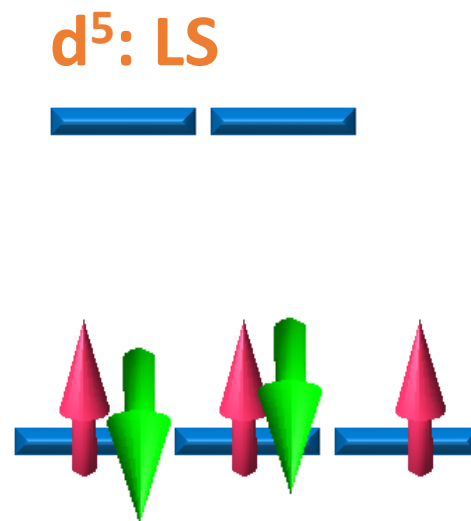
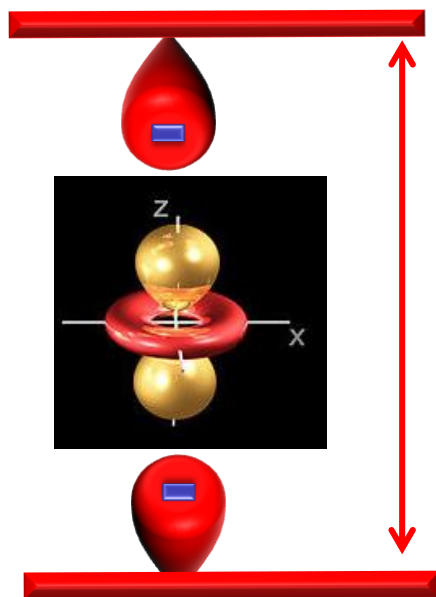
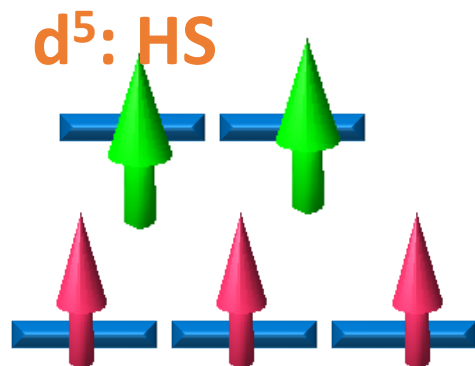


Tutorial – II

Coordination Chemistry

Q01. When high pressure is applied equally in all direction, what type of electronic configuration is favoured for an octahedral high-spin d^5 transition metal complex?

Low spin; because it leads to low electron density between the metal and the ligand (i.e., along the bond axis).



Q02. Using the crystal field stabilization energy as criterion, indicate whether you expect the following spinels to be normal or inverse: Fe_3O_4 ; Co_3O_4 .

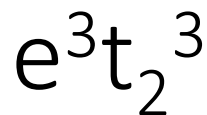
Spinel by definition, the 3+ ion has to go to the O_h site leaving the 2+ ion in T_d .

Fe_3O_4 is composed of Fe(II) T_d and Fe(III) O_h ions with d6 and d5 configurations respectively. Since d⁵ has no CFSE, it is more advantageous to put it in a T_d environment than in O_h . In other words, by placing d⁶ ions in O_h environment there is more gain in more CFSE than keeping this in T_d environment. Here the Fe_3O_4 structure is inverse spinel.

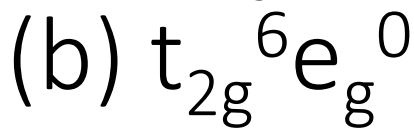
Co_3O_4 has a similar structure with d7 and d6 configurations for 2+ and 3+ ions respectively. Co(III) d6 ion is low spin because (a) high charge (even with weak ligands like oxo) and (b) maximum gain in CFSE. So the Co_3O_4 structure is normal spinel.

Q03. By showing the details, determine the CFSE for the following complexes:

(a) $[\text{FeCl}_4]^{2-}$; (b) $\text{W}(\text{CO})_6$.



$$\text{CFSE} = -0.6 \Delta_t$$

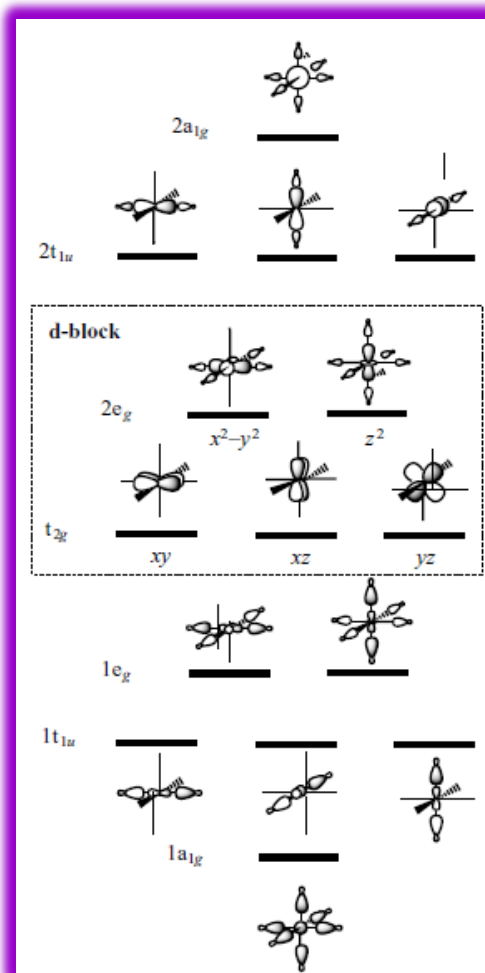
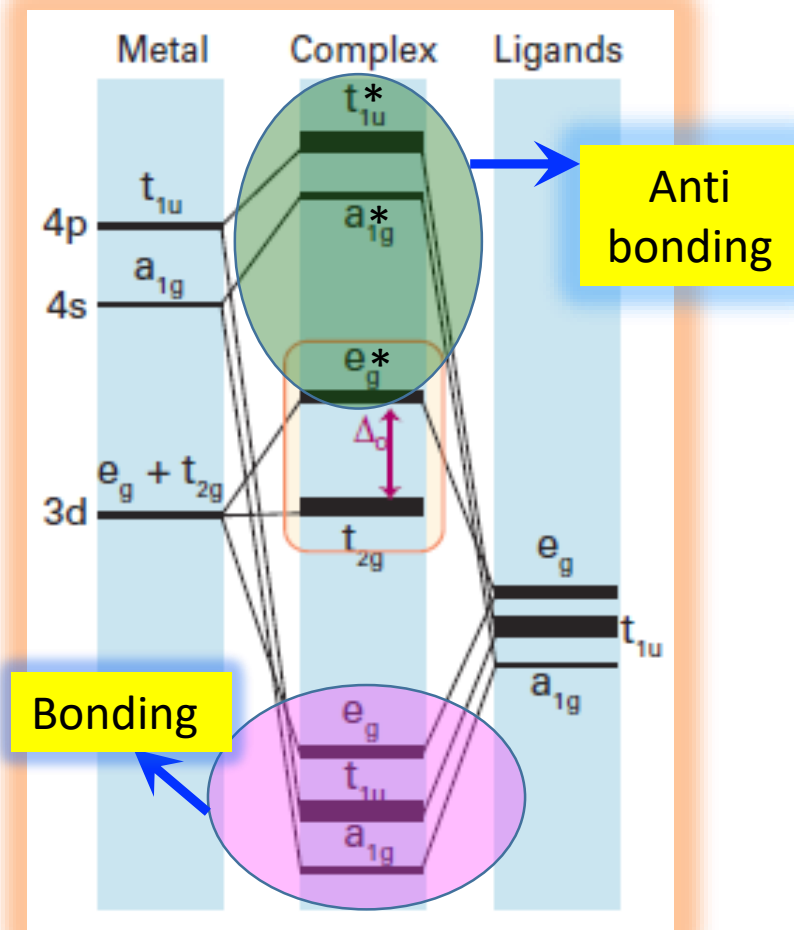


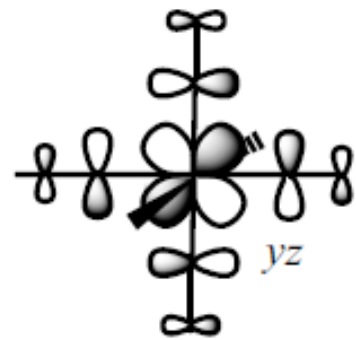
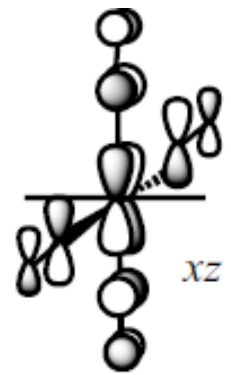
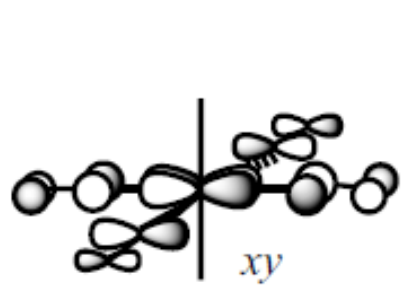
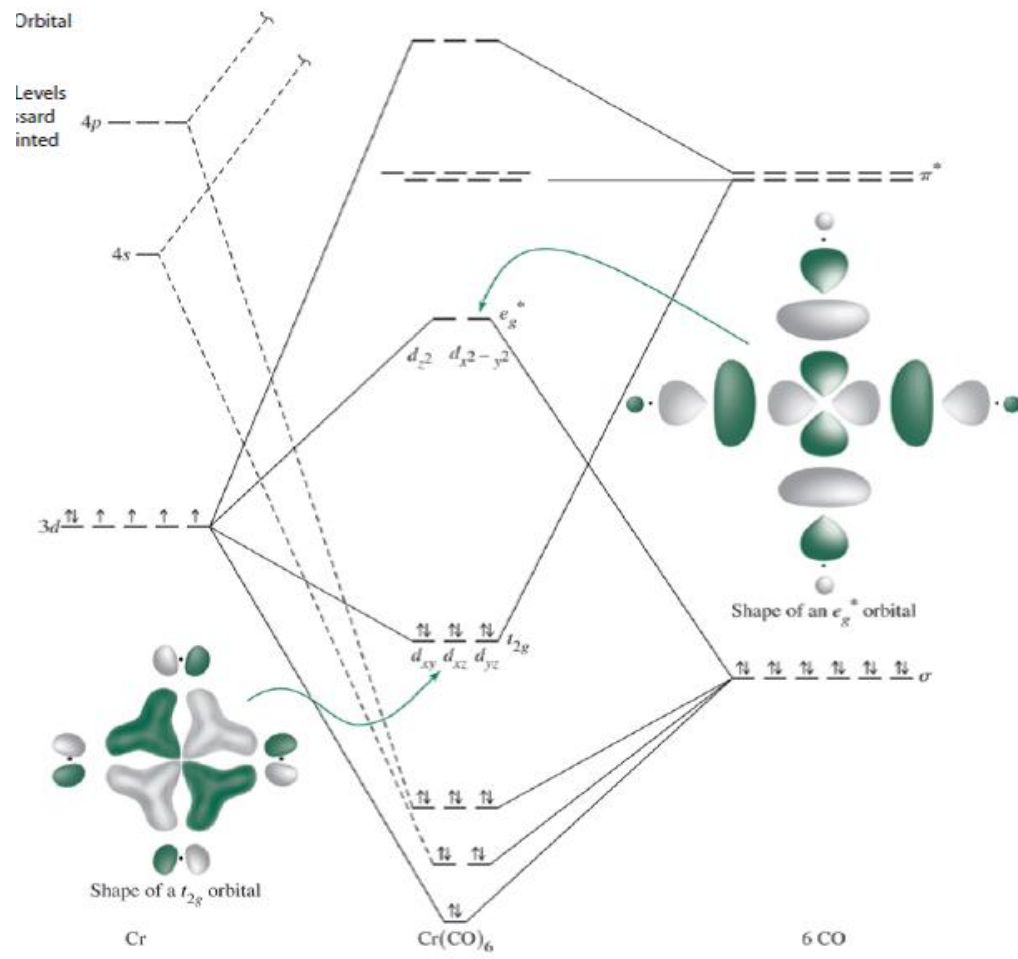
$$\text{CFSE} = -2.4 \Delta_o$$

Q04. $[\text{Cr}(\text{CO})_6]$ is a stable molecule while $[\text{Ni}(\text{CO})_6]$ is very unstable. Rationalize this observation employing Molecular Orbital Theory and draw the corresponding molecular orbital diagrams.

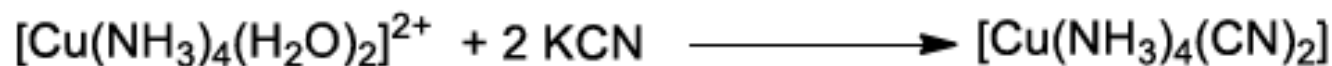
One is 18 electron complex and other is 22 electron complex. As per MOT, filling the anti-bonding orbital will lead to instability. As this is the case for the $[\text{Ni}(\text{CO})_6]$, this is unstable.

M-L \rightarrow σ -bonding



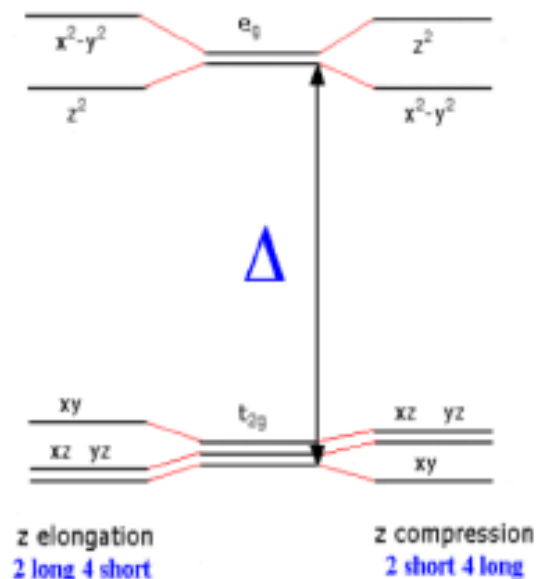


Q05. $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex reacts with two equivalent of KCN leading to the formation of $[\text{Cu}(\text{NH}_3)_4(\text{CN})_2]$. Based on crystal field theory, predict the orbital splitting and the expected geometry for both complexes.

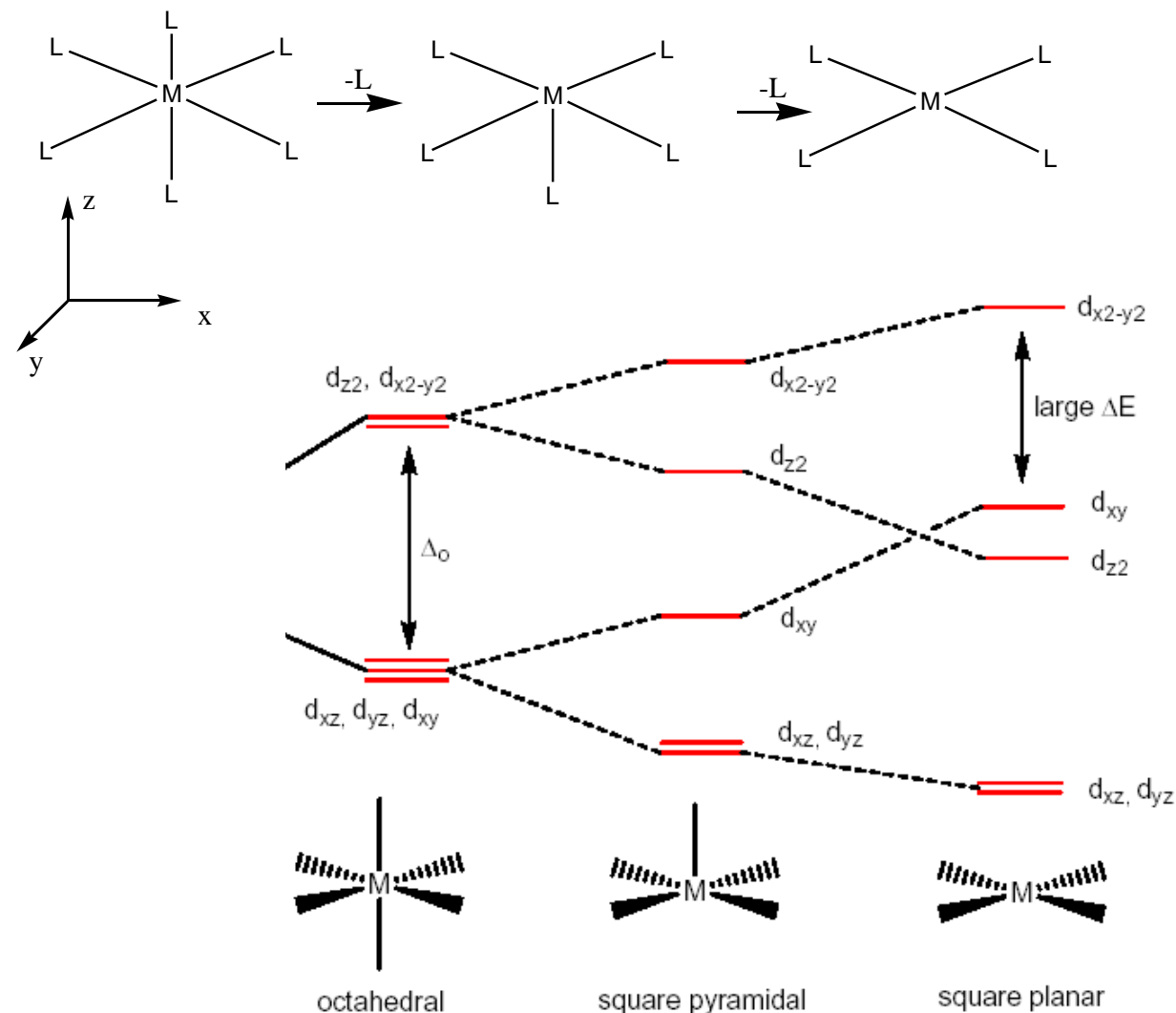


Axially
elongated

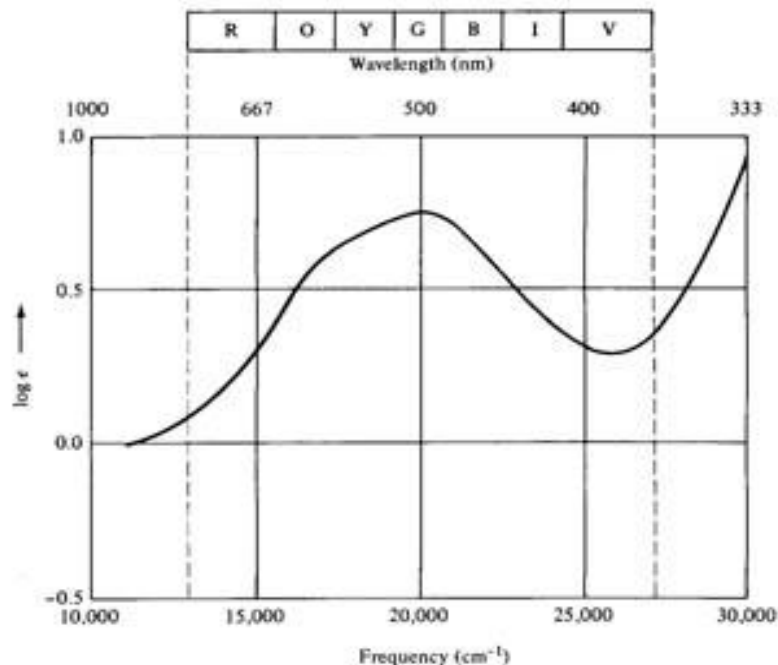
Axially
Compressed



Q06. Draw the orbital splitting for the following geometries given .
 (Assume ligand L as weak field ligand and also label the orbitals).



Q 07. For the following compounds $[M(\text{NH}_3)_6]^{3+}$ ($M=\text{Ti, Zr, Hf}$), draw the tentative absorption spectra of these compounds.



For Ti, $20,300 \text{ cm}^{-1}$ as we go down in the periodic table the crystal field splitting increases, therefore much larger splitting is expected for Zr and Hf with the trend of $\text{Ti} < \text{Zr} < \text{Hf}$. Show the bands tentatively at higher energy for Zr and Hf.