CHEMISTRY -THEORY
(CYI 101)
Inorganic Chemistry

Instructor: Dr. R P John

Department of Chemistry & Chemical Biology

Evaluation and Study Material

Examination/Class tests/others

- See Academic Calendar
- Will be informed time to time

Course Material

- What the instructor teaches!
- Books: *Inorganic chemistry: Huheey, Keiter and Keiter*
  Inorganic Chemistry: Housecroft and Sharpe

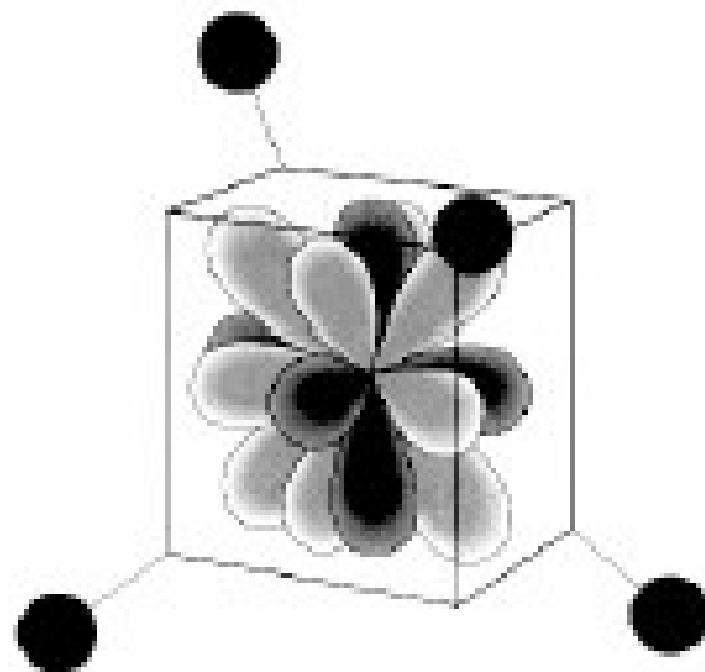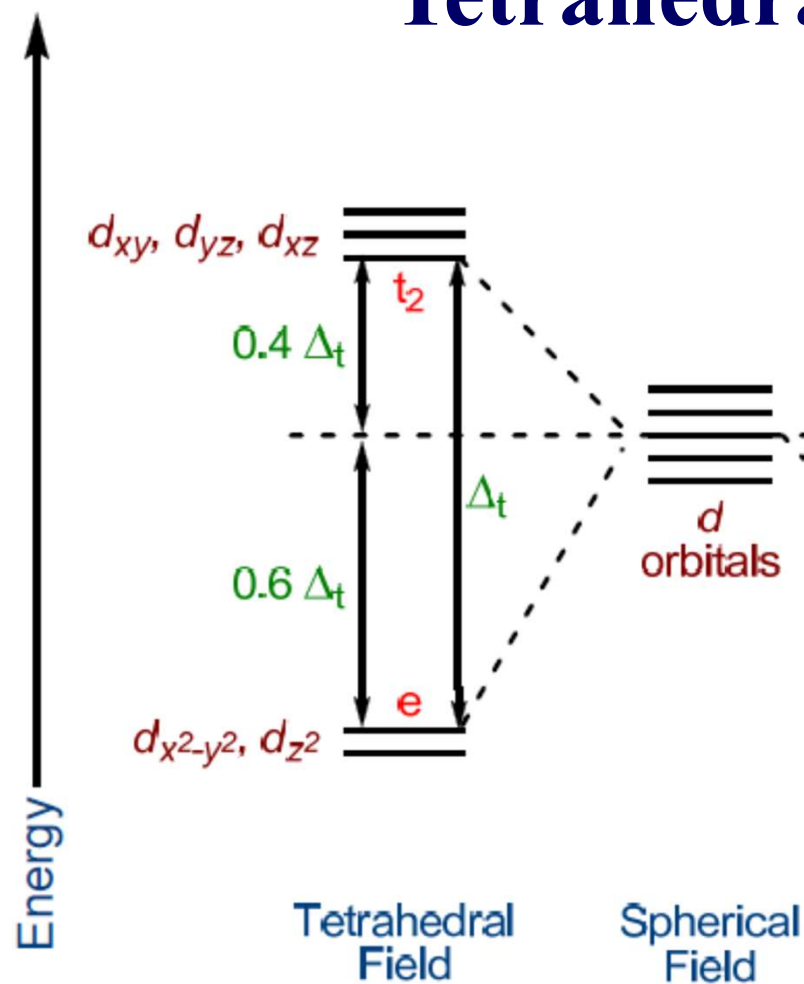*Shriver Atkin's Inorganic Chemistry: Atkins, Overton, Rourke, Weller and Armstrong*

Tetrahedral Field

Tetrahedral Field

Tetrahedral Field

d_{xy}, d_{yz}, d_{xz}

t_2

0.4 Δ_t

Δ_t

0.6 Δ_t

e

$d_{x^2-y^2}$, d_{z^2}

d orbitals

Energy
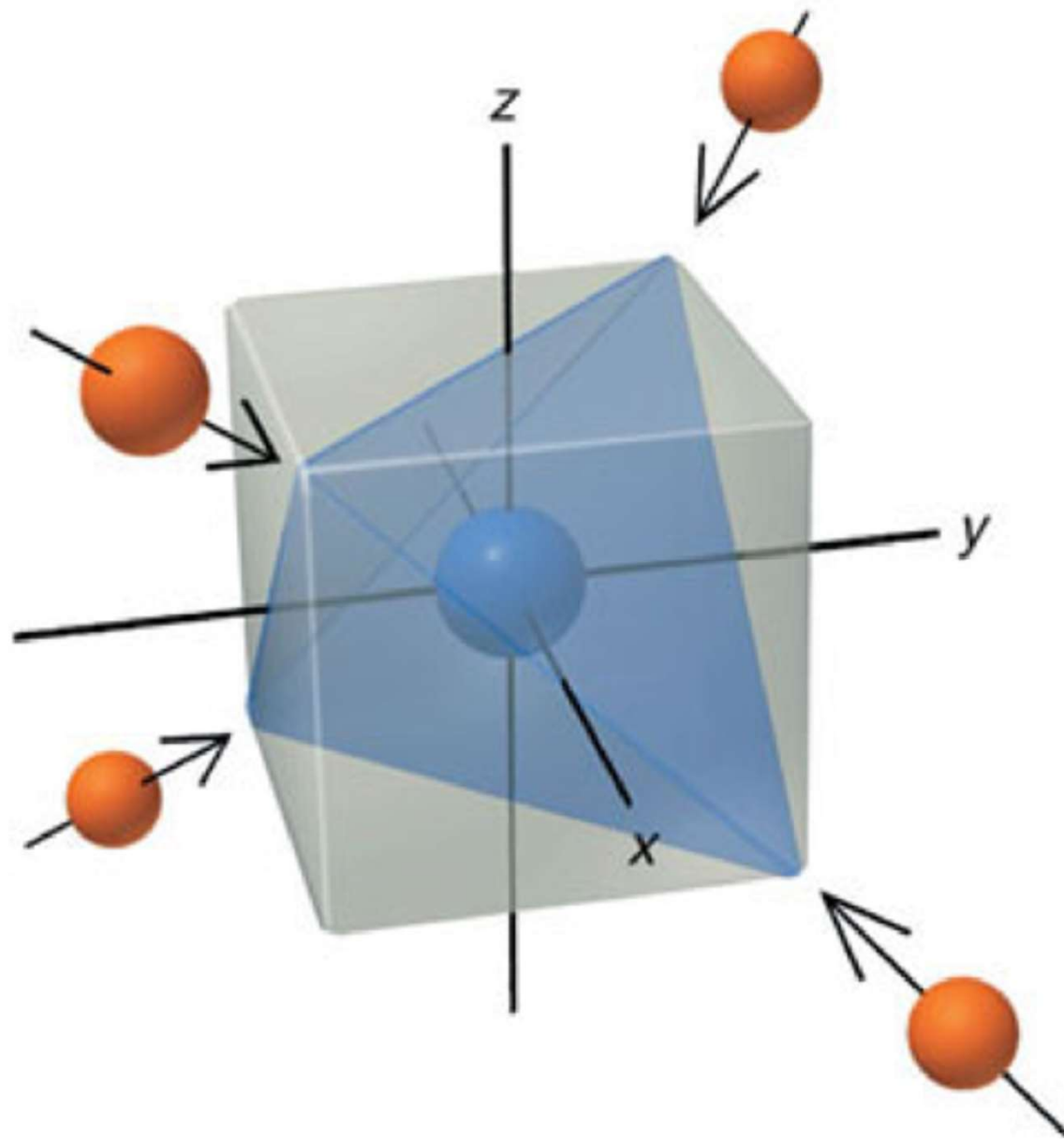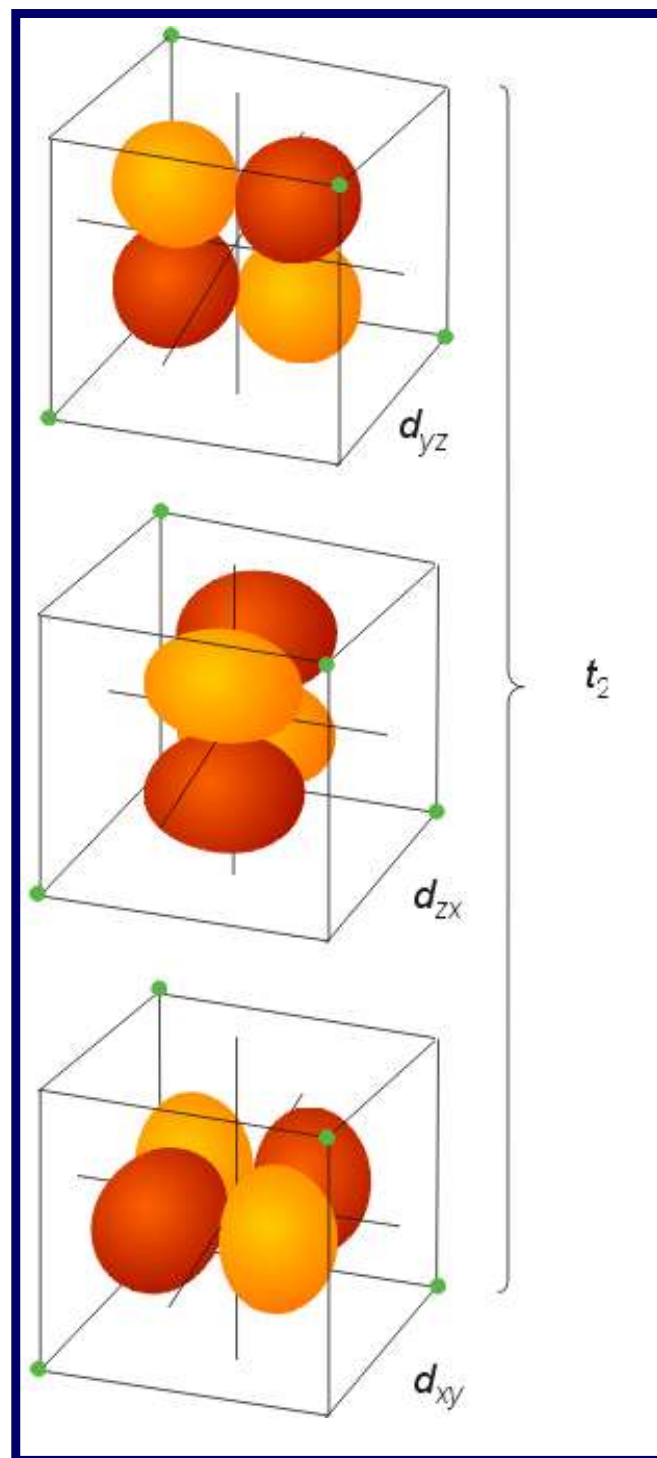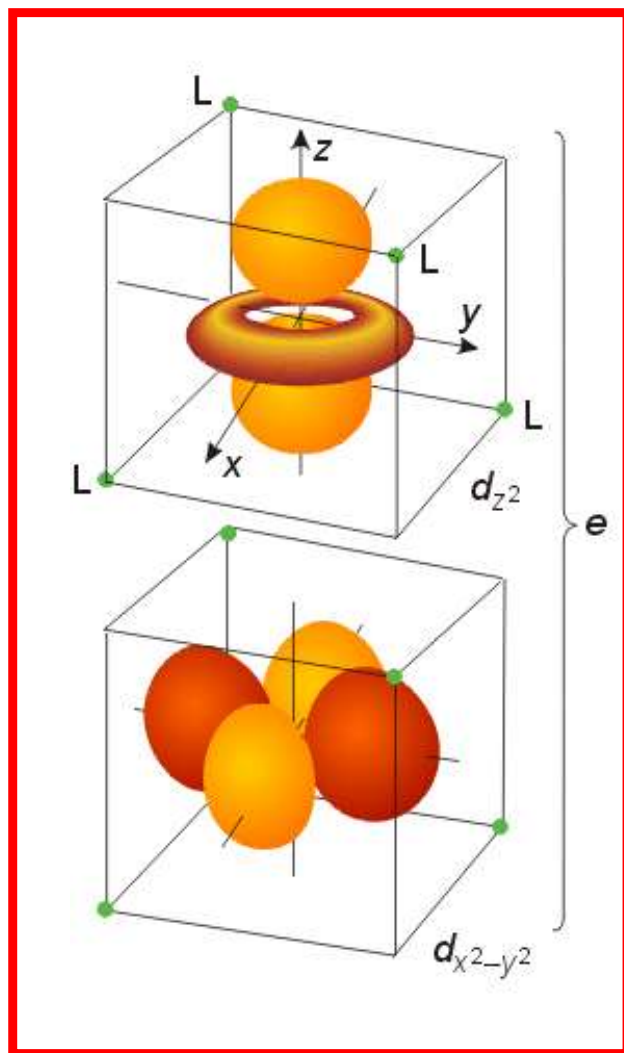
Tetrahedral Field

Spherical Field

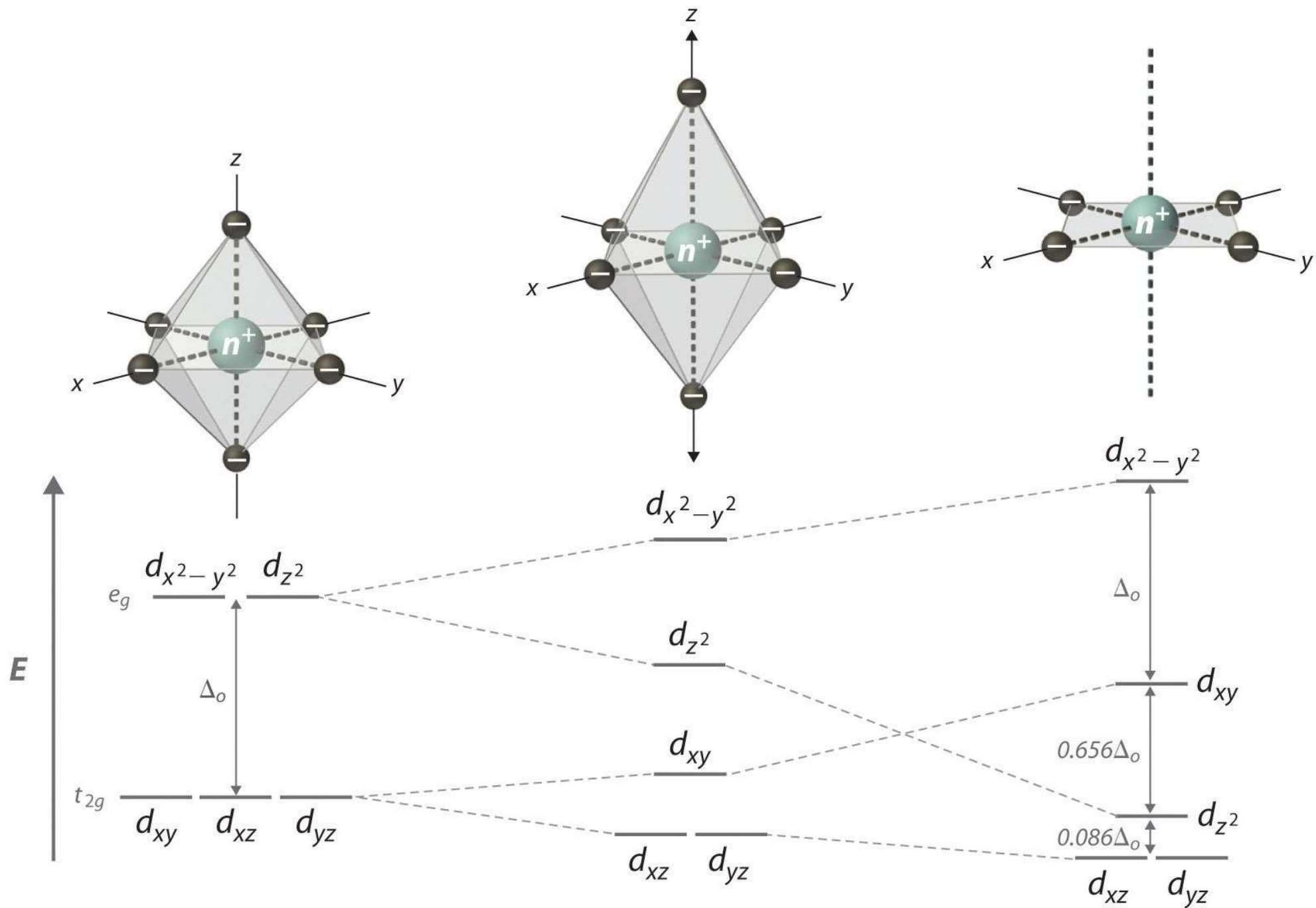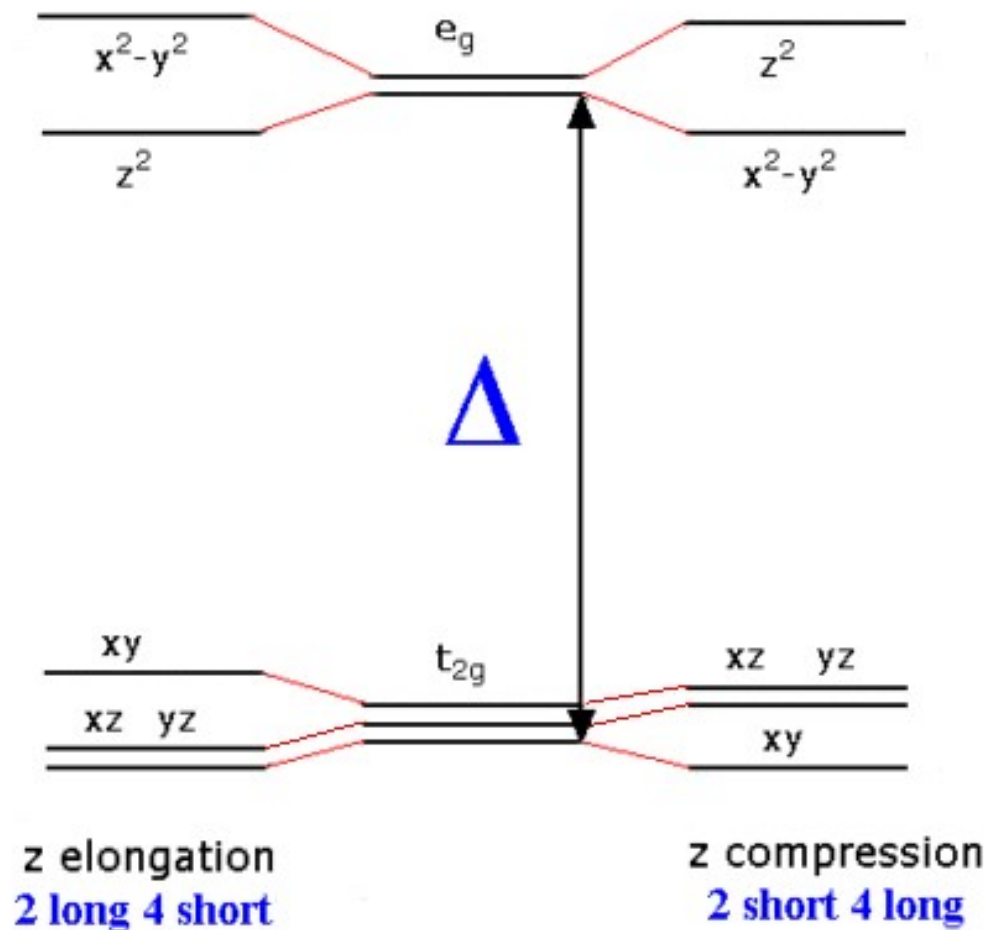$\Delta_t < \Delta_o$

$\Delta_t = 0.45\ \Delta_o$

For the same metal and ligands and the same internuclear distances

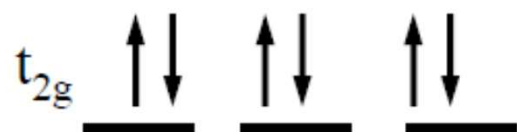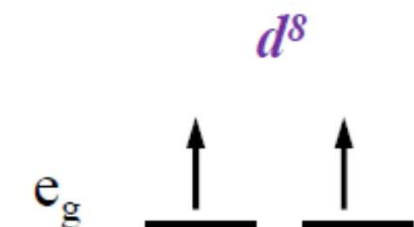# Distortions of Octahedral Complexes

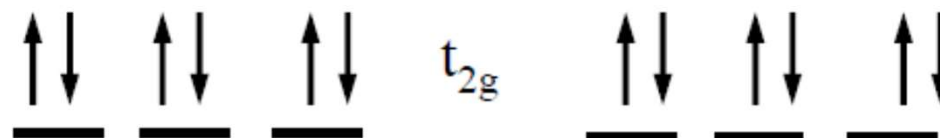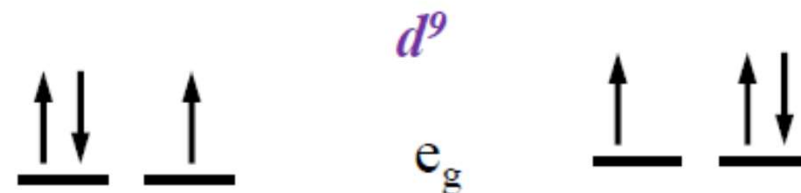# Distortions of Octahedral Complexes: Jahn-Teller effect

'*Any non-linear molecule having an orbitally degenerate electronic configuration is unstable, and the system undergo distortion to remove the degeneracy.*'

z elongation
2 long 4 short

z compression
2 short 4 long

Distortions of Octahedral Complexes

d^8

e_g ↑   ↑

t_{2g} ↑↓   ↑↓   ↑↓

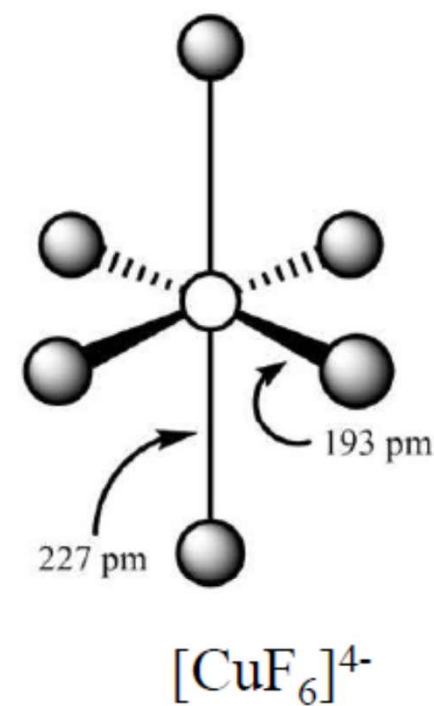Ni^{2+}: Only one way of filling the orbitals; not degenerate and no Jahn-Teller Distortion

d^9

↑↓   ↑ e_g ↑   ↑↓

↑↓   ↑↓   ↑↓ t_{2g} ↑↓   ↑↓   ↑↓

Cu^{2+}: Two ways of filling the e_g orbitals; there is degeneracy and Jahn-Teller Distortion is observed

Distortions of Octahedral Complexes

energy

e_g ↑↓ ↑

t_{2g} ↑↓ ↑↓ ↑↓

Cu(II) in regular octa-
hedral environment

↑ $d_{x^2-y^2}$

↑↓ d_{z^2}

↑↓ d_{xy}

↑↓ ↑↓ d_{xz} d_{yz}

Cu(II) after J-T distortion

193 pm

227 pm

$[CuF_6]^{4-}$
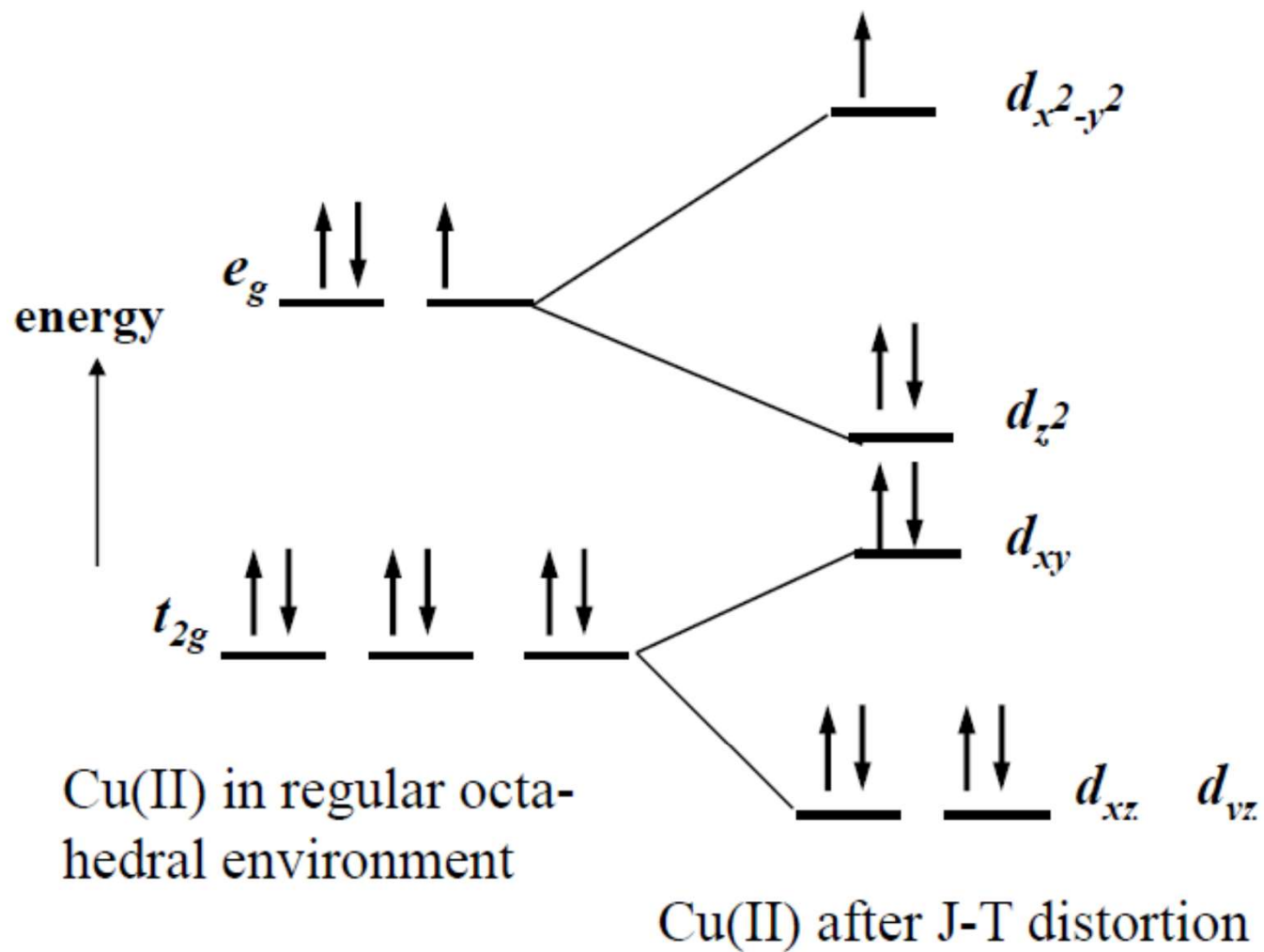
Jahn-Teller Distortion in d^9 Complexes
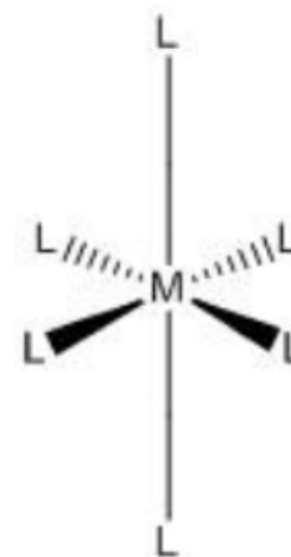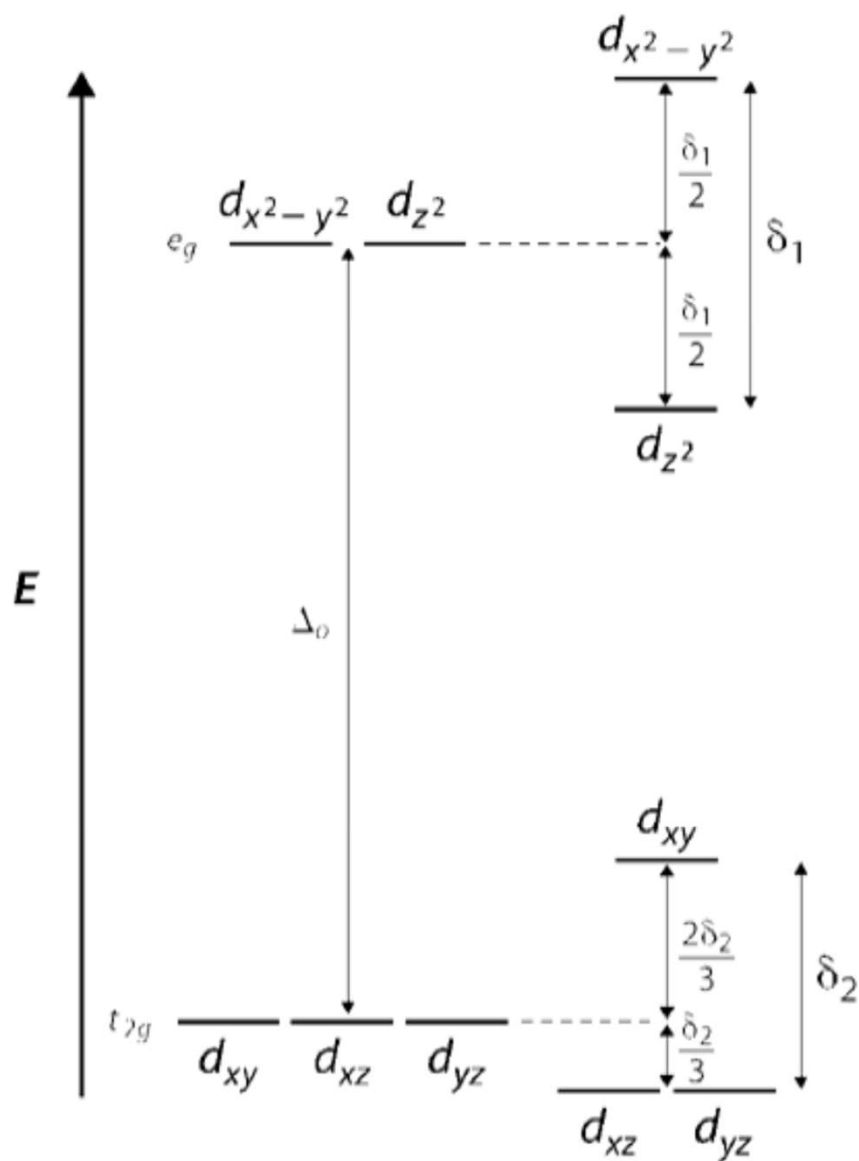
$\Delta o \gg \delta 1 > \delta 2.$

Jahn-Teller Distortion in d^1 Complexes

d^1 Vs d^9

$$\Delta \gg \delta_1 > \delta_2$$
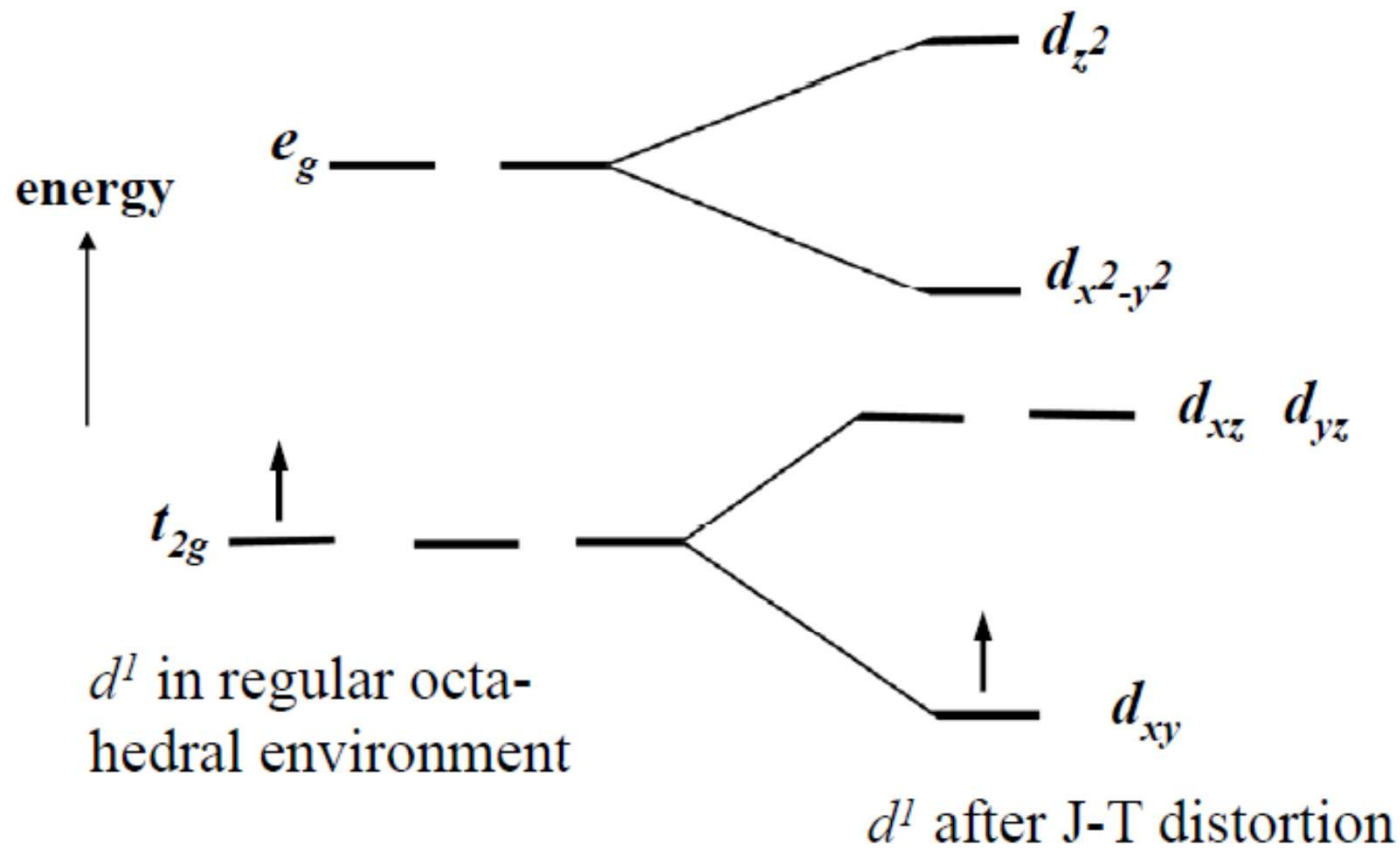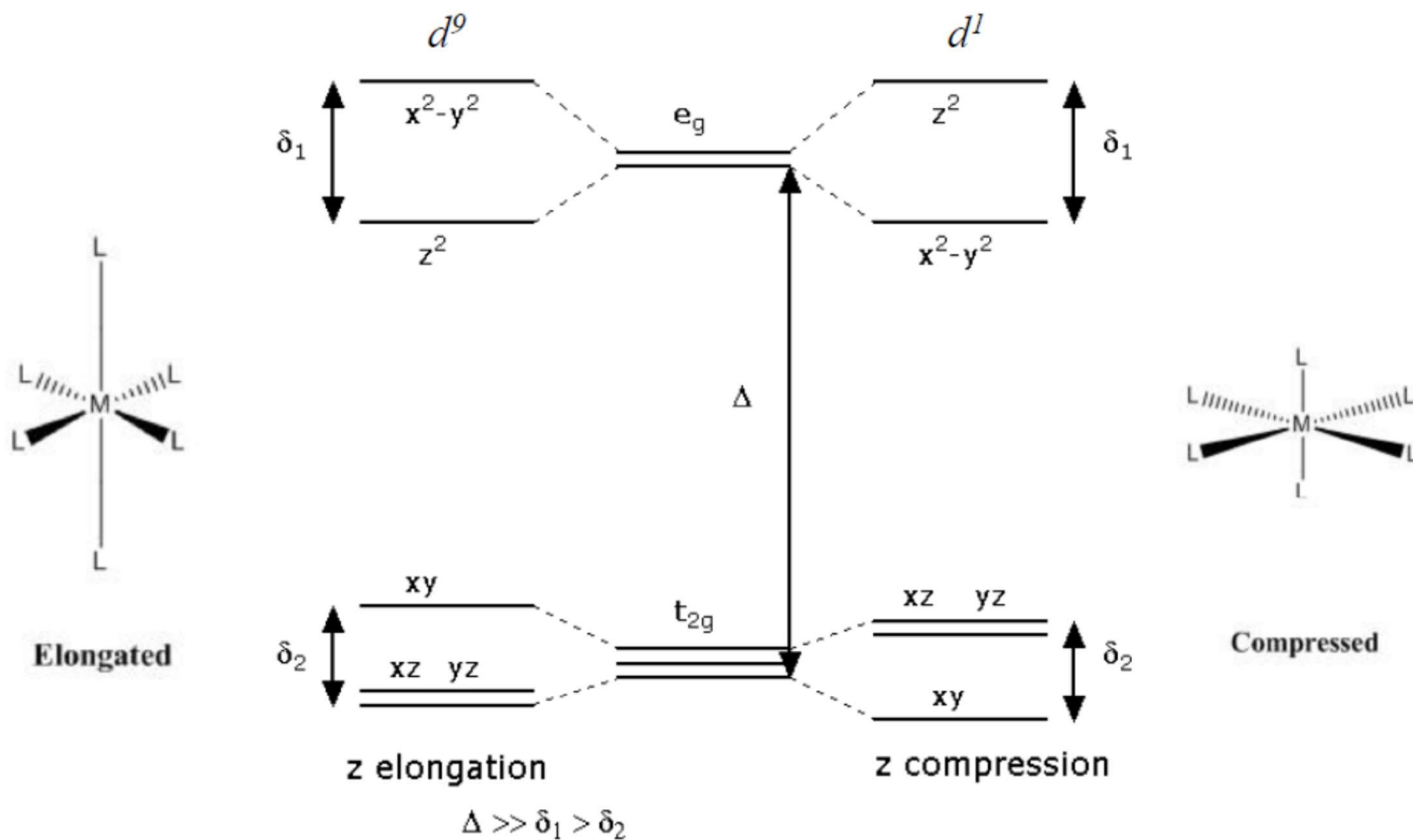
Distortions are more pronounced if the degeneracy occurs in an e_g orbital

Distortions in Low-Spin Complexes
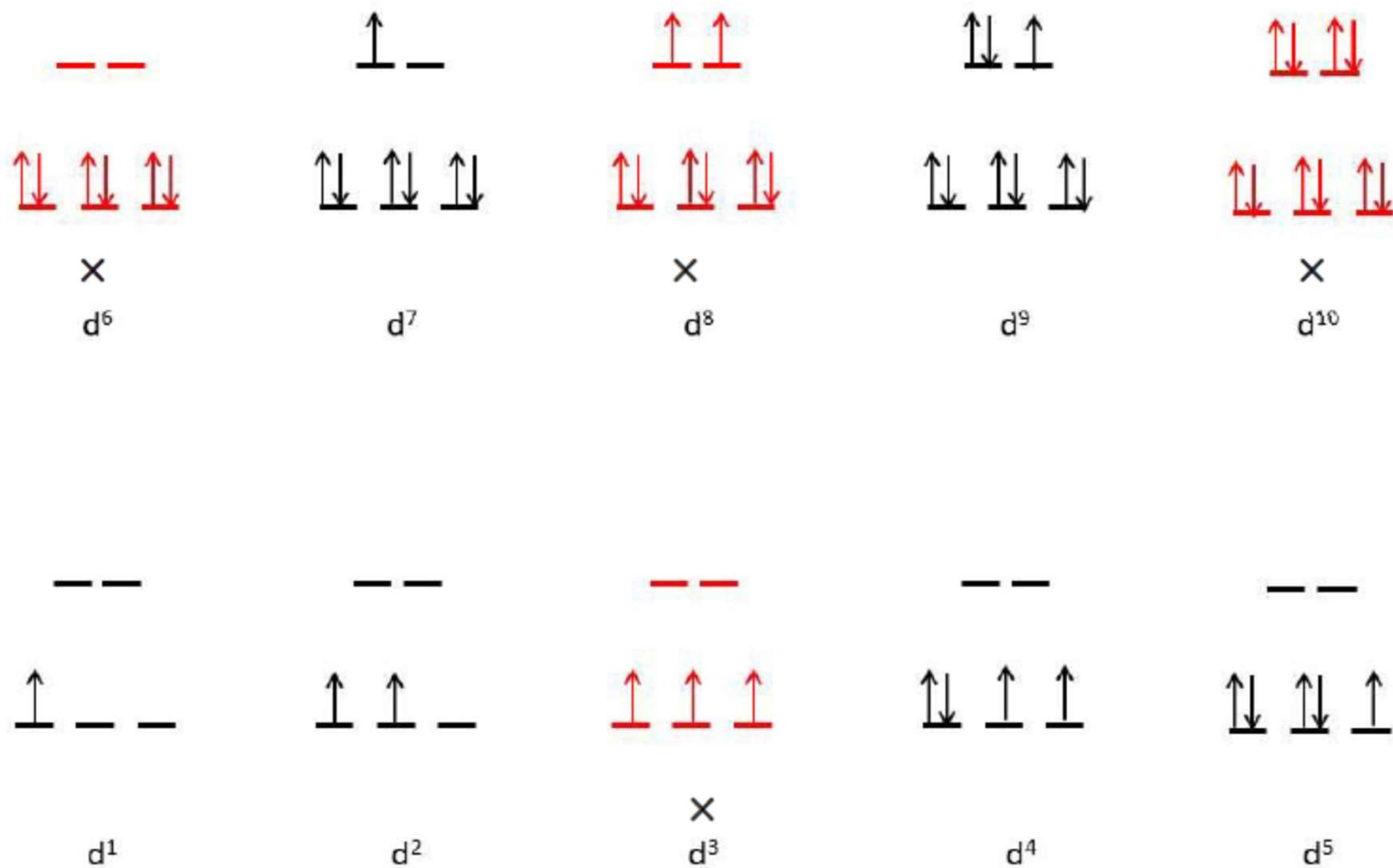
Distortions in High-Spin Complexes

d^6 d^7 d^8 d^9 d^{10}

d^1 d^2 d^3 d^4 d^5
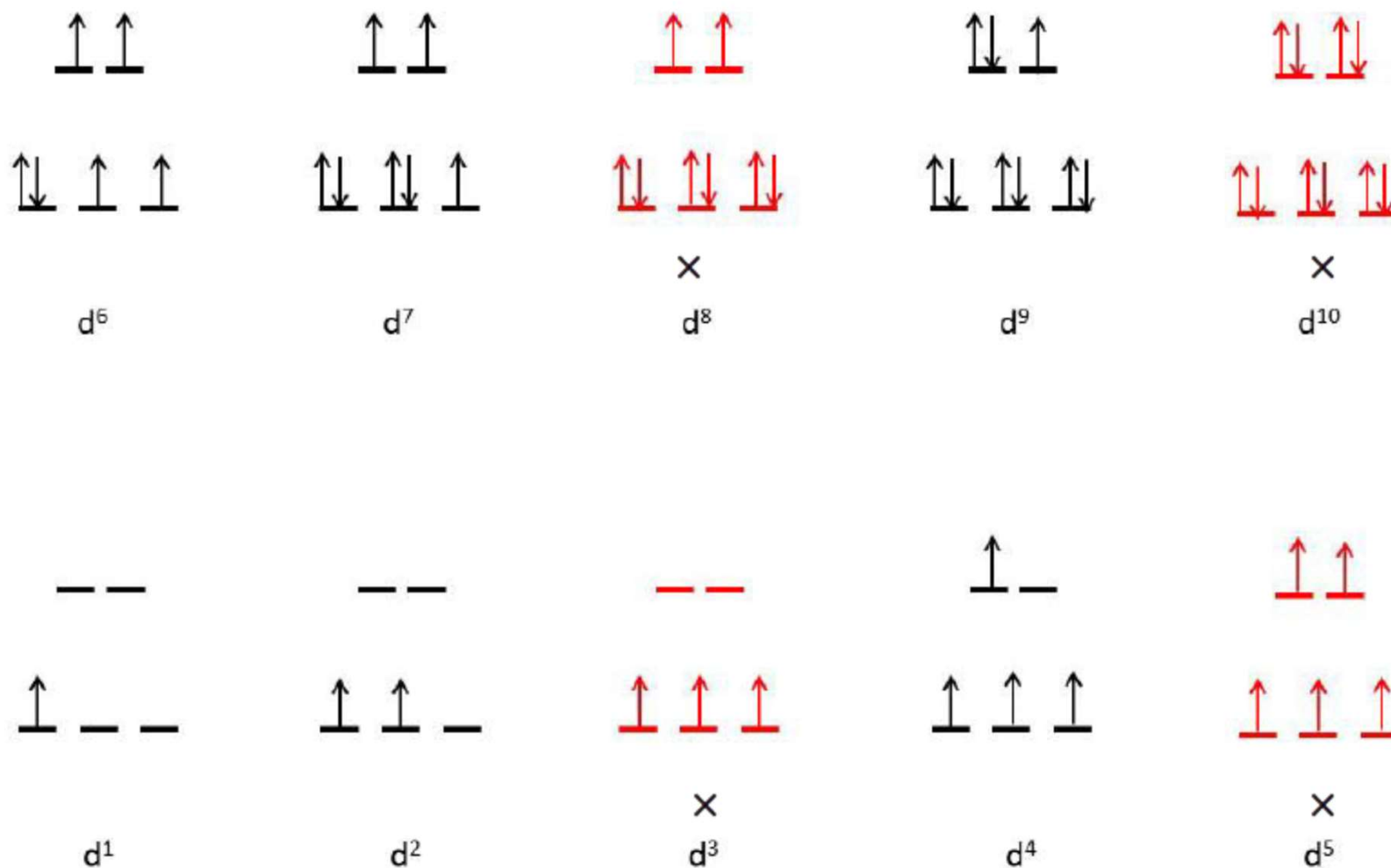
Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum   orbital angular momentum
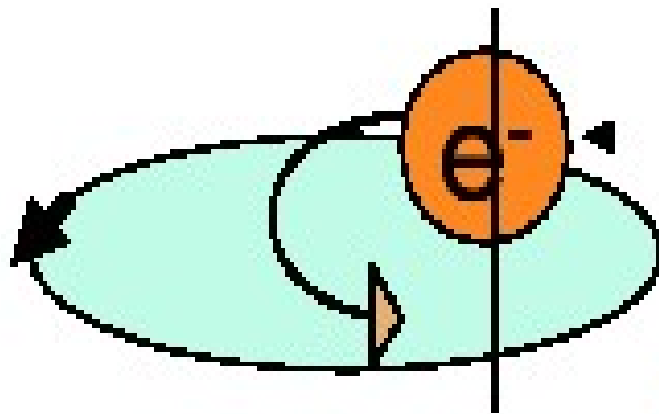
Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

n = no. of unpaired electrons

$$\mu = \{n(n+2)\}^{1/2} \, \mu_B$$

Ion	n	S	μ/μ_B Calculated	Experimental
Ti^{3+}	1	1/2	1.73	1.7 – 1.8
V^{3+}	2	1	2.83	2.7 – 2.9
Cr^{3+}	3	3/2	3.87	3.8
Mn^{3+}	4	2	4.90	4.8 – 4.9
Mn^{2+}	5	5/2	5.92	5.9 - 6.3

Similar Calculation can be done for Low-spin Complex

The d^8 complexes $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ are square planar and tetrahedral respectively. Will these complexes be paramagnetic or diamagnetic?

Tetrahedral
$[NiCl_4]^{2-}$

Square planar
$[Ni(CN)_4]^{2-}$
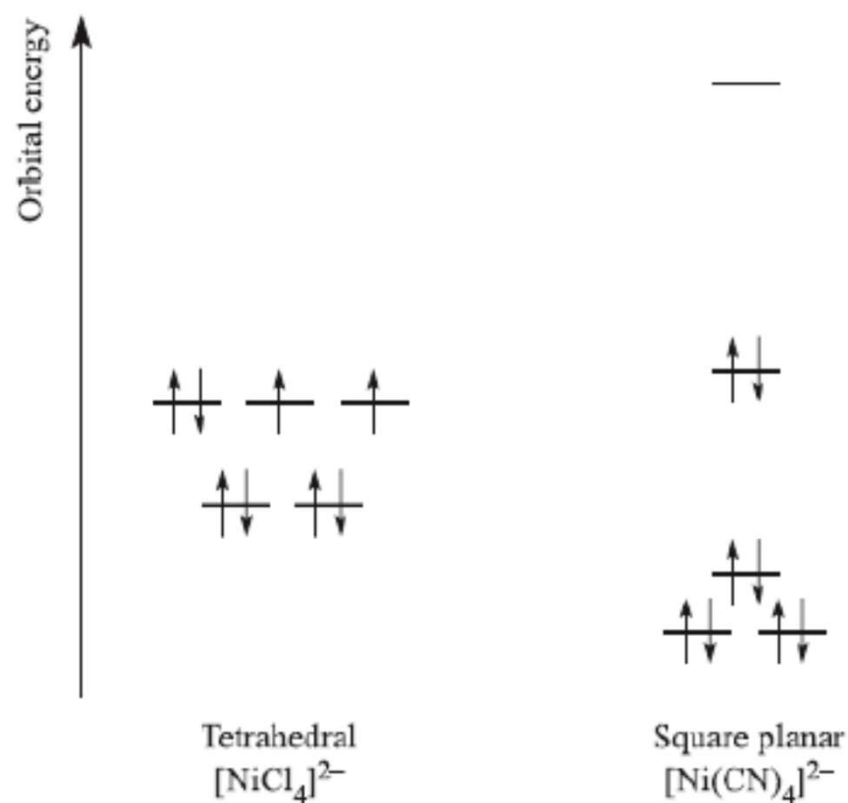
Thus, $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic.

The origin of the color of the transition metal compounds
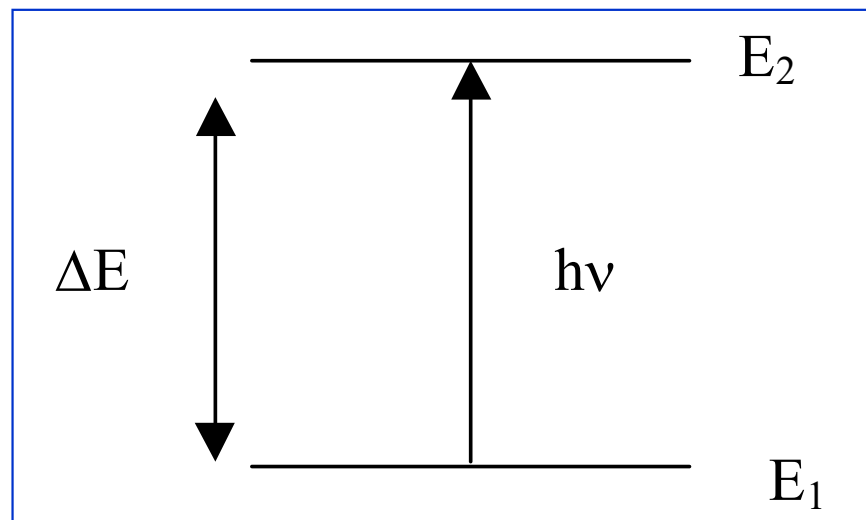
$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_O, therefore the colour

absorbed color
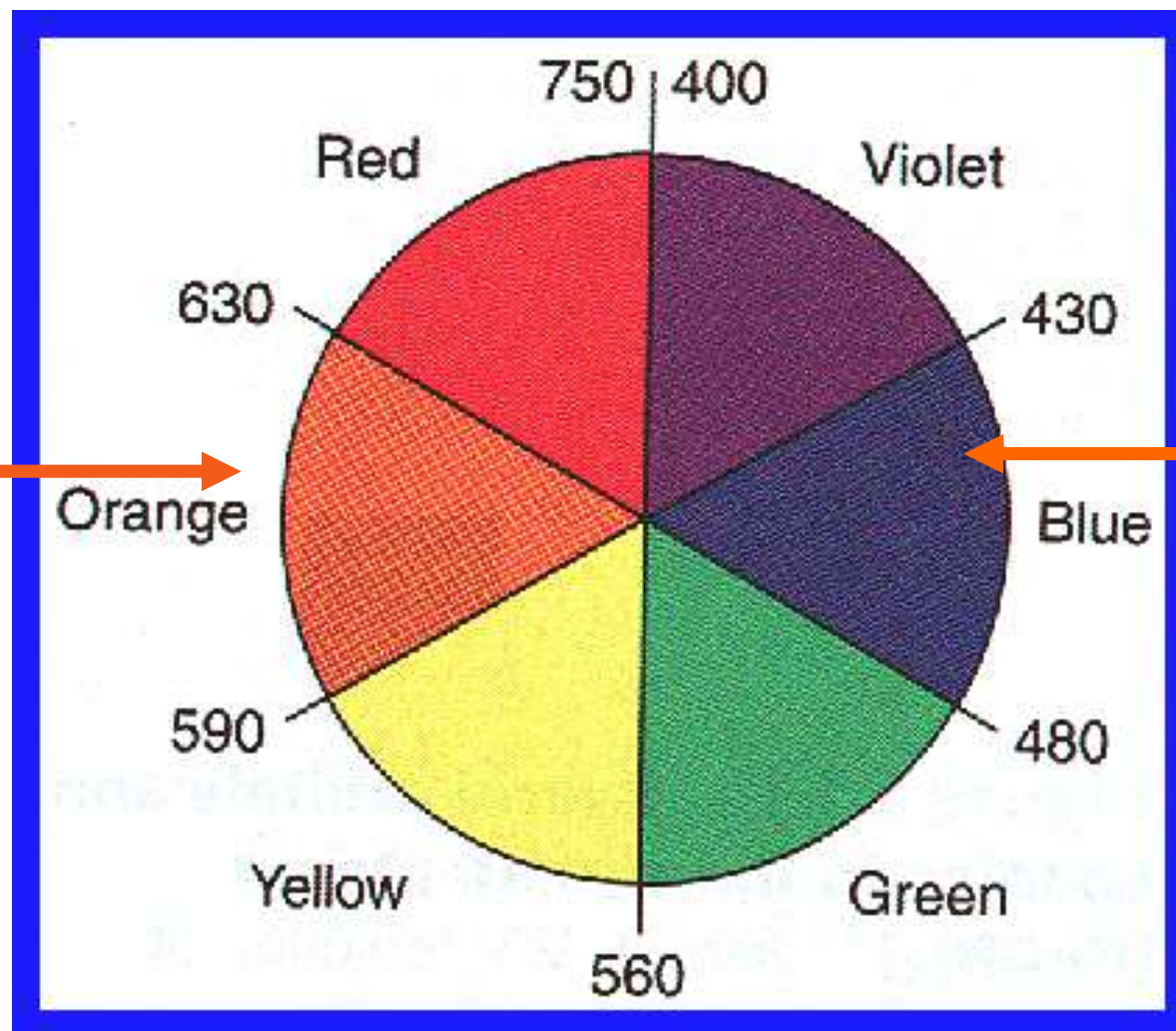
observed color

The colour can change depending on a number of factors e.g.

1. Metal charge
2. Ligand strength

$[CoI(NH_3)_5](NO_3)_2$

$[CoBr(NH_3)_5](NO_3)_2$

$[CoCl(NH_3)_5](NO_3)_2$

$[Co(NO_2)(NH_3)_5](NO_3)_2$

$[Co(SO_4)(NH_3)_5]NO_3$

$[Co(CO_3)(NH_3)_5]NO_3$

Energy

$[CrF_6]^{3-}$ $[Cr(H_2O)_6]^{3+}$ $[Cr(NH_3)_6]^{3+}$ $[Cr(CN)_6]^{3-}$
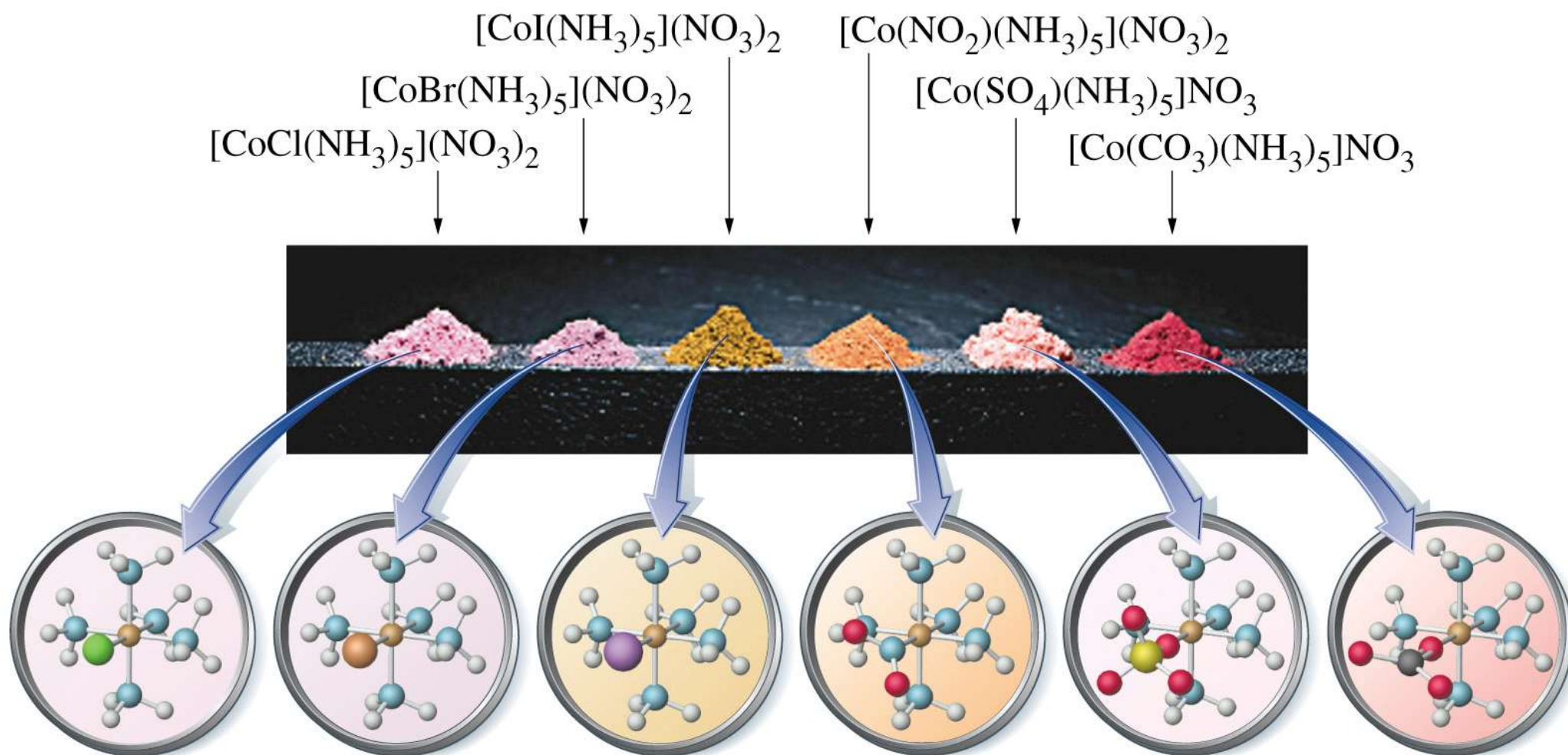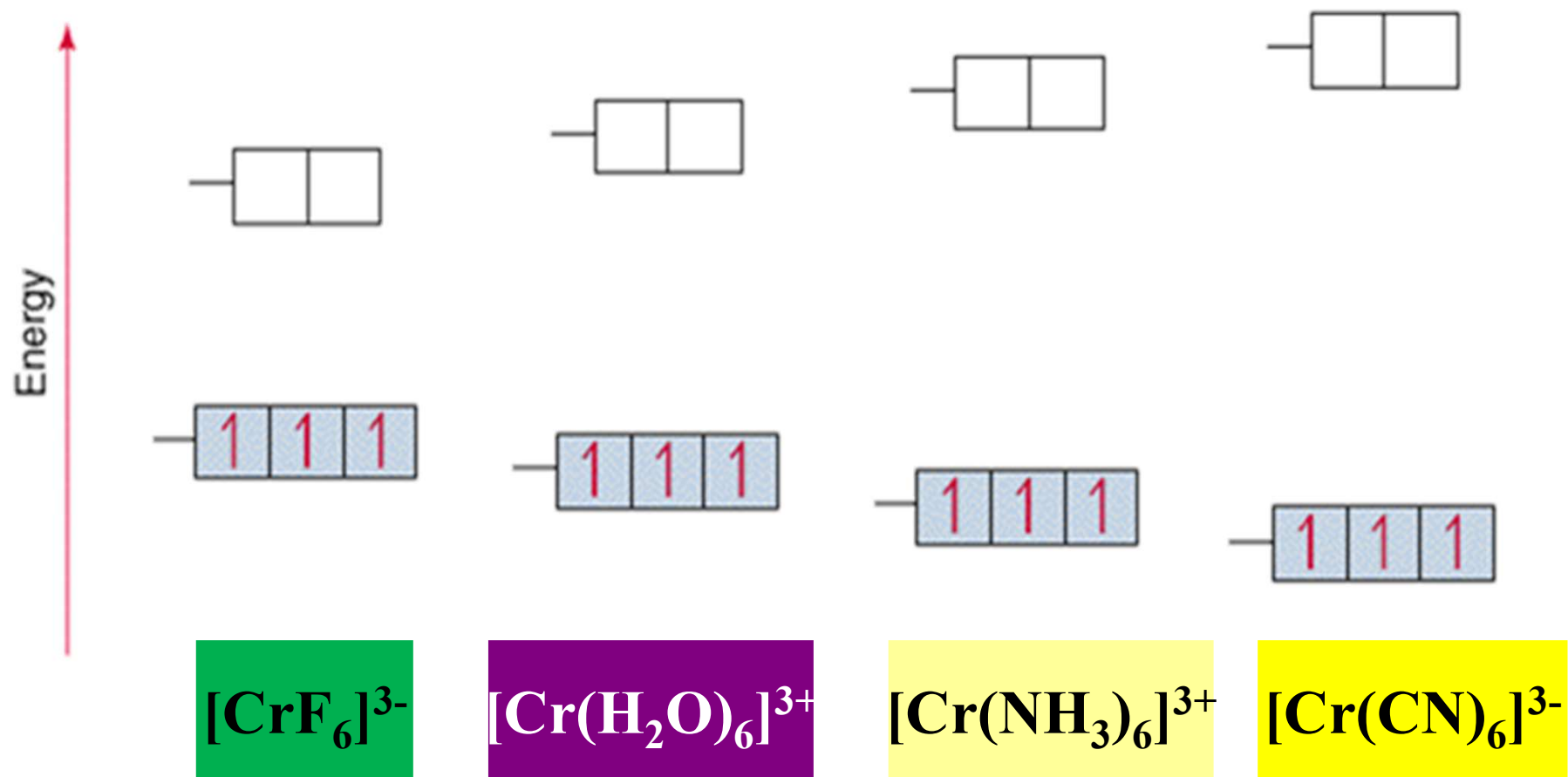
As **Cr³⁺** goes from being attached **to a weak field** ligand to a **strong field ligand,** Δ **increases** and the **color of the complex changes from green to** yellow.

Calculate Δ_o for $[Ti(OH_2)_6]^{3+}$

$\lambda_{max} = 493$ nm

$\tilde{v}_{max} = 20\ 300$ cm^{-1}
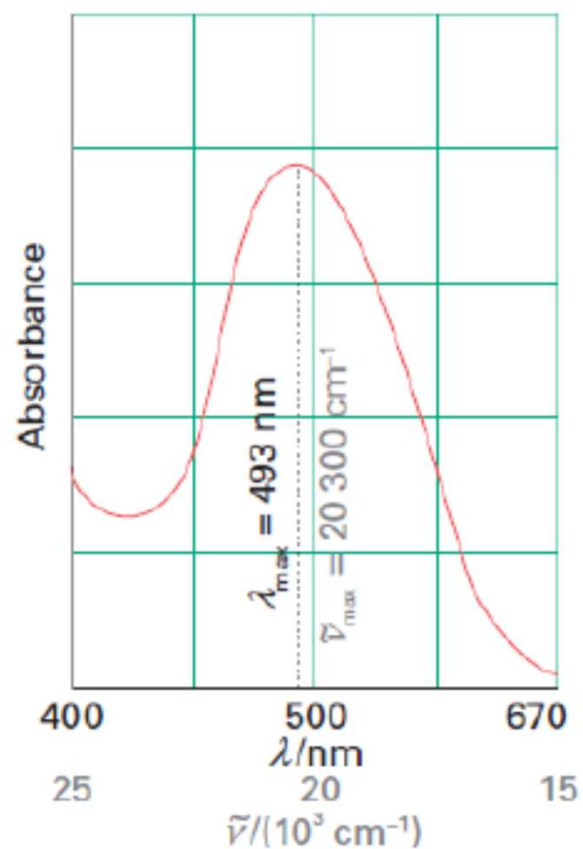
Absorbance

λ/nm

400   500   670

25   20   15

$\tilde{v}/(10^3$ cm$^{-1})$

The optical absorption spectrum of $[Ti(OH_2)_6]^{3+}$

A more resolved absorption spectrum of the complex has a shoulder

Aqueous TiCl₃

$Ti^{3+}(d^1)$

d_{z^2}

$d_{x^2-y^2}$

d_{xz} d_{yz}

d_{xy}
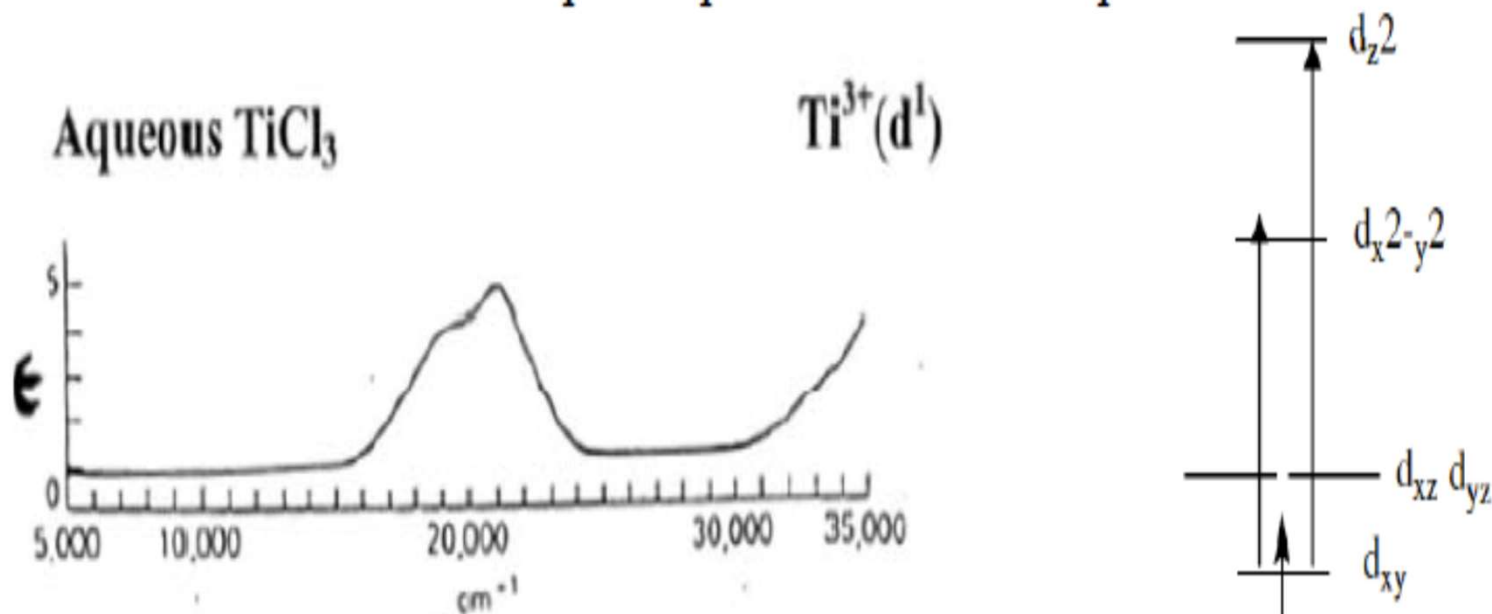
Home work Assignment 1

1. What are the limitations of crystal field theory?
2. Show the filling of electrons in the d-orbitals and calculate the spin only magnetic moments of a) *trans*-[Cu(NH₃)₄(H₂O)₂]²⁺, b) *trans*-[V(py)Cl₄], c) [MnCl₆]³⁻, d) [Ni(H₂O)₆]²⁺, e) *trans*-Ni(py)₄(H₂O)₂]²⁺, f) [NiCN₄]²⁻, g) [Ni(CN₆)]³⁻
3. A complex [Mn(H₂O)₆]³⁺ absorbs at 560nm. Identify the ground state and excited state electronic configuration and calculate the energy of transition between HOMO and LUMO in cm⁻¹.

Limitations of CFT

Considers Ligand as Point charge/dipole only
Does not take into account of the overlap of ligand and metal orbitals

Consequence

e.g. Fails to explain why CO is stronger ligand than CN^- in complexes having metal in low oxidation state

Homework assignment 2

1, Identify Jahn- Teller distortions and the consequent ordering of energy levels in the following. $K_3[Co(CN)_6]$, $[Cu(en)_3]Cl_2$, $K_2[VOCl_4]$, $[Mn(H_2O)_6]SO_4$

2. Predict the spin only magnetic moment of the octahedral complexes formed by the reaction of Mn^{3+} with H_2O and CN^-. Given: the Pairing energy (P) for Mn^{3+} = 28,000 cm^{-1}, Δ_o (H_2O) = 21000 cm^{-1}, Δ_o (CN^-) = 38000 cm^{-1}.