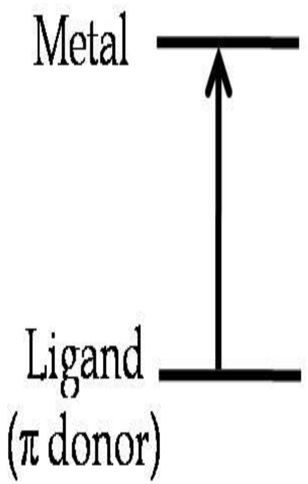
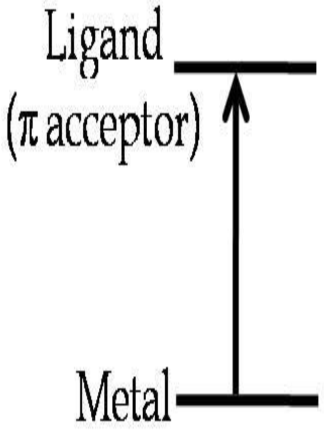
# CHARGE TRANSFER SPECTRA



LMCT



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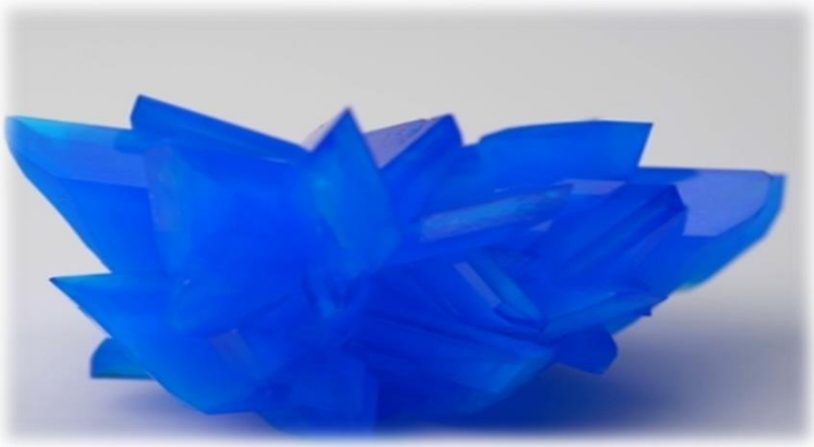
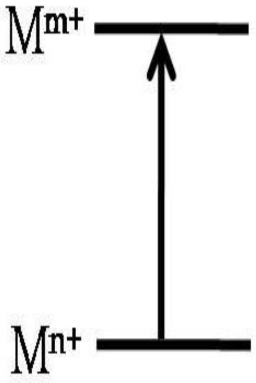
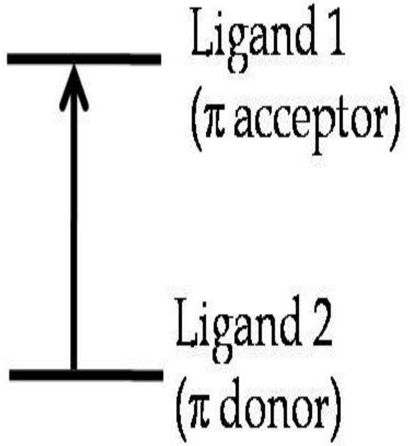




MMCT



LLCT

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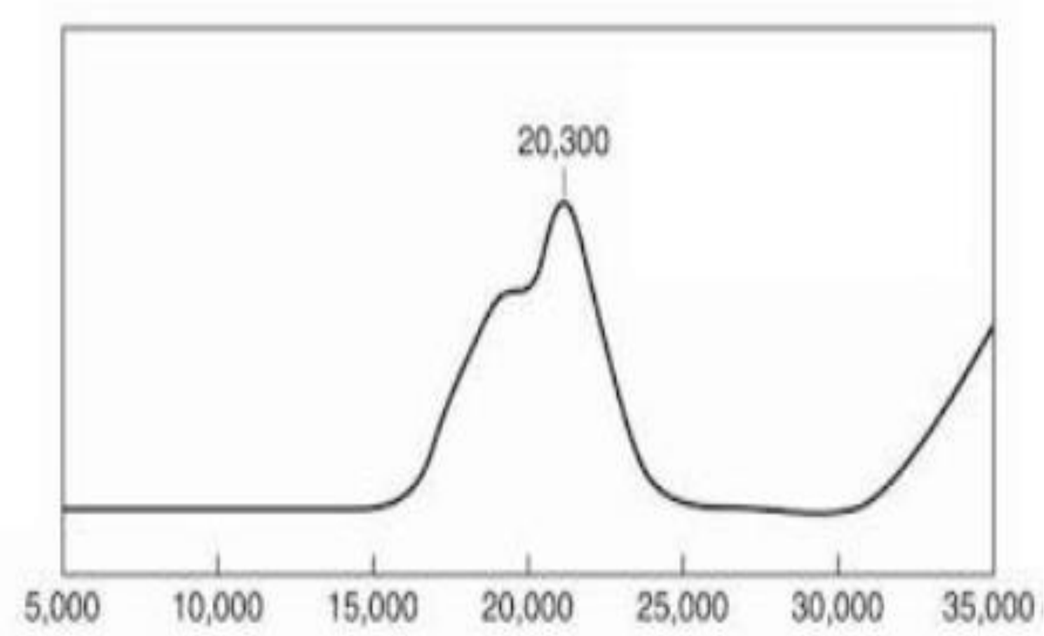
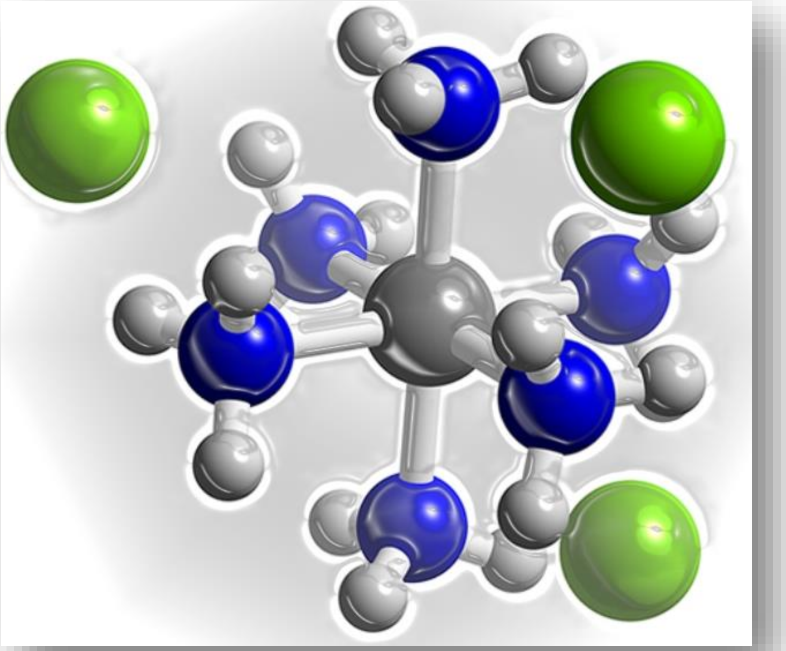
# Electronic Transitions in Coordination Compounds

1. Spectrum of ligands.
2. Spectrum of Counter ion.
3. d-d transition spectrum.
4. Charge transfer spectrum.





# Electronic Transitions in Coordination Compounds

## 1.Spectrum of ligands:

These arise due to characteristic absorptions by the ligands which are normally lie in the UV region. These bands persists in the spectra of complexes formed by these ligands but may be somewhat modified.

**Types**

(i) n- $\sigma^*$ transition.

(ii) n-$\pi^*$ transition.

(iii) $\pi$-$\pi^*$ transition.

It is often difficult to balance spectroscopic cells with water above 50,000 $cm^{-1}$ or with chloroform above 40,000 $cm^{-1}$ because of the presence of intense absorption bands by these solvents.

# Electronic Transitions in Coordination Compounds

## 2. Spectrum of Counter ion:

This arises from the absorption in the UV or visible region by common counter ions usually present with an ionic complex species.

**Types**

(i) n- $\sigma^*$ transition.

(ii) n-$\pi^*$ transition.

(iii) $\pi$-$\pi^*$ transition.

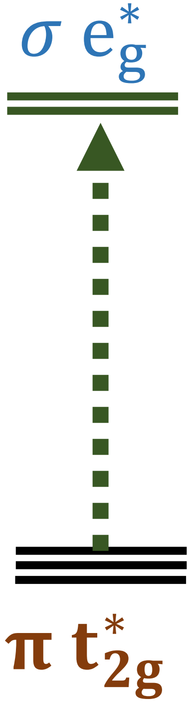
**Common anions like $Cl^-$, $SO_4^{2-}$ and $ClO_4^-$ do not absorb radiation in the UV or visible regions but $NO_3^-$ and $NO_2^-$ have intense absorption bands in the ultraviolet region.**

# Electronic Transitions in Coordination Compounds

## 3. d-d transition spectrum:

**CFT:** Metal d orbital to metal d orbital transition.

**LFT:** Non bonding metal d orbital to anti-bonding MO having greater metal character transition or, MO having greater metal character to MO having greater metal character transition.

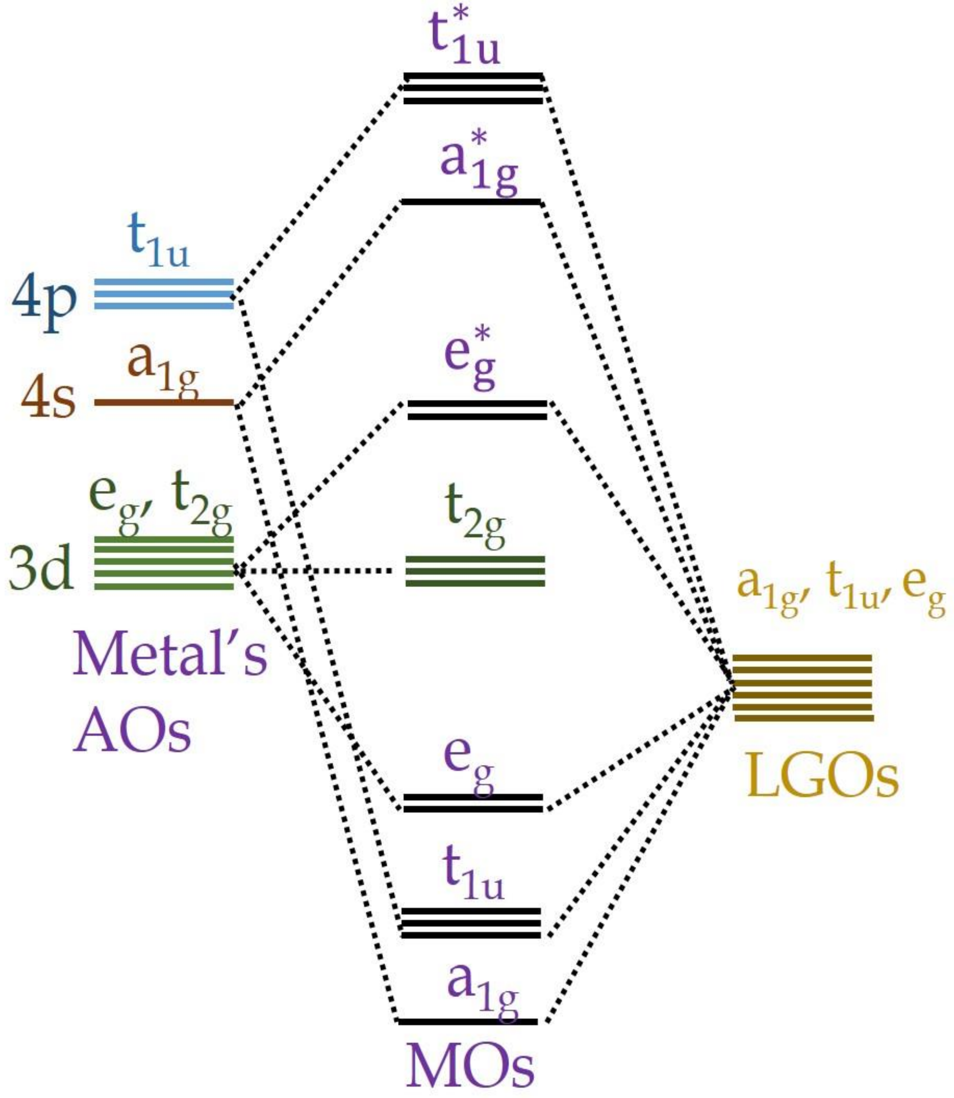


# Electronic Transitions in Coordination Compounds

## 4. Charge transfer spectrum:

It involves movement of electron mainly from a molecular orbitals having greater ligand character to a molecular orbital having greater metal character and vice versa.

**The charge distribution in the excited state differs considerably from the ground state. Hence these transitions are redox in nature and are called charge transfer spectra.**



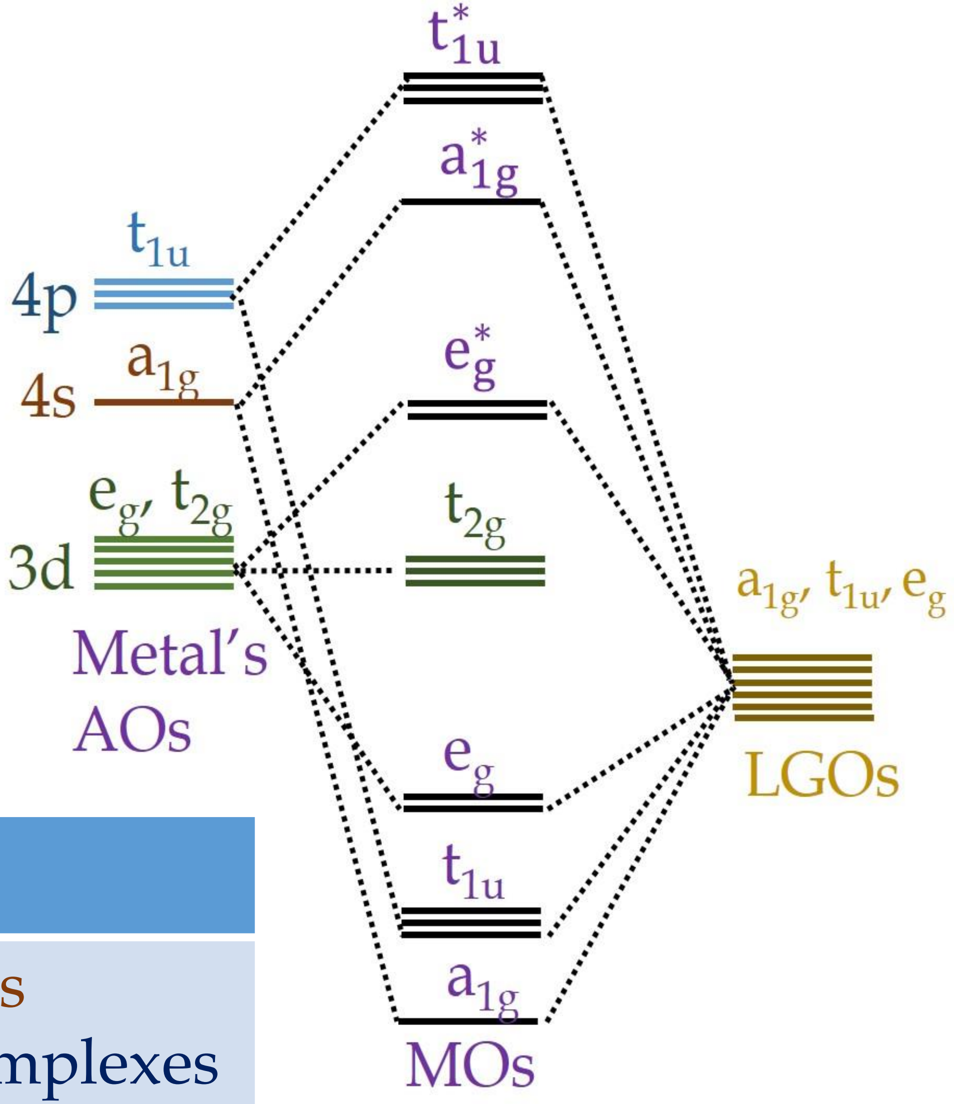
# CHARGE TRANSFER SPECTRUM

## Nature of charge transfer spectra:

(i) These are Laporte and spin allowed transitions.

(ii) Mostly occur in UV region and visible region. **Charge transfer transitions only in visible region are responsible for the color of the complexes.**

(iii) It is observed almost in all complexes.

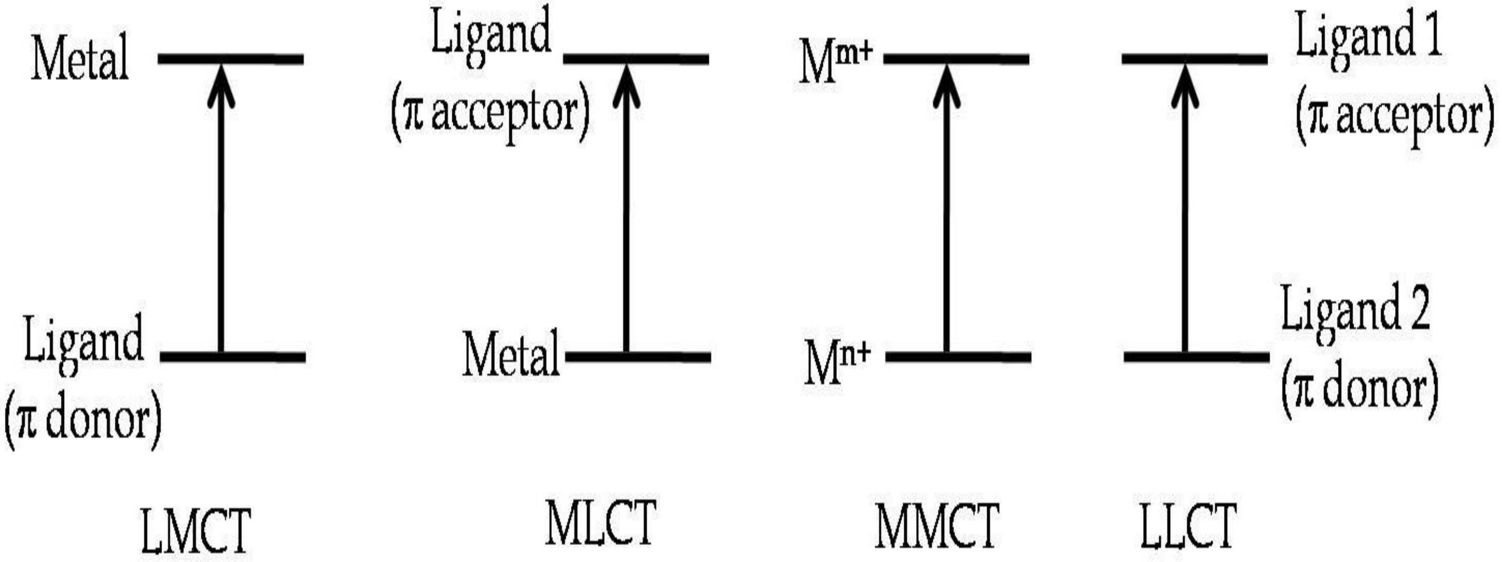


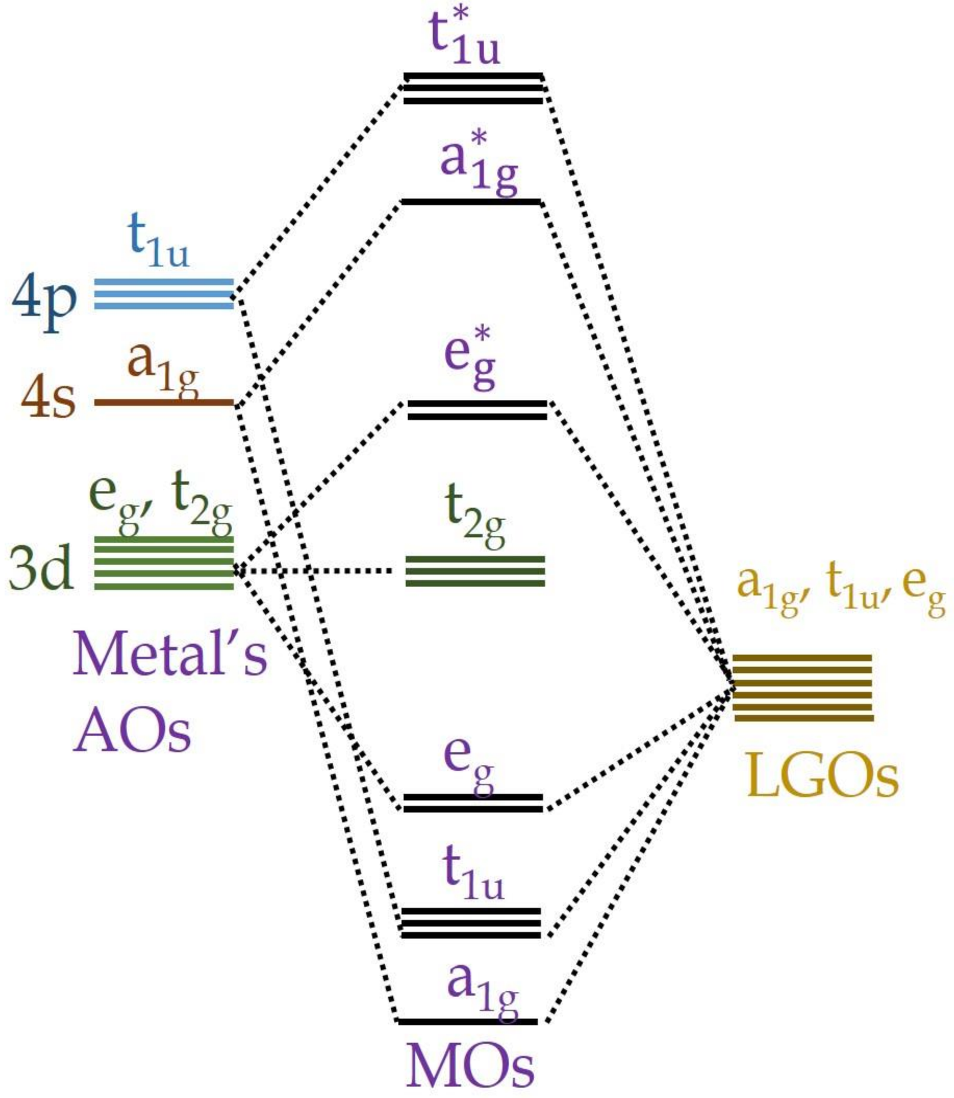
| Transition | ε, dm$^3$ mol$^{-1}$ cm$^{-1}$ |
|---|---|
| Spin allowed d-d transition | 1-10 for centrosymmetric complexes<br>10-100 for non-centrosymmetric complexes |
| Charge transfer | 10000-50000 |

# CHARGE TRANSFER SPECTRUM

## Types:

(i) Ligand to metal charge transfer spectra (LMCT)
(ii) Metal to ligand charge transfer spectra (MLCT)
(iii) Metal to metal charge transfer spectra (MMCT)
(iv) Ligand to ligand charge transfer spectra (LLCT)

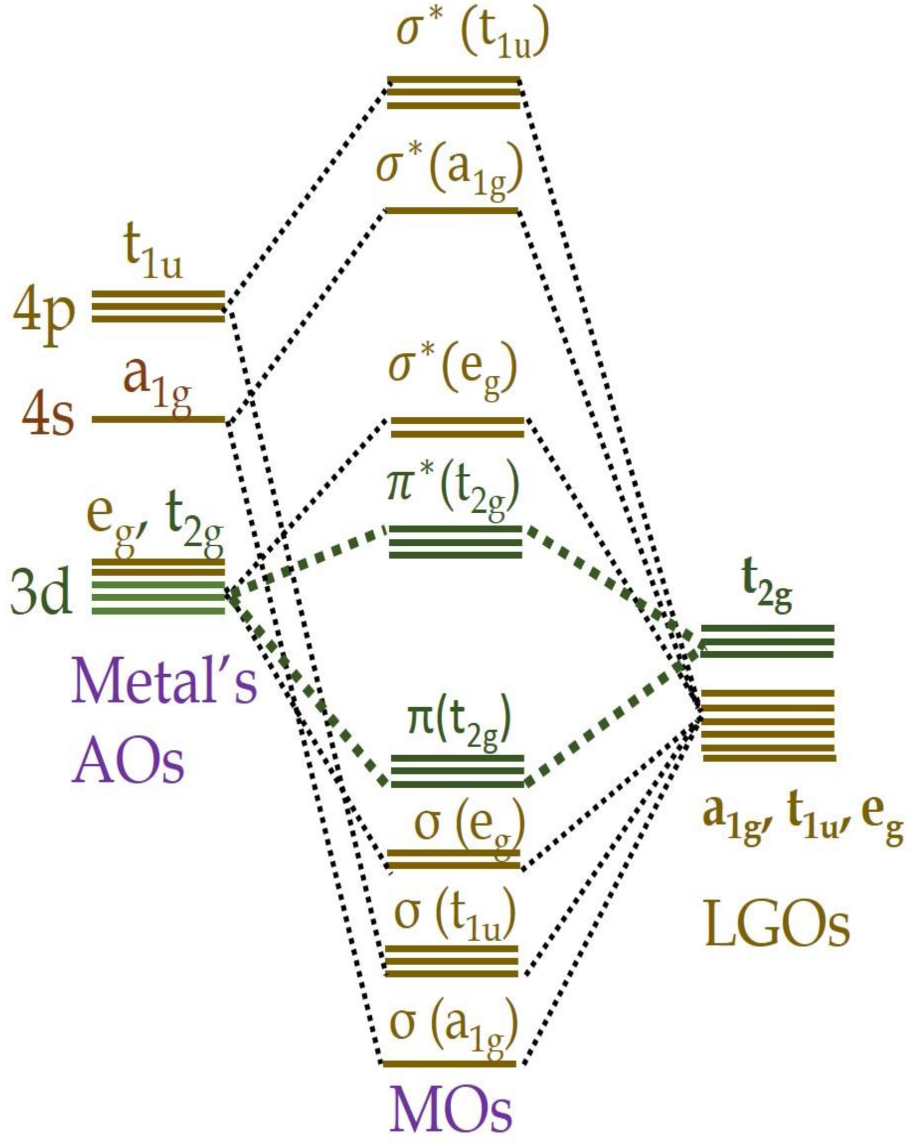




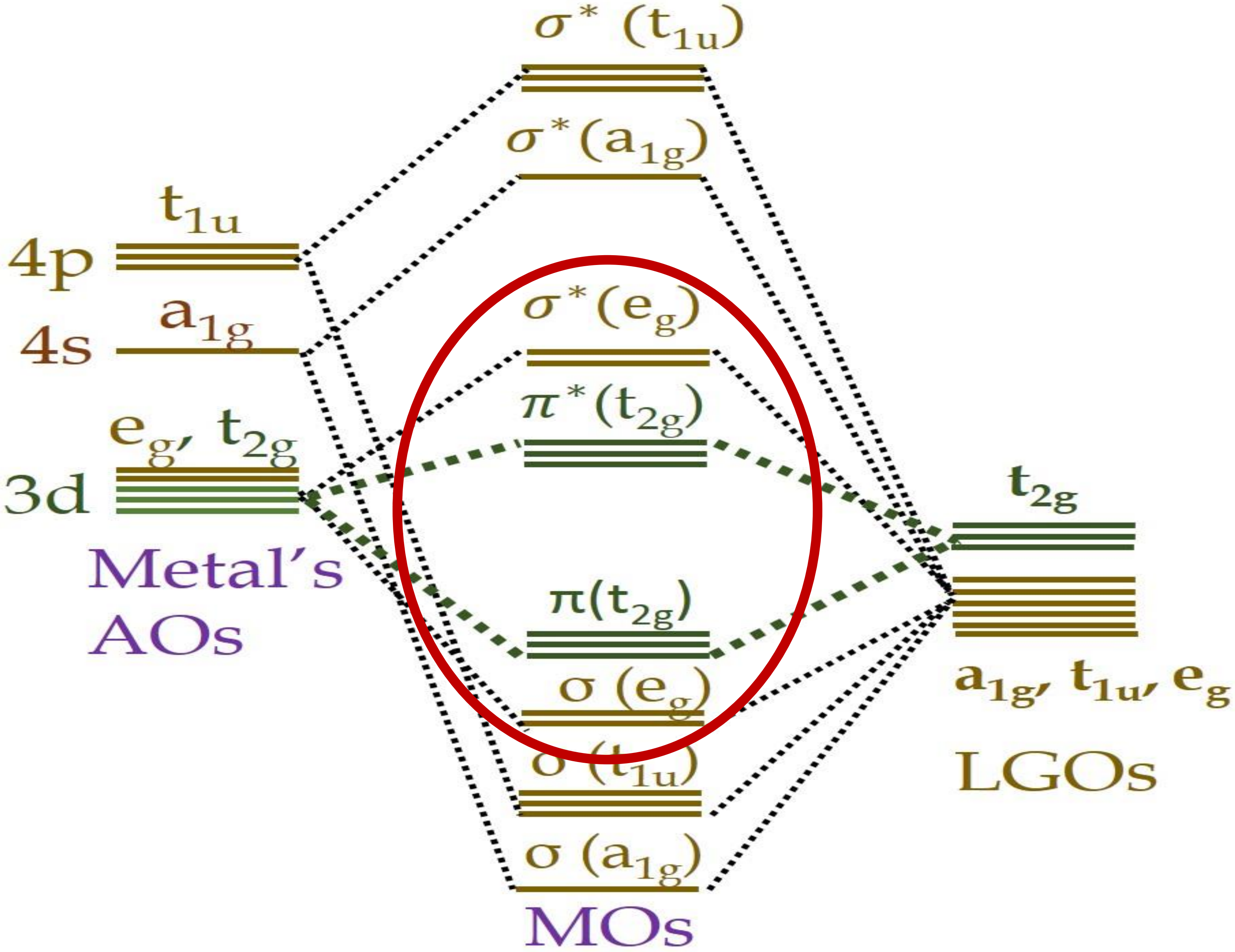
# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)

**LMCT:**

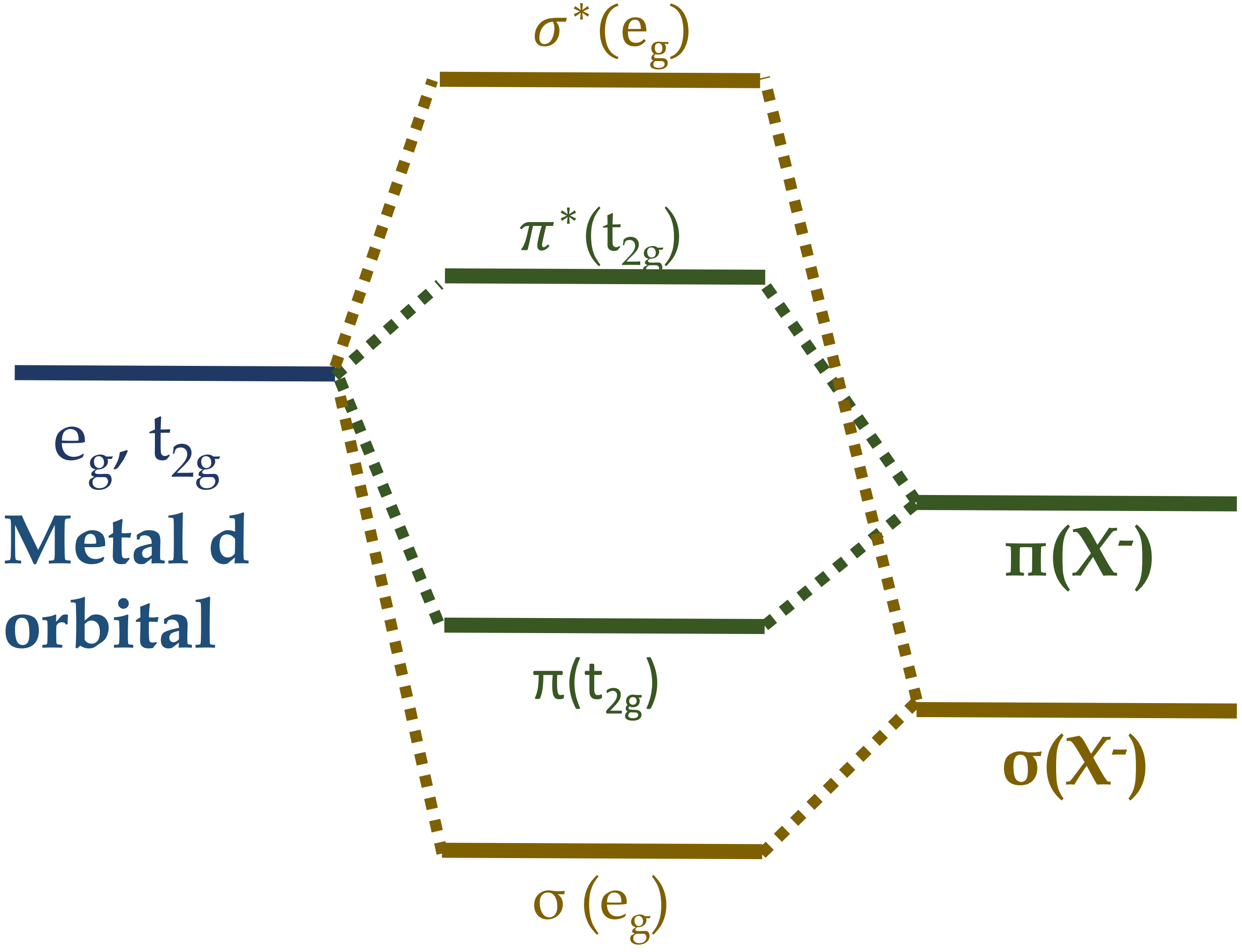
- Electronic transition from ligand based MO to metal based MO.
- The $\pi$ donor ligands generally show LMCT spectra in the visible range.
- Metal should be in high oxidation state.
- These transitions take place with lower energy as the metal becomes more easily reducible and the ligand gets readily oxidizable.



# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)

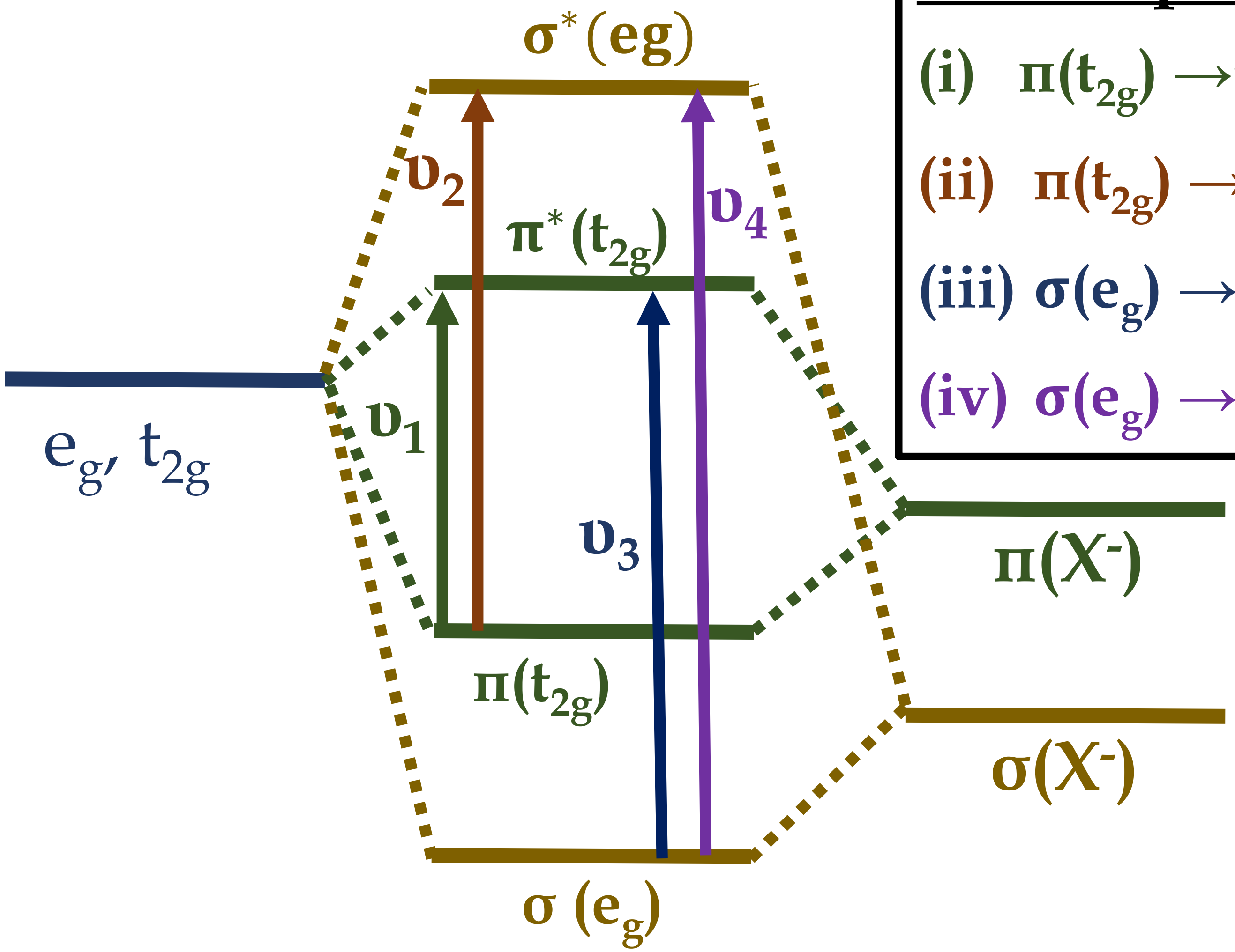


# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)



MO of $MX_6^{n-}$

# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)



**Four expected transitions:**

(i) $\pi(t_{2g}) \rightarrow \pi^*(t_{2g})$ (Low energy transition-VIS region)

(ii) $\pi(t_{2g}) \rightarrow \sigma^*(e_g)$

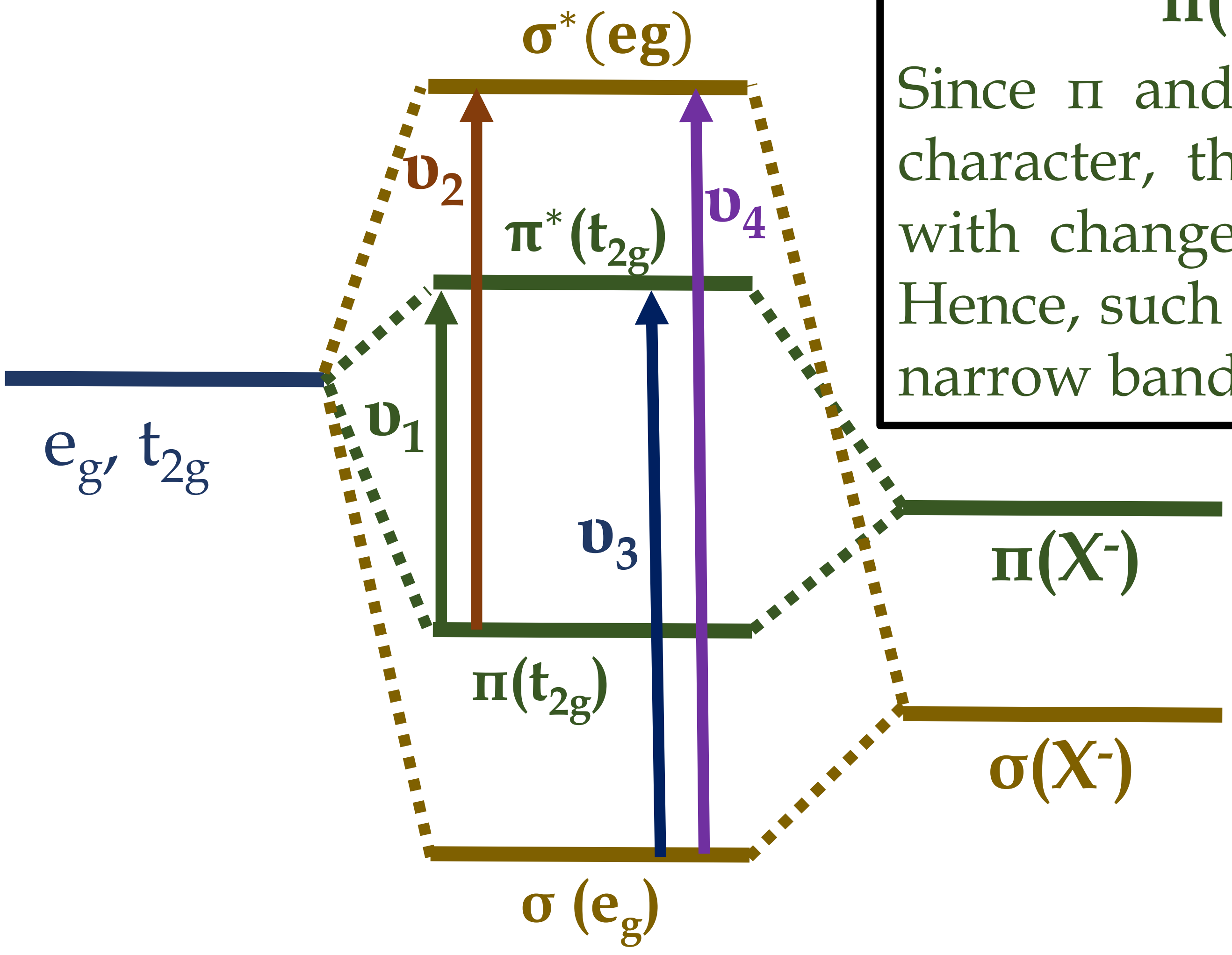
(iii) $\sigma(e_g) \rightarrow \pi^*(t_{2g})$

(iv) $\sigma(e_g) \rightarrow \sigma^*(e_g)$

High energy transition-UV region.

No question of π- π* transition when π* level is filled with metal electrons, as in the case of $d^6$ metal ions. Such cases, the π-$\sigma^*$ transition is the lowest energy transition.

# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)



**$\pi(t_{2g}) \rightarrow \pi^*(t_{2g})$ transition ($\upsilon_1$).**

Since π and π* orbitals are largely non-bonding in character, their energy will not fluctuate noticeably with change in M-L distance as the ligand vibrate. Hence, such transitions are expected to give relatively narrow band.

**$\pi(t_{2g}) \rightarrow \sigma^*(e_g)$ transition ($\upsilon_2$).**

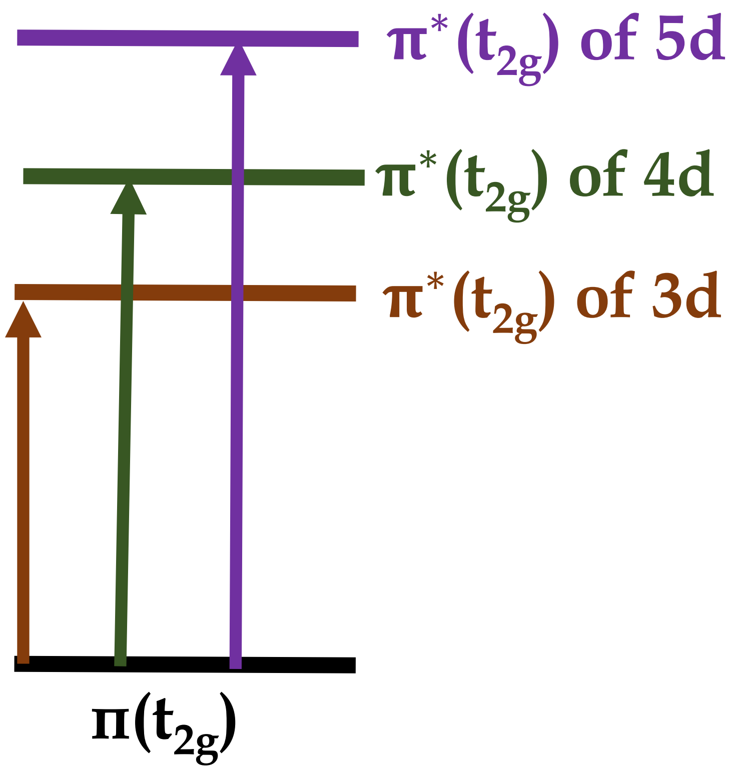
Such transitions take place from a mainly non-bonding orbital to an antibonding one, hence their energy varies noticeably with change in M-L distance as the ligand vibrate. Hence these bands are broad band.

# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)

## Energy of LMCT

**(i) Moving top to bottom of a group:**

For a particular ligand, moving from the top to bottom of a group in the periodic table, LMCT energy increases.



$\pi^*(t_{2g})$ of 5d

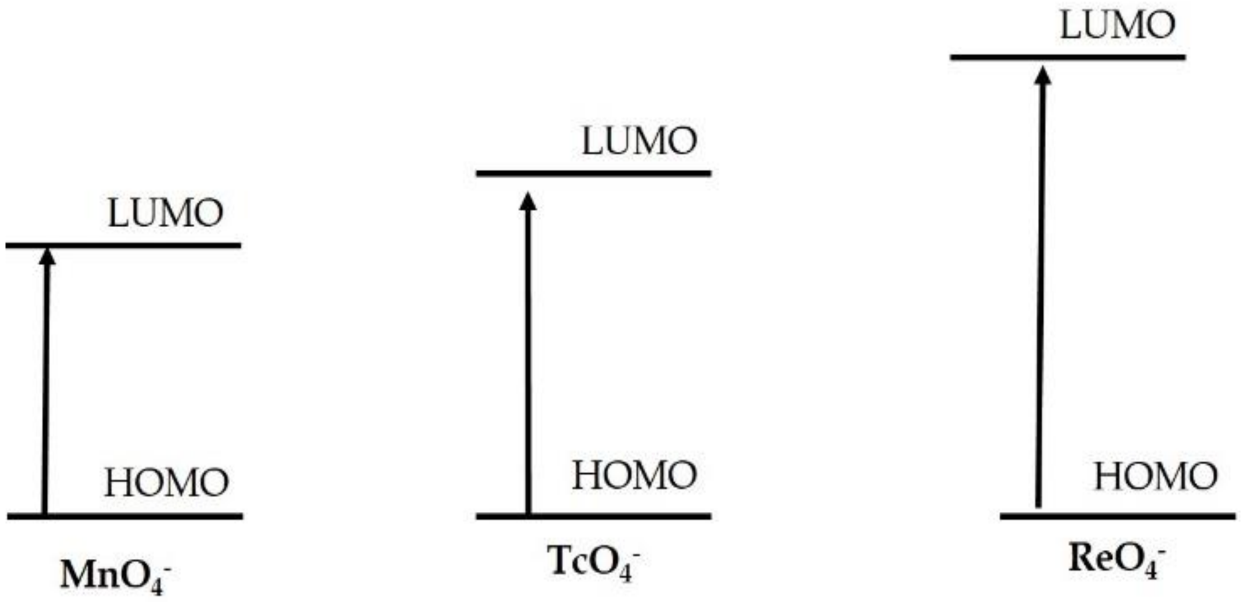
$\pi^*(t_{2g})$ of 4d

$\pi^*(t_{2g})$ of 3d

$\pi(t_{2g})$

**Q1.** Explain the order of charge transfer transition energies: $MnO_4^- < TcO_4^- < ReO_4^-$

**Hints.** Mn, Tc and Re belong to the same group in the periodic table and here their oxidation states are also same (+7 and $d^0$). $O^{2-}$ is a π donor ligand which results LMCT.

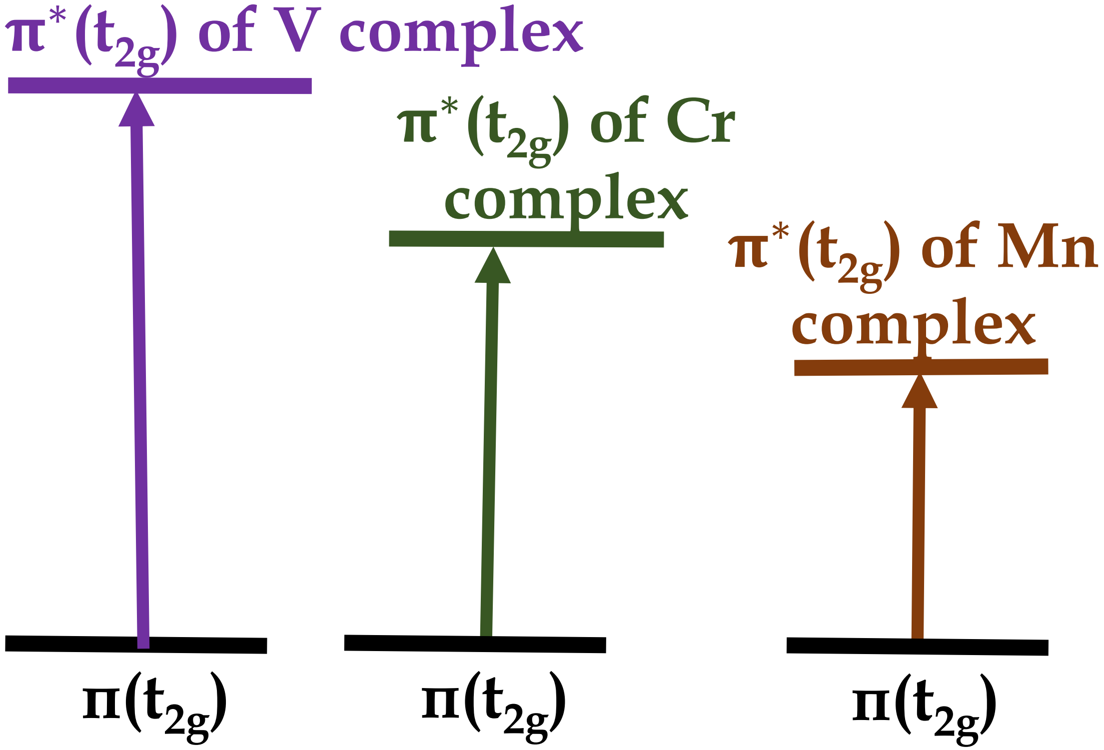


# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)

## Energy of LMCT

### (ii) Moving left to right of a period:

Moving from left to right of a period, effective nuclear charge increases which causes decrease of metal atomic orbital energy. Hence, LMCT energy decreases.



$\pi^*(t_{2g})$ of V complex

$\pi^*(t_{2g})$ of Cr complex

$\pi^*(t_{2g})$ of Mn complex

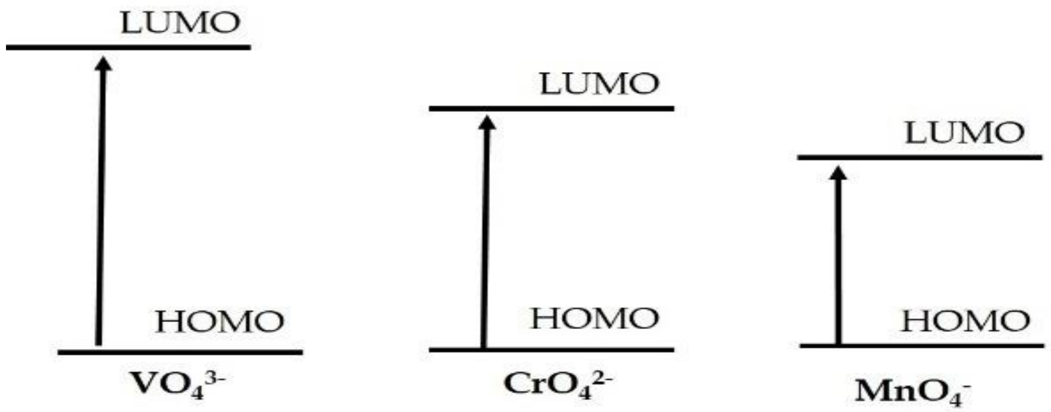
$\pi(t_{2g})$

$\pi(t_{2g})$

$\pi(t_{2g})$

**Q2. Explain the order of charge transfer transition energies: $VO_4^{3-} > CrO_4^{2-} > MnO_4^-$**

**Hints.** $O^{2-}$ is a π-donor ligand and all the metal ions are $d^0$ systems. HOMO of the complexes has greater ligand character and LUMO has greater metal character. Order of energy of LUMO is **$VO_4^{3-} > CrO_4^{2-} > MnO_4^-$.** Order of wavelength of LMCT transitions is $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$.

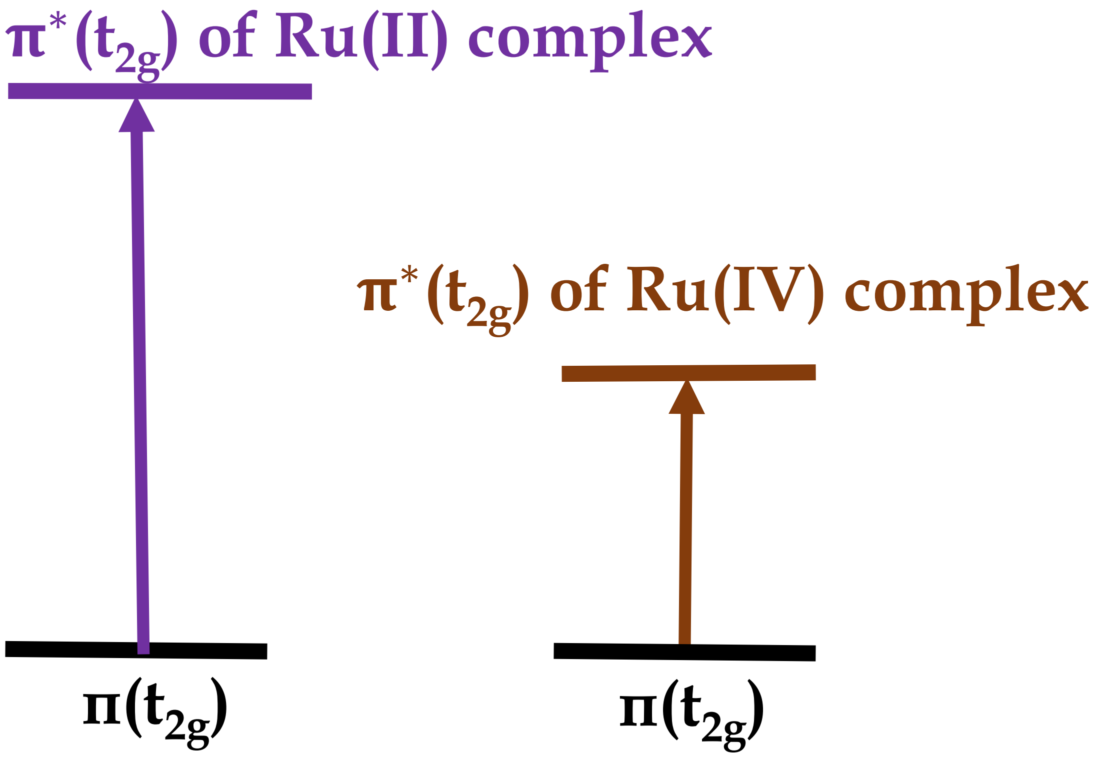


# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)

## Energy of LMCT

### (iii) Oxidation state of metal ion:

With increasing the oxidation state of a metal effective nuclear charge increases, causes low energy of metal atomic orbital. Hence, LMCT energy decreases.

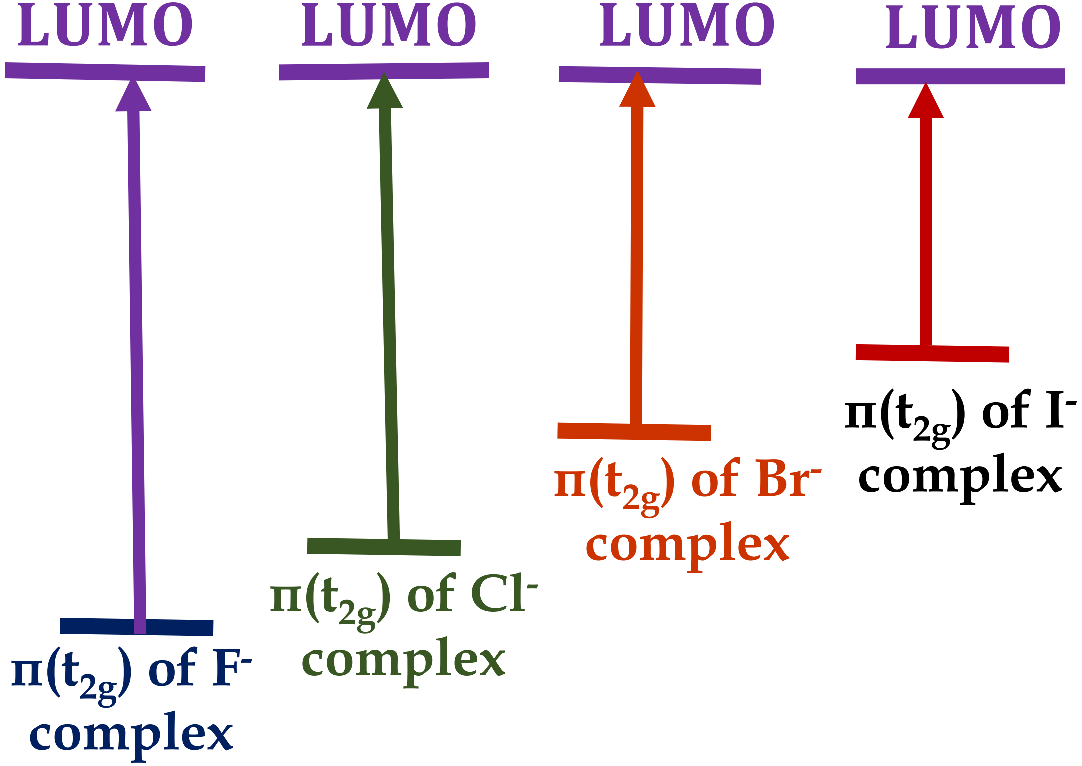


# LIGAND TO METAL CHARGE TRANSFER SPECTRA (LMCT)

## Energy of LMCT

### (iv) Nature of ligands.

For a particular metal ion, LMCT energy changes with changing the π-donor ligand.



**LUMO** **LUMO** **LUMO** **LUMO**

**$\pi(t_{2g})$ of $F^-$ complex**

**$\pi(t_{2g})$ of $Cl^-$ complex**

**$\pi(t_{2g})$ of $Br^-$ complex**

**$\pi(t_{2g})$ of $I^-$ complex**

**Q4.** Colors of $HgCl_2$, $HgBr_2$ and $HgI_2$ are white, yellow and green respectively. Explain.

**Hints.** $Cl^-$, $Br^-$ and $I^-$ are π donor ligands, hence LMCT transitions are occur in $HgCl_2$, $HgBr_2$ and $HgI_2$ compounds.

- The LMCT energy is highest in $HgCl_2$ and it falls under UV region. Thus $HgCl_2$ is a white colored compound.
- The LMCT energy in $HgBr_2$ is in between that of in $HgCl_2$ and $HgI_2$. $HgBr_2$ absorbs visible light in violet region, thus it is a yellow colored compound.
- The LMCT energy is lowest in $HgI_2$. It absorbs visible light in green region, thus it is a red colored compound.

# METAL TO LIGAND CHARGE TRANSFER SPECTRA (MLCT)

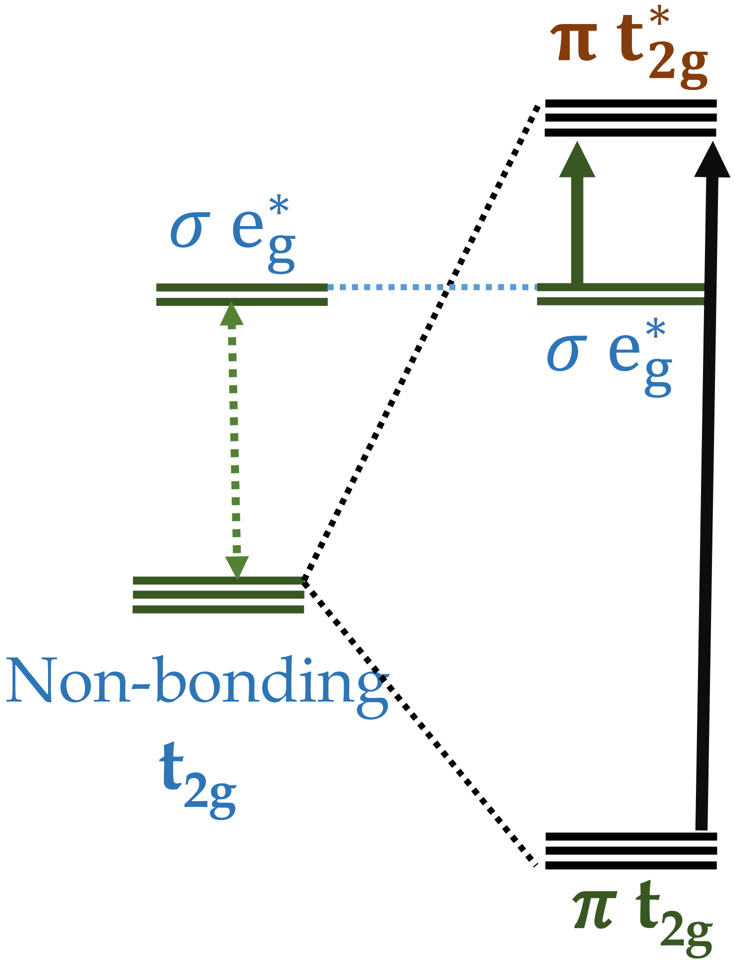
**Some features:**

(i) Electron transferred from metal orbital to ligand orbital.

(ii) Ligand must have vacant high energy **π* orbital (CO, CN-, NO, py, bpy, phen etc.)**.

(iii) Metal must have electrons in the d orbitals.

(iv) Metal must have in lower oxidation state.



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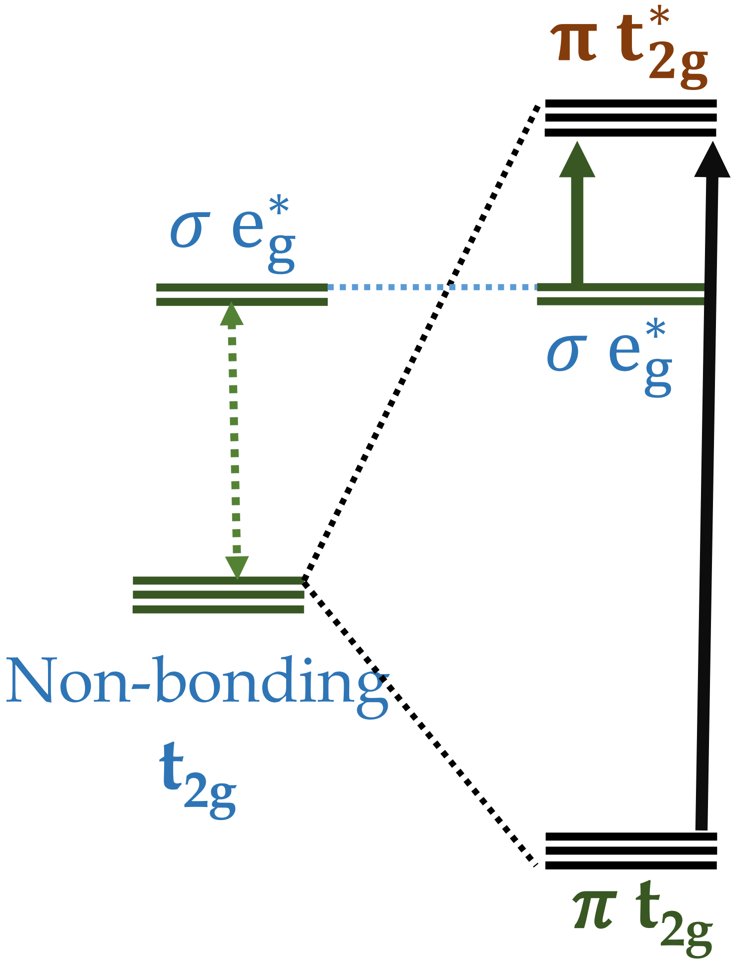
**Π-acceptor ligands stabilize lower oxidation state of metal and π-donor ligands stabilize higher oxidation state of metal.**

**Problem 1. Between $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ in which complex metal-ligand bond strength is higher.**

**Ans. $[Fe(CN)_6]^{4-}$**



**Problem 2.** Among the following metal carbonyl species, the one with the highest metal-carbon back bonding is

(A) $[Ti(CO)_6]^{2-}$ (B) $[V(CO)_6]^{-}$ (C) $Cr(CO)_6$ (D) $[Mn(CO)_6]^{+}$

# METAL TO LIGAND CHARGE TRANSFER SPECTRA (MLCT)

## Some features:

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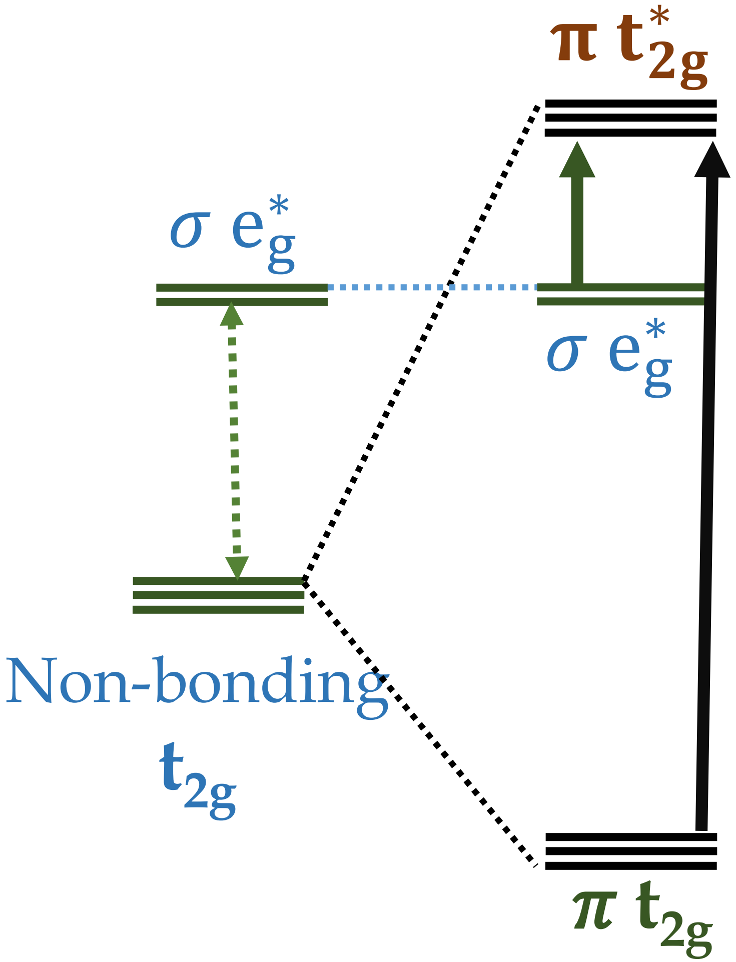


- ❖ Here crystal field splitting energy is very high.
- ❖ Transition $e_g$* to $t_{2g}$* falls under visible region. Hence, electron rich metals which $e_g$ electrons ($d^7$ to $d^{10}$) show color.
- ❖ Transition $t_{2g}$ to $t_{2g}$* is high energy transition.

**Example: $[Fe(py)_6]^{2+}$, $[Fe(bpy)_3]^{2+}$, $[Fe(o\text{-}Phen)_3]^{2+}$**

# METAL TO LIGAND CHARGE TRANSFER SPECTRA (MLCT)

**Some features:**

(i) Electron transferred from metal orbital to ligand orbital.

(ii) Ligand must have vacant high energy **π* orbital (CO, CN-, NO, py, bpy, phen etc.)**.

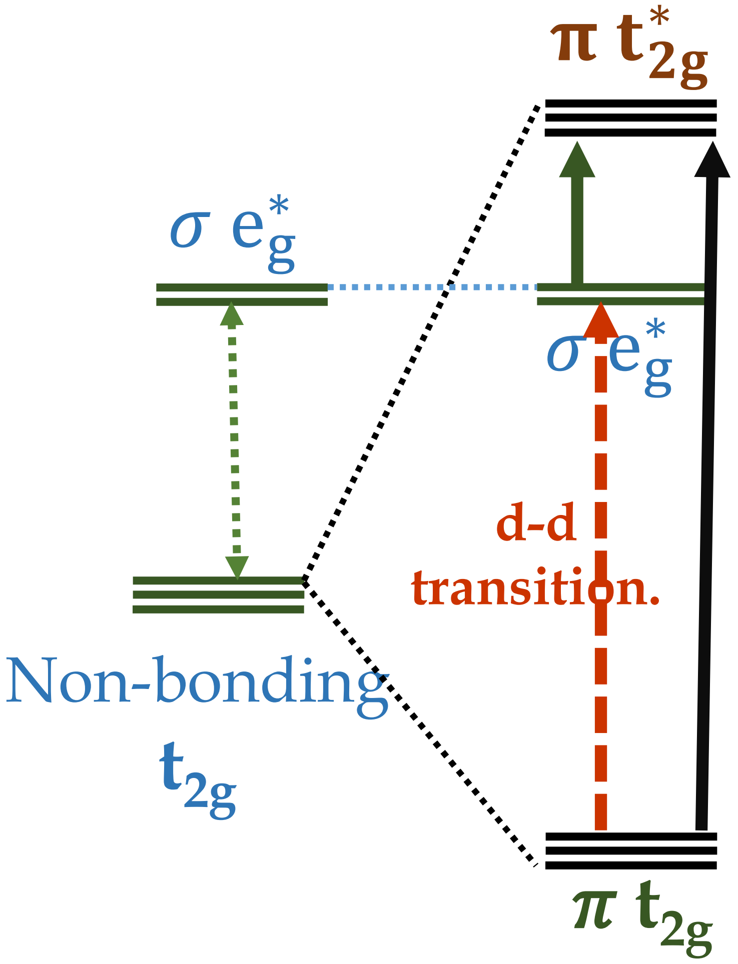
(iii) Metal must have electrons in the d orbitals.

(iv) Metal must have in lower oxidation state.

❖ Here crystal field splitting energy is very high.

❖ Transition $e_g^*$ to $t_{2g}^*$ falls under visible region. Hence, electron rich metals which $e_g$ electrons ($d^7$ to $d^{10}$) show color.

❖ Transition $t_{2g}$ to $t_{2g}^*$ is high energy transition.



**Example: $[Fe(py)_6]^{2+}$, $[Fe(bpy)_3]^{2+}$, $[Fe(o\text{-}Phen)_3]^{2+}$**

# METAL TO LIGAND CHARGE TRANSFER SPECTRA (MLCT)

**Some features:**

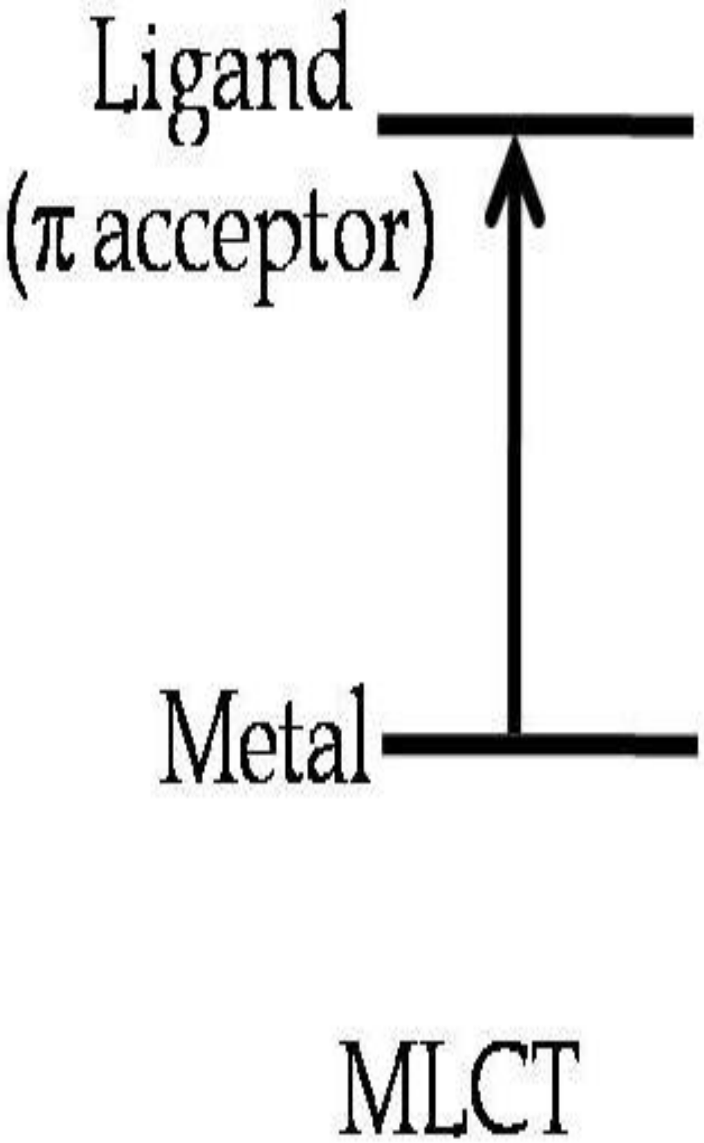
(i) Electron transferred from metal orbital to ligand orbital.

(ii) Ligand must have vacant high energy **π* orbital (CO, CN-, NO, py, bpy, phen etc.)**.

(iii) Metal must have electrons in the d orbitals.

(iv) Metal must have in lower oxidation state.

**Compare the MLCT wavelengths of $[Fe(py)_6]^{2+}$, $[Fe(bpy)_3]^{2+}$, $[Fe(oPhen)_3]^{2+}$ complexes.**



# FEW PROBLEMS

**Problem 1**. F$^-$ stabilizes higher valent while CO stabilizes lower valent state of the metal ions.

F$^-$ ligand acts as a π-donor ligand *i.e.* F$^-$ donate its π electrons to the metal center. The metal center will capable to accept this electron cloud if the metal center is in higher valent state. Thus, the F$^-$ stabilizes the higher valent metal ions.

CO ligand acts as a π-acceptor ligand i.e. CO accepts electron from metal ion center. If the metal center is in lower valent state, then electron donation from metal to ligand will facilitate and, if the metal center is in higher valent state, then electron donation from metal to ligand will retard. Thus, the CO stabilizes the lower valent metal ions.

# FEW PROBLEMS

**Problem 2.** The color of potassium dichromate is due to
(a) d-d transition (b) transition in $K^+$ ion (c) LMCT (d) MLCT (JAM 2010)

- In potassium dichromate, oxidation state of Cr is +6 . Hence, no d-d transition is possible ($d^0$ system).
- Ligand to metal charge transfer will occur if the ligand is oxidisable and metal is reducible (i.e. it is electron deficient and is at high oxidation state).
- Metal to ligand charge transfer will occur if the metal is oxidisable (i.e. it is at low oxidation state) and ligand is reducible (i.e. it is electron acceptor).
- Here, $Cr^{+6}$ is highly reducible and ligand $O^{2-}$ is highly oxidisable.
- Orange color of potassium dichromate is due to ligand to metal charge transfer.

# FEW PROBLEMS

## Problem 3.

The electronic transitions possible for the color of $K_2Cr_2O_7$ and porphine in their solid state respectively are : (JAM 2014)

(a) d-d, π- π* (b) MLCT, π- π*

(c) LMCT, π- π* (d) LMCT, d-d

## Problem 4.

A filter paper moistened with cadmium acetate solution turns yellow upon exposure to $H_2S$. The transition responsible for the yellow color is (JAM 2015)

(a) d-d (b) MLCT

(c) LMCT (d) σ-σ*

# FEW PROBLEMS

**Problem 5.**

Among $[Cr(C_2O_4)_3]^{3-}$, $[CrO_4]^{2-}$, $[ReO_4]^-$ and $[NiO_2]^{2-}$ which exhibit only charge transfer bands in UV-visible region? **(JAM 2016)**

**Ans.** $[CrO_4]^{2-}$and $[ReO_4]^-$

**Problem 6.**

**Complex $[CuCl_4]^{2-}$ exists but $[CuI_4]^{2-}$ does not. Explain**

**Hints.** $Cu^{2+}$ is reduced to $Cu^+$ by $I^-$, but not by $Cl^-$, that is why$[CuI_4]^{2-}$ does not exist.

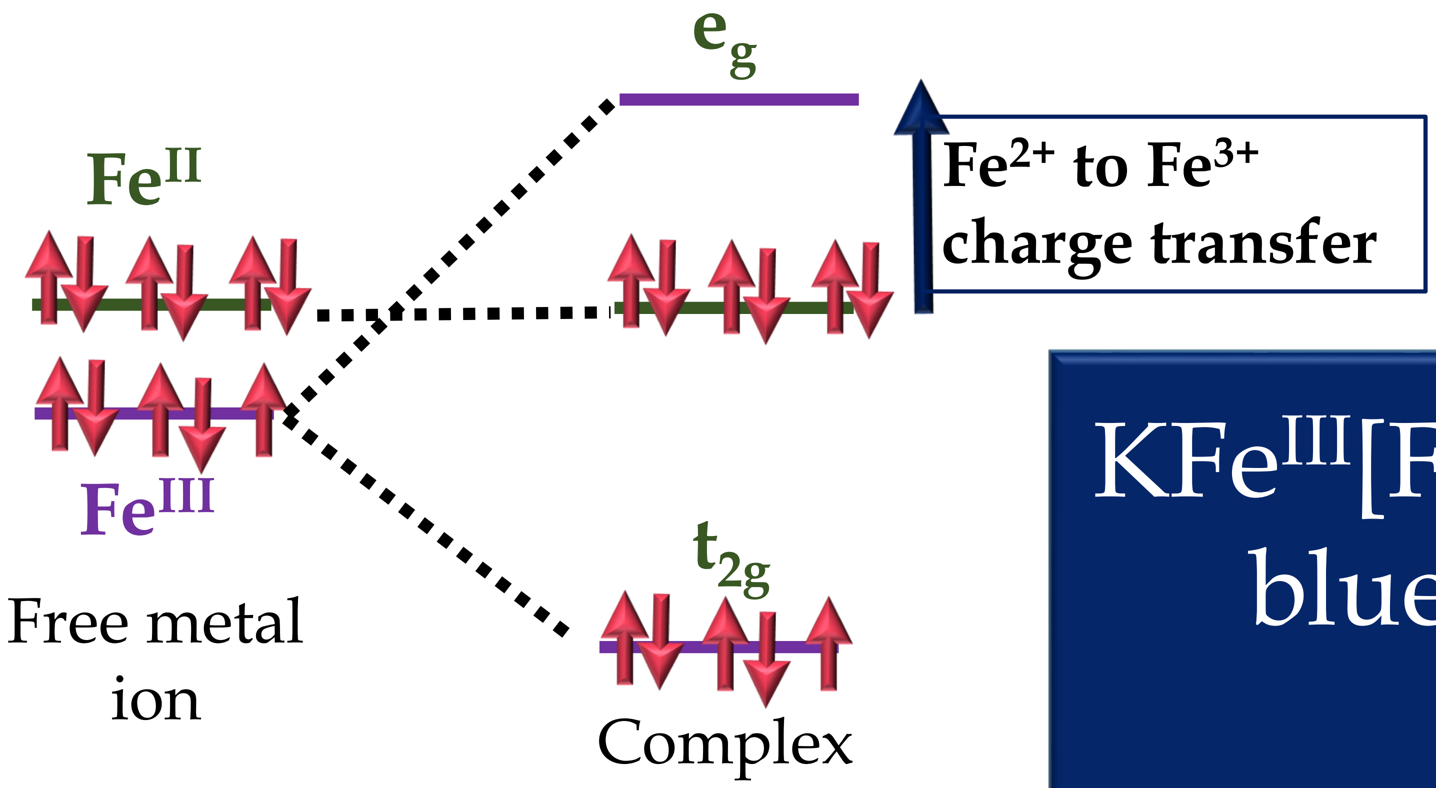
- The charge transfer process is closely related to an oxidation and reduction process. The energy of transition measures the tendency of the reaction to take place.
- If the ligands have low electronegativity and low reduction potentials, then actual electron transfer from the ligand to metal may take place.
- The dark color of $[CuCl_4]^{2-}$ is due to LMCT.
- The $[CuI_4]^{2-}$ is so unstable that lose electron to orbitals centered entirely on the copper. $2Cu^{2+} + 4I^- = 2CuI + I_2$

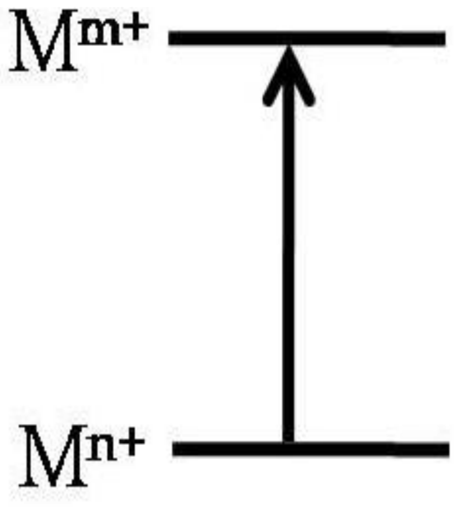
# METAL TO METAL CHARGE TRANSFER SPECTRA (MMCT)

**MMCT:**

‘Intravalence’ charge transfer take place in compounds containing a metal in two different oxidation states.

**Example 1.** Turn blue color of $KFe^{II}[Fe^{III}(CN)_6]$.





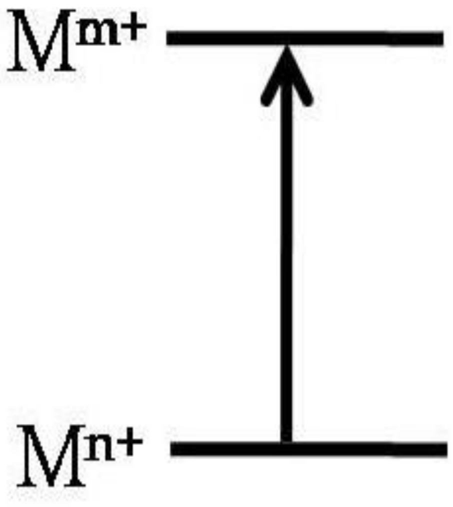
MMCT

$KFe^{III}[Fe^{II}(CN)_6]$ is prussian blue color because of MMCT.

# METAL TO METAL CHARGE TRANSFER SPECTRA (MMCT)

**MMCT:**

'Intravalence' charge transfer take place in compounds containing a metal in two different oxidation states.



MMCT

## Other examples

- If spinels are colored it mainly due to MMCT. Rust ($Fe_3O_4$) is reddish brown due to $Fe^{2+} \rightarrow Fe^{3+}$ MMCT.
- $Pb_3O_4$ (mixed oxide of $Pb^{2+}$ and $Pb^{4+}$) is colored due $Pb^{2+} \rightarrow Pb^{4+}$ MMCT.
- $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$.
- $[Pt^{IV}(NH_3)_2Br_2]$ $[Pt^{II}(NH_3)_2Br_4]$.

# LIGAND TO LIGAND CHARGE TRANSFER SPECTRA (LLCT)

## LLCT:

The metal complexes in which both oxidizing (π acceptor) and reducing (π donor) ligands are present, ligand to ligand charge transfer takes place there.

## Examples:

- Yellow color of $[Tl(bpy)I_2]$.
- $[Be(CO)_3X_3]$