CHEM F111 : General Chemistry
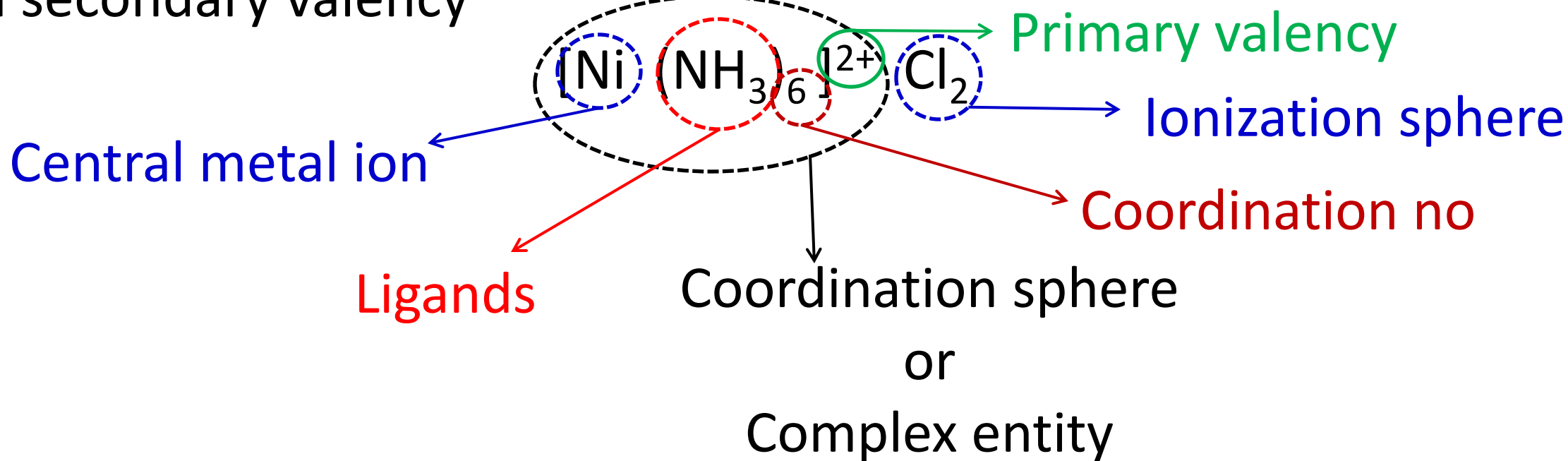## Semester II: AY 2017-18
Lecture-22, 14-03-2018

Discussed topics……

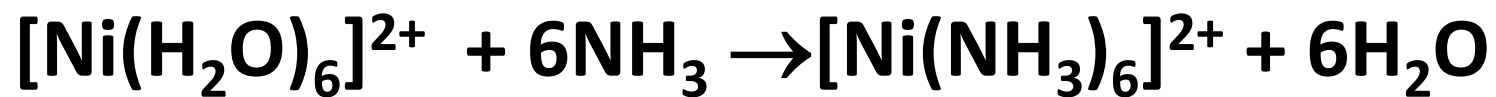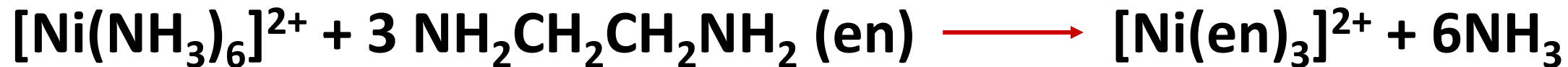➢ <u>Werner's work:</u> Coordination sphere, Coordination No, Primary and secondary valency

Primary valency

Ionization sphere

Central metal ion

Coordination no

Ligands

Coordination sphere
or
Complex entity

$[Ni(NH_3)_6]^{2+} Cl_2$

➢ EAN, EAN violation, Stability of complexes, Effect of chelation, Chelate formation, and isomerism

$$[Ni(NH_3)_6]^{2+} + 3\ NH_2CH_2CH_2NH_2\ (en) \longrightarrow [Ni(en)_3]^{2+} + 6NH_3$$

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

- en and NH_3 have similar N-donor environment
- en is bidentate and *chelating* ligand
- reaction proceeds towards right, ΔG negative
- $\Delta G = \Delta H - T\Delta S$ (ΔH -ve, ΔS ++ve)
- reaction proceeds due to entropy gain
- ΔS ++ve is the major factor behind chelate effect

Re-visit VBT

The language of valence bonding:
The nature of bond types, Promotion, Hybridization, Resonance

Drawbacks of VBT
- ✓ This theory does not discuss energies of electrons.
- ✓ The assumptions about the electrons being localized to specific locations
- ✓ Cannot account for colour of complexes
- ✓ May predict magnetism wrongly
- ✓ Cannot account for spectrochemical series

Crystal Field Theory

Crystal Field Theory

- ➢ Model for bonding in transition metal complexes
- ➢ Focuses on d-orbitals
- ➢ Ligands are considered as *point negative charges*
- ➢ Assumes ionic bonding: *electrostatic interactions*
- ➢ Electrostatic interactions: metal ions (+ve centre) attracted to ligands (-ve centre)

d-orbital expressions

$$\Psi_{3d_{\pm 1}} \;=\; Mr^2 e^{-Zr/3a_0} \sin 2\theta\, e^{\pm i\phi}$$

$$\Psi_{3d_{\pm 2}} \;=\; Mr^2 e^{-Zr/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$$

$$\Psi_{3d_{xz}} \;=\; Mr^2 e^{-Zr/3a_0} \sin 2\theta \cos\phi$$

$$\Psi_{3d_{yz}} \;=\; Mr^2 e^{-Zr/3a_0} \sin 2\theta \sin\phi$$

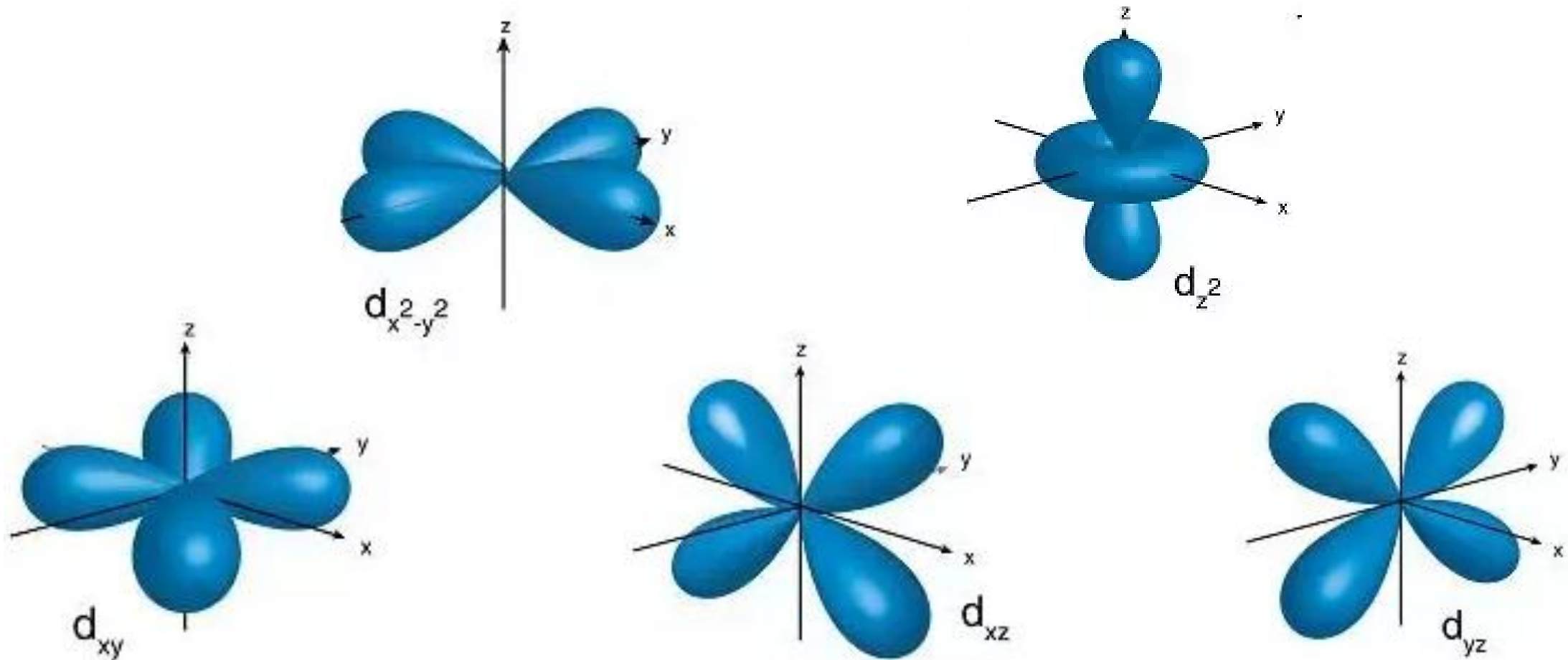$$\Psi_{3d_{x^2-y^2}} \;=\; Mr^2 e^{-Zr/3a_0} \sin^2\theta \cos 2\phi$$

$$\Psi_{3d_{xy}} \;=\; Mr^2 e^{-Zr/3a_0} \sin^2\theta \sin 2\phi$$

n=3, l=2

(not in syllabus)

Shapes of d-orbital

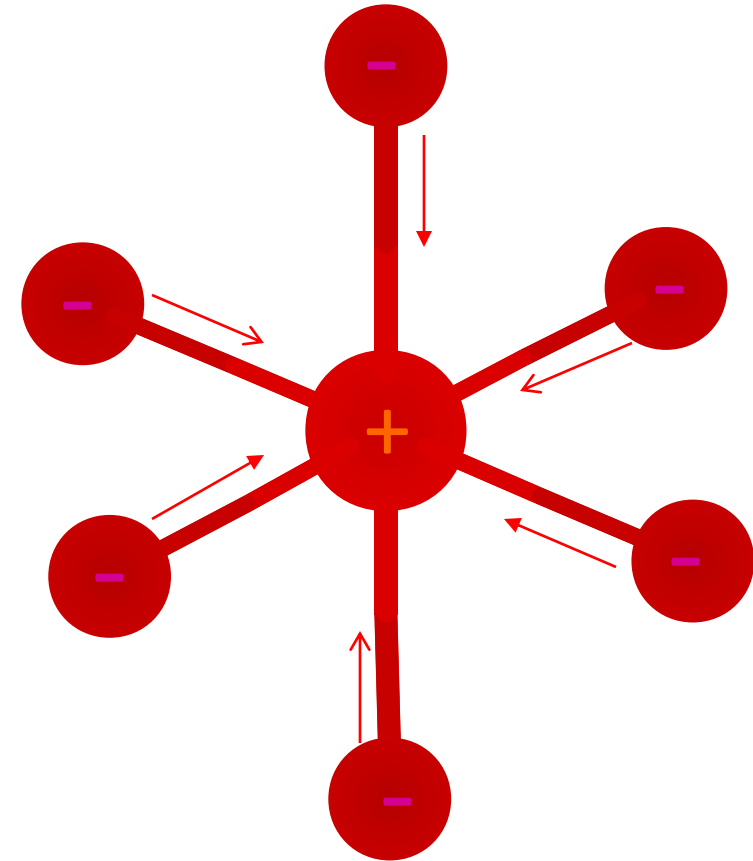CFT: Accounts for observed properties of transition metal complexes focuses on d-orbitals

Crystal Field Theory

Octahedral Crystal Field

(-) Ligands attracted to (+) metal ion; provides stability

d orbital e⁻'s repulsed by (–) ligands; increases d orbital potential energy
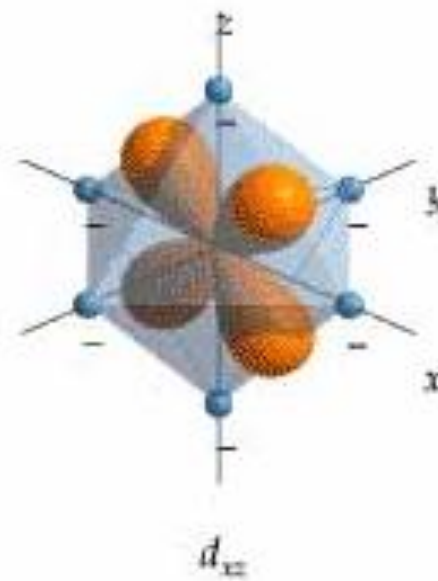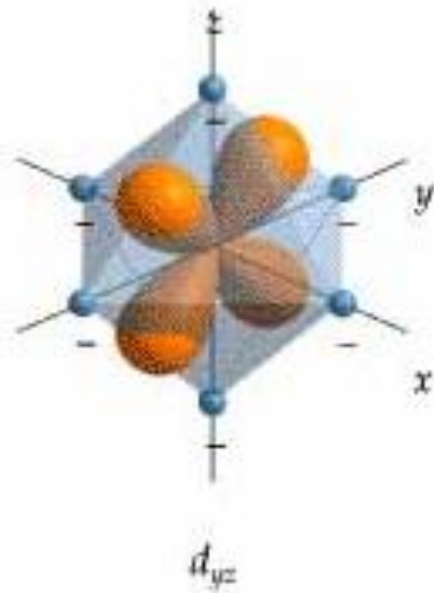

ligands approach along x, y, z axes
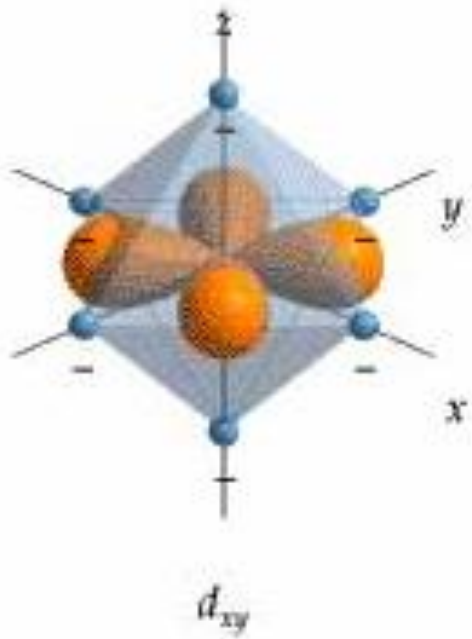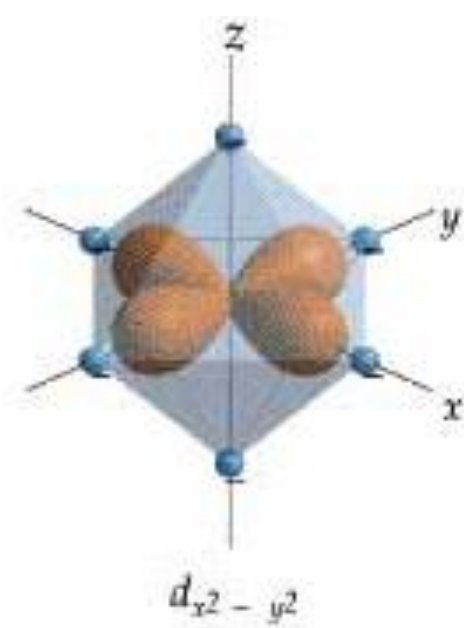
Crystal Field Theory

d_{z^2}

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

d_{xy}

d_{yz}

d_{xz}

Crystal Field Theory

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

d_{z^2}
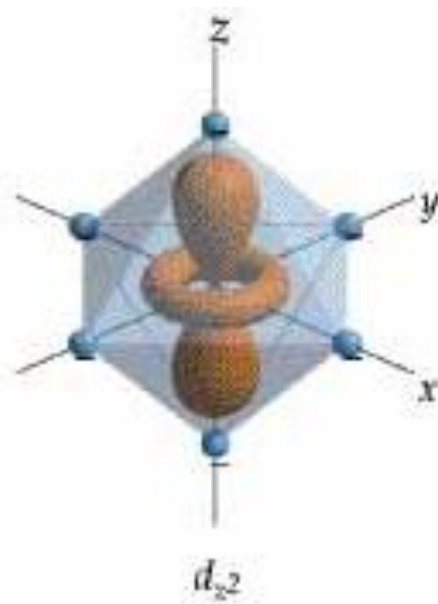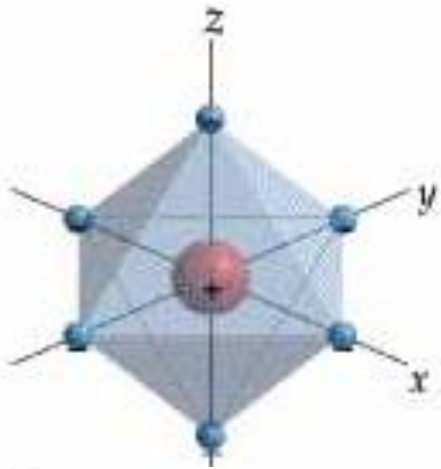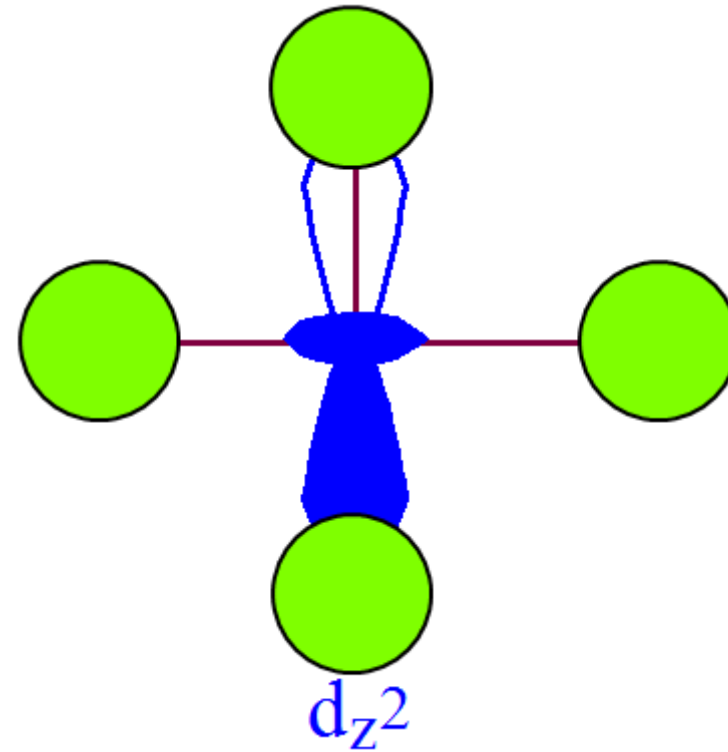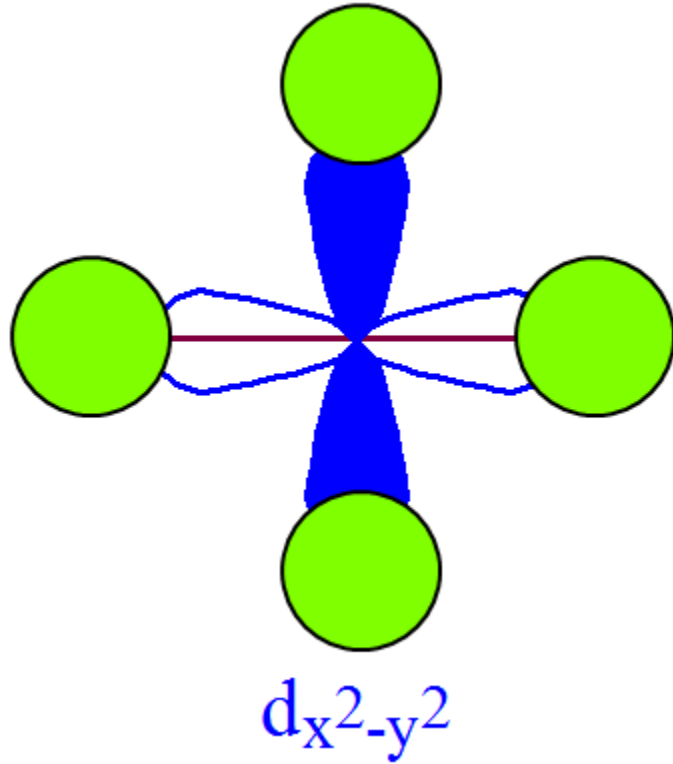
Lobes are directed towards ligands

greater electrostatic repulsion = higher potential energy

Crystal Field Theory

d_{xy}

d_{xz}

d_{yz}
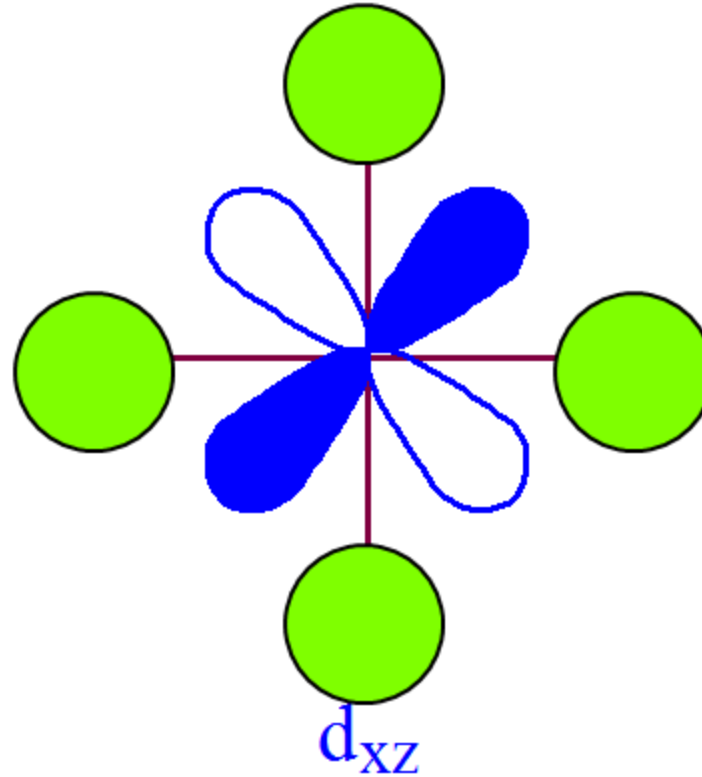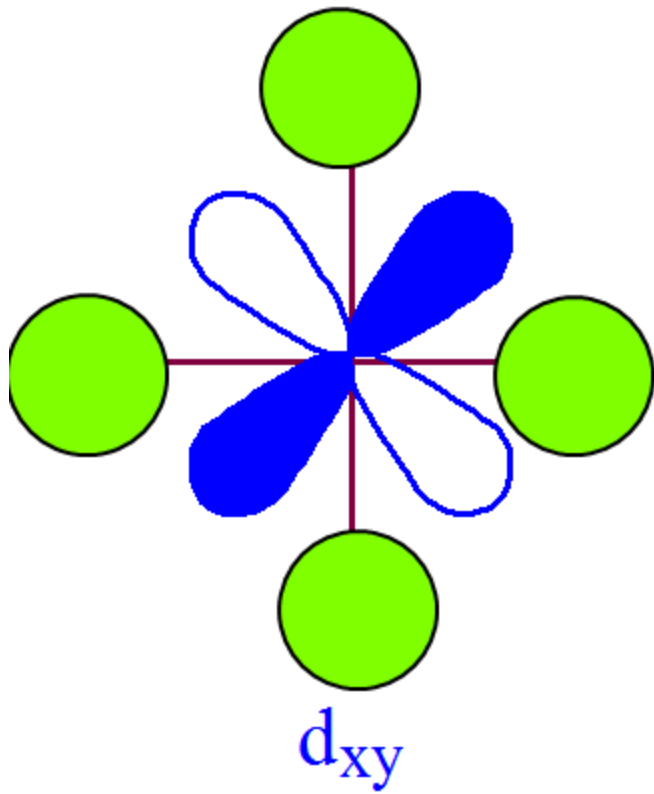
Lobes are directed between the ligands
less electrostatic repulsion = lower potential energy

Crystal Field Theory

Octahedral crystal field

d orbital energy levels

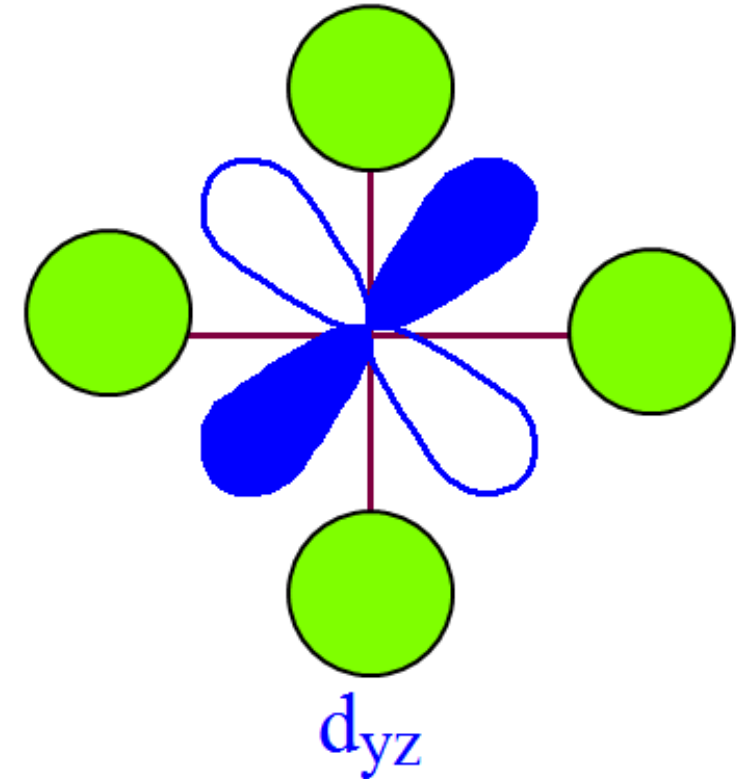isolated metal ion

E

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

Δ

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

d-orbitals

Under ligand field
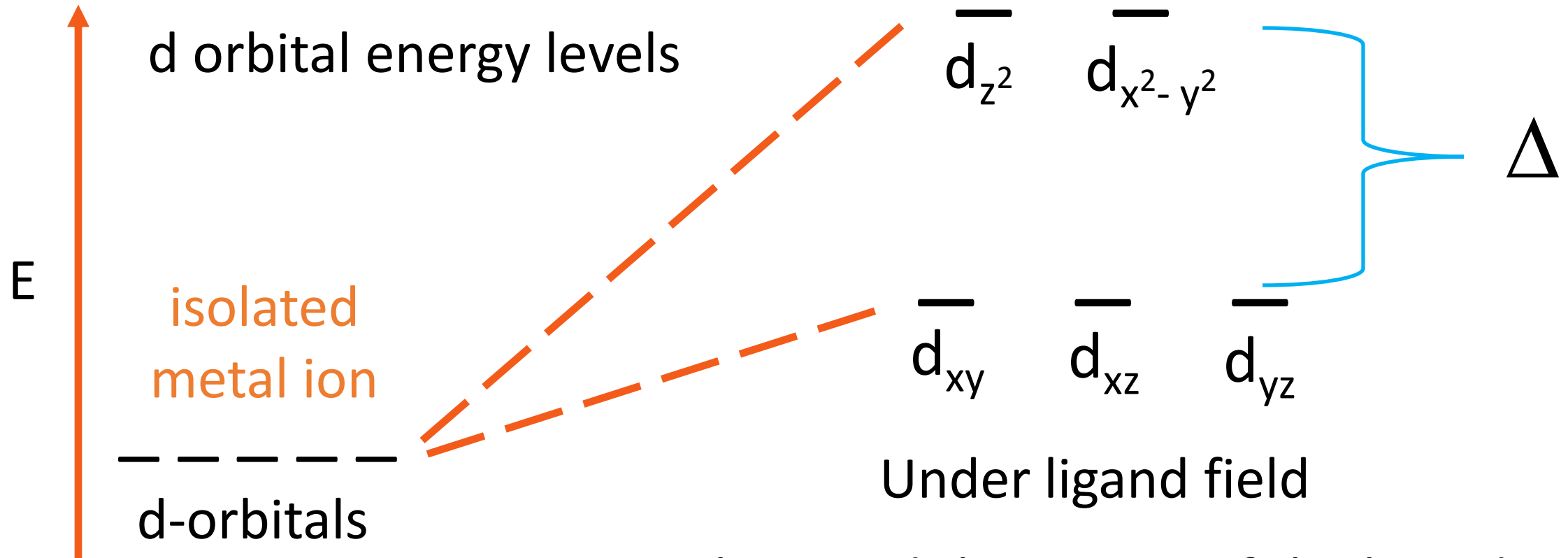
Metal ion and the nature of the ligand determines Δ

Crystal Field Theory

d orbital energy levels

Crystal field splitting in an octahedral field

E

d-orbitals

e_g

Δ_O

Determined by metal ion and ligand

t_{2g}

In octahedral crystal field

Crystal Field Theory

✓ e_g orbitals ($d_{x^2-y^2}$, d_{z^2}) are <u>along</u> Inter Nuclear Axes (Metal-Ligand bond axes) : more repulsion : high energy

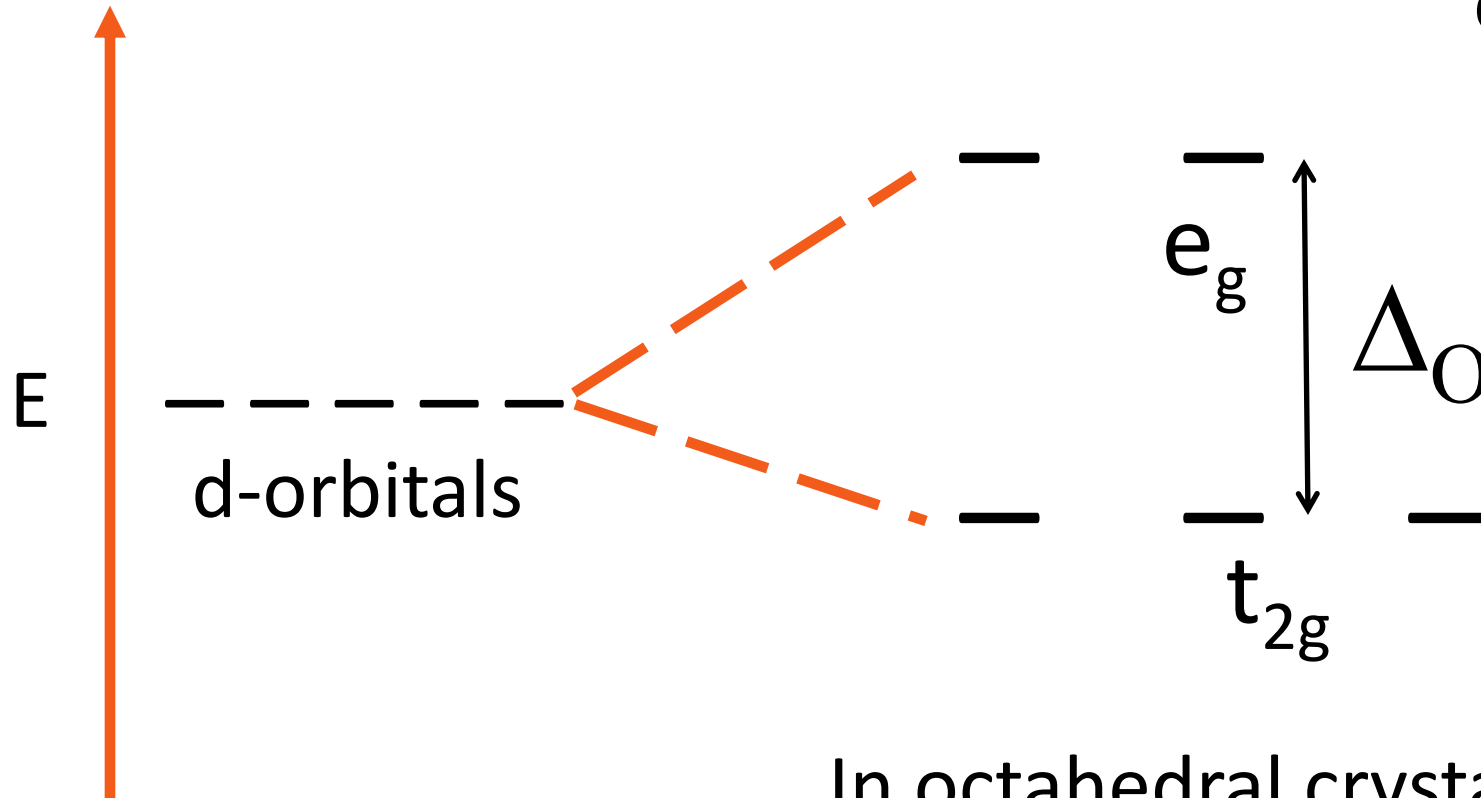✓ t_{2g} orbitals (d_{xy}, d_{yz}, d_{zx}) are <u>away</u> from Inter Nuclear Axis (Metal-Ligand bond axes): less repulsion : low energy

✓ We don't refer to isolated metal atom/ion any more; The weighted mean of these two levels is assumed to be zero; called Bari center.

$\Delta_{oct} = \Delta_o = 10\ Dq$ (different notations for the splitting)

Crystal Field Theory

$10\,Dq = \Delta_O$

How to estimate Δ_O
electronic spectroscopy

6 Dq = 0.6 Δ_O and 4 Dq = 0.4 Δ_O
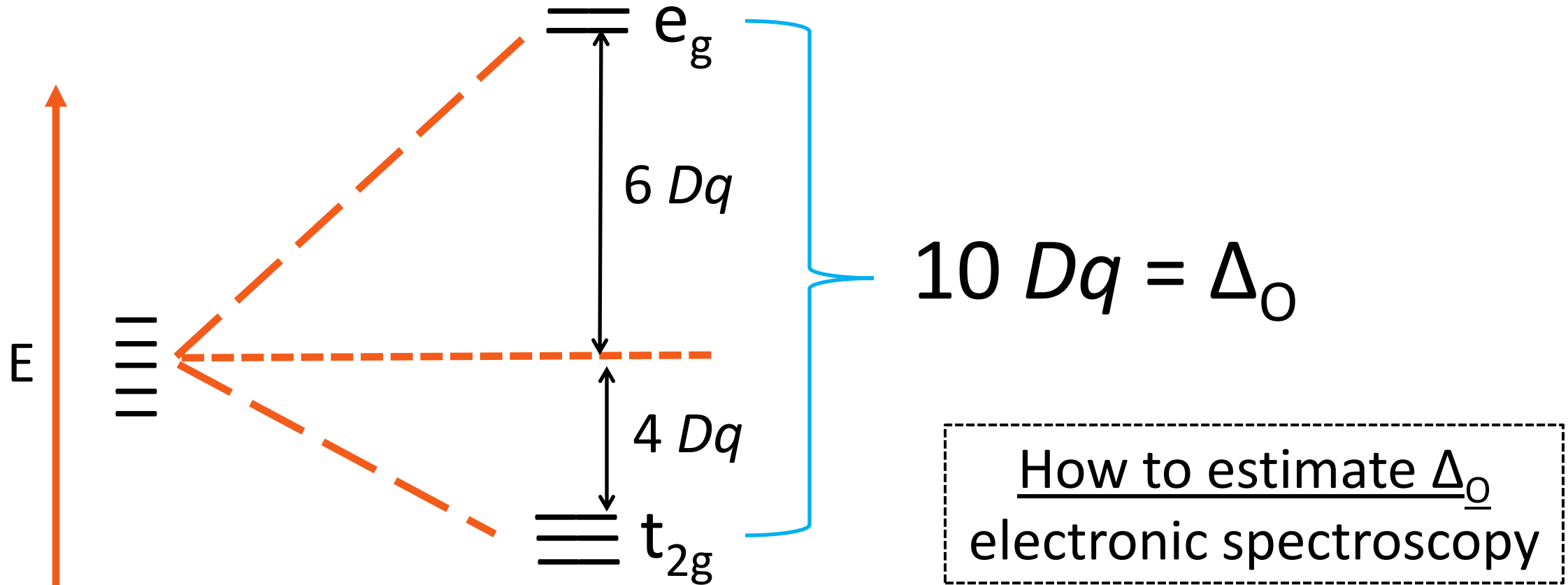
Estimation of Δ_o

Δ_o can be measured directly from electronic spectra for d^1 and d^9 systems;

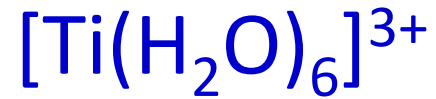In other d^n cases we can obtain it from calculations using the spectral data.

Consider $[Ti(H_2O)_6]^{3+}$, Ti^{3+}: $3d^1$ therefore, $t_{2g} \rightarrow e_g$ transition

__ __ e_g ⬆ __ e_g

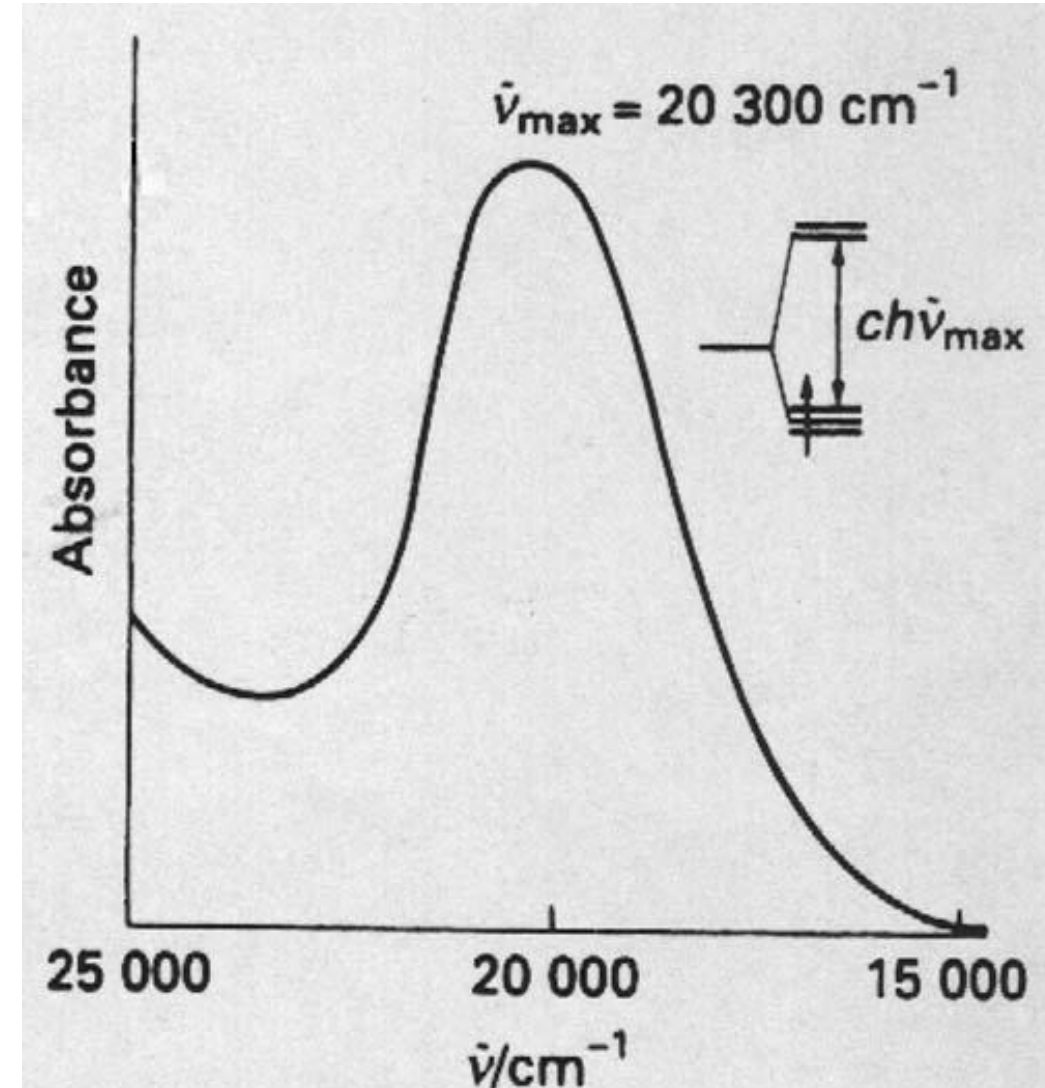⬆ __ __ t_{2g} __ __ __ t_{2g}

Estimation of Δ_o

$$[Ti(H_2O)_6]^{3+}$$

Δ_o = 20,300/83.7 = 243 kJmol^{-1}

Complex is <u>reddish violet in color</u>;

Yellow and green light are absorbed and hence the complementary color is seen.

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

$ch\tilde{v}_{max}$

Absorbance

25 000   20 000   15 000

$\tilde{v}/cm^{-1}$

Crystal Field Theory
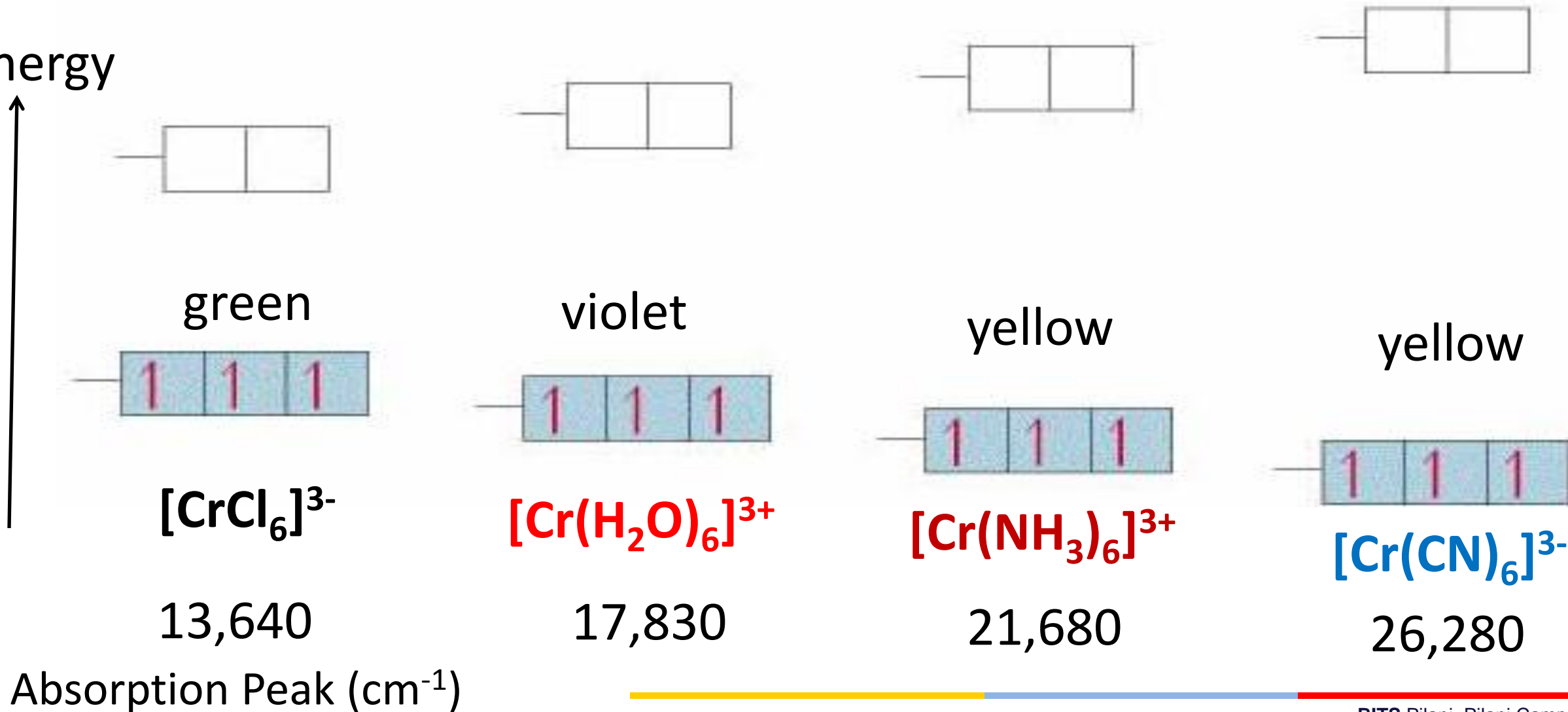
The magnitude (value) of Δ_o depends on

1. Nature/type of the ligand

2. Charge on the metal ion

3. Size of the metal ion; i.e., whether the metal ion belongs to I, II, or III row transition elements

Nature/type of the ligand

All other factors SAME while making comparisons. Consider Cr^{3+} (d^3 system)

energy

green

violet

yellow

yellow

$[CrCl_6]^{3-}$

$[Cr(H_2O)_6]^{3+}$

$[Cr(NH_3)_6]^{3+}$

$[Cr(CN)_6]^{3-}$

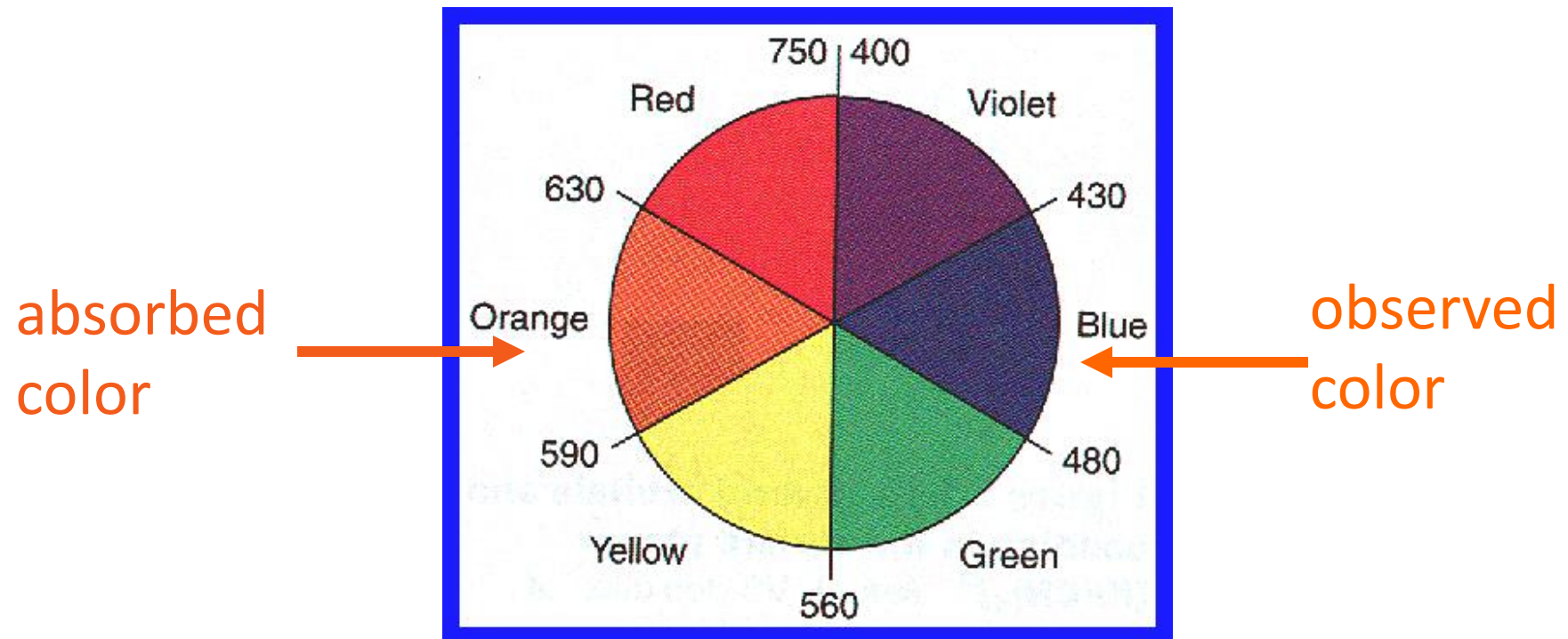13,640

17,830

21,680

26,280

Absorption Peak (cm^{-1})

Color of Transition metal comp

Compounds/complexes that have color:

- absorb specific wavelengths of visible light (400 –700 nm)
- color observed = complementary color of color absorbed

absorbed color

observed color

Nature/type of the ligand

From the previous data of chromium complexes, we can write the Δ_o value for

$$Cl^- < H_2O < NH_3 < CN^-$$

weak field   strong field

This experimentally determined series is known as spectrochemical series

Δ_o values range from 7000 cm^{-1} to 30,000 cm^{-1}

Nature/type of the ligand

- The position of λ_{max} and hence Δ_o varies w.r.t. the chemical nature of the ligand

- Ligands which cause only a small degree of crystal field splitting (low Δo value) are called <u>WEAK</u> ligands

- Ligands which cause large crystal field splitting (high Δo value) are called <u>STRONG</u> ligands

Spectrochemical series

Smallest Δ

(<u>weak</u>) I⁻ < Br⁻ < S²⁻ < <u>S</u>CN⁻ < Cl⁻ < NO₃⁻ < F⁻ < OH⁻ < EtOH (ethanol) < C₂O₄²⁻ (oxalate) < H₂O < EDTA < <u>N</u>CS⁻ < CH₃CN < NH₃ < en < bipy < phen < <u>N</u>O₂⁻ < PPh₃ < CN⁻ < CO   (<u>strong</u>)

Largest Δ

➤ There is no visible pattern

➤ No charge or size correlation

➤ Both the sigma and pi bonding nature along with electrostatic attractions determine the crystal field splitting Δ$_o$
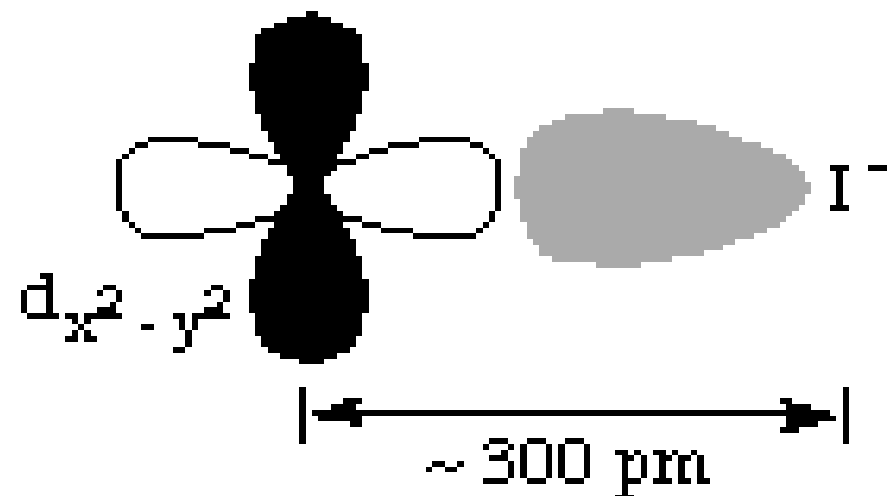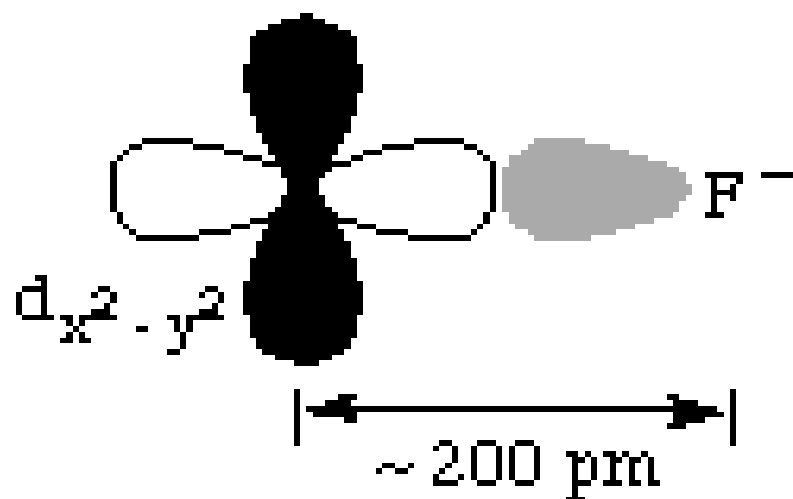
➤ A pattern of increasing sigma donation

Halide donors < O donors < N donors < C donors

Spectrochemical series

Within halide donors for Δ_o: $I^- < Br^- < Cl^- < F^-$.

This can be explained in terms of electrostatic repulsions. F^- is of small size and hence more closer bonding and more repulsion (higher Δ_o)

Spectrochemical series

Consider $PPh_3 < CN^- < CO$

• Δ_o of CN^- is almost double that of I^- ; This can not be explained by simple CFT. Covalent bonding of σ and π types of bonding is to be included.

• Carbonyl, phosphines are *neutral ligands* and still produce the maximum splitting of d orbitals which implies electrostatic-point charge model is not sufficient.

π (pi) back bonding from metal t_{2g}
→ vacant ligand orbital
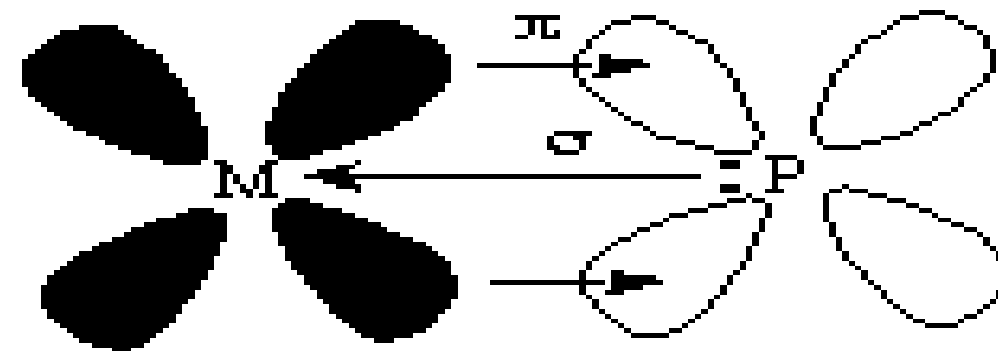
PPh_3 , CN^- , CO   are called π acceptors.

Electronic configuration in Oh com.

Expected orbital filling tendencies for e⁻'s:

- ✓ occupy a set of equal energy orbitals one at a time (Hund's rule), which minimizes repulsions
- ✓ occupy lowest energy vacant orbitals first

d orbital occupancy depends on <u>Δ and pairing energy, P</u>

- If Δ > P (Δ large; strong field ligand)
  - ➢ e⁻'s pair up in lower energy d subshell first
- If Δ < P (Δ small; weak field ligand)
  - ➢ e⁻'s spread out among all d orbitals before any pair up

d orbital occupancy

d¹

d²

high spin

$\Delta < P$

d⁴

low spin

$\Delta > P$
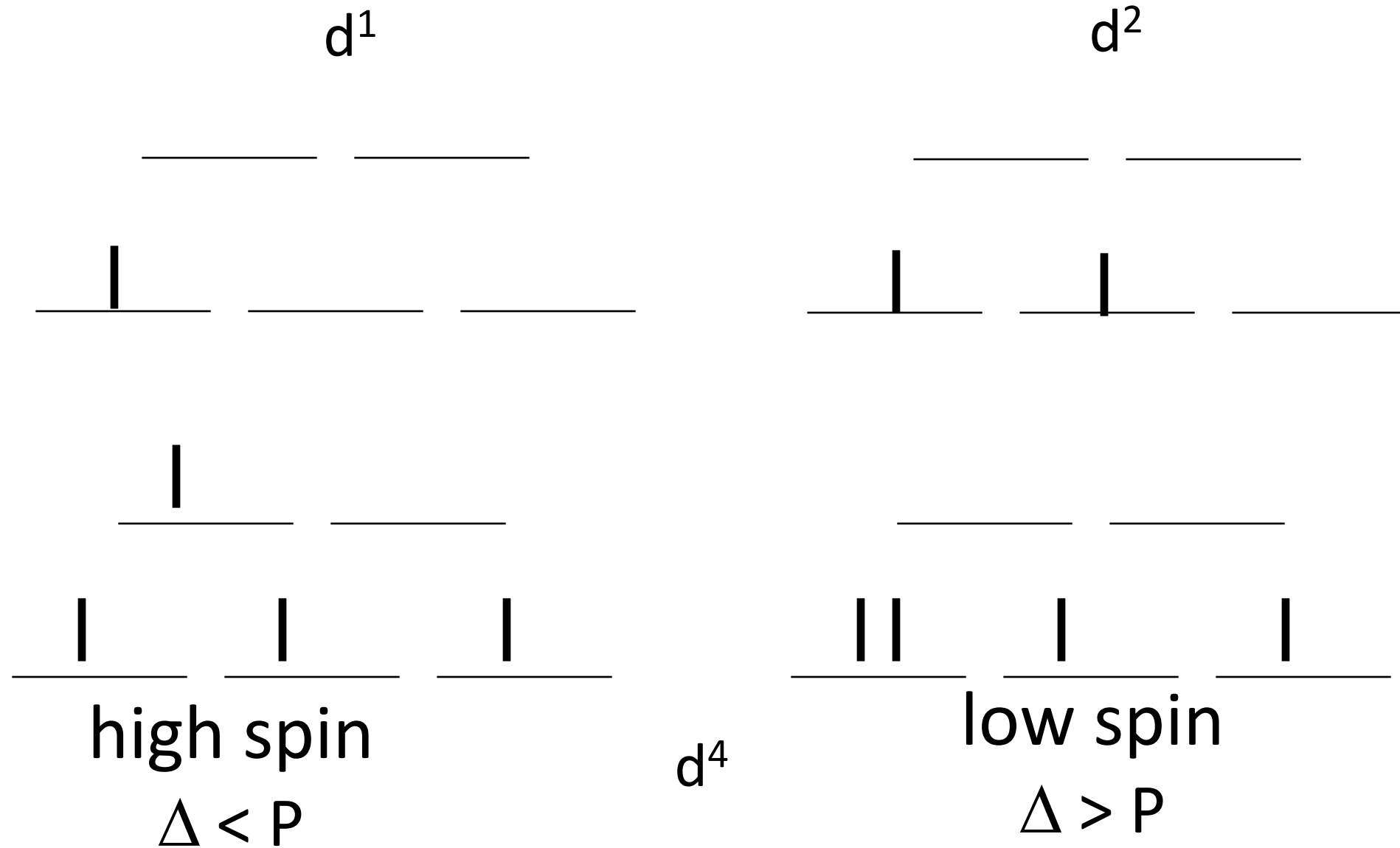
Nature of metal cation

(i) Different Charges on the cation of the same metal:

Δ_o for $[Fe(H_2O)_6]^{2+}$ = 10,400 cm^{-1}

Δ_o for $[Fe(H_2O)_6]^{3+}$ = 13,700 cm^{-1}

The metal cation with a higher oxidation state has a larger value of Δ_o than that with lower oxidation state.

(ii) Different charges on the cation of different metal: Two different cation with the same number of d- electrons but with different charge (metals within a same period):

Δ_o for $[V(H_2O)_6]^{2+}$ = 12,400 cm^{-1}

Δ_o for $[Cr(H_2O)_6]^{3+}$ = 17,400 cm^{-1}

Size of the metallic species

If all other factors are same, the period to which the metal belongs matters

Complex	Δ_o (kJ/mol)	Config.
$[Co(NH_3)_6]^{3+}$	296	$3d^6$
$[Rh(NH_3)_6]^{3+}$	406	$4d^6$
$[Ir(NH_3)_6]^{3+}$	490	$5d^6$

➢ Larger the d orbital size it is easier to split
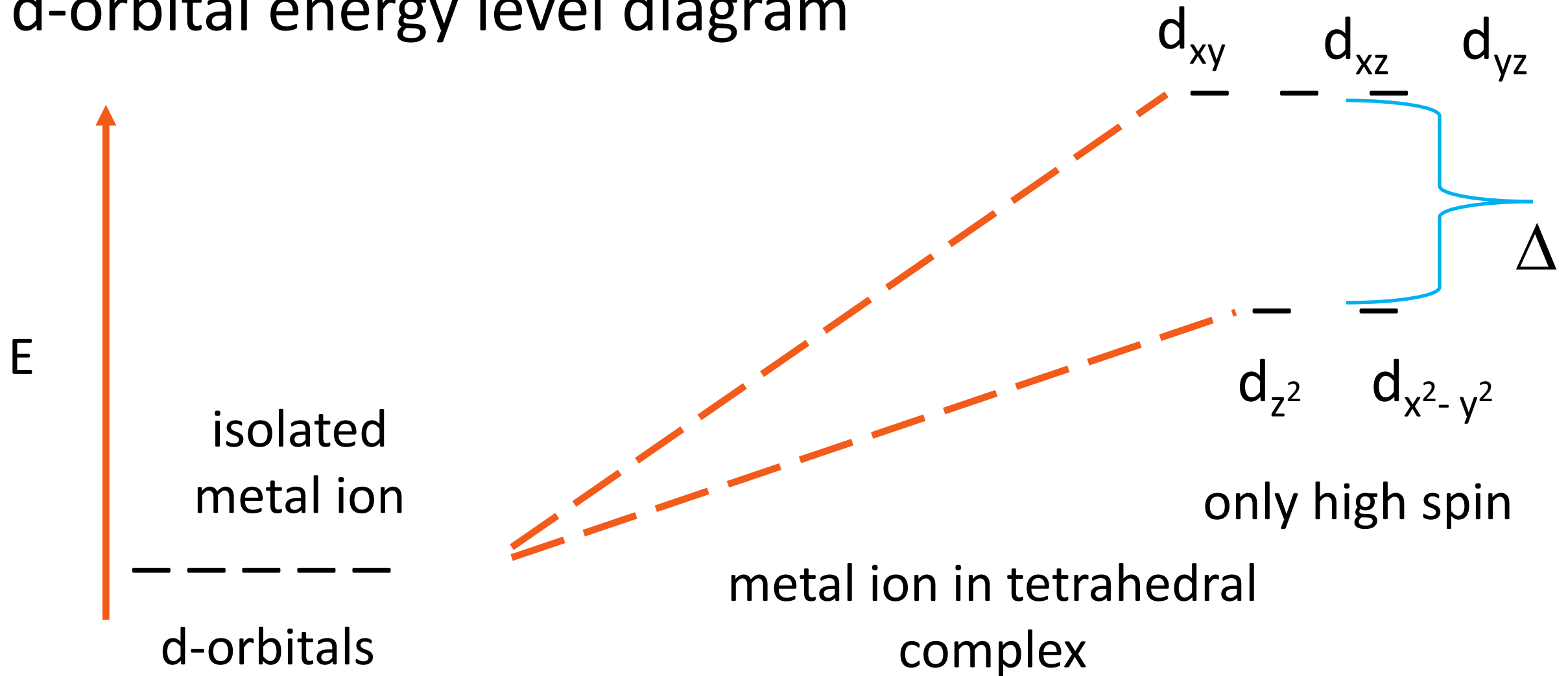➢ 5d orbitals split larger than 4d orbitals and so on

Tetrahedral complex
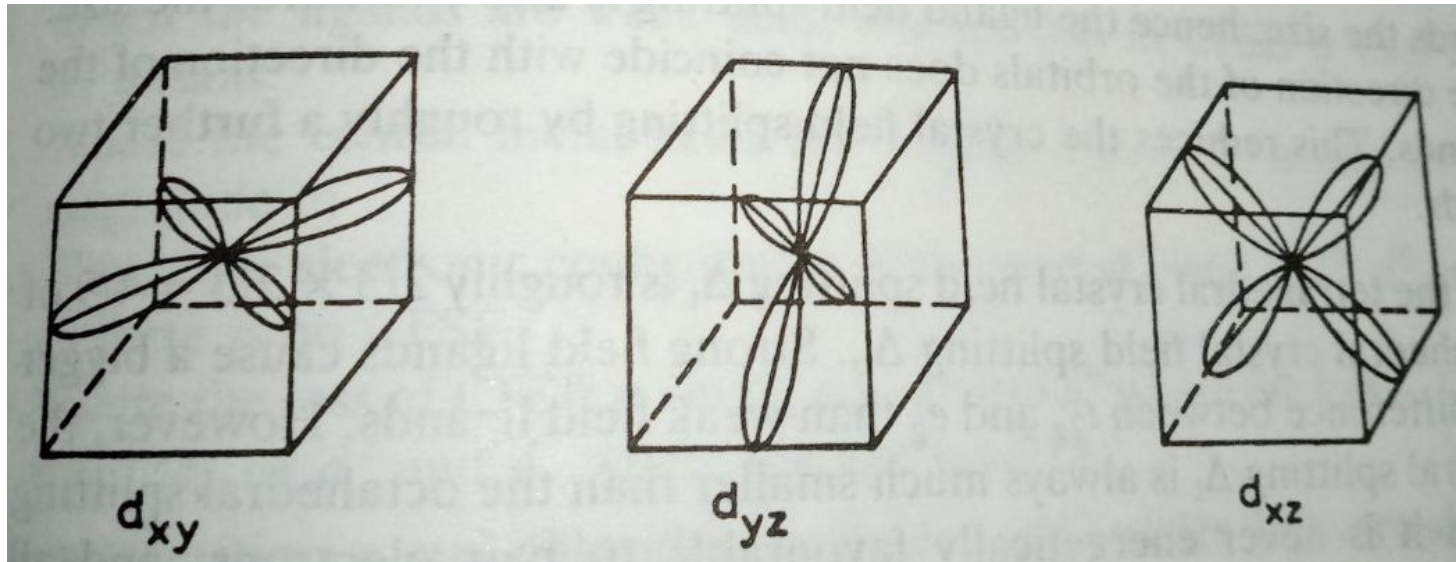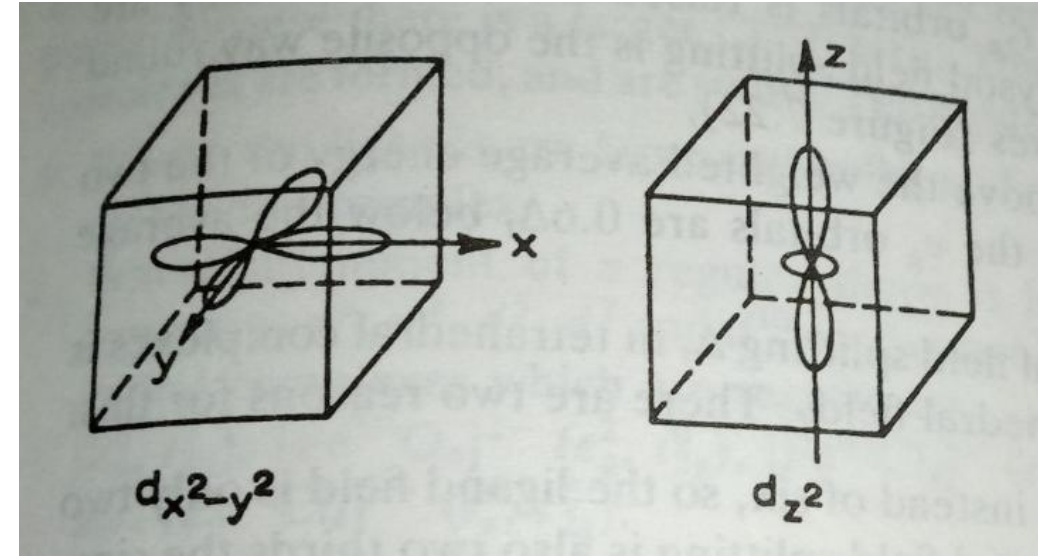
Splitting in tetrahedral complex

d-orbital energy level diagram

d_{xy} — — d_{xz} d_{yz}

Δ

d_{z^2} — — $d_{x^2-y^2}$

E

isolated
metal ion

only high spin

— — — — —

d-orbitals

metal ion in tetrahedral
complex

Discussed topics……

- ✓ shapes of d orbitals

- ✓ crystal field theory

- ✓ octahedral complexes

- ✓ spectrochemical series

- ✓ d-orbital splitting in tetrahedral complex
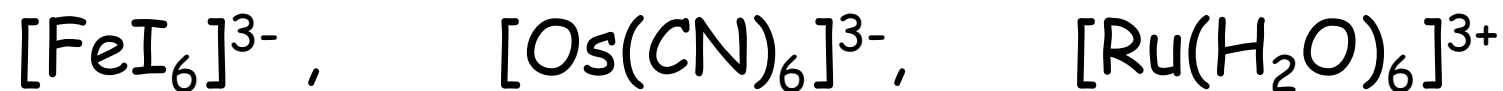
d orbital electrons (supporting slide)

d-orbital energy level diagrams:

- determine oxidation number of the metal
- determine number of d e$^-$'s
- determine if ligand is weak field or strong field
- draw energy level diagram

Which of the following species will have highest crystal field splitting?

$[FeI_6]^{3-}$, $[Os(CN)_6]^{3-}$, $[Ru(H_2O)_6]^{3+}$

Ans: $[Os(CN)_6]^{3-}$

Reason: Δ_o for $Fe^{3+} < Ru^{3+} < Os^{3+}$ and

Δ_o for $I^- < H_2O < CN^-$

This has strong filed ligand as well as metal with 5d electrons