

Basic Concept of Photo Chemistry of Coordination Compound

Lecture - 2

M. Sc. Chemistry 4th Sem (402-I / U-IV)
Ph. D. Course Work -Section-II/U-II

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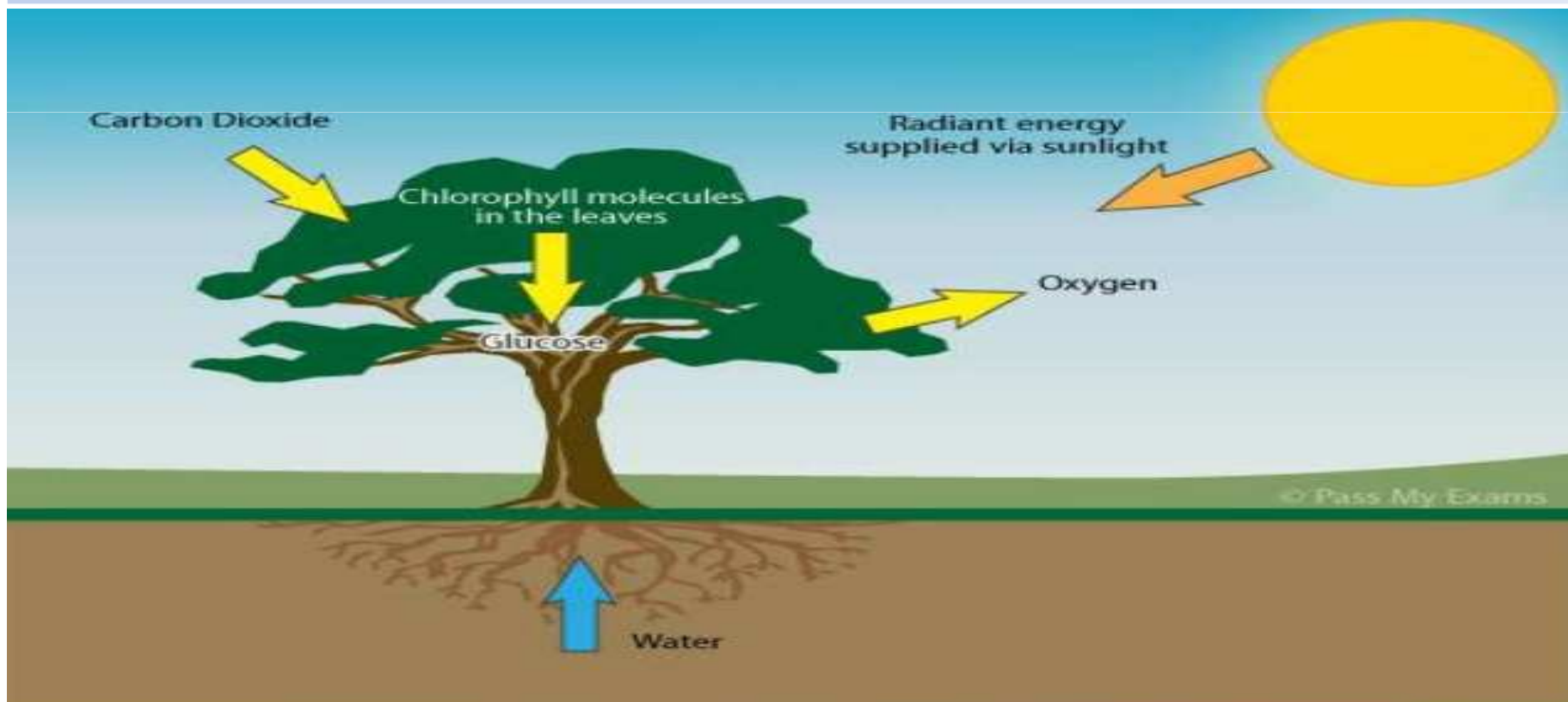
Inorganic Photo Chemistry

Photo Chemistry of Coordination Compound

Photochemistry is the branch of chemistry which deals with the exposure of light on chemical reaction & fate of incident light as well as fate of chemical reaction. It also deals rate & mechanism of photochemical reaction (PCR).



Here, there are two main parts of PCR (a) Photo (light) (b) Chemicals
So we have to deal fate of photo & chemicals one by one.



Fate of incident light:

When light (photon) energy is passed through aqueous solution of a substance than it may be either transmitted or reflected or absorbed

$$\text{i.e. } I = I_a + I_r + I_t$$

$$E = hc/\lambda$$

Where I = Energy of Incident light

I_a = Absorbed light

I_r = Reflected light

I_t = Transmitted light

λ = UV-Visible (λ = 100-800 nm)

- able to excite bonding e- in molecule
- Capable of breaking of bond in molecule

- (Photo dissociation)

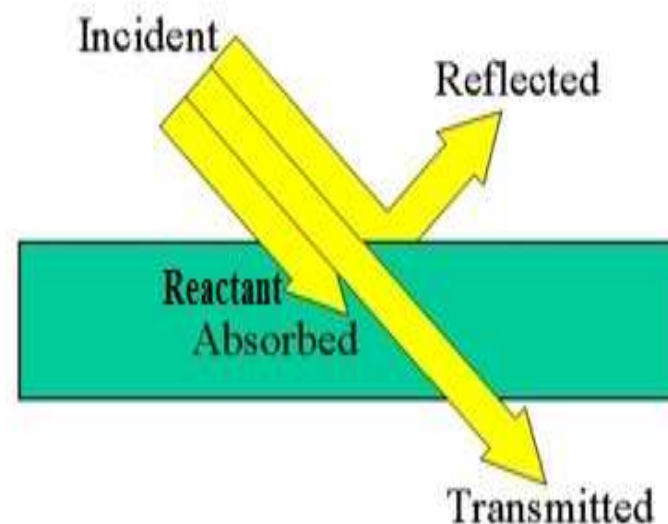
= UV photons (λ = 100-300)

- can break more & stronger bonds

= IR (λ = 0.8-300 μm)

- excites vibrational motion in a

molecules not able to break chemical bond.



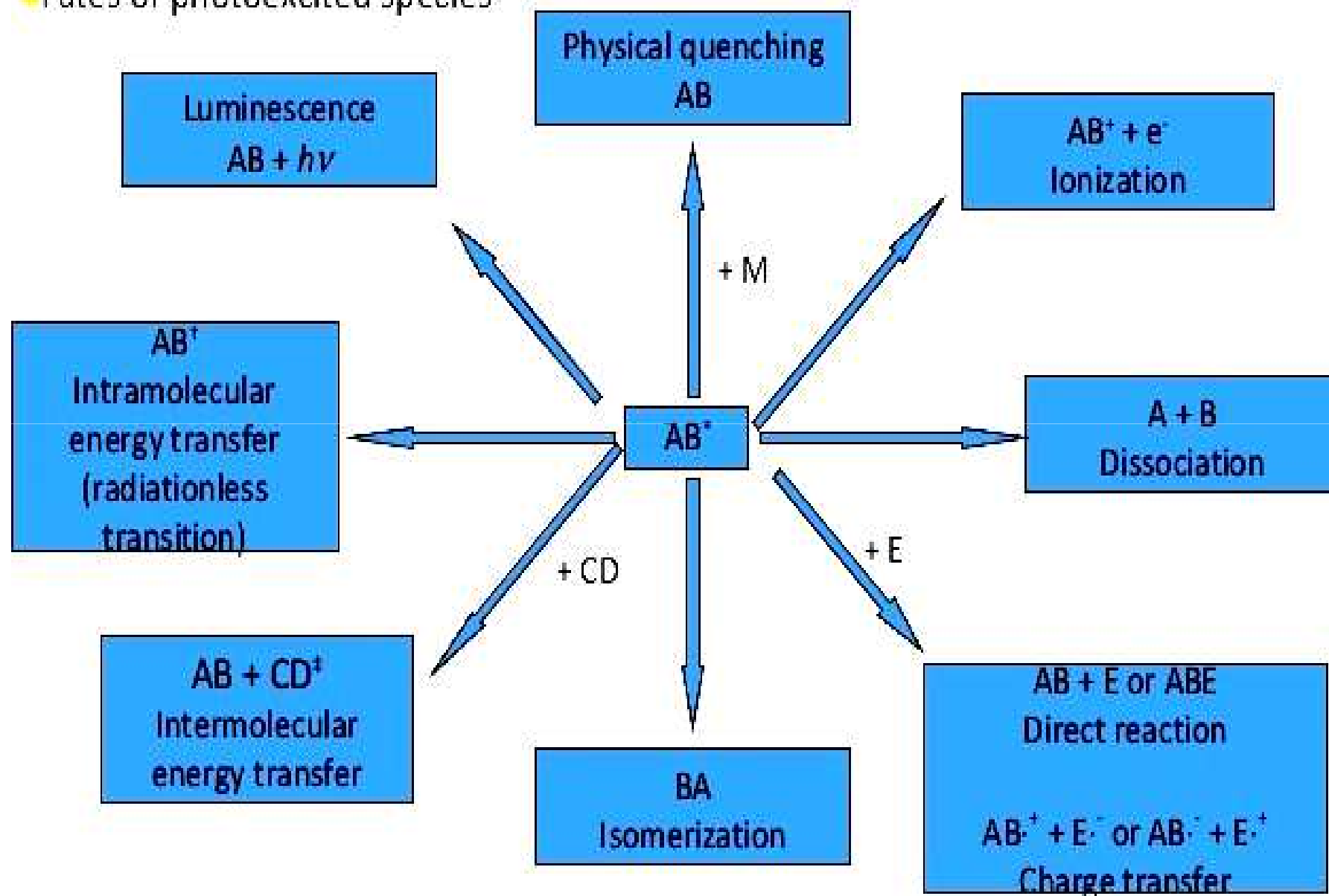
Fate of photo excited species

when light is absorbed by the molecule than it get excited AB^* which properties is different from original reactant A & B.



- Excited state are stronger acid & stronger reductant than original state.
- when a other molecule come near the excited state (molecule) than interaction takes place & there may be,
 - charge transfer b/w different energy level of metal & ligand molecular orbitals (LMCT, MLCT, MMCT & LLCT)
 - inter molecular or intra molecular transfer of energy,
 - transition of e^- ,
 - dissociation of photo excited species,
 - ionization quenching,
 - isomerization,
 - b/w the two energy level of excited state & ground state.

Fates of photoexcited species



Fate of electronic transition

There are mainly two types of electronic transition occurs in coordination compound of transition metal:

1. d-d transition or ligand field transition
2. Charge transfer b/w/within Metal orbital & ligand orbital.

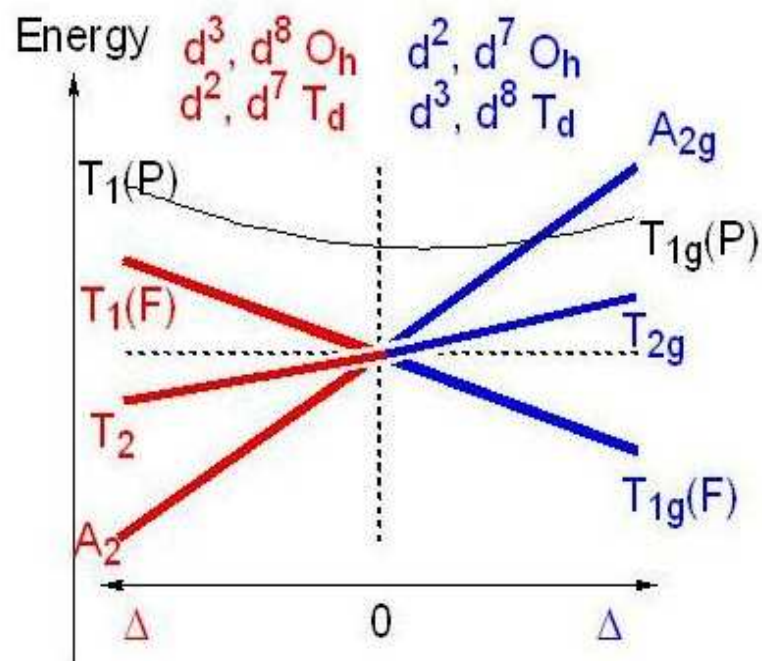
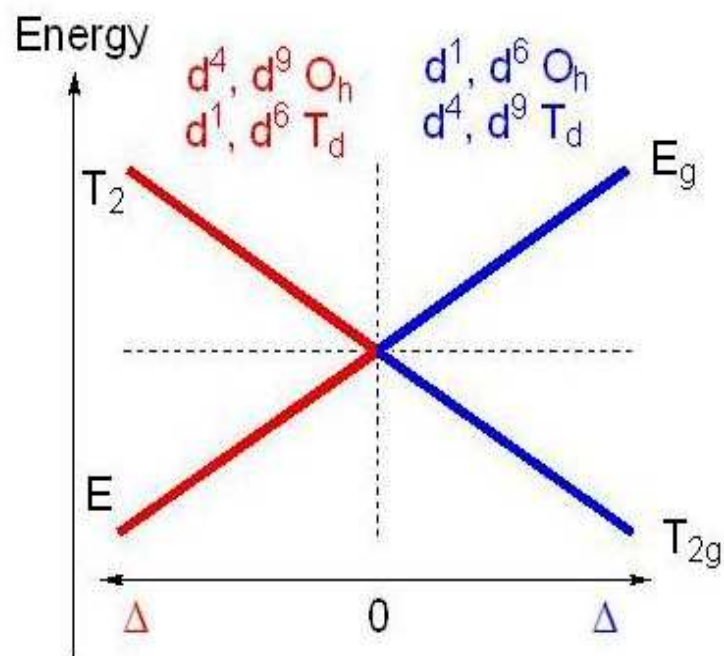
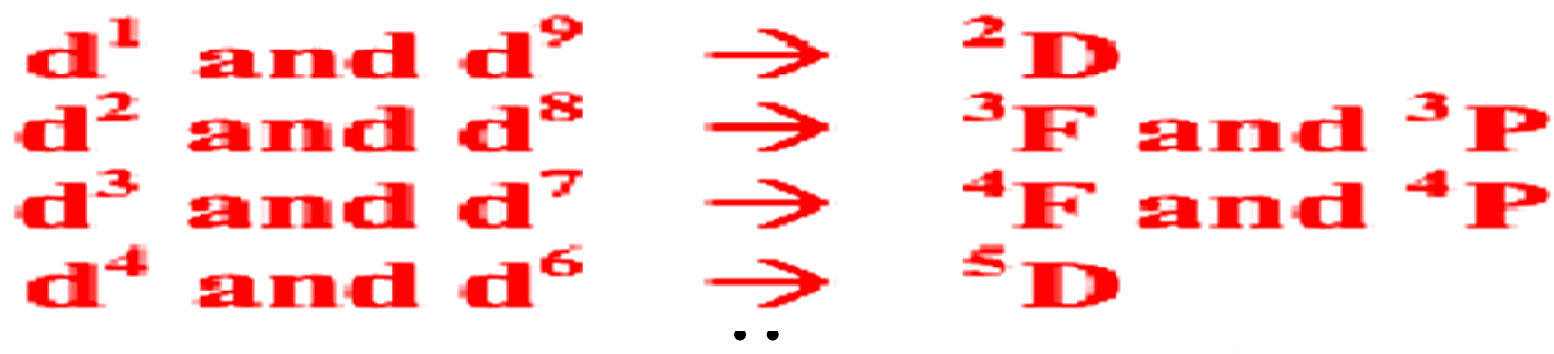
Intensity of color due to transition of e-
is proportional to the

- number of transition
- feasibility of transition
- 1/ energy difference (ΔE) b/w two level
- ΔE (\downarrow), V (\downarrow), V^- (\downarrow), λ (\uparrow)

d-d transition or ligand field transition:

Transition of electron from one orbital to another orbital by absorption or emission of light (energy) is called d-d transition. Due to d-d transition it gives spectra is called electronic spectra. It depends upon no. of electron in d orbital & geometry of complexes & nature of ligand

Splitting of term of d^n e- are guided by Orgel diagram as well as Tanabe-Sugano which gives color & spectral properties of coordination compd.



CO, CN⁻ > phen > NO₂⁻ > en > NH₃ > NCS⁻ > H₂O > F⁻ > RCO₂⁻ > OH⁻ > Cl⁻ > Br⁻ > I⁻

Low spin

Strong field

Large Δ

π acceptors

σ donor only

High spin

Weak field

Small Δ

π donors

TABLE 10.5 Spin States and Ligand Field Strength

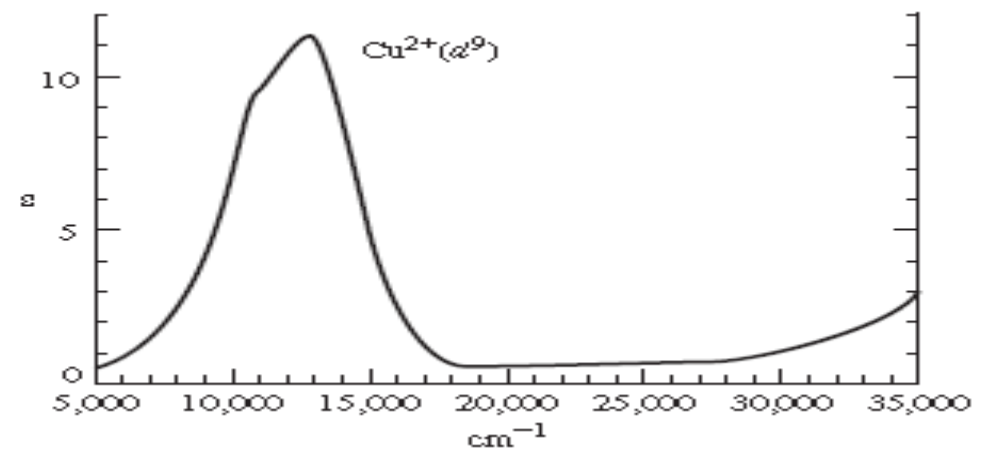
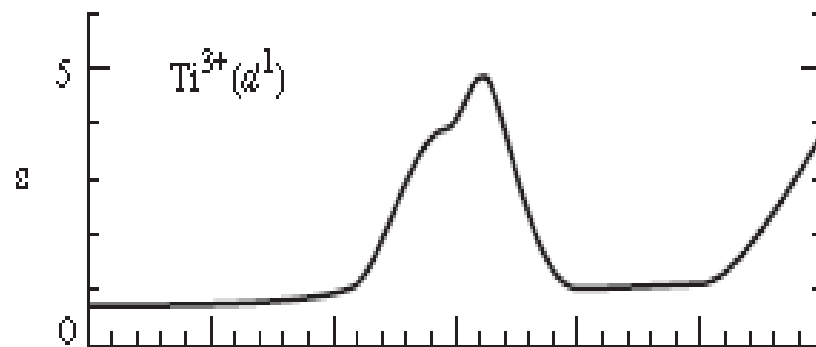
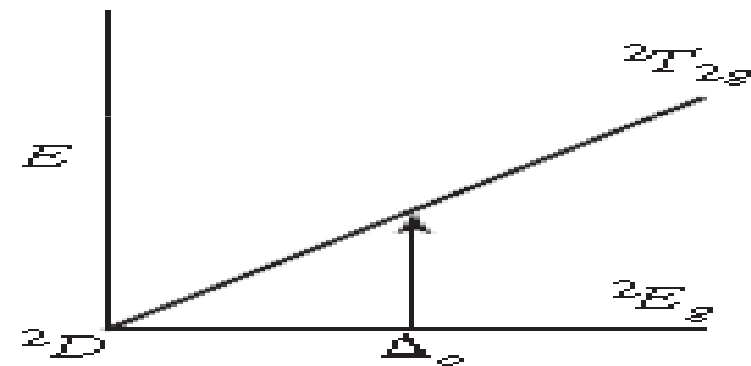
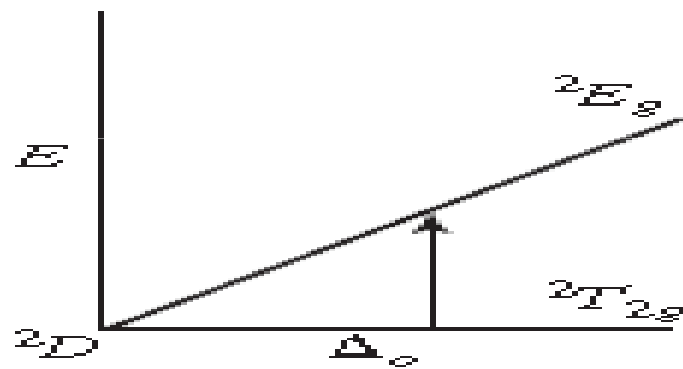
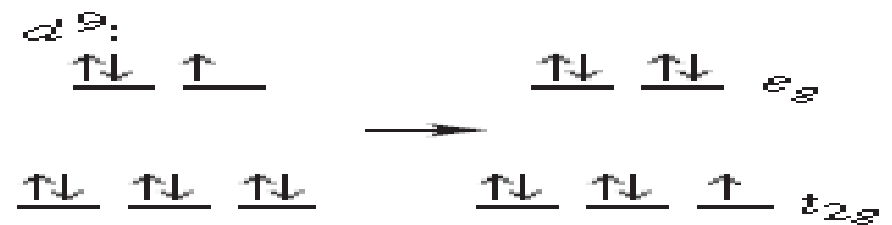
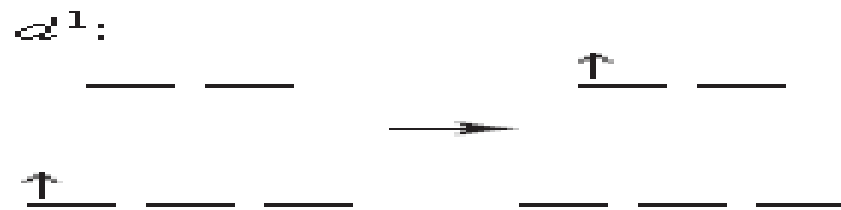
Complex with Weak-Field Ligands (High Spin)

Δ _o					
	d ¹	d ²	d ³	d ⁴	d ⁵
Δ _o					
	d ⁶	d ⁷	d ⁸	d ⁹	d ¹⁰

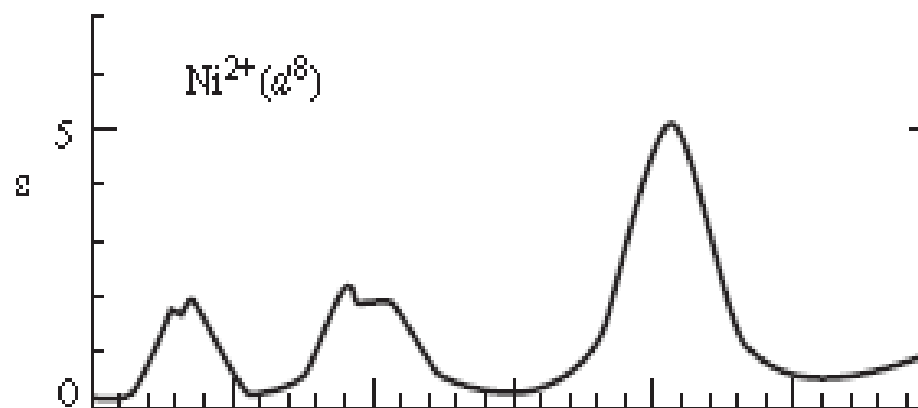
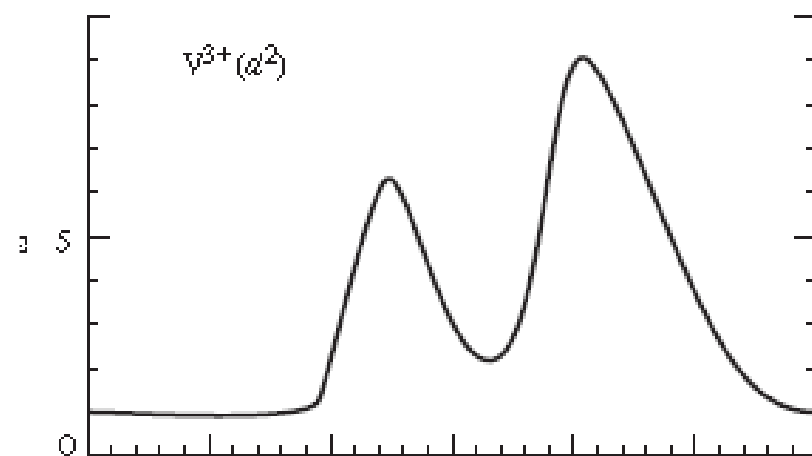
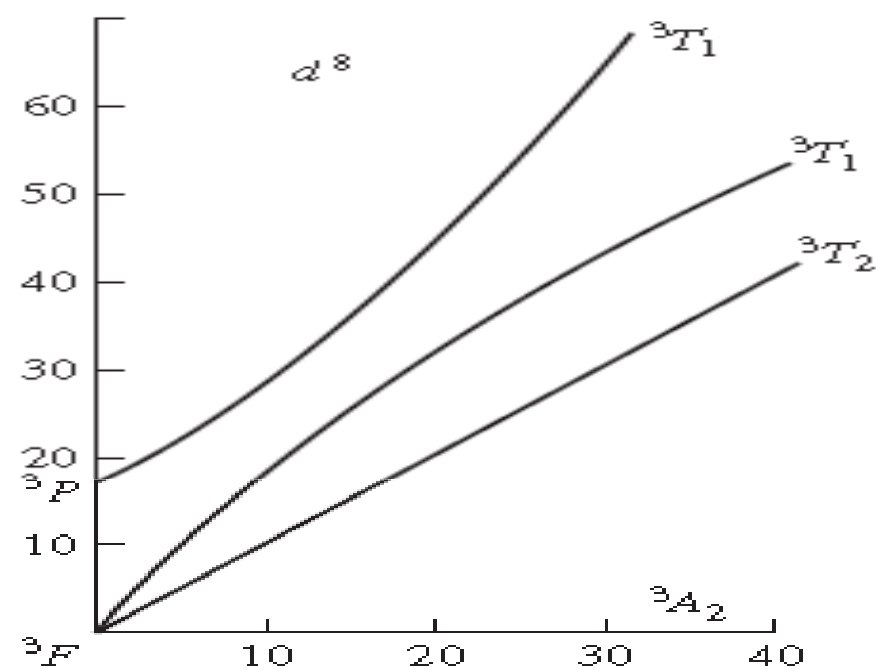
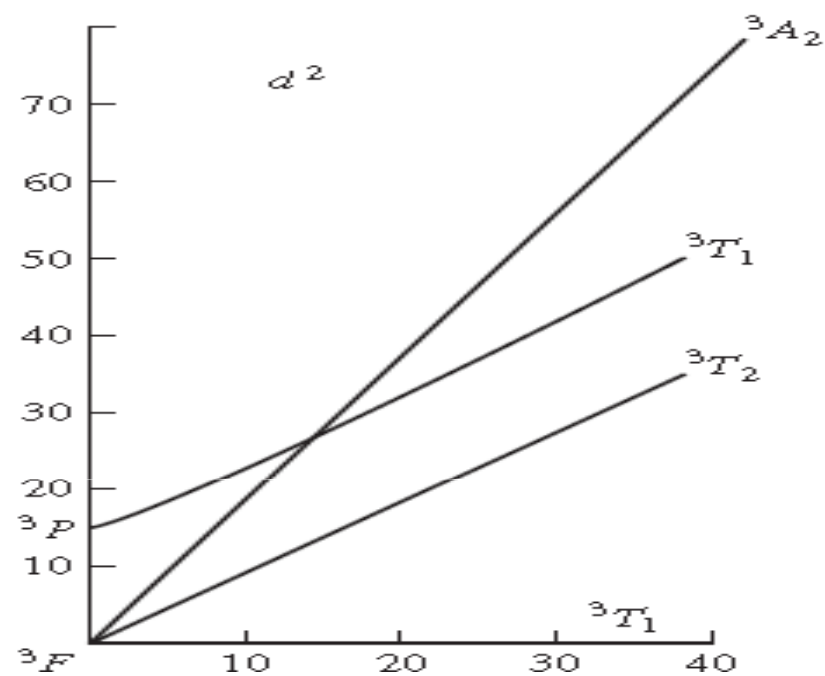
Complex with Strong-Field Ligands (Low Spin)

Δ _o					
	d ¹	d ²	d ³	d ⁴	d ⁵
Δ _o					
	d ⁶	d ⁷	d ⁸	d ⁹	d ¹⁰

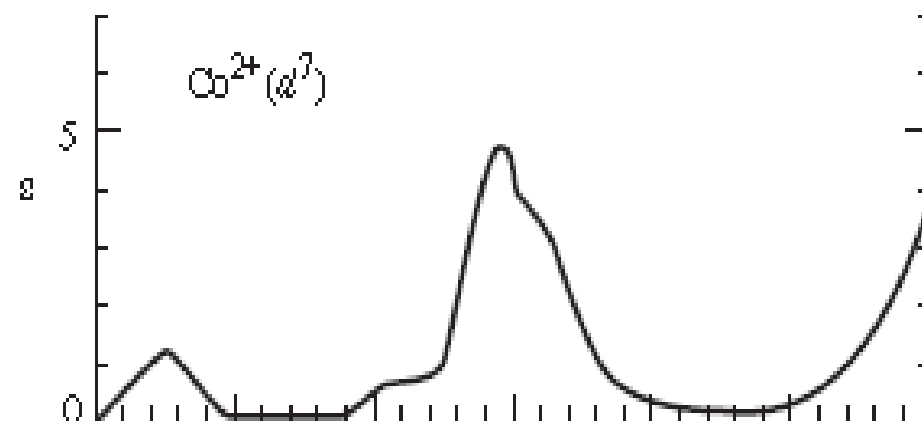
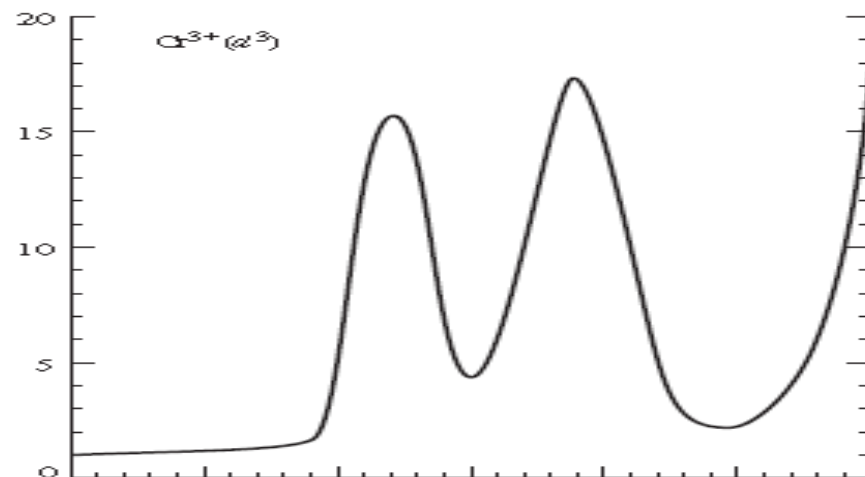
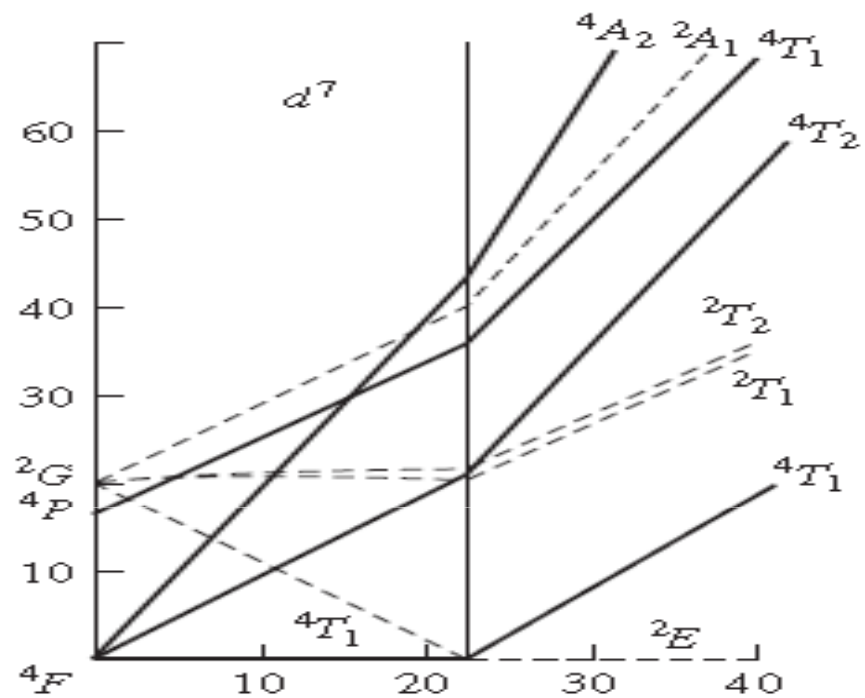
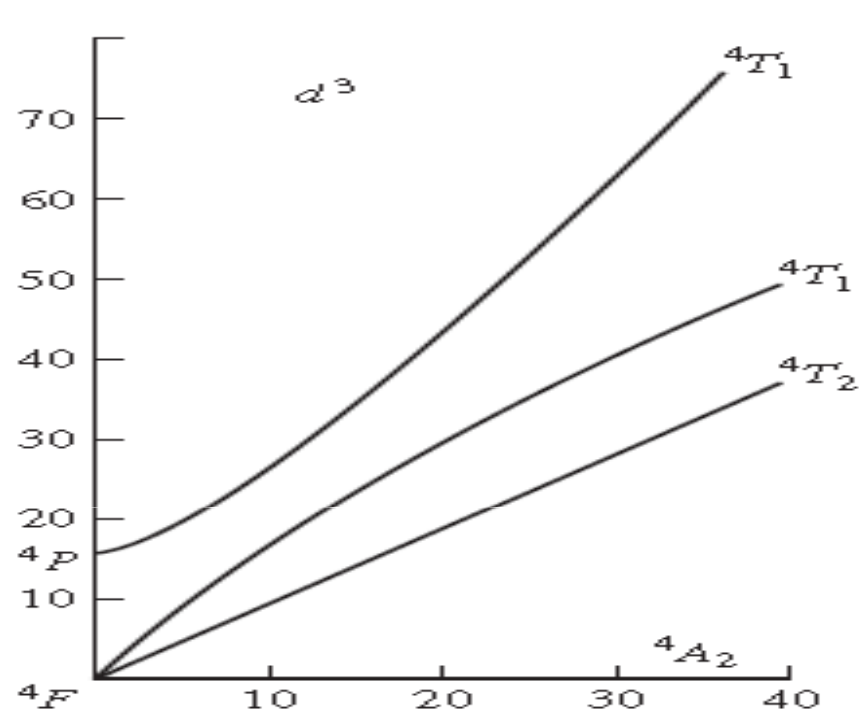
d¹, d⁹ Oh. transition



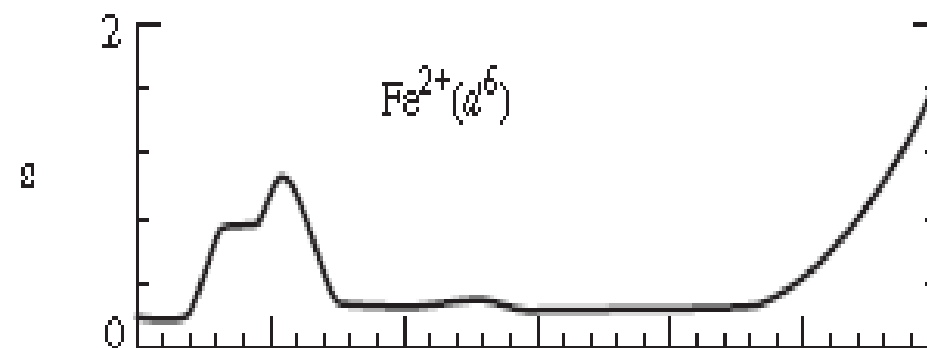
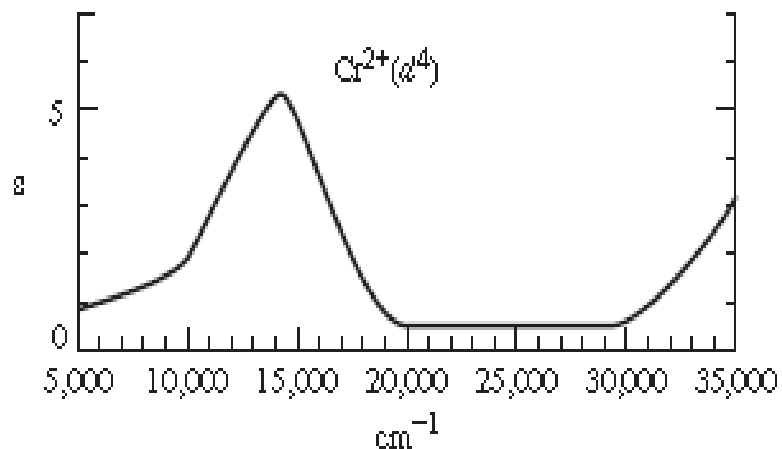
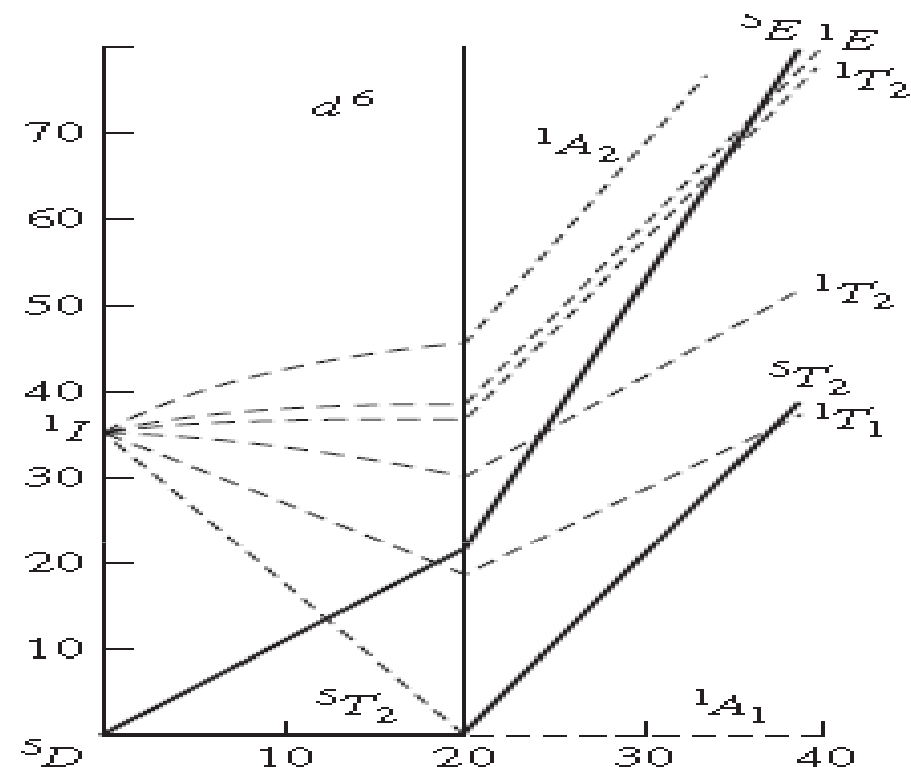
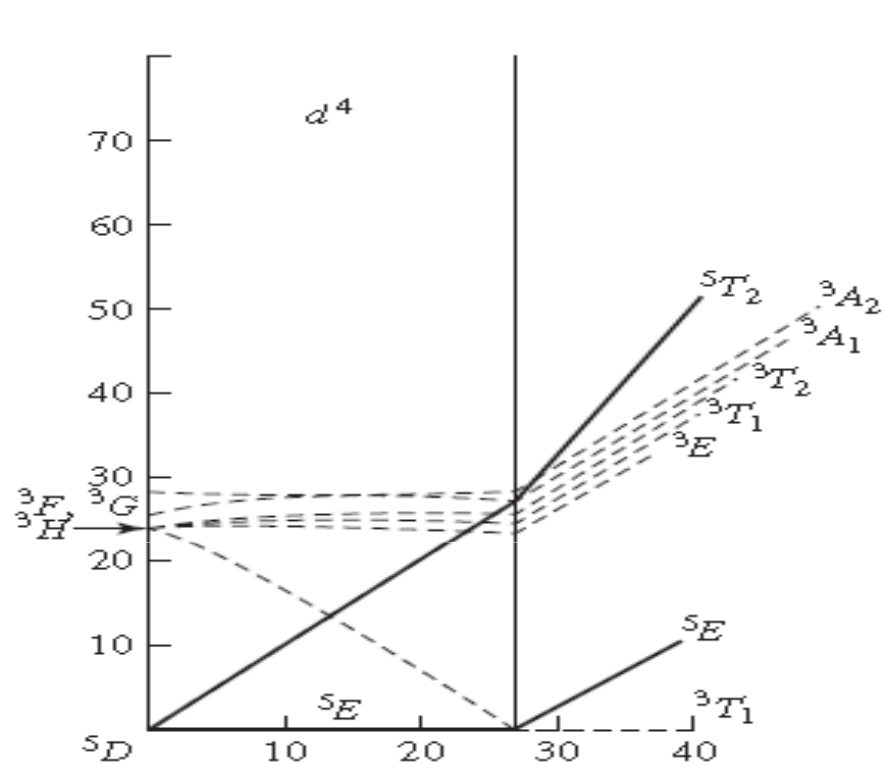
d^2, d^8 Oh. transition



d^3, d^7 Oh. transition

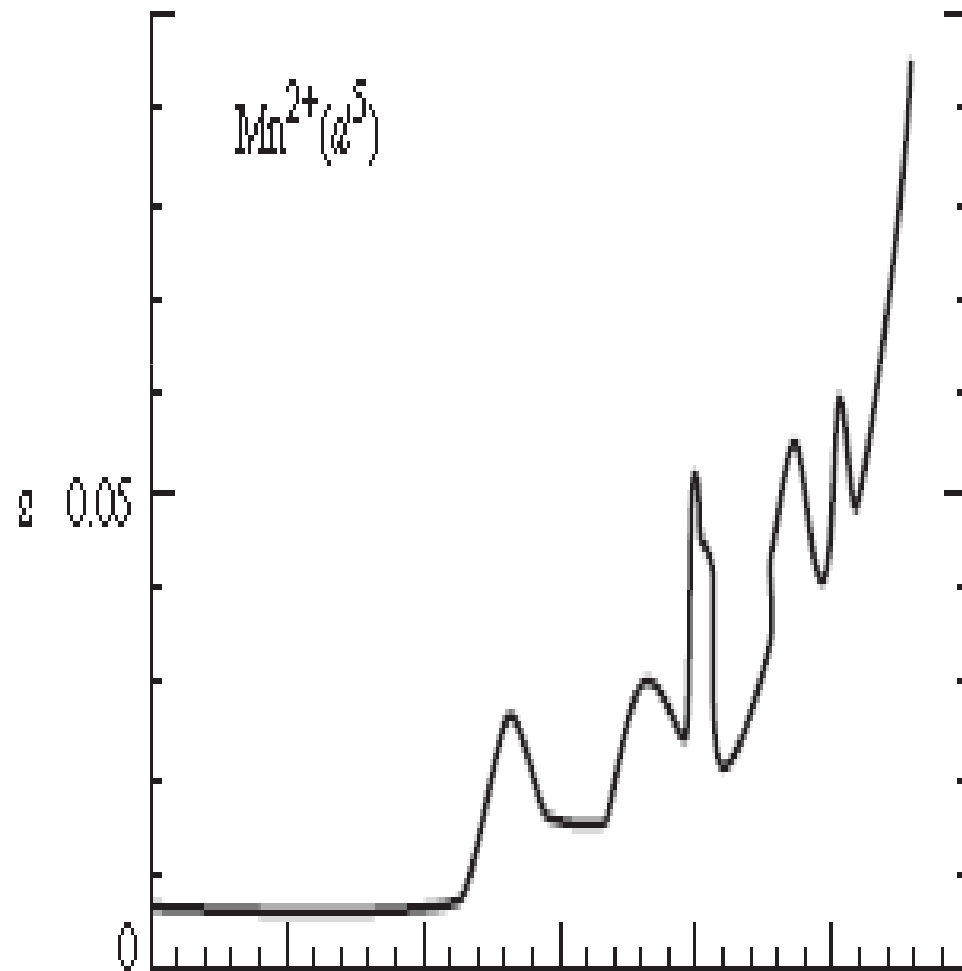
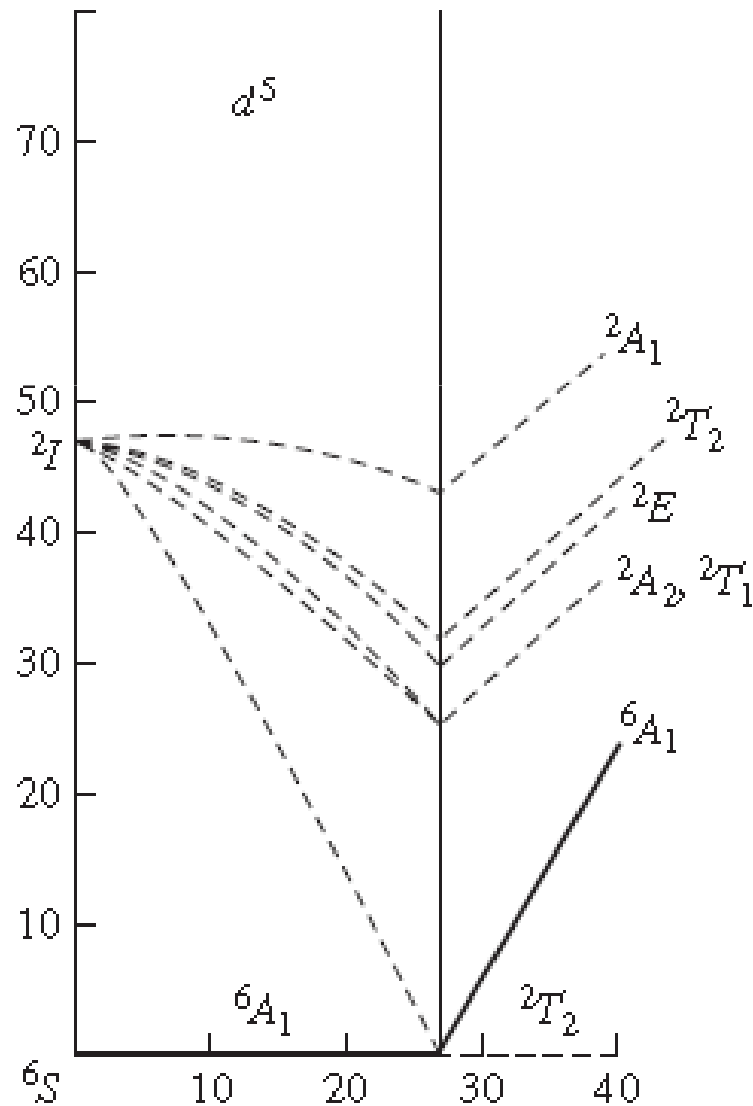


d^4, d^6 Oh. transition



d⁵ Oh. Transition

d⁵ system has no any d-d transition but it shows color due to charge transfer.



Charge transfer:

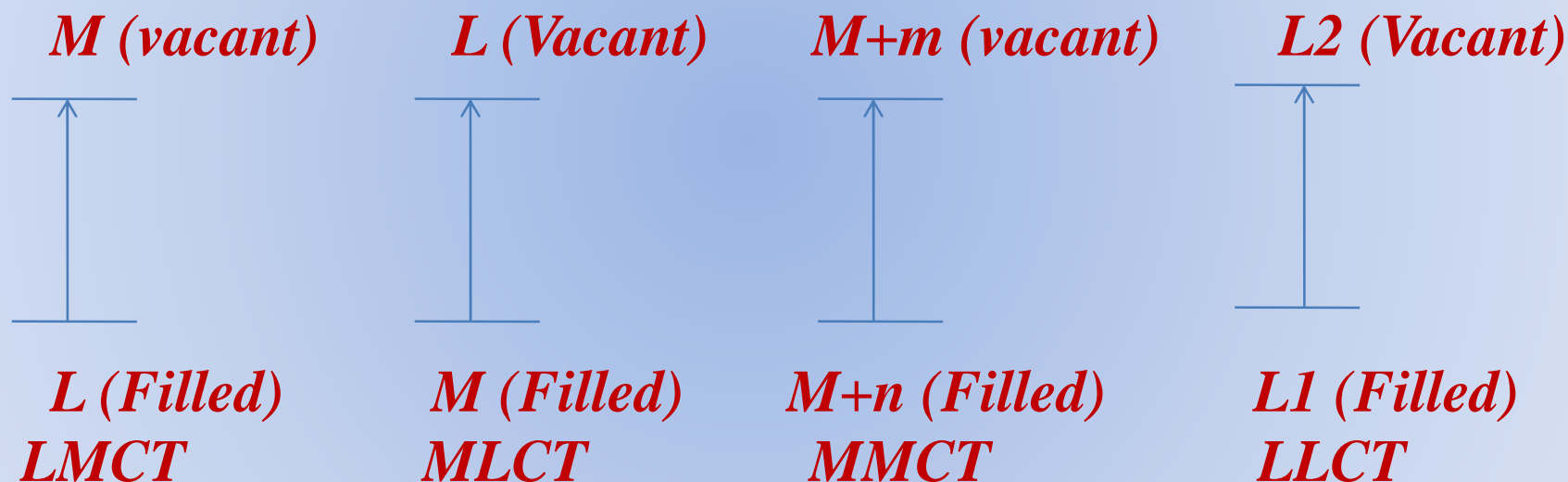
There are mainly four ways of charge transfer in transition metal complexes.

(a) **Ligand-to-Metal Charge-Transfer** (*LMCT*)

(b) **Metal-to-Ligand Charge-Transfer** (*MLCT*)

(c) **Metal-to-Metal Charge-Transfer** (*MMCT or IVCT*)

(d) **Ligand-to-Ligand Charge-Transfer** (*LLCT or ILCT*)



In these electronic transitions, the electronic transitions are laporte and spin allowed, i.e., $\Delta l = \pm 1$ and $\Delta S = 0$.

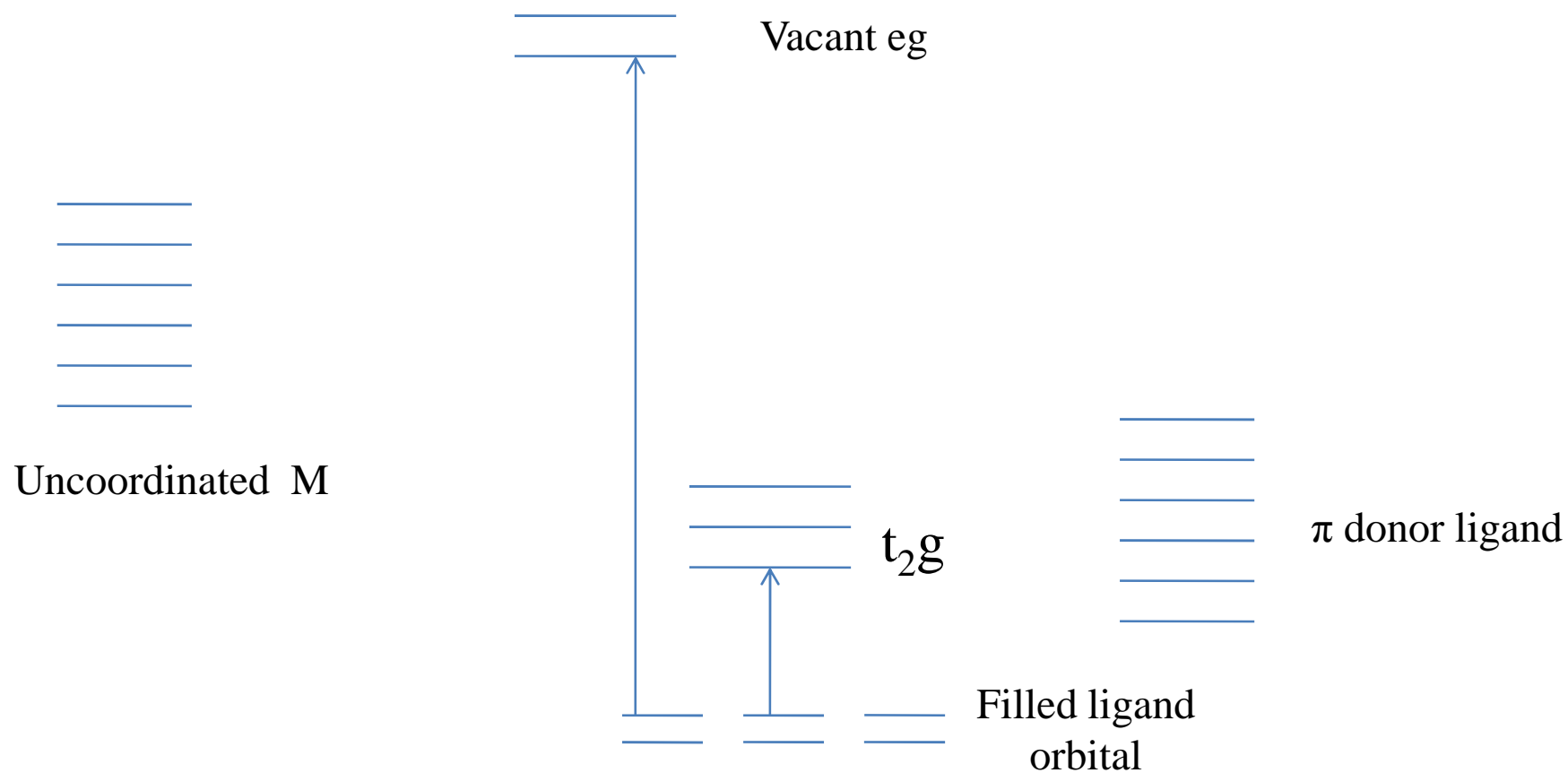
A charge transfer transition may be regarded as an internal redox process.

Ligand to Metal Charge Transfer (LMCT)

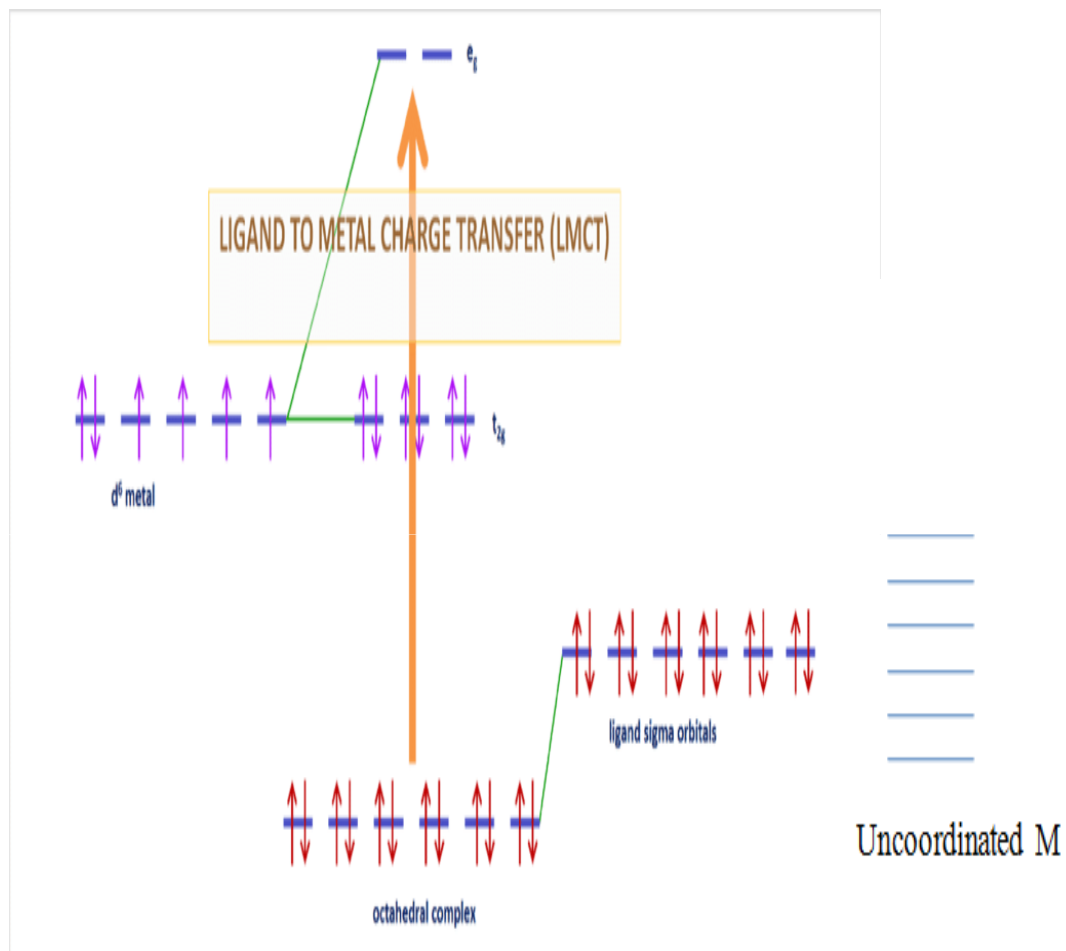
If the migration of electron is from ligand to the metal, then the charge transfer is called ligand to metal charge transfer (LMCT). To make the electron transfer from ligand to metal more favorable,

- L orbital is filled & M orbital is vacant
- L is π donor (X^- , O^{--} , S^{--} , Se^{--} , N_3^- , RO^-) etc.
- L should have low energy filled orbital
- The net result of such a metal-ligand combination would be that the orbitals involved in an LMCT process would be close enough in energy that the transition could be induced by a photon in the visible or near-ultraviolet region.

LMCT

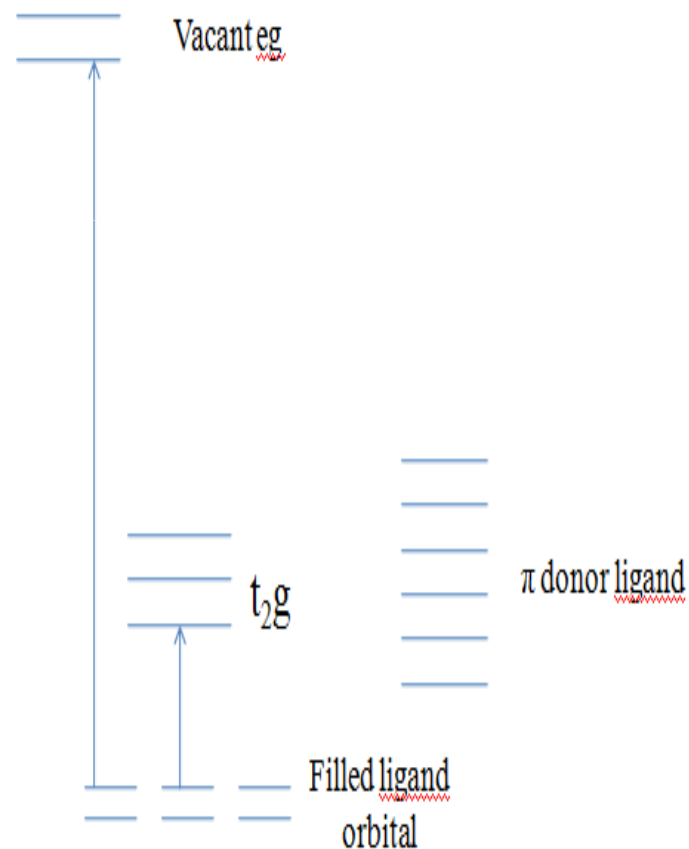


Charge transfer have been explained by the help of MO diagram as



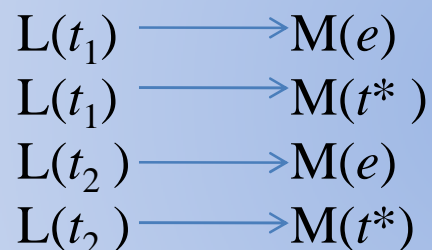
t_{1u} to t_{2g}
 t_{1u} to e_g

LMCT



In any tetrahedral complex, the four lowest energy σ -bonding orbitals will be filled and will be primarily ligand in character. Next there are two sets of σ - nonbonding MO's, one ligand-centered and one metal-centered. The permanganate, these orbitals would correspond to filled oxygen πp orbitals and empty manganese $3d$ orbitals, respectively.

All of the higher energy antibonding molecular orbitals would be unoccupied for a manganese (VII) complex. Hence there are four possible ligand-to-metal transitions:



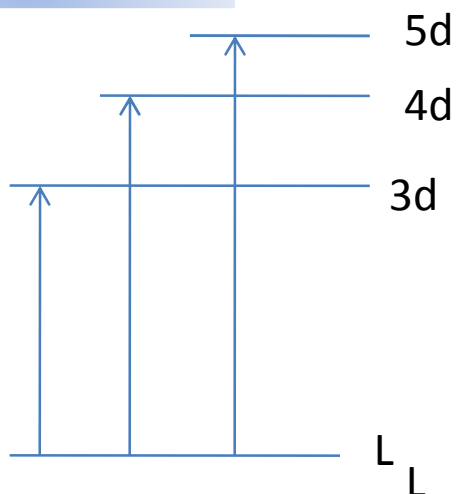
For MnO_4^- all four of these transitions have been observed:

$(t_1 \rightarrow e);$	$17,700 \text{ cm}^{-1}$
$(t_1 \rightarrow t^*);$	29500 cm^{-1}
$(t_2 \rightarrow e);$	and $30,300 \text{ cm}^{-1}$
$(t_2 \rightarrow t^*)$	$44,400 \text{ cm}^{-1}.$

Only the absorption at $17,700 \text{ cm}^{-1}$ falls within the visible range ($14,000 - 28,000 \text{ cm}^{-1}$), and it is responsible for the familiar deep purple color of MnO_4^- .

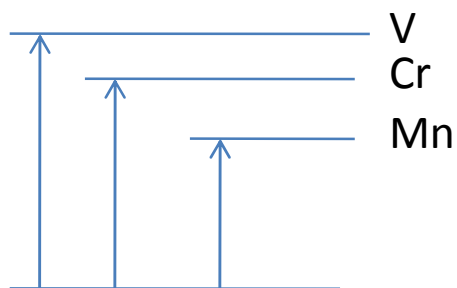
Intensity of LMCT also depends upon nature of d orbital

A – in group of PT



Intensity of LMCT increases due to increasing in size of metal $3d < 4d < 5d$

B – in period of PT



Intensity of LMCT decreases due to lowering of size & increasing in nuclear charge

Metal to Ligand Charge Transfer (MLCT)

Migration of electron from metal to ligand, then charge transfer is called metal to ligand charge transfer (MLCT).

Characteristics of MLCT

1. **MLCT** are favored in complexes that have
Metal side

- i. O.N. should be low
- ii. Energy of metal should have high
- iii. M should be easily oxidisable
- iv. M have filled orbital/occupied metal-centered orbitals
- v. Able to back bonding

Ligand Side

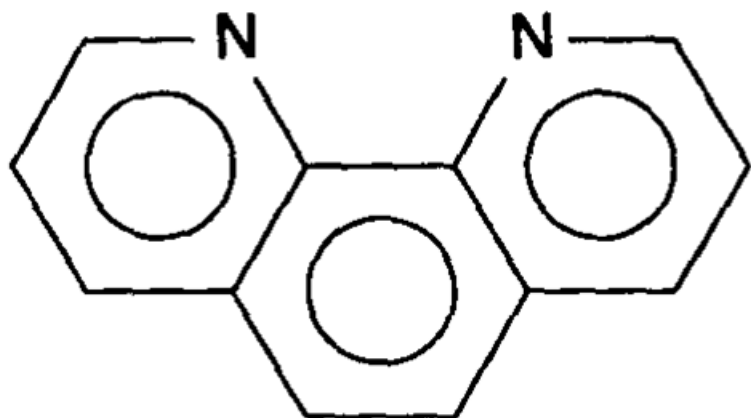
- i. L have vacant orbital/vacant low lying π^* orbital's ligand
- ii. L should be easily reducible
- iii. Ligands which have empty π antibonding orbitals
like CN^- , SCN^- , CO, pyridine, bipyridine, pyrazine, *o*-phenanthroline, dithiolene ($\text{S}_2\text{C}_2\text{R}_2$), dithiocarbamate (S_2CNR_2) & aromatic ligand

The red color of tris (bipyridyl)iron(II), electron makes a transition for a d orbital of the central metal into a π^* orbital of the ligand.

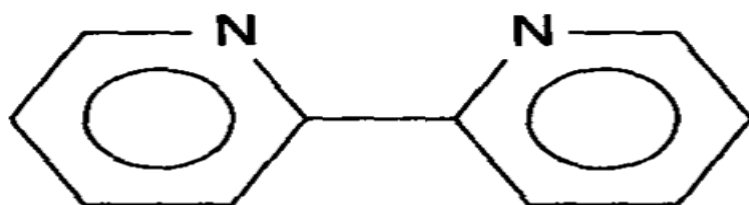
- Diamines, which have two N donor atoms: two important examples are 2, 2'-bipyridine and 1, 10- phenanthroline.

- Complexes of diimines with strong MLCT bands include tris(diimine) species such as tris (2, 2'bipyridyl)ruthenium(II), which is orange on account of its MLCT band.

- A diimine ligand may also be easily substituted into a complex with other ligands that favor a low oxidation state. $[\text{W}(\text{CO})_4(\text{phen})]$ and $[\text{Fe}(\text{CO})_3(\text{bipy})]$ shows MLCT transitions is by no means limited to diimine ligands.

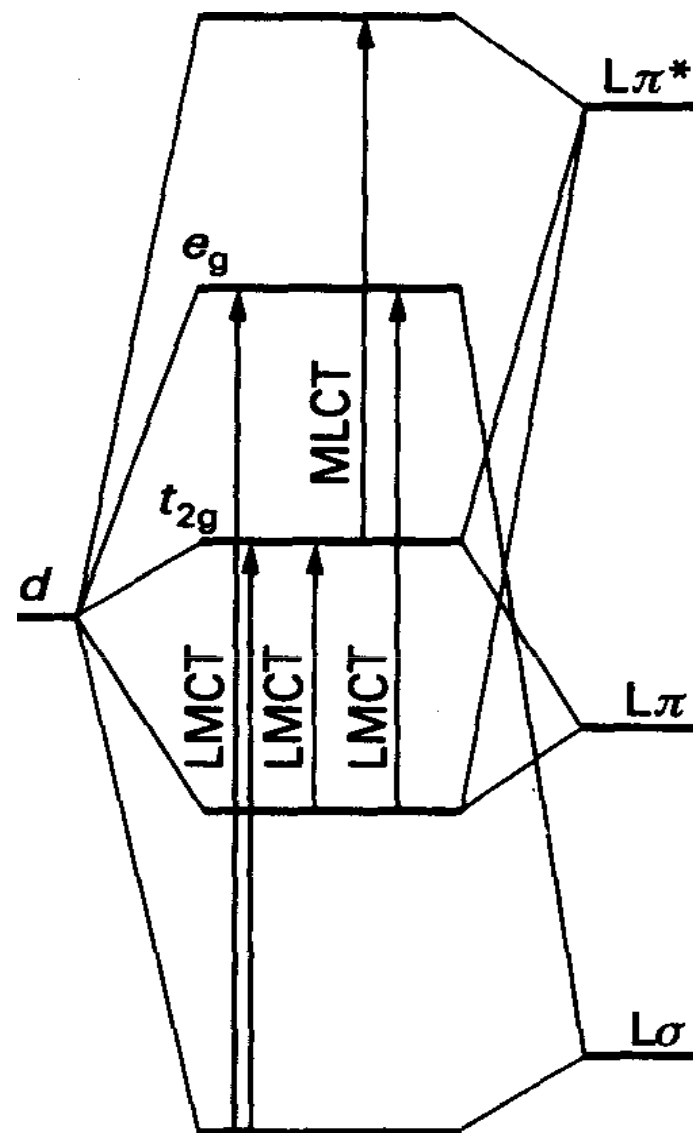


1,10-Phenanthroline (phen)



2,2'-Bipyridine (bipy)

Having π^* MO & non bonding e-



Having low lying π^* MO

MMCT or IVCT

Transfer of e^- from one metal to another metal having different O.N. is called metal-metal charge transfer or intra valent charge transfer. It must have more than one metal ion having different O.S. & energy level.

In spinal (M_3O_4) MMCT takes place where M^{+2} & M^{+3} are present. Fe_3O_4 due to transfer of e^- from Fe^{+2} to Fe^{+3}

$Fe^{+3} [Fe^{+2}(CN)_6]$ Prussian Blue

$Fe^{+2} [Fe^{+3}(CN)_6]$ Turnbulls Blue

-Rust is radish brown Fe_3O_4 due to $Fe^{+2}=Fe^{+3}$

LLCT or ILCT or LC

Transfer of e^- from lower energy level of ligand to higher energy level of ligand

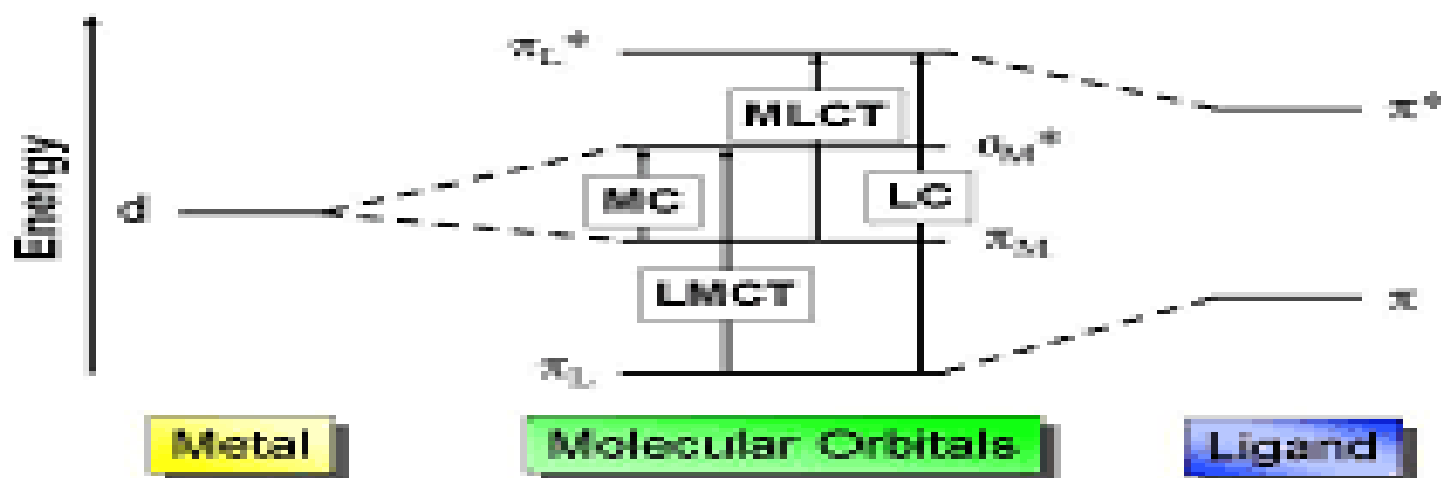
i.e. transfer of e^- from filled orbital of one ligand to vacant orbital of another ligand

i.e. it occurs in complex of mixed ligands

i.e. it should have π donor (like halide) & π acceptor (CO, CN^- , Py, biPy etc)

$\text{Be}(\text{CO})_3 \text{X}_3$, $[\text{Tl}(\text{biPy}) \text{I}_2]$ where x & I are π donor & transfer e^- to CO & biPy which are π acceptor

Excited States of Organometallic Complexes



References & further reading

S & Atkins, Oxford Inorganic Chemistry, Fourth Edition

Alagappa university, M. Sc. Chemistry

Pearson, Inorganic chemistry

Fmiza Hammer Synthesis & reaction of organometallic compound

Thank
you!