TS-Diagram for d^2

$[V(OH_2)_6]^{3+}$

$V^{III} \Rightarrow d^2$

$\nu_1 = 17,800\,cm^{-1}$

$\nu_2 = 25,700\,cm^{-1}$

$\nu_3 = 38000\,cm^{-1}$

$\frac{\nu_1}{\nu_2} = 1$

$\frac{\nu_2}{\nu_1} = 1.45$

$\frac{\nu_3}{\nu_1} = 2.1$

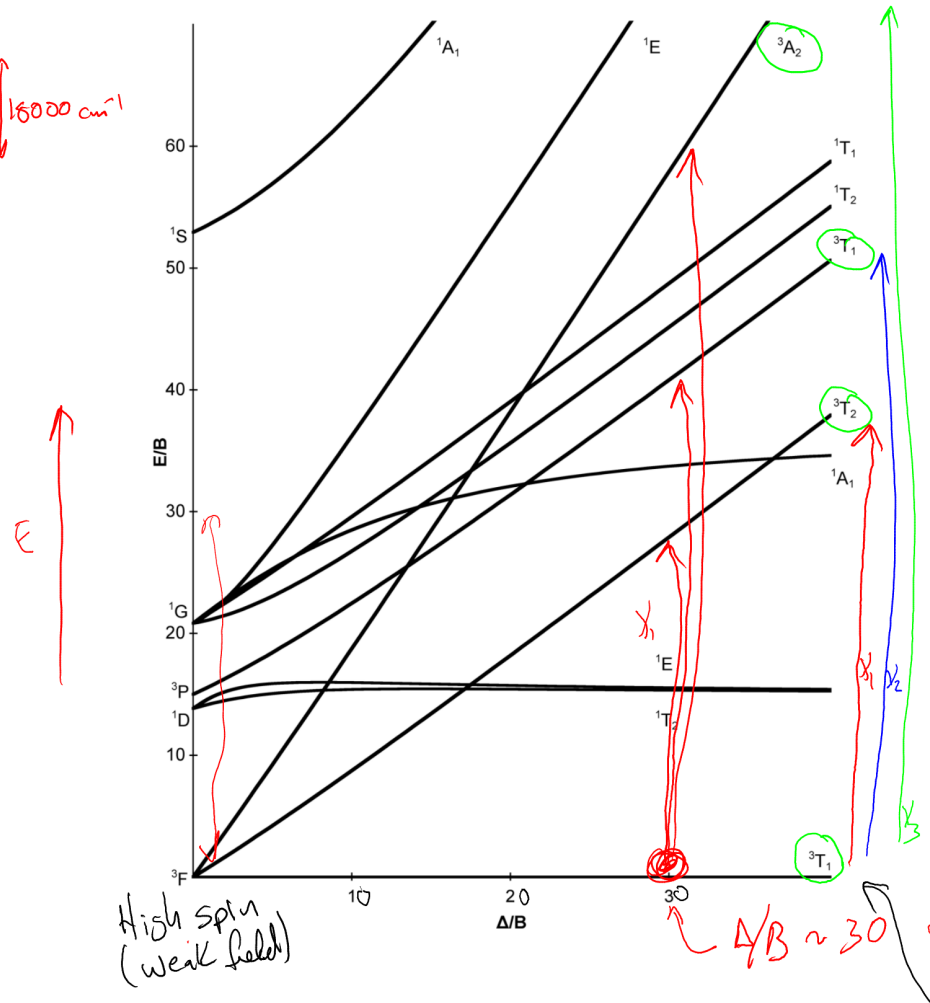
$\uparrow\downarrow$ $\uparrow\downarrow$ $\_$

$1 \quad 1 \quad \_$

$18000\,cm^{-1}$

$2S+1 = 3$

triplet



High spin (weak field)

$\Delta/B \sim 30$ for $[V^{III}(OH_2)]^{3+}$

Low spin (strong field)

$\nu_1 \sim 17,800\,cm^{-1}$ at $E/B = 30$

$17,800 \div 30 \longrightarrow B = 600\,cm^{-1}$

$\hookrightarrow E/B$ at $\Delta/B = 30$

$(\Delta/B)(B) = \Delta = 30(600\,cm^{-1}) \Rightarrow 18000\,cm^{-1}$

$\hookrightarrow \Delta/B \quad \hookrightarrow B$

Consider d^4 in O_h

High Spin

eg ↑ —

t_{2g} 1 1 1 ↕ Δ_o small (weak field)

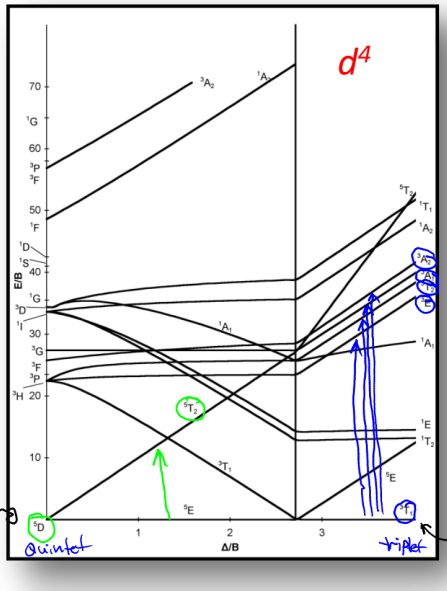
$S = 2$; $2S+1 = 5$

Low Spin

— — eg

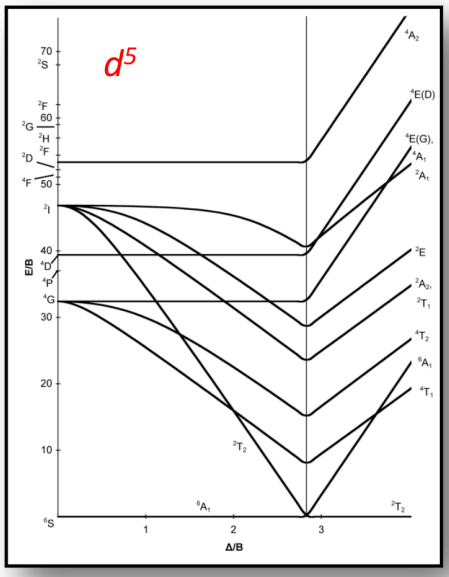
t_{2g} ↑↓ 1 1 ↕ Δ_o large (Strong field)

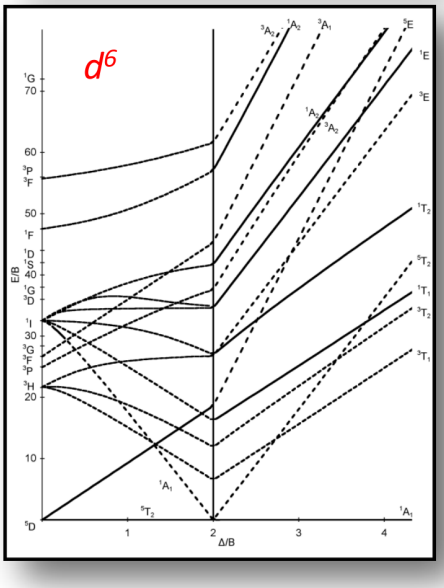
$S = 1$; $2S+1 = 3$

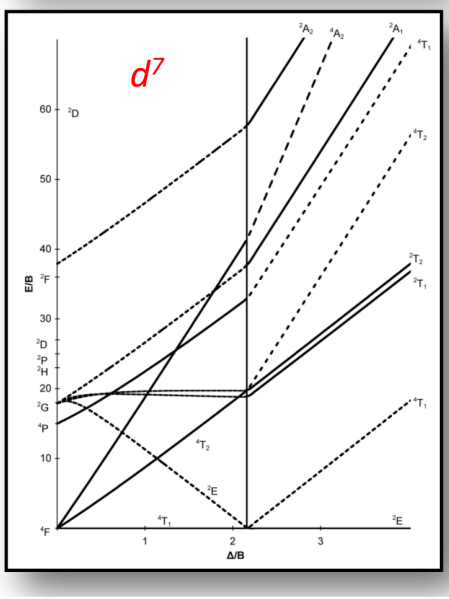


(HS) weak field

(LS) Strong field







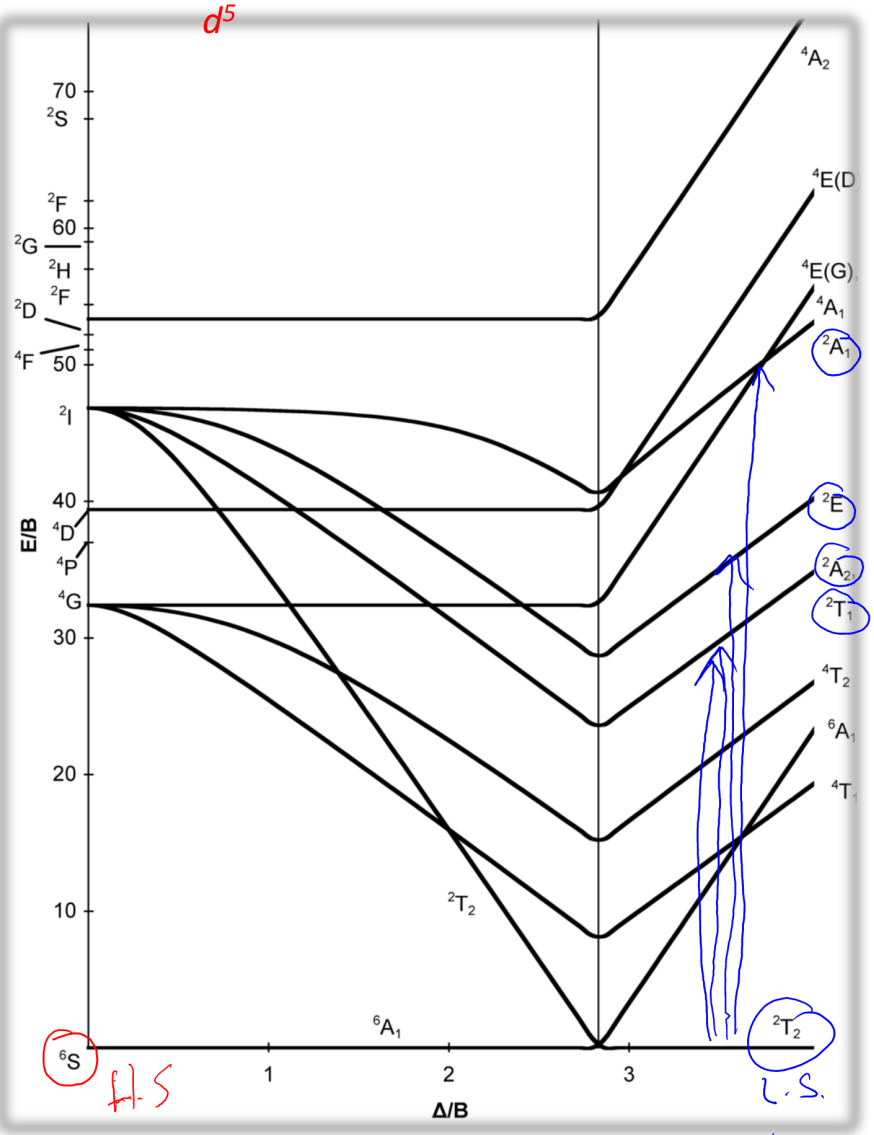
This divergence in spin states + allowed transitions is especially stark for d^5

Consider $[Mn(OH_2)_6]^{2+}$ $Mn^{II} \Rightarrow d^5$ → weak field complex (H.S.)

$\uparrow\ \uparrow$ e_g

$\uparrow\ \uparrow\ \uparrow$ t_{2g}

$2S+1=6$



No Allowed transitions!

Most Mn^{II} salts are white

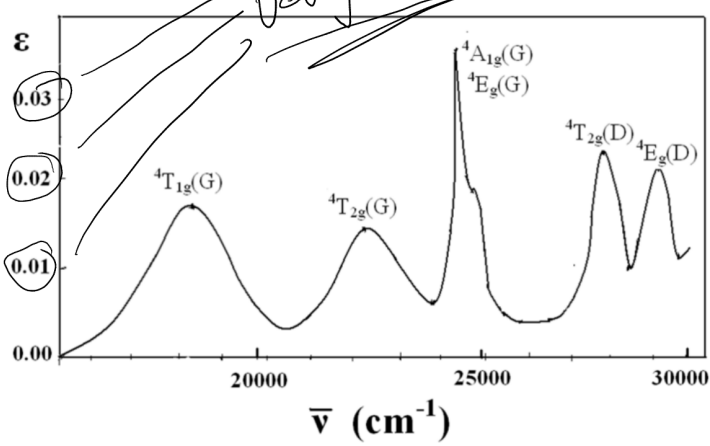
$\uparrow\ \uparrow$

$h\nu$ →

$\uparrow\ \uparrow\ \uparrow$

Spin Forbidden transitions!

very weak



$[Mn(OH_2)_6]^{2+}$

deep purple color

$[Mn(CN)_6]^{4-} \Rightarrow Mn^{II}$ d^5

— —

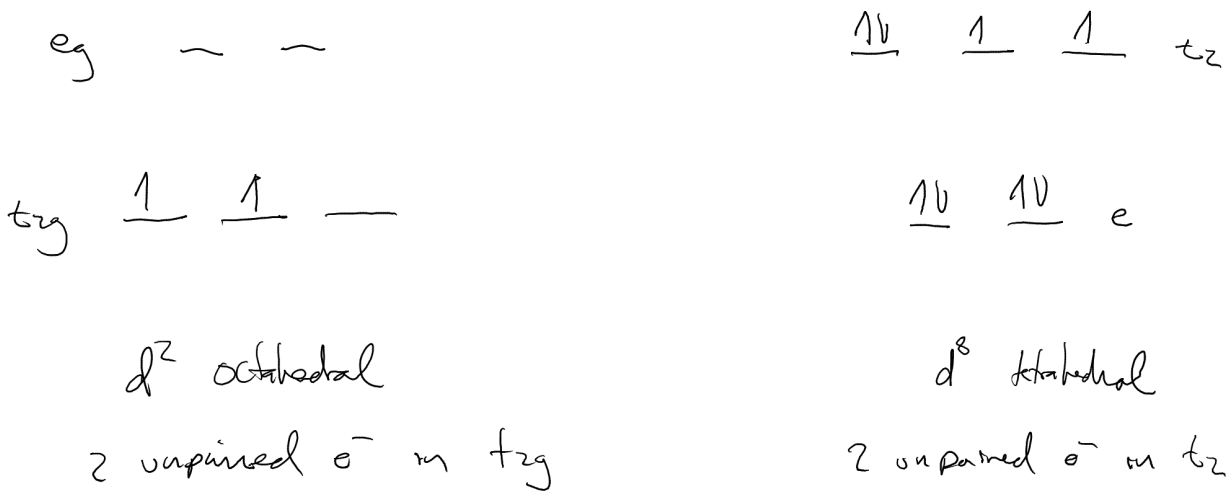
$\uparrow\downarrow\ \uparrow\downarrow\ \uparrow$ Δ_o large

$2S+1=2$ (doublet

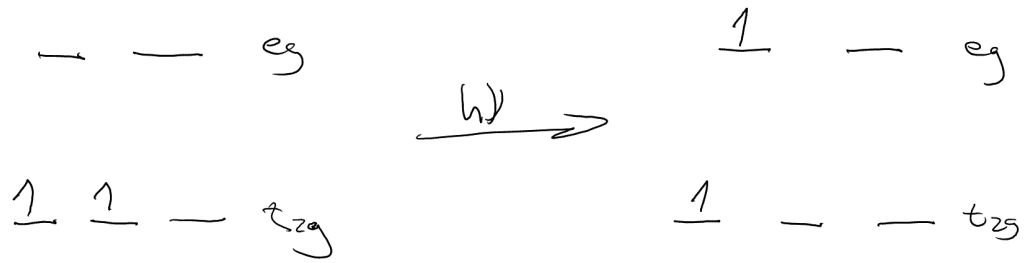
Tetrahedral Complexes

- Tetrahedral complexes are more strongly-colored than octahedral complexes
  - ↳ A consequence of the Laporte Selection Rule (No inversion center in Td)

We can use Octahedral TS diagrams for tetrahedral complexes



Light absorbtion for d^2 in O_h is associated w/ e^- promotion from $t_{2g} \rightarrow e_g$



Light absorbtion for d^8 in Td is associated w/ hole demotion from $t_2 \rightarrow e$

∴ We can analyze Td absorption spectra for a given d^n using the TS-diagram that corresponds to the d^{10-n} electron count

For d^2 Td ⟶ d^8 O_h
For d^3 Td ⟶ d^7 O_h
etc.....

Charge Transfer Transition ε on the order of 5000 or greater

↳ Commonly observed for TM complexes...

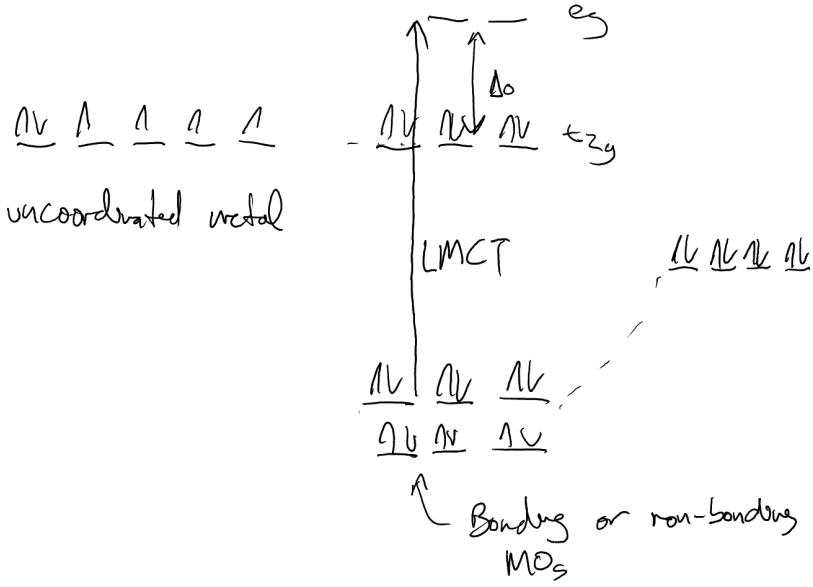
① LMCT – Ligand to Metal Charge Transfer

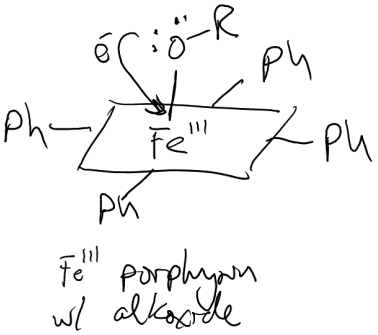
② MLCT – Metal to Ligand Charge Transfer

LMCT

Involve ligands w/ donor orbitals:

Halides, oxides, amides alkoxides, etc...

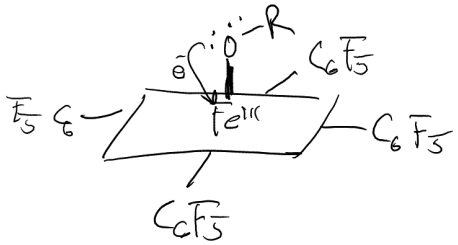




Fe^{III} porphyrin w/ alkoxide

LMCT $\varepsilon \sim 20000\ cm^{-1} \cdot M^{-1}$

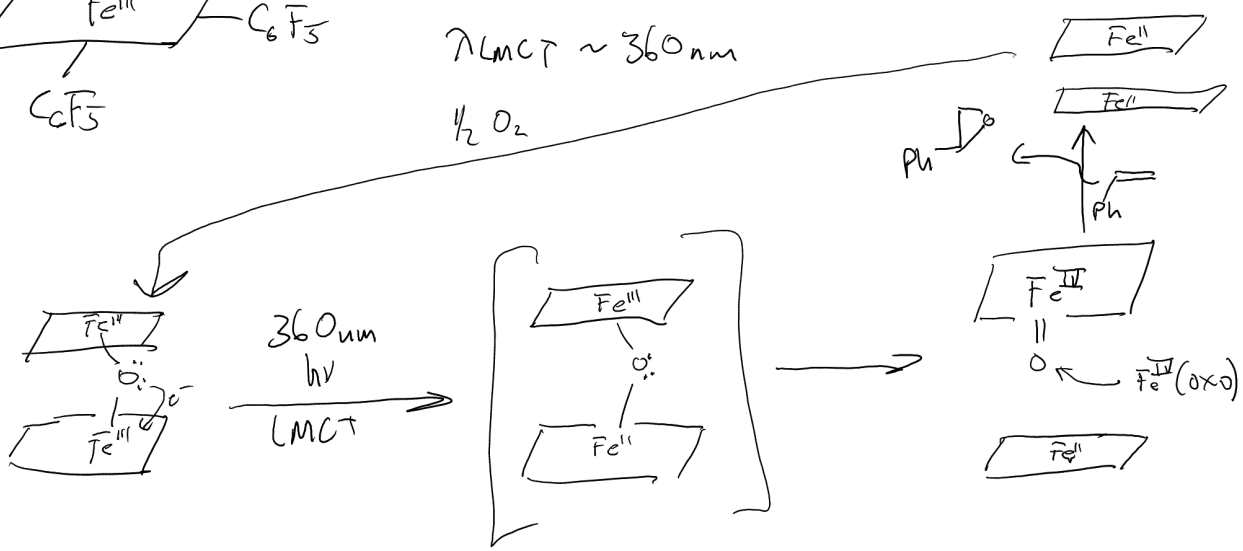
$\lambda_{LMCT} \sim 320\ nm$



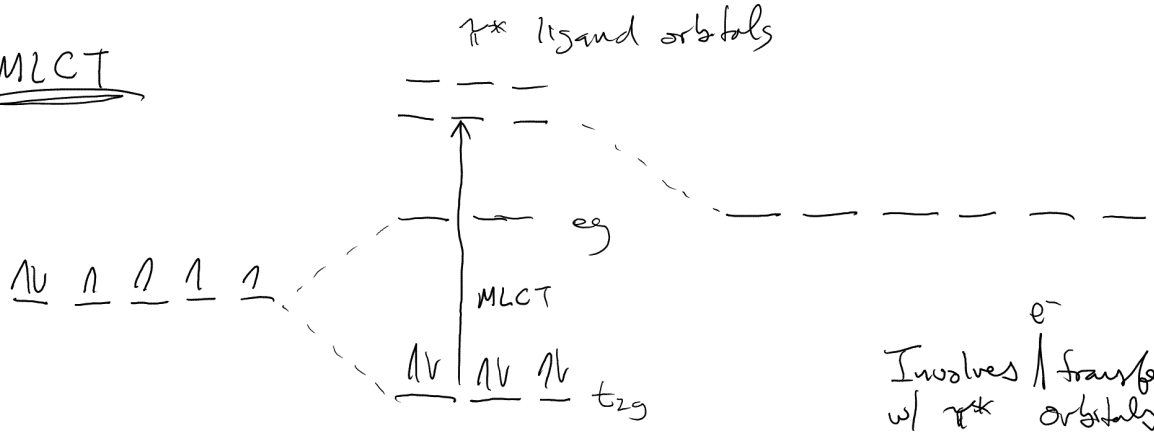
LMCT $\varepsilon \sim 20000\ cm^{-1} \cdot M^{-1}$

$\lambda_{LMCT} \sim 360\ nm$

$\frac{1}{2}\ O_2$

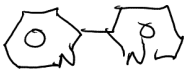


MLCT



Involves e^- transfer to ligands w/ π* orbitals

CN^-, CO, NO^+, Ph, bpy

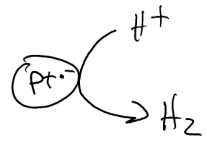


$[Ru^{II}(bpy)_3]^{2+}$ $\xrightarrow[\text{MLCT}]{h\nu}$ $[Ru^{III}(bpy)_2(bpy^{\bullet-})]^{2+}$

400–500 nm

MLCT state

transfer an e^- to Pt NP



$[Ru^{III}(bpy)_3]^{3+}$

Reductant