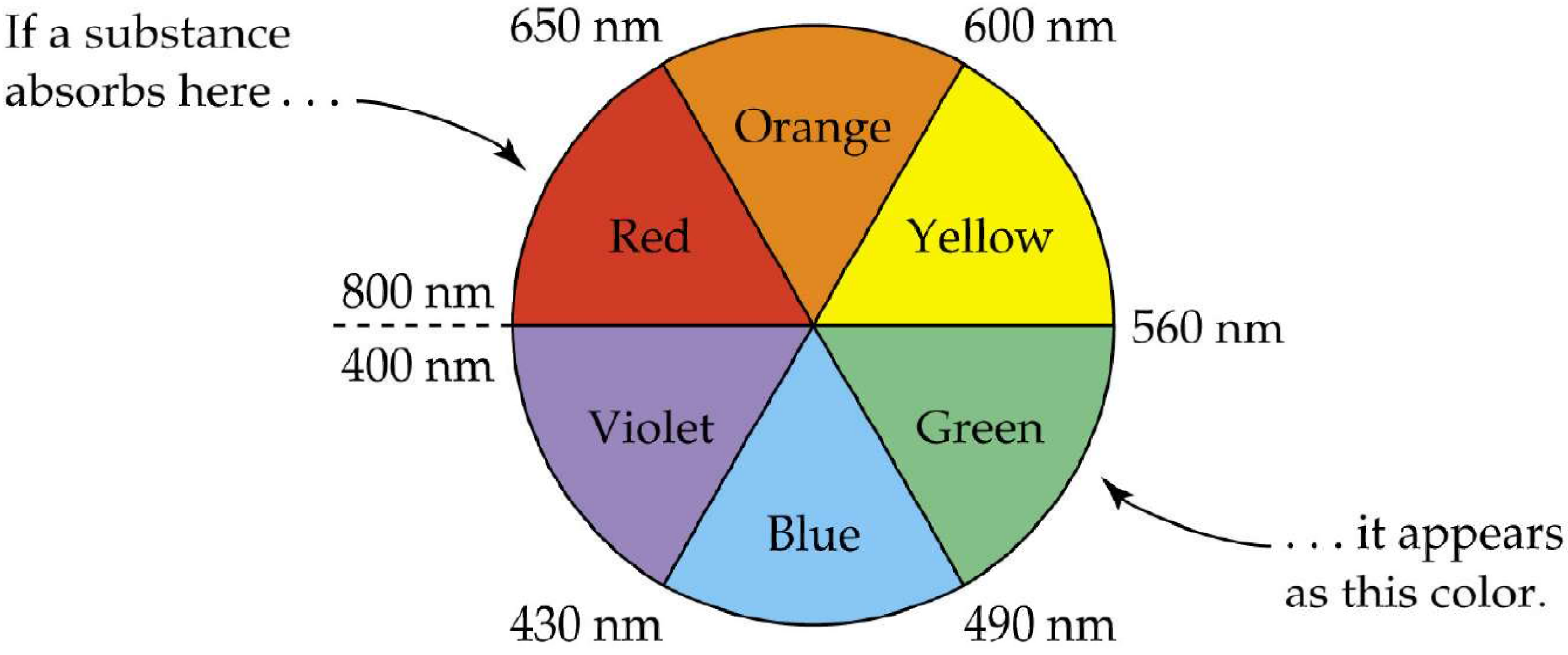
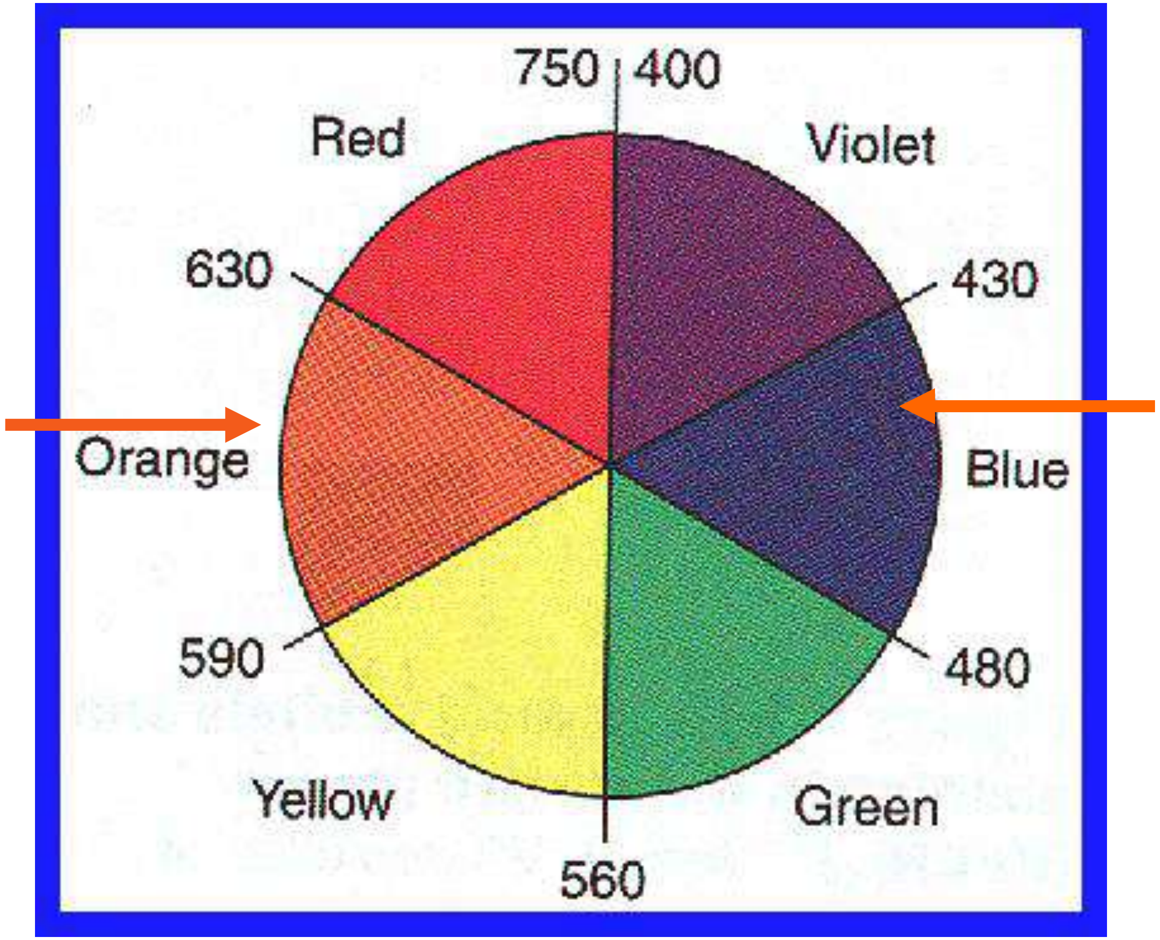
The artist's wheel

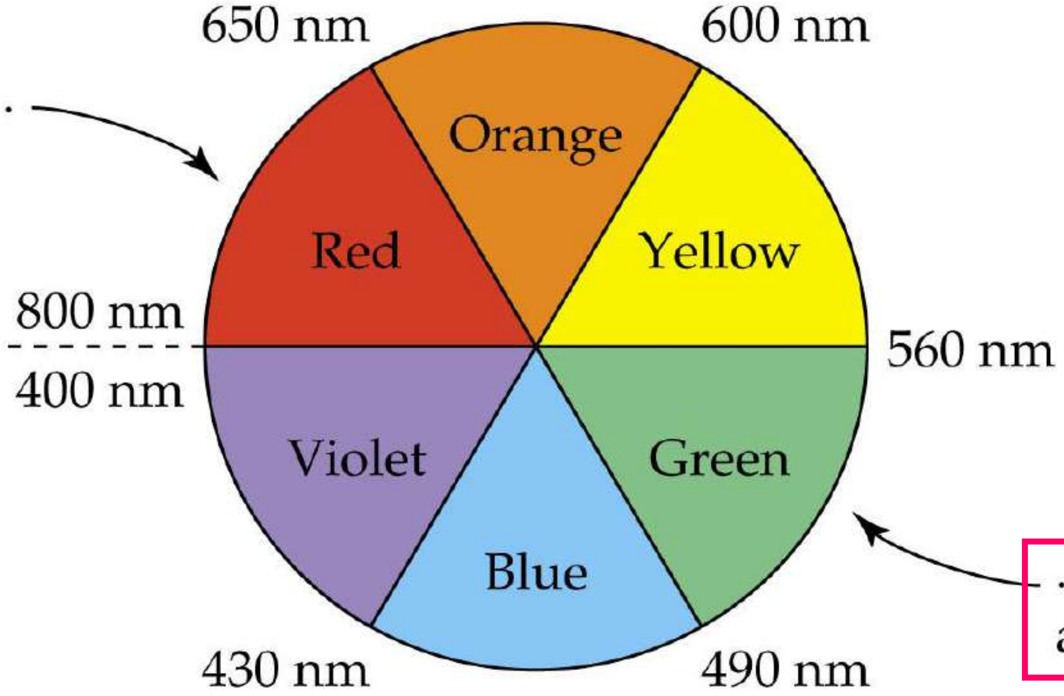




absorbed color

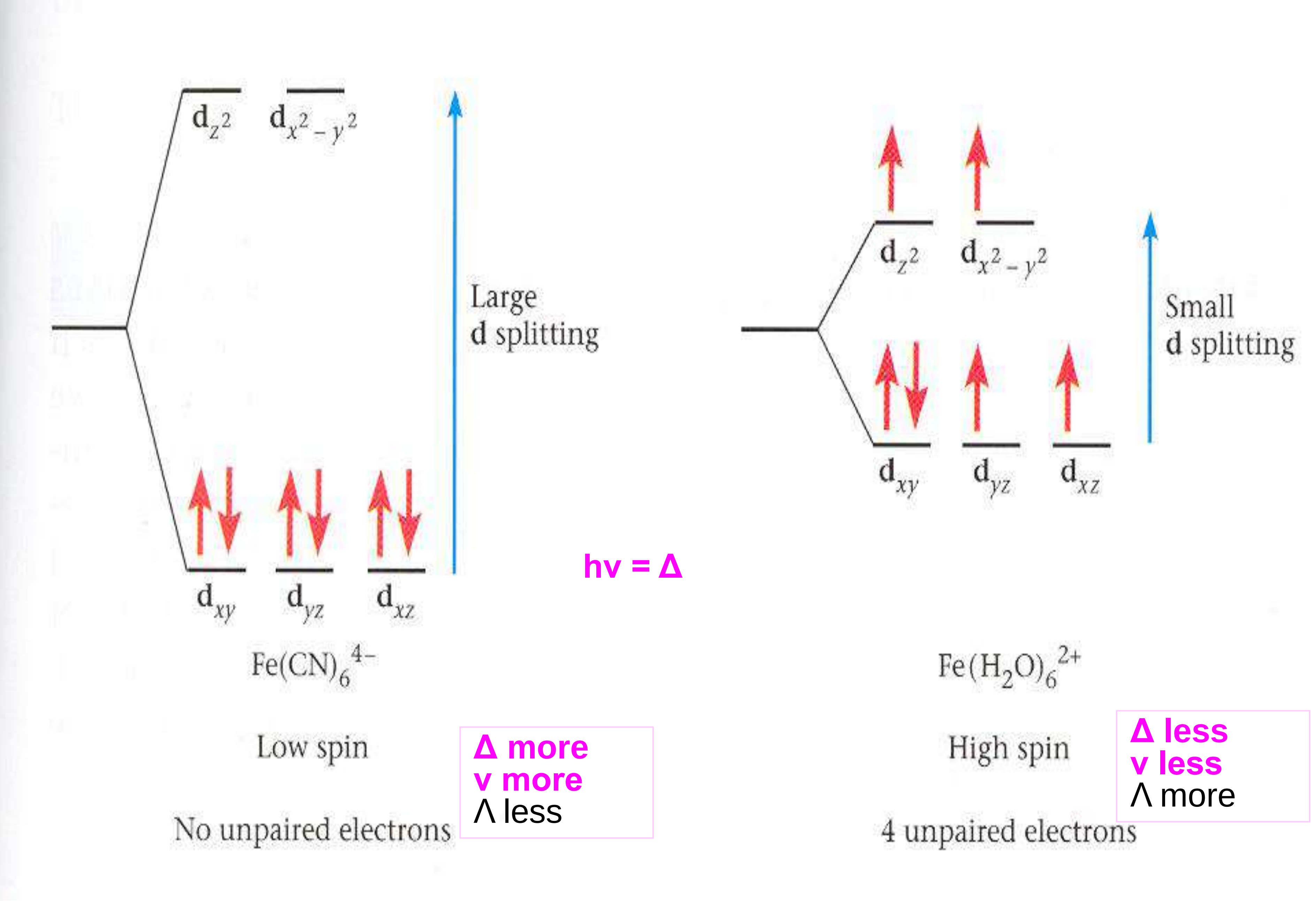
observed color

If a substance absorbs here . . .



. . . it appears as this color.

The larger the crystal-field splitiing （Δ）, the higher will be the frequency of light absorbed most strongly （ν）, and the shorter its wavelength （λ）.

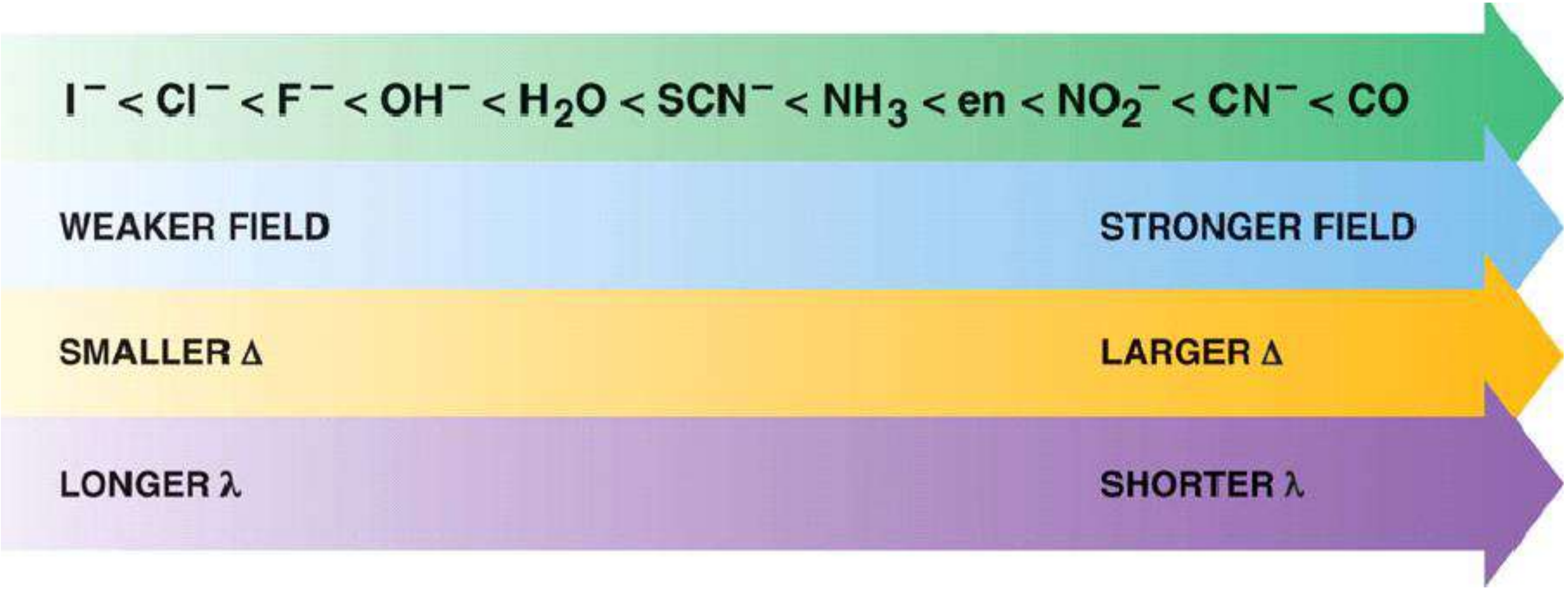


$h\nu = \Delta$

Δ more
ν more
Λ less

Δ less
ν less
Λ more

Spectrochemical Series

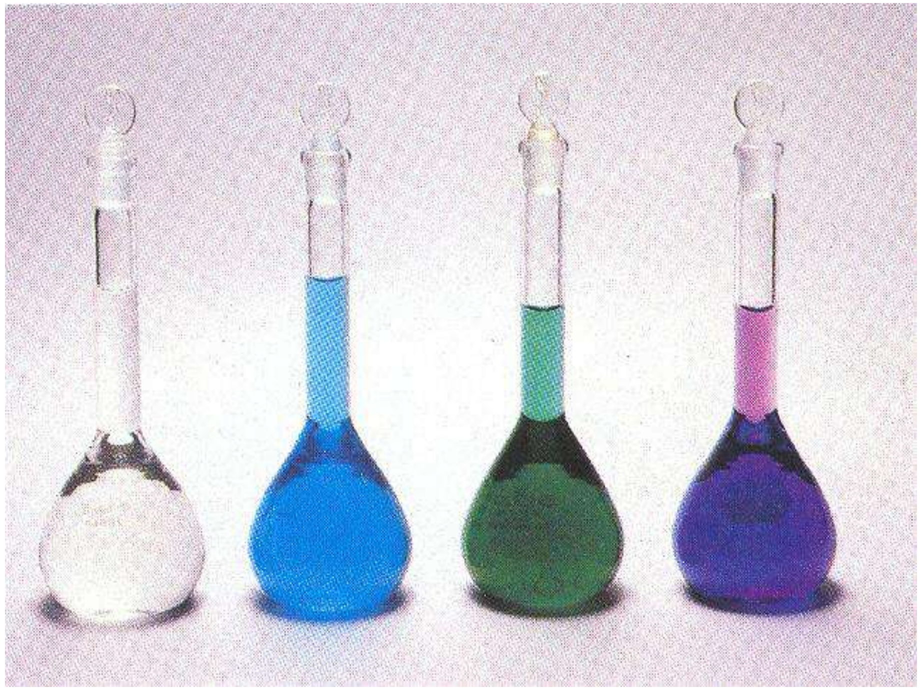


$I^- < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < en < NO_2^- < CN^- < CO$

WEAKER FIELD — STRONGER FIELD

SMALLER Δ — LARGER Δ

LONGER λ — SHORTER λ



- On the other hand, coordination compounds of transition metals with weak-field ligands are blue-green, blue, or indigo since they absorb lower-energy yellow, orange, or red light.

- As we have noted earlier, strong-field ligands cause a large split in the energies of the d orbitals of the central metal atom.
- Transition metal coordination compounds with these ligands are yellow, orange, or red since they absorb higher-energy violet or blue light.

$[Co(NH_3)_5Cl]^{2+}$ → Purple compound

absorbs yellow green region

(wavelength of 530 nm)

$[Co(NH_3)_6]^{3+}$ orange compound

absorbs → violet region

(wavelength of 410nm)

d^{10} (Zn^{2+}, Ag^{+} complexes) is colorless

C. K. Jørgensen's *f* and *g* factors

Δ_o = f (ligand) · g (metal)
Δ_o in 1000 cm^{-1} (Kkiesers)

g factors	*f* factors
$3d^5$ Mn(II) 8.0	Br^- 0.72
$3d^8$ Ni (II) 8.7	$\underline{S}CN^-$ 0.73
$3d^7$ Co(II) 9.0	Cl^- 0.78
$3d^3$ V(II) 12.0	N_3^- 0.83
$3d^5$ Fe(III) 14.0	F^- 0.90
$3d^3$ Cr(III) 17.4	oxalate^{2-} 0.99
$3d^6$ Co(III) 18.2	H_2O 1.00
$3d^9$ Cu(II) 9.5	$\underline{N}CS^-$ 1.02
$3d^4$ Cr(II) 9.5	$CH_3C\underline{N}$ 1.22
$4d^6$ Ru(II) 20.0	pyridine 1.23
$3d^3$ Mn(IV) 23.0	NH_3 1.25
$3d^3$ Mo(III) 24.6	en (ethylenediamine) 1.28
$4d^6$ Rh(III) 27.0	bipy (2,2'-bipyridine) 1.33
$4d^3$ Tc(IV) 30.0	Phen (1:10-phenanthroline) 1.34
$5d^6$ Ir(III) 32.0	$\underline{C}N^-$ 1.70
$5d^6$ Pt(IV) 36.0	

Charge-Transfer transition

- Charge-transfer band arise from the movement of electrons between orbitals that are predominantly ligand in character and orbitals that are predominantly metal in character.

- These transitions are identified by their high intensity and the sensitivity of their energies to solvent polarity.

- Absorption for charge transfer transition is more intense than d–d transitions. *($\mathcal{E}_{d\text{-}d}$ =20 L mol^{-1} cm^{-1} or less, $\mathcal{E}_{charge\text{-}transfer}$ =50,000 L mol^{-1} cm^{-1} or greater)*

Charge-Transfer transition

Charge-Transfer transition is classified into:

➢Ligand-to-Metal Charge-Transfer transition.

(LMCT transition)

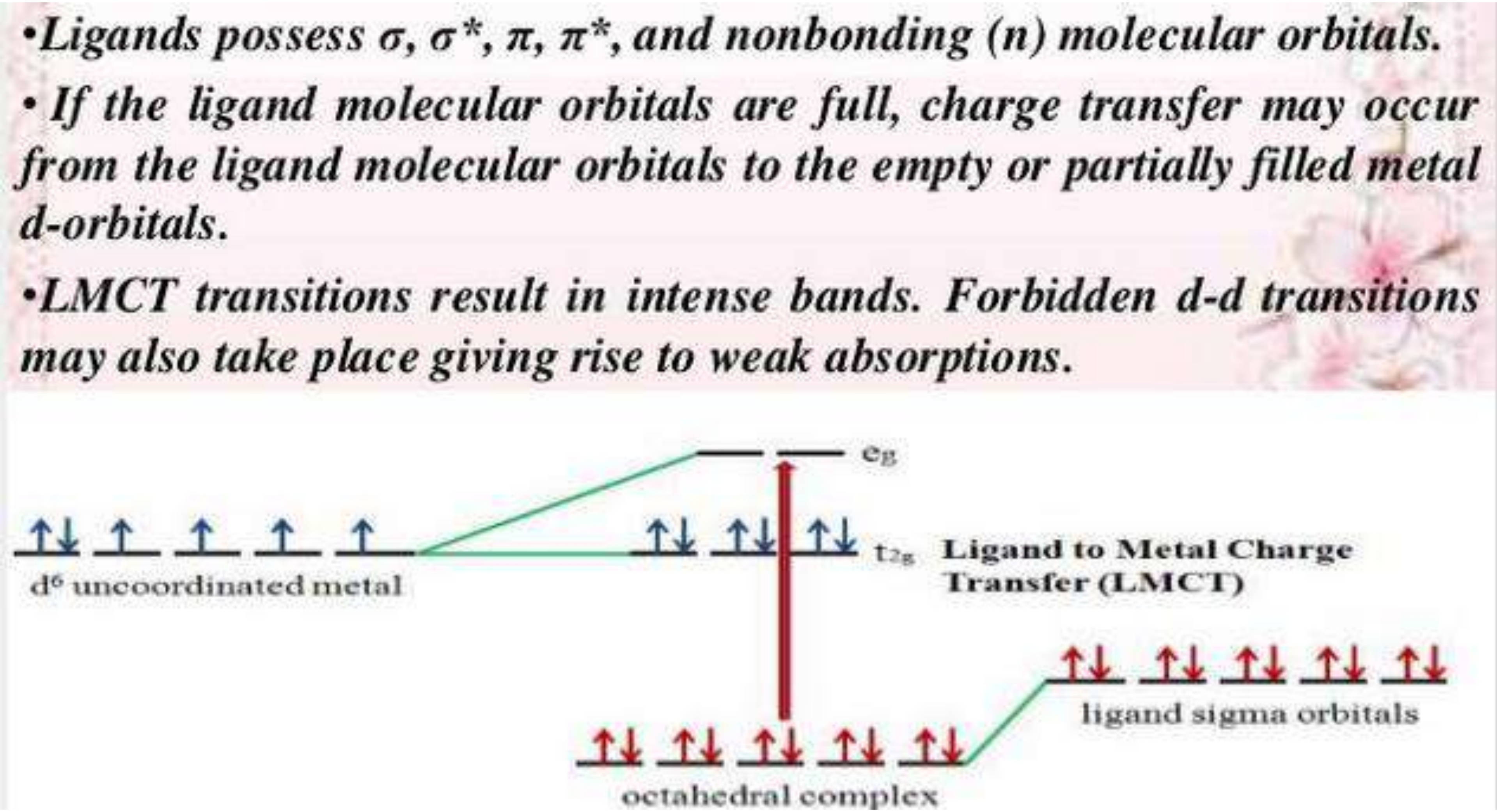
If the migration of the electron is from the ligand to the metal.

➢Metal-to-Ligand Charge-Transfer transition.

(MLCT transition)

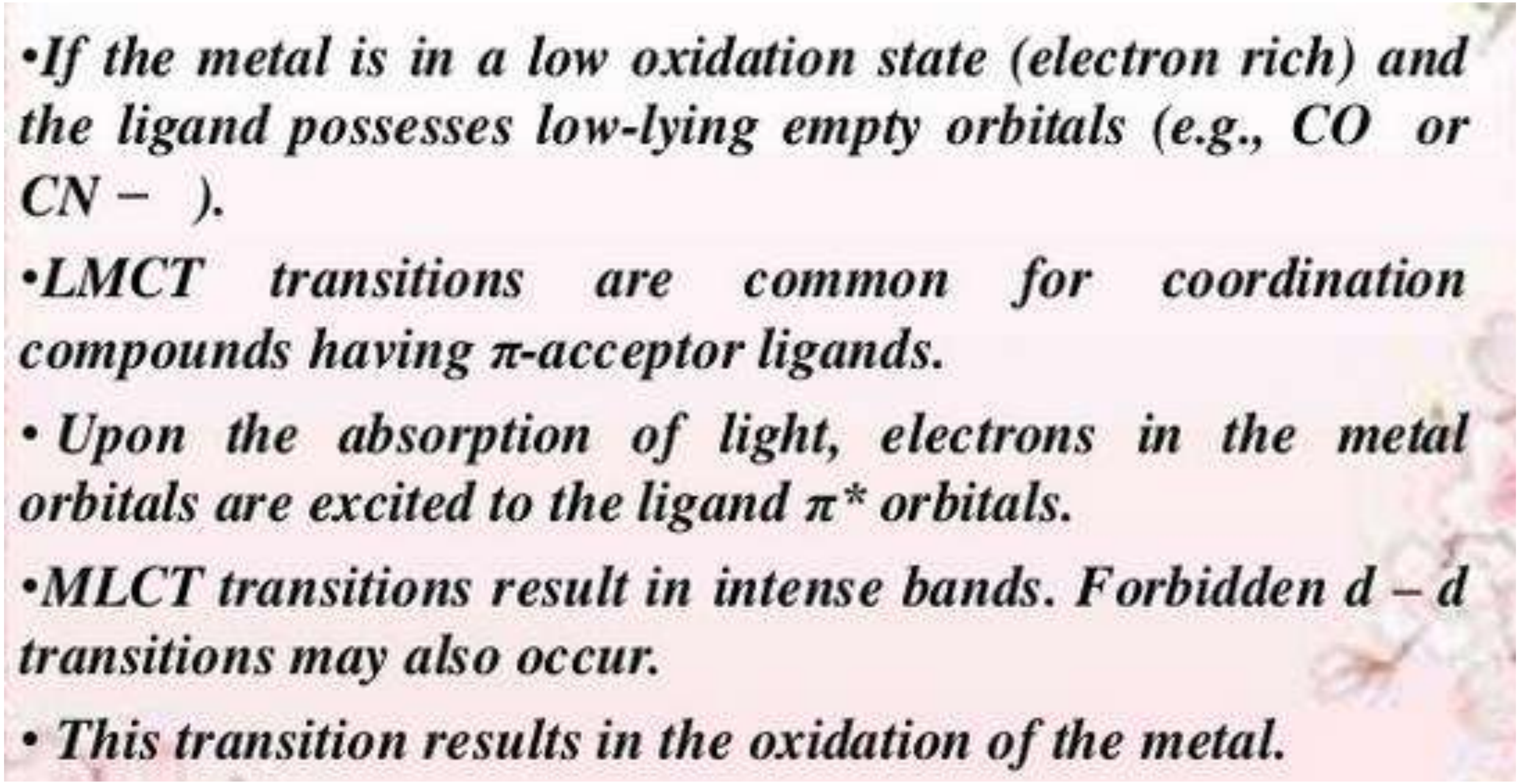
If the migration of the electron is from the metal to the ligand .

LMCT :

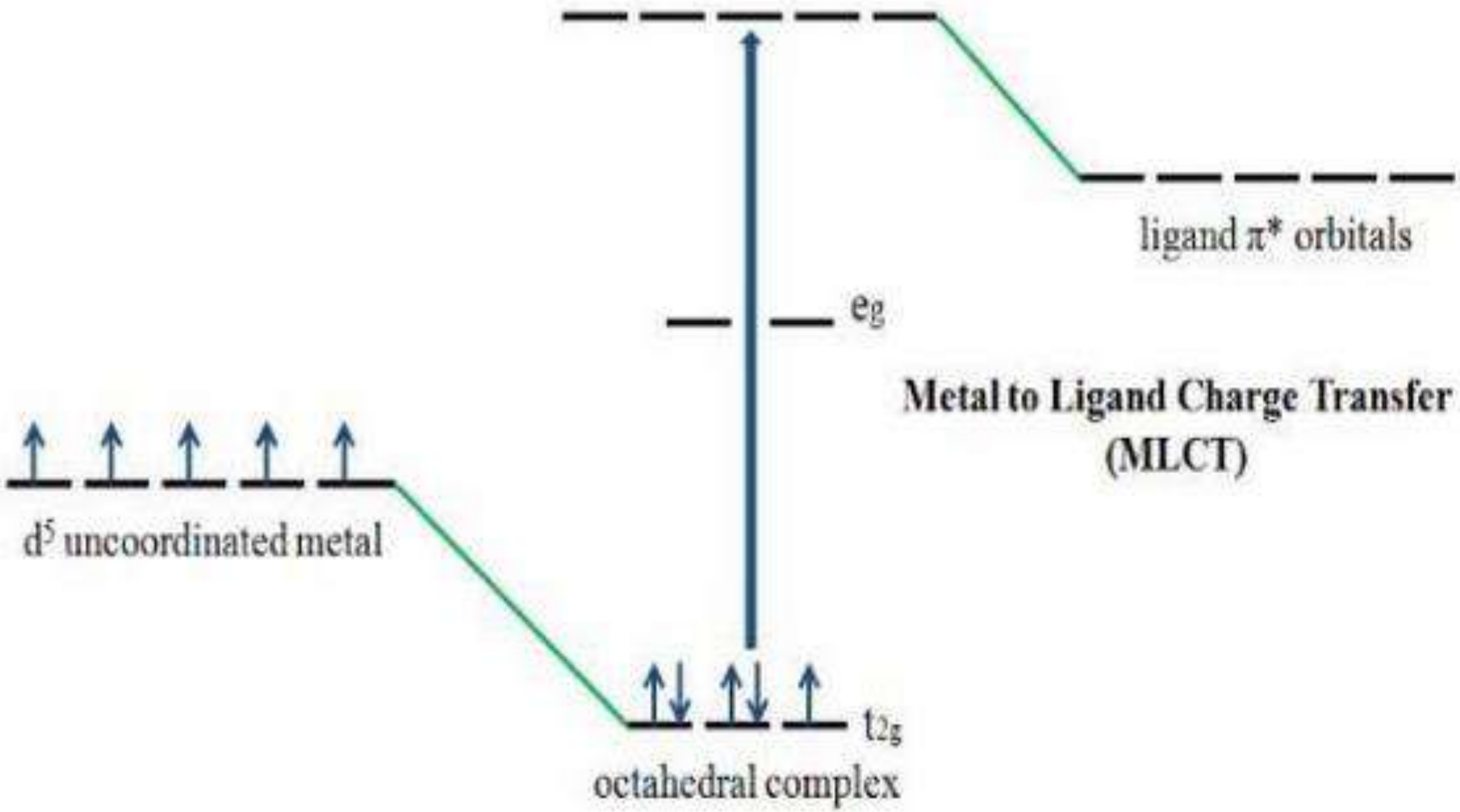


- *Ligands possess σ, σ*, π, π*, and nonbonding (n) molecular orbitals.*
- *If the ligand molecular orbitals are full, charge transfer may occur from the ligand molecular orbitals to the empty or partially filled metal d-orbitals.*
- *LMCT transitions result in intense bands. Forbidden d-d transitions may also take place giving rise to weak absorptions.*

MLCT :



- *If the metal is in a low oxidation state (electron rich) and the ligand possesses low-lying empty orbitals (e.g., CO or CN −).*
- *LMCT transitions are common for coordination compounds having π-acceptor ligands.*
- *Upon the absorption of light, electrons in the metal orbitals are excited to the ligand π* orbitals.*
- *MLCT transitions result in intense bands. Forbidden d – d transitions may also occur.*
- *This transition results in the oxidation of the metal.*



Metal to Ligand Charge Transfer (MLCT)

Charge-Transfer Absorptions

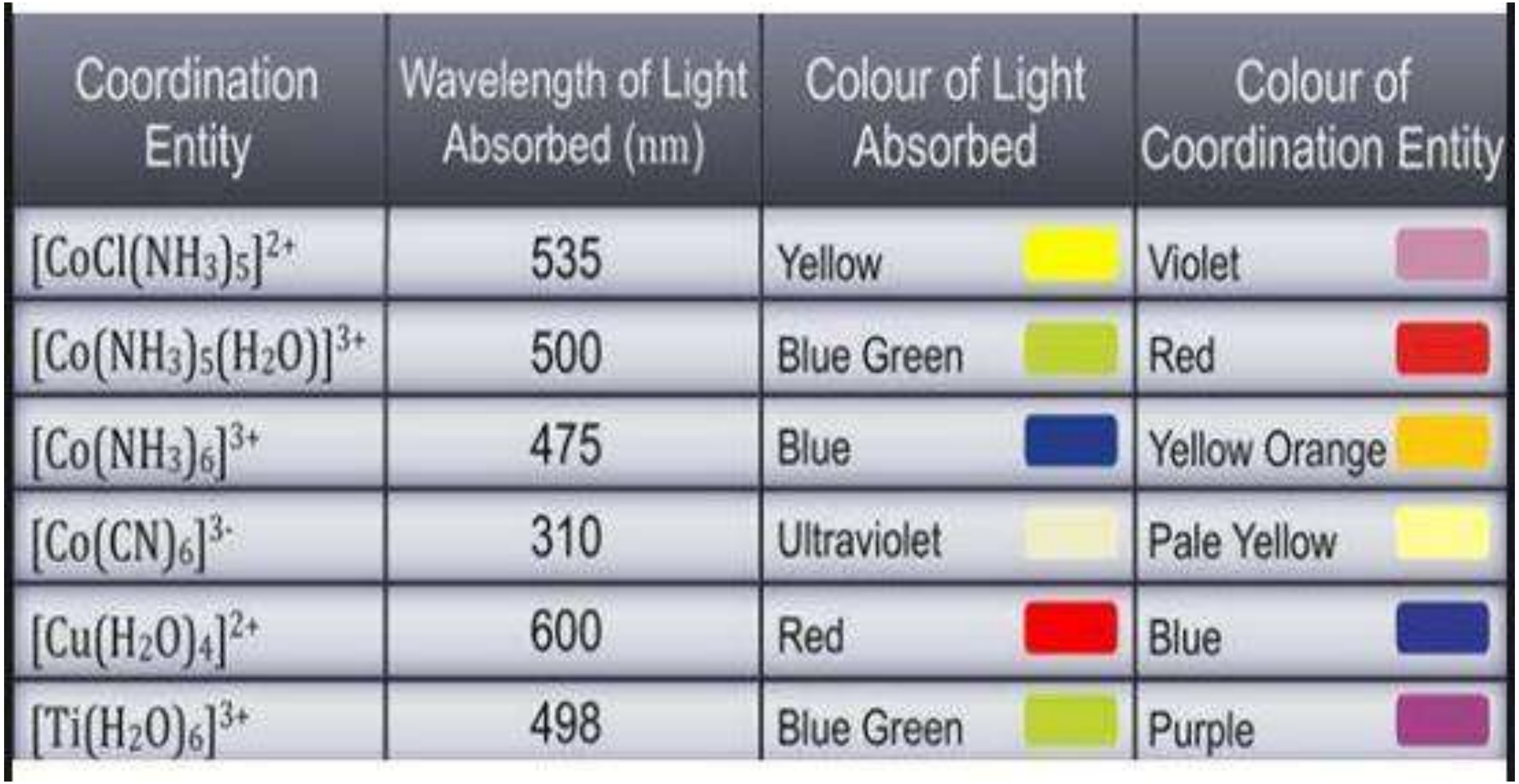
- ❖ Movement of electrons between metal and ligand.
- ❖ Often 1000 times stronger than d-d transition bands.

LMCT

- *e.g.* transfer of an electron from p-orbital on a choride (u symmetry) to a metal's d-orbital (g symmetry).
- Favourable when metal centre is in a high oxidation state.
- Common for π-donor ligands (F^-, O^{2-}, N^{3-}, OH^-)
- e.g. Colour of $KMnO_4$ (d^0 complex)

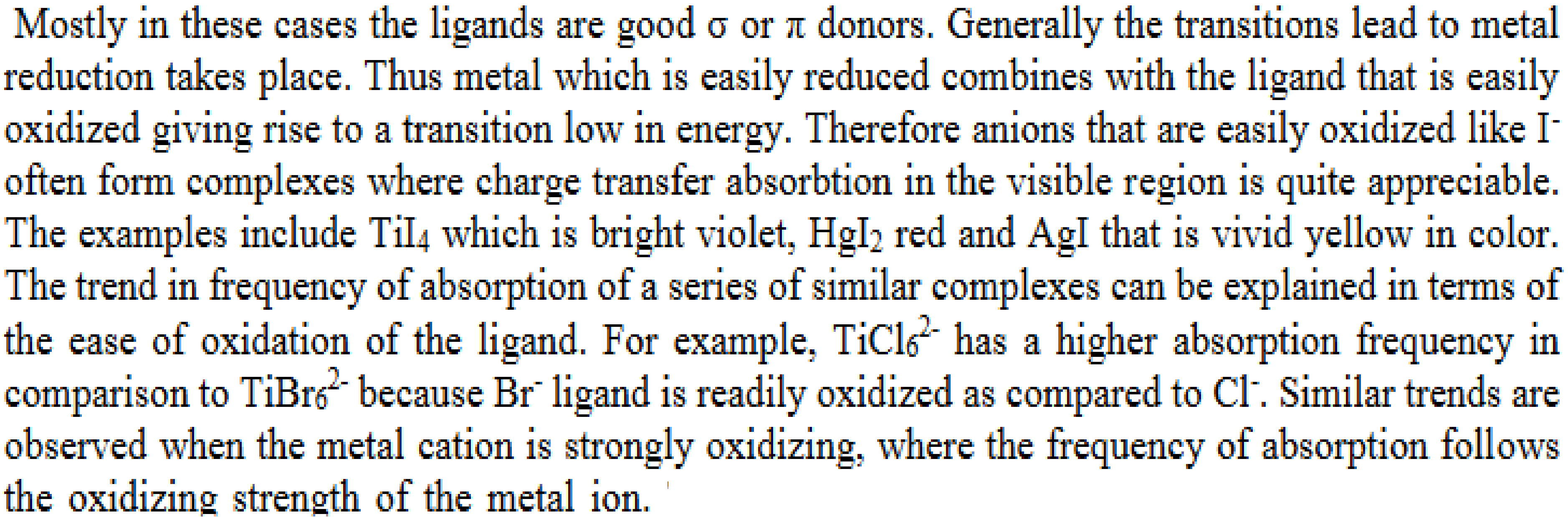
MLCT

- e.g. transferred of electron from metal's d-orbital to π^* orbital of CO ligand
- Favoured electron rich metal centres and those ligated by π-acceptors
- Often higher in energy (in the UV region)



Coordination Entity	Wavelength of Light Absorbed (nm)	Colour of Light Absorbed	Colour of Coordination Entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow 🟨	Violet 🟪
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green 🟩	Red 🟥
$[Co(NH_3)_6]^{3+}$	475	Blue 🟦	Yellow Orange 🟧
$[Co(CN)_6]^{3-}$	310	Ultraviolet ⬜	Pale Yellow 🟨
$[Cu(H_2O)_4]^{2+}$	600	Red 🟥	Blue 🟦
$[Ti(H_2O)_6]^{3+}$	498	Blue Green 🟩	Purple 🟪

LMCT :



Mostly in these cases the ligands are good σ or π donors. Generally the transitions lead to metal reduction takes place. Thus metal which is easily reduced combines with the ligand that is easily oxidized giving rise to a transition low in energy. Therefore anions that are easily oxidized like I^- often form complexes where charge transfer absorbtion in the visible region is quite appreciable. The examples include TiI_4 which is bright violet, HgI_2 red and AgI that is vivid yellow in color. The trend in frequency of absorption of a series of similar complexes can be explained in terms of the ease of oxidation of the ligand. For example, $TiCl_6^{2-}$ has a higher absorption frequency in comparison to $TiBr_6^{2-}$ because Br^- ligand is readily oxidized as compared to Cl^-. Similar trends are observed when the metal cation is strongly oxidizing, where the frequency of absorption follows the oxidizing strength of the metal ion.

Probing 4d/5d :

Higher oxidation states of the metal ions are easy to be reduced than the lower ones

Comparison amongst 3d,4d and 5d indicated that, 3d are comparatively easy to be reduced than 4d/5d

3d		4d		5d	
MnO_4^-	<	TcO_4^-	<	ReO_4^-	M^{7+}
∧		∧		∧	
CrO_4^{2-}	<	MoO_4^{2-}	<	WO_4^{2-}	M^{6+}
∧		∧		∧	
VO_4^{3-}	<	NbO_4^{3-}	<	TaO_4^{3-}	M^{5+}

The charge transfer process is similar to the internal redox process because electron transfer takes place during this process from **metal to ligand** or **ligand to metal** within a complex/compound. **In heavier transition metal complexes the latter is generally observed**. Thus, it is possible to classify and rank the metal ions according to their oxidising power $Rh^{4+} > Ru^{4+} > Ru^{3+} > Pd^{2+} > Rh^{3+}$, etc. Greater the oxidising power of the metal ion and also greater the reducing power of the ligands, lower the energy at which the C.T. bands appear.

Among the oxo ions of 4d series elements, the decreasing order of energy of ligand to metal charge transfer is as follows: $NbO_4^{3-} > MoO_4^{2-} > TcO_4^{-}$

But, the energy of charge transfer increases for the similar ions of 5d-series elements. For the above ions, the energy difference between 2p-orbitals of oxide ion and 4d-orbitals of the metal ions is very large lying in UV region and hence these ions are colourless.

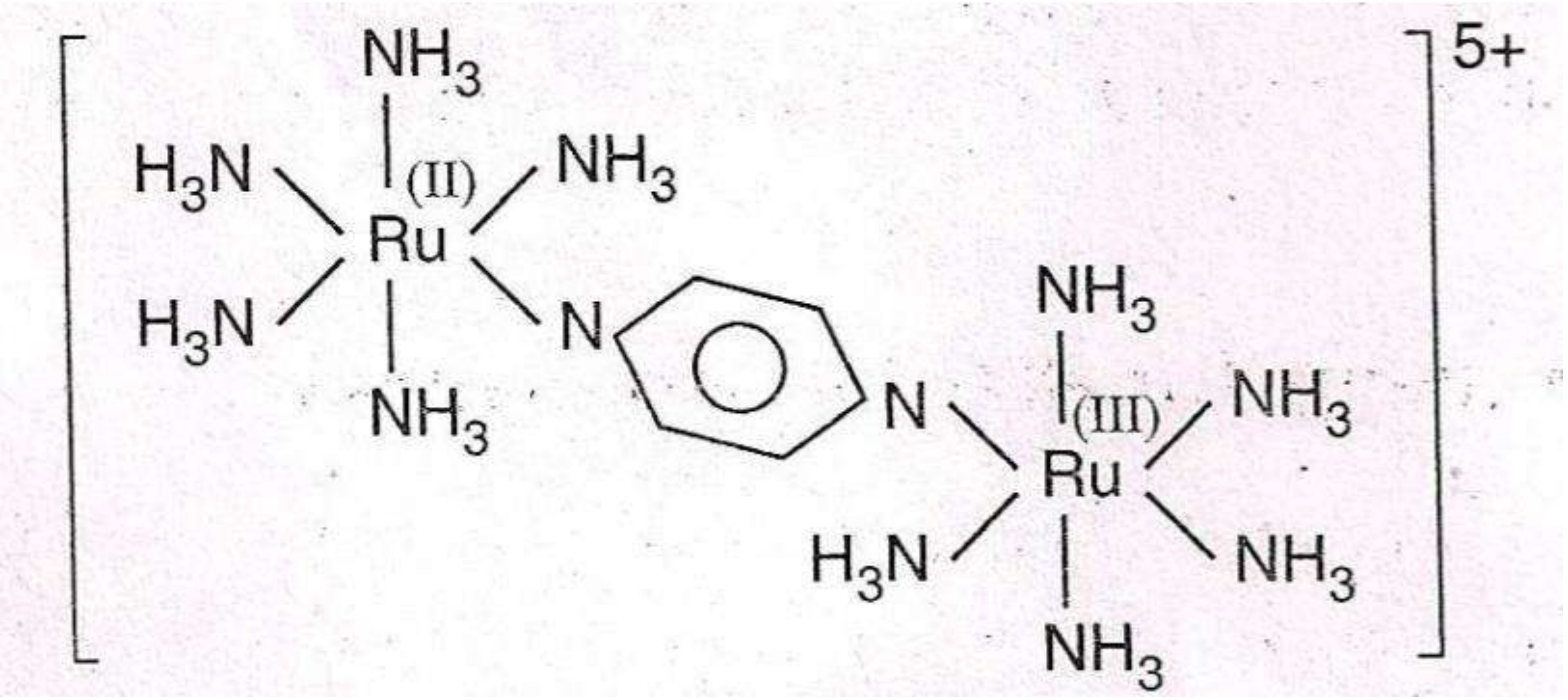
It has been observed that the d-d transitions (electronic spectra) of the compounds/complexes of third transition (5d-) series elements are less important than those of the complexes of first transition series elements because more energy is required for causing d-d transitions due to greater value of Δ, the crystal field splitting energy. In the octahedral ligand field the increasing Δ_0 is as follows: **$Ir^{3+} < Re^{4+} < Pt^{4+}$, etc**

For 5d-series, because of the larger magnitude of Δ (crystal field splitting energy), the d-d bands are found at lower wavelengths or higher frequency and hence, overlap with the charge transfer bands.

Thus, it is possible to classify and rank metal ions according to their oxidising power: **$Os^{4+} > Re^{4+} = Os^{3+} = Pt^{4+} > Pt^{2+} > Ir^{3+}$**

Greater the oxidising power of the metal ion and also greater the reducing power of the ligand, lower the energy at which the charge transfer (L→M) bands appear.

MMCT :



electronic transition occurs from Ru(II) to Ru(III) through Pyz-bridging ligand leading to intense coloured above complex

Similarly, $Mo_2Cl_8^{4-}$ is red coloured

Probing 4d/5d :

3d elements are readily reduced than 4d/5d congeners. This is due to larger intensity of 3d metal charge transfer bands than 4d/5d congeners.

Higher the OS of M ion, more is the tendency of M to get reduced and larger is the intensity of absorption of respective charge transfer band

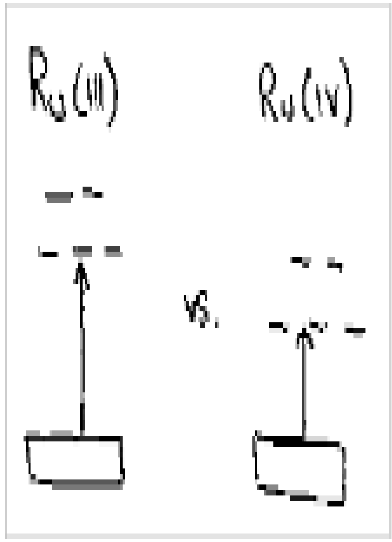
Probing 4d/5d :

Within any periodic group, Δ_o increases down a group (3d < 4d < 5d). This is due to the larger size of the 4d or 5d orbitals compared with the compact 3d orbitals and the consequent stronger interactions with the ligands.

With this, corresponding energy transition increases and λ decreases

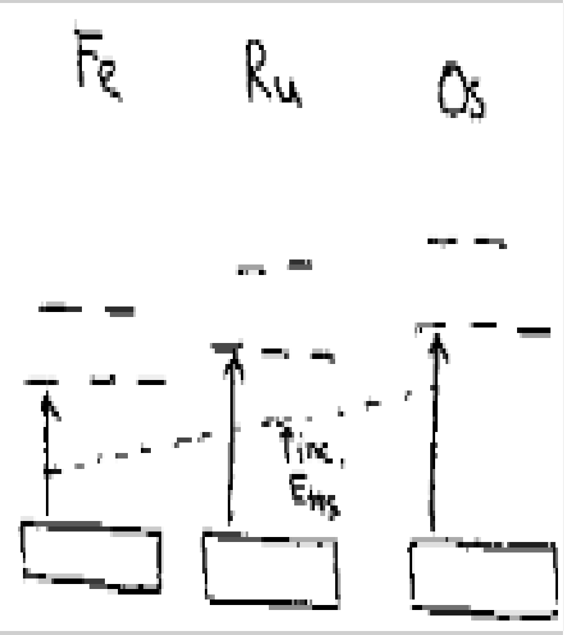
Probing 4d/5d :

Comparing metals with different oxidation states, for a higher oxidation state, the d-orbitals are lower in energy, since the increased charge of the nucleus stabilises them. Thus, the energy gap is reduced, and the Transition Energy is lower.



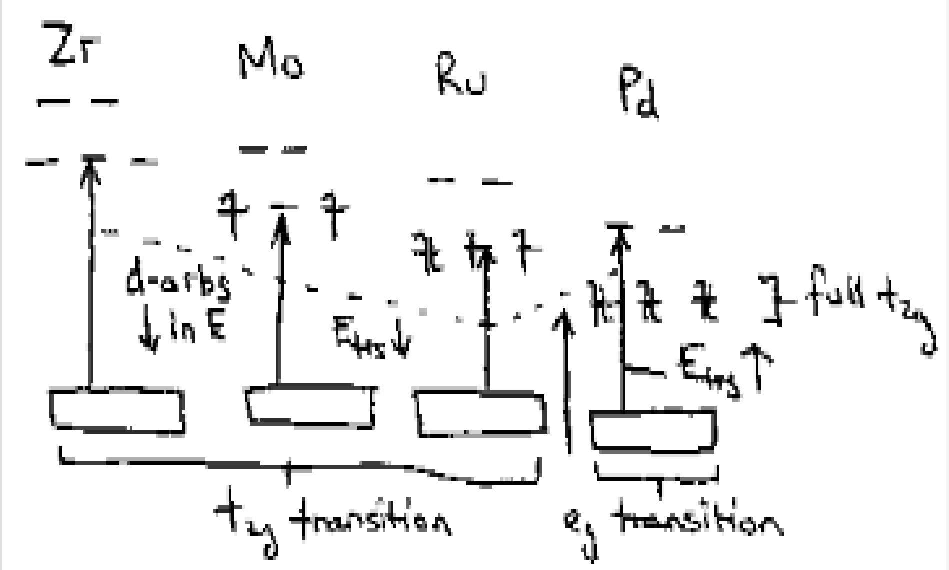
Probing 4d/5d :

Moving down a Group, 4d and 5d transition metals, the 4d and 5d orbitals are higher in energy and so the Transition Energy is increased.



Probing 4d/5d :

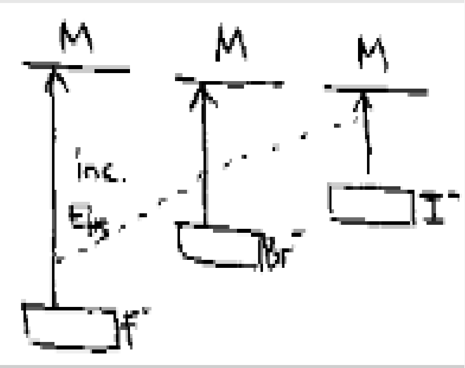
Moving across the Period, the d-orbitals decrease in energy, reducing the Transition Energy. However, d-electrons are increasingly populating these orbitals, and this can have important consequences. For example, the energy of transition for Pd is higher than for Ru because the electron has to enter an e_g orbital instead of t_{2g}, so the energy gap is larger.



Probing 4d/5d :

Variation with Ligands

Comparing Ligands, again orbital energy is the key to the transition energies. For example, down the halides, their non-bonding orbitals increase in energy, giving:



Thus, the Transition Energy will decrease for lower halides.

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