CHARGE TRANSFER SPECTRA →

* d-d Spectra, f-f Spectra in terms of e^- transitions as
  ① Spin allowed as well as
  ② Laparte orbital forbidden
* C.T Spectra are, spin allowed as well as Laporte orbital allowed hance its intensity is quit high $\epsilon_{max} > 10,000$
* $KMnO_4$ Solution in H_2O show C.T. Spectra and produces very Intence Colour
* C.T transition occured very high energy.
* It is a type of Redox process. ie one species lost the e^- and other Species gain the e^- (Reduces)

types of C.T Spectra

(i) Ligand To Metal charge transfer (L→MCT)
(ii) Metal to Ligand charge transfer (M→LCT)
(iii) Intervalent charge transfer (MMCT)
(iv) Intraligand charge transfer (LLMT)

(1.) LMCT

* e^- density is transfer from Ligand based orbital to metal based orbital.

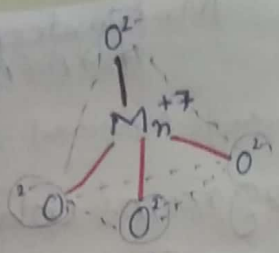
Conditions -
① → Ligand should be e^- rich Species.
eg O^{--}, halides
② → Metal should be in high positive oxidation state.

* Thus complexes if show the colour, than it is very Intance. If transition does not show colour than it may be in UV region.

Colour range = 14000 - 28000 cm^{-1} (visible region)

→ Eg
$KMnO_4$ - Purple
$K_2Cr_2O_7$ - Orange
K_2CrO_4 - Yellow
$Fe(S.CN)_3$ - Blood red
$FeCl_3$ - Brown (Dark)
CdS - Yellow
HgI_2 - Red
BiI_2 - Orange Red
PbI_2 - Yellow
HgS - Vermilion (सिंदूरी)
NaCl - White (U.V)

MnO_4^-



$Mn = 3d^5\ 4s^2$

$Mn^{+7} = 3d^0$ $\quad d \rightarrow d$ (Transition) (not allowed)

* Charge transition take place (Pink colour)
* The following four Transition May take Place
  - ✓ 17,700 cm^{-1} (visible Region)
  - 29,500 cm^{-1}
  - 30 300 cm^{-1}
  - 44400 cm^{-1} (U.V)

$L(\sigma) \rightarrow M$

$L(\pi) \rightarrow M$

oxid^n state of Mn

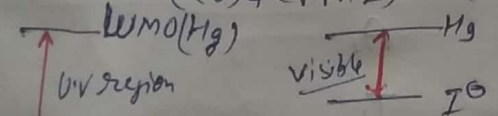
(2) MLCT

* the e$^-$ density transfer from metal based orbital to ligand based orbital.
* Metal should be zero or low positive or low negative oxid^n state
* Metal should be e$^-$ rich.
* Ligand should be good e$^-$ acceptor (π acceptor)
  (i) Ligand must have π^* orbital such as CN, NO, CO etc
  (ii) Vacant d-orbital eg- P, Ph_3P, PR_3, S, As, Se, PF_3, $P(OPh)_3$, $P(OMe)_3$ etc.
* Aromatic or heteroaromatic system show C.T. spectra
* MLCT occurs in Metal Carbonyl.

eg- ① $V(CO)_6$ dark green

② $Cr(CO)_6$ — white Solid
$Mo(CO)_6$
$Mo(CO)_5(Ph_3P)$ light yellow
$Mo(CO)_4(PPh_3)$
$Mo(CO)_4(PPh_2)$ (Maroon)

$HgCl_2$ — white
HgI_2 — Red
$Fe_2(CO)_9$ — Red orange
$Fe_3(CO)_{12}$ — Dark green



* Due to difference in the energy level gap b/w LUMO (Hg) and HOMO (halide), the transition occurs in diffrent range hance in case of HgI_2 transition occurs in visible range hance showing the red colour. while $HgCl_2$, show No colour (U.V region)

3. M-MCT

If transfer of charge or e$^-$ take place from metal to metal-le Metal base orbital → Metal based orbital C.T. occur (H.W)

4. LLCT

I_2 Vapour Colour - arise due to $\pi^* \rightarrow \sigma^*$

* This transition occurs purple colour (LLCT)
* The MMCT and LLCT occurs in very rare complexes