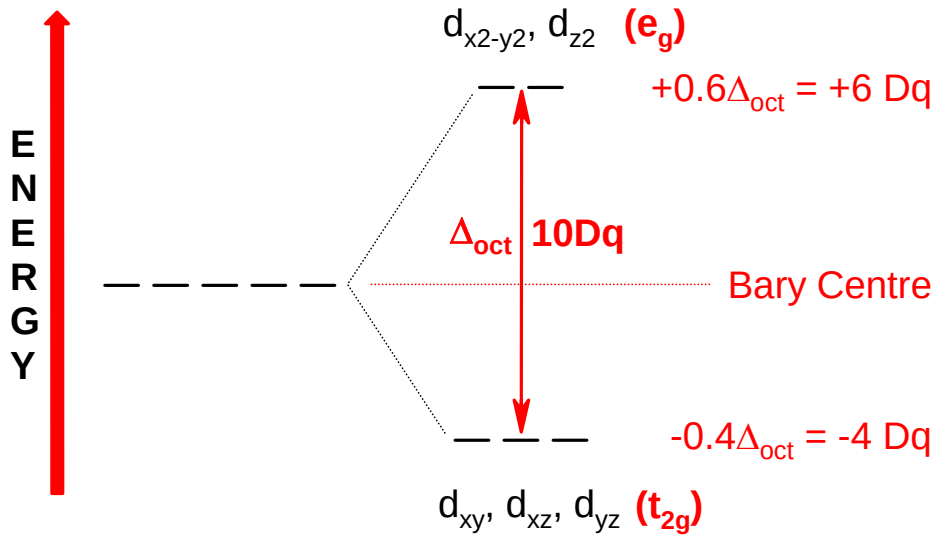
- works for several oxidation states and geometries
- allows prediction of properties such as structures, colours, magnetism

CFT examines *relative* d orbital energies when a M^{n+} ion is placed in an '*electrical field*' created by the ligand (donor) electrons:

- electrostatic ***attraction*** between M^{n+} and L
- electrostatic ***repulsion*** between d electrons and L electrons (considered as point charges) ***destabilizes d electrons differentially depending upon their orientation in space***



CFT for an Oh complex:



a, b = singly degenerate labels
e = doubly degenerate
t = triply degenerate

g = gerade (symmetrical about origin)
u = ungerade (unsymmetrical about origin)

size of Δ_{oct} or (Δ_o) is determined by the ***'crystal field strength'***

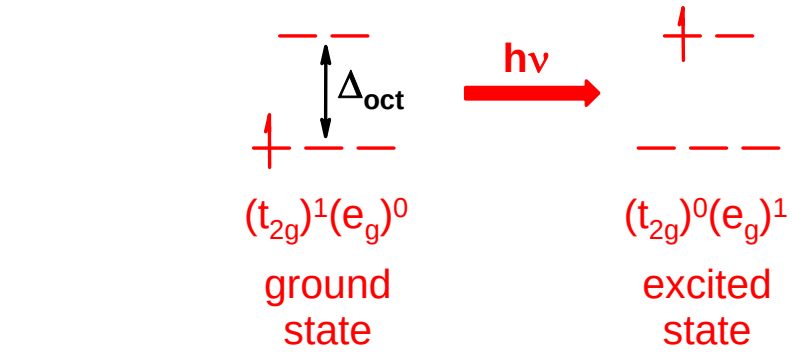
Δ_{oct} (weak field) < Δ_{oct} (strong field)

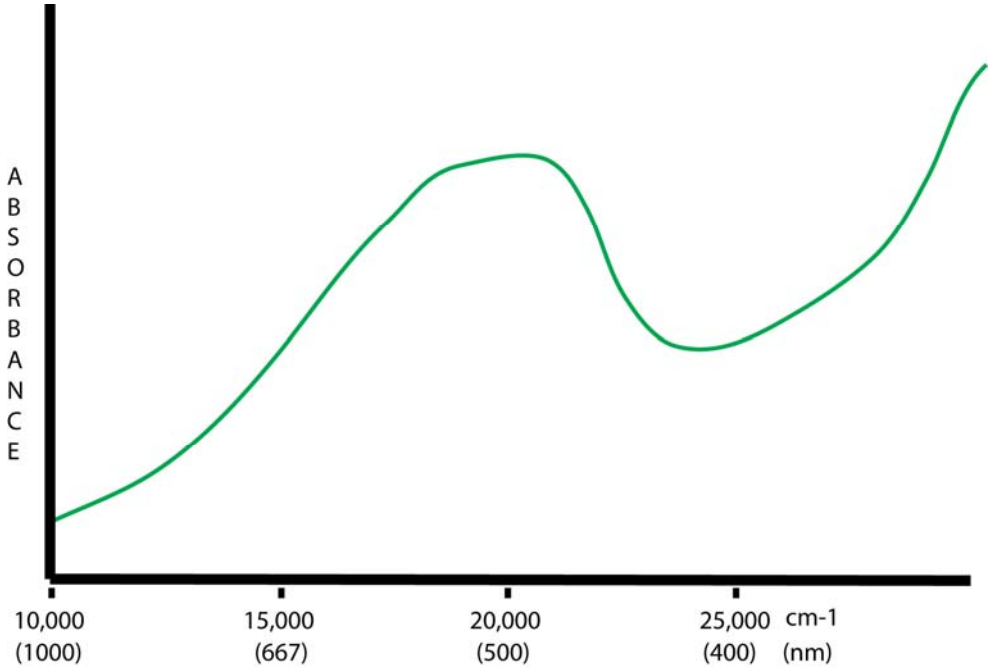
factors affecting the **size of Δ_{oct}** include:

- identity and Ox. St. of the metal (larger for $2^{nd}/3^{rd}$ row than 1^{st} row d block)
- nature of the ligands (σ and π bonding ability)

Electronic spectra (UV-Vis) can provide a measure of Δ_{oct} because transitions between d orbitals ($\mathbf{t_{2g} \rightarrow e_g}$) fall in this region:

eg. $[Ti(H_2O)_6]^{3+}$ d^1





- Δ_{oct} is a measurable quantity

- in this case, Ti^{3+} has a λ_{max} = 20,300 cm^{-1} or 243 kJ mol^{-1} for the energy required to promote an electron from the **t_{2g} to e_g set**

Electronic spectroscopy of many Oh complexes gives a *relative* ranking of the crystal field strengths of ligands called the ***spectrochemical series***:

$I^- < Br^- < NCS^- < Cl^- < NO_3^- < F^- < OH^- < ox^{2-} \sim H_2O <$
weak field → increasing Δ_{oct} →

$NCS^- < py < NH_3 < en < bipy < phen < NO_2^- < PPh_3 < CN^- \sim CO$
increasing Δ_{oct} → strong field

A few points about the spectrochemical series:

1 For a given M^{n+} ion, varying L gives ***predictable trends*** BUT NOT absolute values for Δ_{oct}

2 For a given ML_n, higher ox. states give larger Δ_{oct}
smaller ionic radius, shorter M-L distance?

3 **Heavier metals of a given triad (2^{nd} and 3^{rd} row) give greater Δ_{oct}** for a given ML_n type complex

4 For a given ML_n type of complex, Δ_{oct} does NOT vary in a predictable way across the row