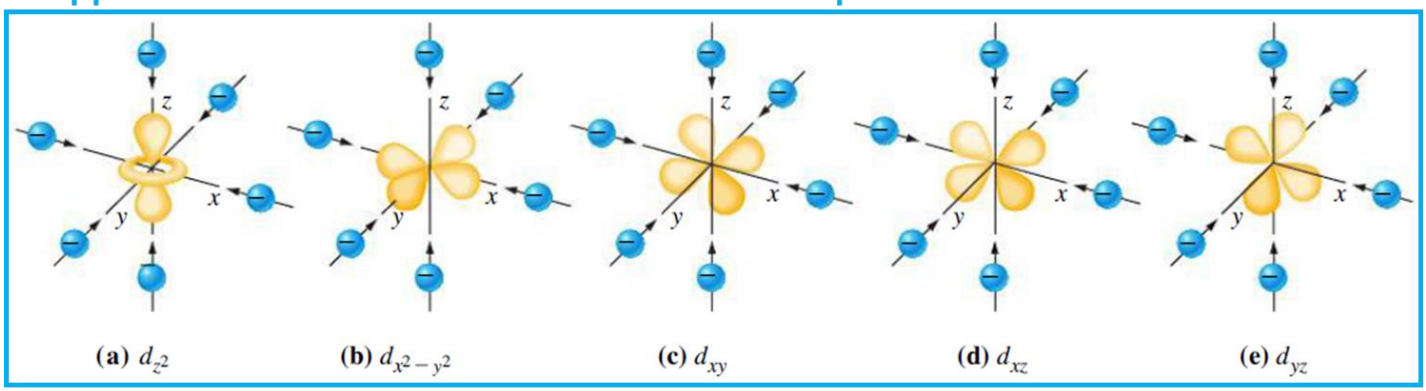
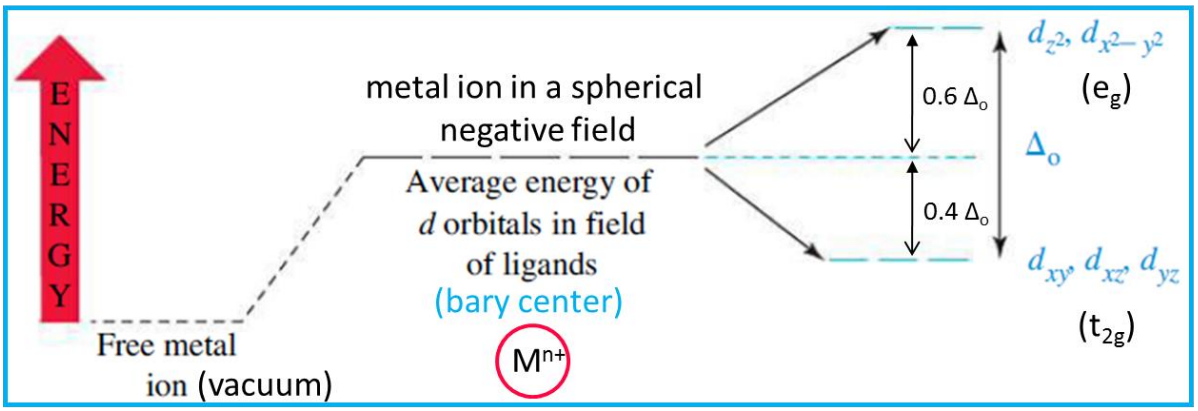
Crystal Field Theory: Octahedral Complexes

Approach of six anions to a metal to form a complex ion with octahedral structure



Splitting of d energy levels in the formation of an octahedral complex ion



Factors that Affect Crystal Field Splitting

1) Nature of the ligand:

Spectrochemical Series

$$I^- < Br^- < S^{2-} < \underline{S}CN^- < Cl^- < \underline{N}O_2^- < N^{3-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O$$
$$< \underline{N}CS^- < CH_3C{\equiv}N < py < NH_3 < en < bpy < phen < \underline{N}O_2^- < PPh_3 < \underline{C}N^- < CO$$

weak field ligands ——— increasing Δ_o ———→ strong field ligands

- Ligands with the same donor atoms are close together in the series.
- Ligands up to H_2O are weak-field ligands and tend to result in high-spin complexes.
- Ligands beyond H_2O are strong-field ligands and tend to result in low-spin complexes.

- CFT can not explain why certain anionic ligands lies lower in the series than neutral ligands, although reverse should be expected based on electrostatic interactions.
- It also can not explain why OH^- lies lower in the series than H_2O and NH_3, although reverse should be expected, since dipole moment of OH^- is greater than H_2O and NH_3.

Factors that Affect Crystal Field Splitting

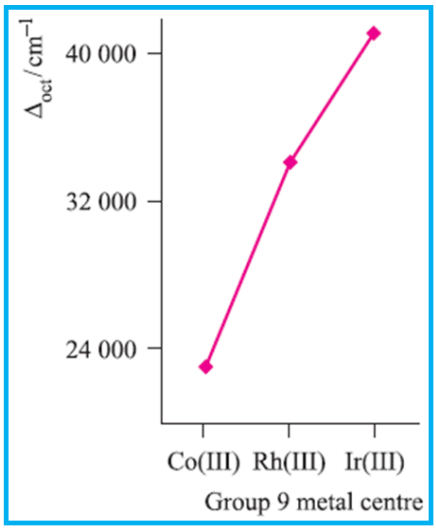
Nature of Ligand

Complex	Δ_o (cm^{-1})
$[CrCl_6]^{3-}$	13640
$[Cr(H_2O)_6]^{3+}$	17830
$[Cr(NH_3)_6]^{3+}$	21680
$[Cr(CN)_6]^{3-}$	26280

Oxidation State of Metal Ion

Complex	Δ_o (cm^{-1})
$[Fe(H_2O)_6]^{2+}$	9400
$[Fe(H_2O)_6]^{3+}$	13700
$[Co(H_2O)_6]^{2+}$	9300
$[Co(H_2O)_6]^{3+}$	18200

Nature of Metal Ion



Complex	Δ_o (cm^{-1})
$[Co(NH_3)_6]^{3+}$	24800
$[Rh(NH_3)_6]^{3+}$	34000
$[Ir(NH_3)_6]^{3+}$	41000