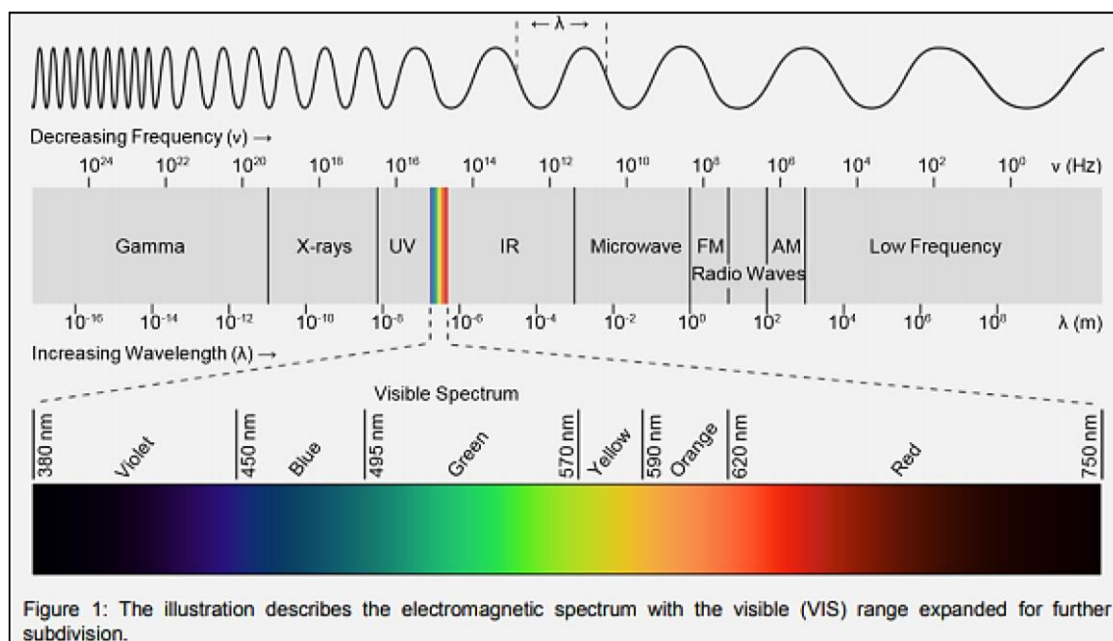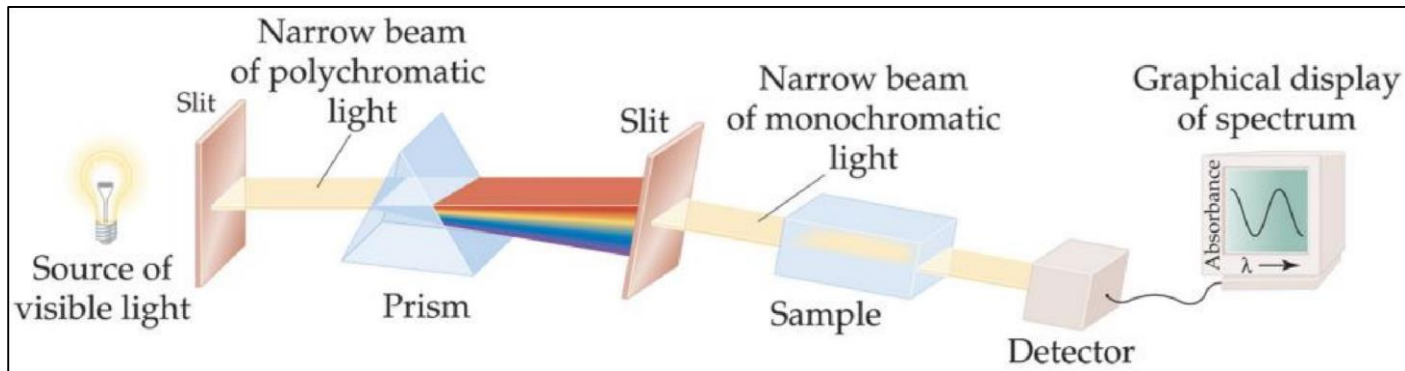# Electronic Spectra of Complexes

The ultra violet and visible spectra of coordination compounds of transition metals involve transitions between the *d* orbitals of metals. Therefore, we will need to look closely at the energies of these orbitals and at the possible ways in which electrons can be raised from lower to higher energy level.

Obviously, the colors produced are intimately related to the magnitude of the spacing between these levels. Since this spacing depends on factors such as the geometry of the complex, the nature of the ligands present, and the oxidation state of the central metal atom, electronic spectra of complexes can provide valuable information related to bonding and structure.

Electronic Spectroscopy

This is also known as UV-Vis spectroscopy and covers the region from 200 to 800 nm of the electromagnetic spectrum. The region from 200 to 400 nm is called ultraviolet (UV) and that from 400 to 800 nm is known as the visible region. A substance appeared colored when the emitted light falls in this visible region. This spectroscopy is used to find out the geometry of complexes because the number of bands seen in the visible region due to *d-d* transitions depends on the geometry of the complex.

Figure 1: The illustration describes the electromagnetic spectrum with the visible (VIS) range expanded for further subdivision.

The spectrophotometer

The absorbance or the optical density of a molecule absorbing in ultraviolet or visible region depends on the molecular structure and its concentration is given by the Beer-lambert relationship:

$$\log \frac{I_o}{I} = A = \varepsilon l c$$

where

A = absorbance

ε = molar absorptivity (L mol^{-1} cm^{-1}) (also known as molar extinction coefficient)

l = path length through solution (cm)

c = concentration of absorbing species (mol L^{-1})

Spectrophotometers commonly obtain spectra as plots of absorbance versus wavelength, this spectrum is a consequence of transitions between states of different energies and can provide valuable information about those states and in turn, about the structure and bonding of molecule or ion.

Although the quantity most commonly used to describe absorbed light is the wavelength, energy and frequency are also used. In addition, the wavenumber (the number of waves per centimeter), a quantity proportional to the energy, is frequently used.

$$E = h\nu = \frac{hc}{\lambda} = hc\left(\frac{1}{\lambda}\right) = hc\bar{\nu}$$

where

E = energy

h = Planck's constant = 6.626×10^{-34} J s

c = speed of light = 2.998×10^{8} m s^{-1}

ν = frequency (s^{-1})

λ = wavelength (often reported in nm)

$\frac{1}{\lambda} = \bar{\nu}$ = wavenumber (cm^{-1})

Absorption of Light

In explaining the colors of coordination compounds, we are dealing with the phenomenon of complementary colors: if a compound absorbs light of one color, we see the complement of that color. For example, when white light (containing a broad spectrum of all visible wavelength) passes through a substance that absorbs red light the color observed is green. Green is the complement of red, so green predominates visually when red light is subtracted from white. Complementary colors can conveniently be remembered as the color pairs on opposite sides of the color wheel.
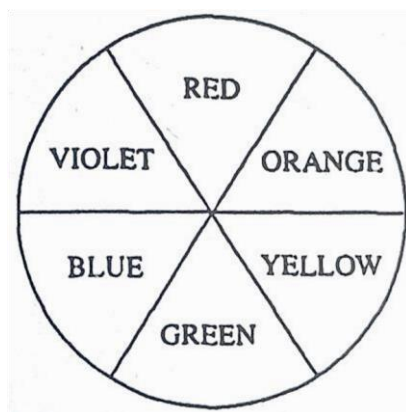
The color wheel

Visible Light and Complementary Colors

Wavelength Range (nm)	Wave Numbers (cm^{-1})	Color	Complementary Color
<400	>25,000	Ultraviolet	
400–450	22,000–25,000	Violet	Yellow
450–490	20,000–22,000	Blue	Orange
490–550	18,000–20,000	Green	Red
550–580	17,000–18,000	Yellow	Violet
580–650	15,000–17,000	Orange	Blue
650–700	14,000–15,000	Red	Green
>700	<14,000	Infrared	

It is not always possible to make a simple prediction of color directly from the absorption spectrum, in large part because many coordination compounds contain two or more absorption bands of different energies and intensities. The net color observed is the color predominating after the various absorptions are removed from white light.

If the color of the aqueous solution is due to the transition of electrons from one d level to another d level, there should be only one color. But the fact that different colors are seen for different compounds shows that the d orbitals are at different energy levels and hence there is not only one transition but many.

In order to understand this, the splitting of d orbitals in different environment is to be understood.

For many coordination compounds, the electronic absorption spectrum provides a convenient method for determining the magnitude of the effect of ligands on the d orbitals of the metal. Although in principle we can study this effect for coordination compounds of many geometry, we will concentrate on the most common geometry, octahedral, and we will examine how the absorption spectrum can be used to determine the magnitude of the octahedral ligand field parameter Δ_0 for a variety of complexes.

Electronic Spectra of Complex Ions

Example (1) : **[Ti(H$_2$O)$_6$]$^{3+}$** ; its electronic spectrum is given in Figure below, which shows only one λ_{max}.

500 nm

Wavelength, λ
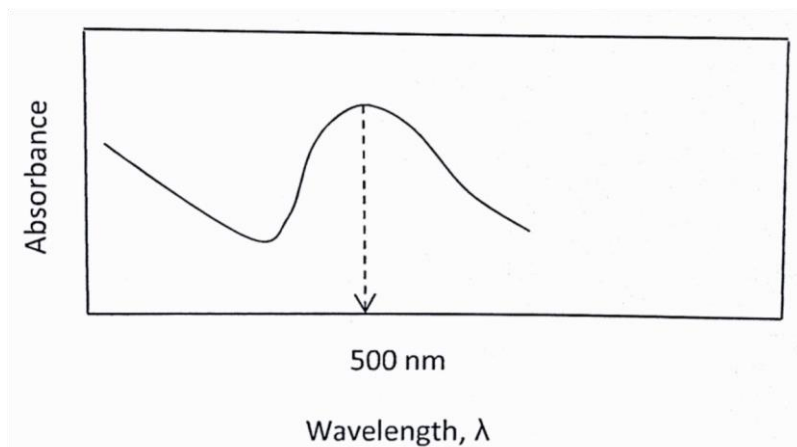
There is only one absorption near 500 nm, which indicates that there is only one transition taking place in this complex. It means that the *d* orbitals are spilt into only two levels.

**Note: To express the value of the crystal field splitting parameter (Δ) for this ion in cm^{-1} : we know that:

Wave number = 1/ Wavelength

= 1/ 500 nm

[1 nm = 10^{-7} cm]
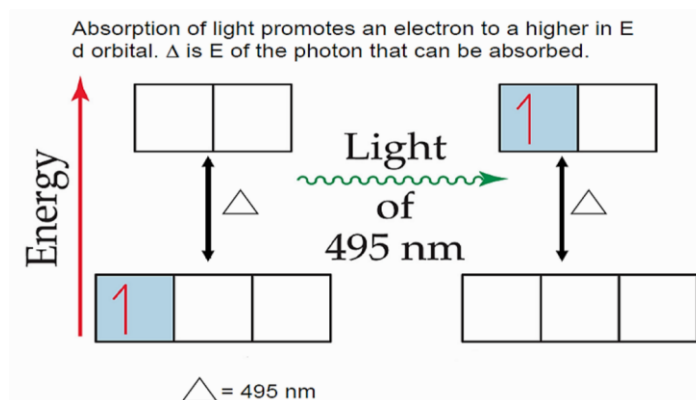
= 0.002 x 10^7 = 20000 cm^{-1}

**Note : To obtain the crystal field splitting energy (Δ) of this complex compound from its absorption spectrum:

The wave number of 20000 cm^{-1} is associated with energy which is equal to 239.23 KJ mol^{-1} as shown below:

We know that since   83.6 cm^{-1} = 1 KJ mol^{-1}

20000/ 83.6 KJ mol^{-1} = 239.23 KJ mol^{-1}

This energy is the energy difference between t$_{2g}$ and e$_g$ sets of orbitals (Figure below)

Absorption of light promotes an electron to a higher in E d orbital. Δ is E of the photon that can be absorbed.

**Note : The higher is the value of the frequency in cm^{-1} (wave number) of the peak of maximum absorption in the absorption spectrum of a given complex ion, greater is the magnitude of (Δ).

Example (2): **[Cr(en)₃]³⁺**, its electronic spectrum (Figure below) shows two λ_{max} indicating two transitions. This shows that *d*-orbitals are split into more than one energy level.
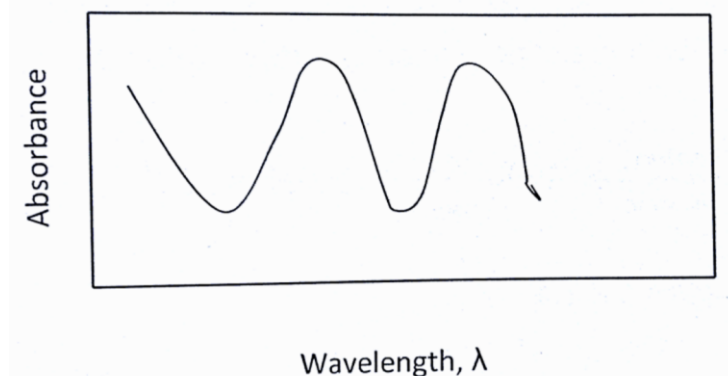
Example (3): **[CrF₆]³⁻**, the electronic spectrum of this complex (Figure below) Shows three absorptions indicating three transitions. This shows the splitting of *d* orbitals in a different way.

Wavelength, λ (nm)
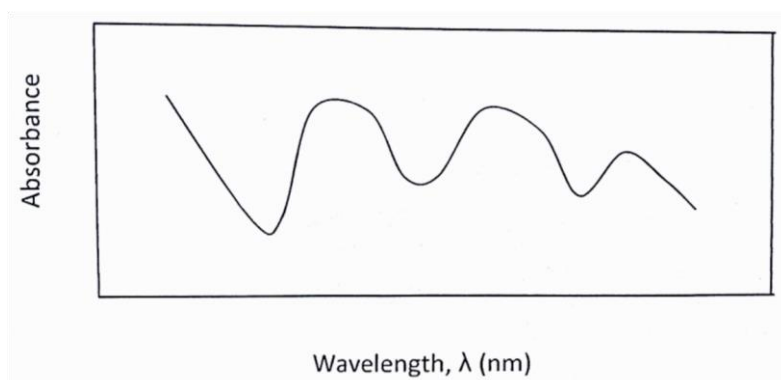
These examples show that the number of absorptions for the complexes varies even though two of them contain chromium and in the oxidation state +3. Moreover, they are octahedral complexes. Hence, the difference in the number of absorptions is due to the nature of the ligands. Similarly, it can be shown that the number of absorptions will also vary depending up on the geometry of the complex as well as the oxidation state.

Types of Electronic Spectra of Complexes

1) Ligand Spectra
2) Charge-transfer Spectra
3) *d-d* Spectra
4) Counter-ion Spectra

1) Ligand Spectra

Most of the organic ligand have absorption bands that usually appear in UV region, especially when these molecules contain π electron system.
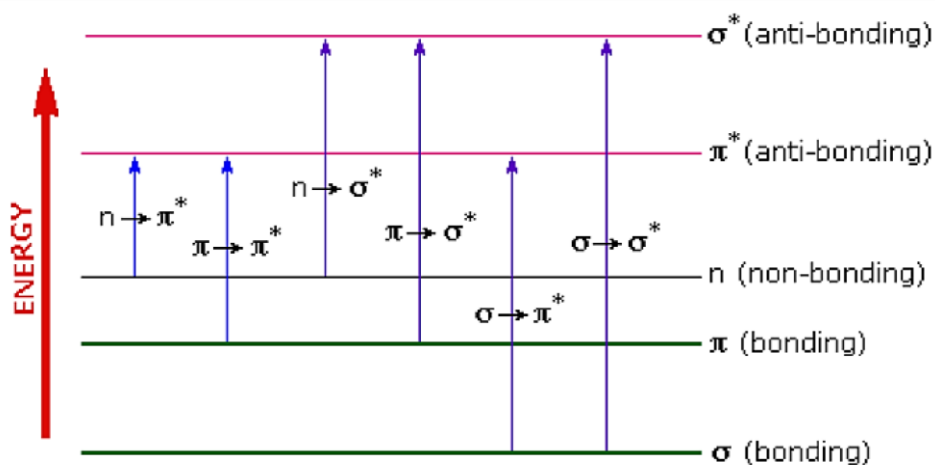
All the (UV-Vis) spectra of the organic ligands show two absorption peaks:

1- $\pi \rightarrow \pi^*$ these transitions found in the molecules that have double or triple bonds and without atoms having nonbonding electrons. Examples olefins and aromatic system; benzene and diene.

2- $n \rightarrow \pi^*$ These transitions found in the molecules that have a lone pair and a π bond. Examples R$-$C$=$O (keton) , R$-$CHO (aldehyde) , C $\equiv$ N and pyridine.

2) Charge-transfer Spectra

There are cases where the absorption bands in the visible or ultraviolet regions ranges between ε value of 1000 to 55,000 Lmol^{-1}cm^{-1}. For these cases such high value of absorption has been suggested due to charge transfer bands which are so much intense since they are allowed transitions that transmit exceptionally deep colors to the respective transition metal complex. Examples include $KMnO_4$, K_2CrO_4, $[Fe(bipy)_3]^{2+}$, $Cr(CO)_6$, $[Ir(Br)_6]^{2-}$, $[Ni(Cl)_4]^{2-}$, etc. In charge transfer transition either electron is donated from the low lying orbitals of the ligand to the metal or from orbitals of the metal to the ligand.
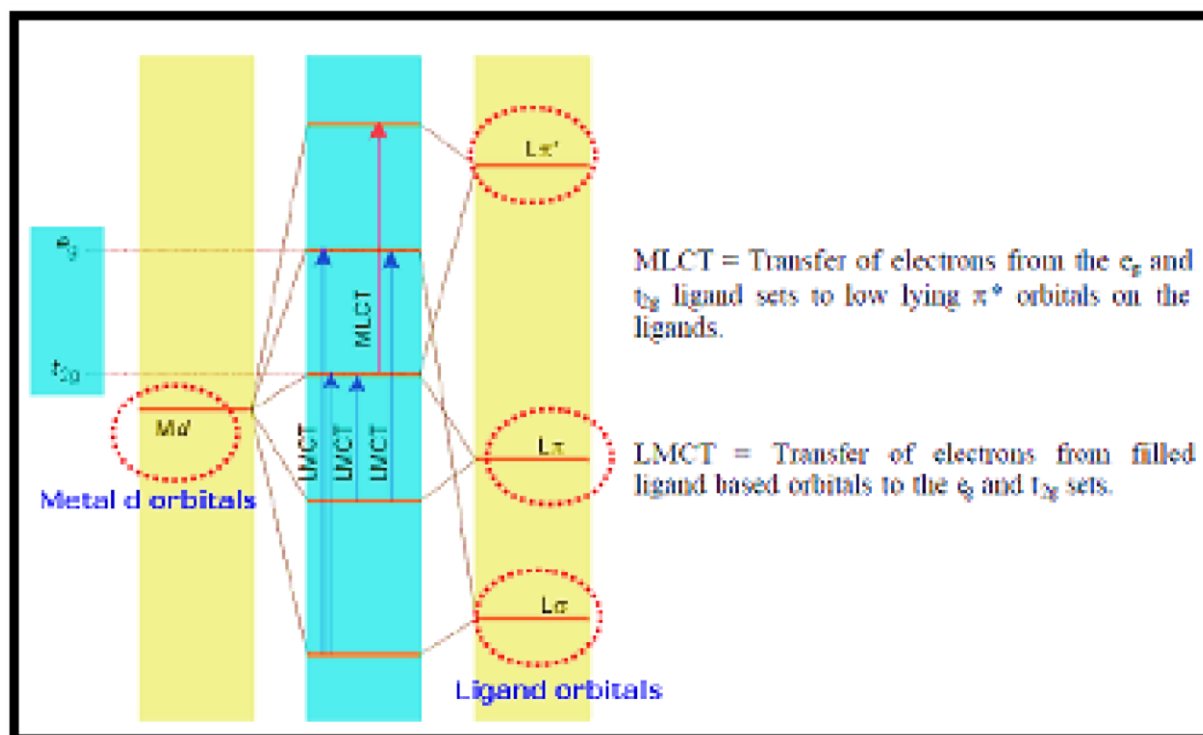
Origin of charge transfer bands

Types of Charge Transfer Spectra

There are chiefly three types of charge transfer spectrum
(a) Ligand to metal charge transfer spectrum (LMCT)
(b) Metal to ligand charge transfer spectrum (MLCT)
(c) Metal to metal charge transfer spectrum (MMCT)

a) Ligand to Metal Charge Transfer Spectrum (LMCT)

In these type of transitions, the transfer of electron occurs from the orbitals that are ligand based to the orbitals that are metal based. An example of these type of complexes includes $[Cr(NH_3)_6]^{3+}$, $[Cr(Cl)(NH_3)_5]^{2+}$. The LMCT charge transfer spectrum has been shown in Figure below.
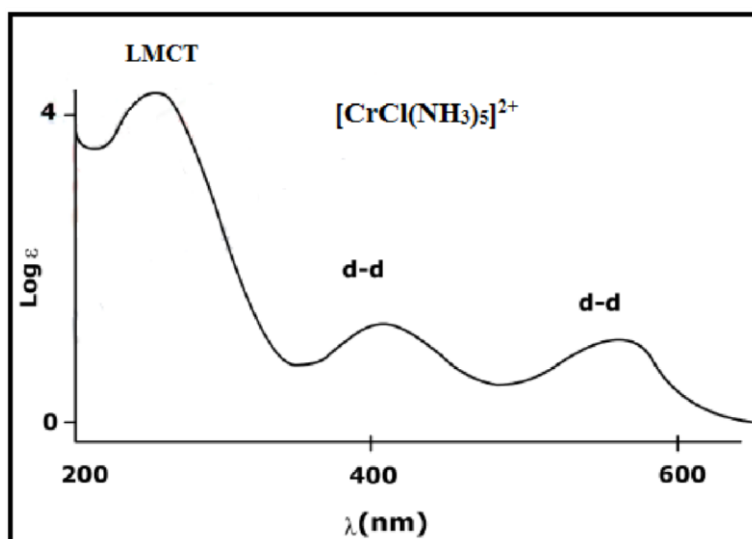
Mostly in these cases the ligands are good σ or π donors. Generally, the transitions lead to metal reduction takes place. Thus metal which is easily reduced combines with the ligand that is easily oxidized giving rise to a transition low in energy. Therefore, anions that are easily oxidized like I^- often form complexes where charge transfer absorption 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.

b) Metal to Ligand Charge Transfer Spectrum (MLCT)

In these type of transitions basically the metal orbitals are involved that can easily supply their electrons present in the low lying molecular orbital to the empty π^* orbitals of the ligand. Example of complexes showing these type of transitions is $[Fe(CO)_3(bipy)]$, $[Ru(bipy)_3]^{2+}$, $[W(CO)_4(phen)]$ etc. in all these cases the π^* empty orbital present on the ligand becomes the receptor of electrons with the introduction of light and the absorption process.

In the process of charge relocation, the metal is oxidized and the ligand is reduced, therefore for this type of charge transfer phenomenon, it is important that the metal oxidation as well as ligand reduction is quite feasible. Easily reducible ligands are those which have a low lying, vacant π^* orbital, such as pyridine, which then forms stable colored complexes with the metal ions that are easily oxidized such as Fe^{2+} and Cu

c) Metal to Metal Charge Transfer Spectrum (MMCT)

Some compounds possess metal ions in two different oxidation states. In these compounds, a charge transfer transition may occur when the electron moves from one metal ion to the other, with one metal ion acting as the reducing agent and the other acting as the oxidizing agent. Compounds of this nature are generally very intensely colored, such as Prussian Blue, $KFe^{III}[Fe^{II}(CN)_6]$.

3) *d-d* Spectra

In case of transition metal complexes with octahedral geometry the most important type of electronic transition taking place is the *d-d* transition where transition of an electron takes place from the lower t_{2g} level to the upper e_g level. Mostly it is the transition which imparts the color to the complex since it occurs in the visible or ultraviolet part of the spectrum. But the value of molar extinction coefficient, ε for these transitions is quite low since, these are Laporte forbidden transitions. Hence for *d-d* transitions, the value of molar extinction coefficient, ε ranges from 0.5 up to 20 $Lmol^{-1}cm^{-1}$.

4) Counter-ion Spectra

Counter ion is the ion (negative or positive) which bound to the complex ion to balance the charge.

There are many ions that have high intensity absorption bands in UV region (250-390 nm) like Oxyanions (NO_3^-, NO_2^-).

Most of ions do not have absorption peaks in UV region like SO_4^{2-}, Cl^- and ClO_4^- thus there is no interference with complex ion spectra, therefore these ions are preferred as counterions.

Example: Identify all the expected electronic transitions in UV-Visible for the following ions: 1- $[Cr(C_2O_4)_3]^{3-}$ 2- $[Ti(H_2O)_6]^{3+}$ **Solution:**

1- $[Cr(C_2O_4)_3]^{3-}$ Cr^{3+}
   $[_{18}Ar]\ 3d^3\ 4s^0$
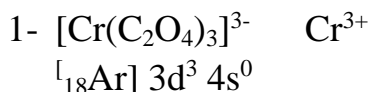
   a) Weak absorption bands in the visible region 400-800 nm attributed to *d-d* transitions of Cr^{3+} ion.

   b) Very intensity absorption bands of charge transfer in the region 300-380 nm are attributed to LMCT.

c) Absorption bands in the region 200-350 nm are assigned to the ligand spectra $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^{*.}$

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

$Ti^{3+} [_{18}Ar] 3d^1 4s^0$

a) There are no transitions of electrons in UV region.
b) Electronic absorption in the visible region 400-800 nm is attributed to *d-d* of Ti^{3+} ion.

Selection Rules for Electronic Transitions

The relative intensities of absorption are governed by a series of selection rules.

On the bases of the symmetry and spin multiplicity of ground and excited electronic states, two of these rules may be stated, these rules help us in finding out the possible transitions between the different energy levels.

Transitions taking place obeying the selection rules are called **allowed transitions** and those taking place without obeying the selection rules are called **forbidden transitions**.

Rule 1: Laporte Selection Rule

Transitions will be allowed only when there is a change in parity. That is, gerade $\rightarrow$ ungerade ($g \rightarrow u$) and vice versa ($u \rightarrow g$); $s \rightarrow p$, $p \rightarrow d$ transitions are allowed , but ($g \rightarrow g$) and ($u \rightarrow u$) ; $d \rightarrow d$, $p \rightarrow p$ are forbidden.

According to this selection rule $\Delta L = \pm 1$ for an allowed transitions.

In centrosymmetric molecules, that is, molecules with center of symmetry, the *d* orbitals have gerade symmetry (g symmetry) and hence, *d-d* transitions are forbidden (not allowed). In other words, if an octahedral complex has a center of symmetry, the *d-d* transitions in that complex are forbidden.

**Note: However, in complexes, *d-d* transitions are taking place in electronic spectra and they not only give important clues about the structure of the complex but also proof the theories of bonding in complexes.

d-p Mixing and the breakdown of Laporte selection rule

In tetrahedral complexes, there is no center of symmetry and hence, this selection rule is not applicable. Moreover, the MOs formed have the character of both *d* and *p* orbitals from which they are formed. This is called *d-p* mixing because the *p* orbitals have (u) character and the *d* orbitals have (g) character.

**Note: In a molecule which is noncentro symmetric (e.g. tetrahedral), p-d mixing can occur to a greater extent and so the probability of d-d transitions is greater than in a centro symmetric complex. This leads to tetrahedral complexes being more intensely colored than octahedral complexes.

Rule 2: Spin Selection Rule

According to this selection rule, $\Delta S = 0$ for an allowed transition (there is no change in the number of unpaired electrons before and after the transition). $\Delta S = S_1 - S_2 = (+1/2) - (+1/2) = 0$
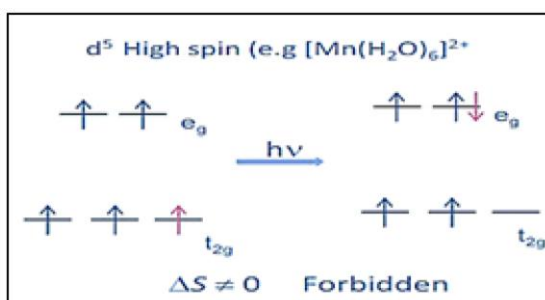
In other words, there should not be any change in the spin of the states and their multiplicities should be the same during the transition of electrons. That is, singlet-singlet and triplet-triplet transitions are allowed like $^3A_{2g} \rightarrow\ ^3T_{2g}$, while singlet-triplet and vice-versa transitions are not allowed like $^1A_{1g} \rightarrow\ ^3T_{1g}$.

Type of transition	Typical ε_{max} / $dm^3\ mol^{-1}\ cm^{-1}$	Example
Spin-forbidden 'd–d'	<1	$[Mn(H_2O)_6]^{2+}$ (high-spin d^5)
Laporte-forbidden, spin-allowed 'd–d'	1–10	Centrosymmetric complexes, e.g. $[Ti(H_2O)_6]^{3+}$ (d^1)
	10–1000	Non-centrosymmetric complexes, e.g. $[NiCl_4]^{2-}$
Charge transfer (fully allowed)	1000–50 000	$[MnO_4]^-$

Term Symbol

Absorptions result in the excitation from lower to higher states energy. Because these states are quantized, we observe absorption in bands. These bands can have determined from interactions or coupling of electrons in terms of their orbital angular momenta (their m_l value) and spin angular momenta (their m_s values). This is called Russell-Saunders coupling (LS coupling).

In a free atom (one in absence of a ligand field) these interactions produce atomic states called microstates which are the detailed electronic configuration of atom or ion.

Term is denoted by symbol, ^nL_j, where   n = (2S+1) and called the
spin multiplicity.

S is the total spin of the electrons.

L is the total orbital angular momentum.

L	0	1	2	3	4	5	6	7
Term	S	P	D	F	G	H	I	K

In the interpretation of spectra of coordination compounds, it is often important to identify the lowest-energy term.

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

Cr^{3+} $[_{18}Ar]$ $3d^3 4s^0$

$L = +2+1+0 = 3$; therefore, F term S
$= 3/2$

Spin multiplicity $=2S+1 = 4$

Therefore, the ground term is ^4F

The relationship between the number of unpaired electrons and multiplicity is shown in Table below:

No. of unpaired e	S	Multiplicity 2S+1	symbole
0	0	1	Singlet
1	1/2	2	Doublet
2	2/2	3	Triplet
3	3/2	4	Quartet
4	4/2	5	Quintet
5	5/2	6	Sextet

Absorption spectra of coordination compounds in most cases involve the *d* orbitals of the metal, and it is consequently important to know the free-ion terms for the possible *d* configurations. For reference, therefore, these are listed for the possible *d* electron configurations in following Table:

Free-Ion Terms for d^n Configurations

Configuration   Free-ion Terms

d^1	^2D					
d^2		$^1S\,^1D\,^1G$	$^3P\,^3F$			
d^3	^2D		$^4P\,^4F$	$^2P\,^2D\,^2F\,^2G\,^2H$		
d^4	^5D	$^1S\,^1D\,^1G$	$^3P\,^3F$	$^3P\,^3D\,^3F\,^3G\,^3H$	$^1S\,^1D\,^1F\,^1G\,^1I$	
d^5	^2D		$^4P\,^4F$	$^2P\,^2D\,^2F\,^2G\,^2H$	$^2S\,^2D\,^2F\,^2G\,^2I$ $^4D\,^4G$ ^6S	
d^6	Same as d^4					
d^7	Same as d^3					
d^8	Same as d^2					
d^9	Same as d^1					
d^{10}	^1S					

Arranging the terms in the increasing order of energy
Hund's rules

Rule 1: Maximum multiplicity will have minimum energy, when we have ^1S, ^1D and ^3P states, ^3P state should be the ground state.

Rule 2: If two states have the same multiplicity, then the one with higher L value will have lower energy.

Example: ^3P and ^3F

L = 1 for P and 3 for F. Hence $^3F < ^3P$

For d^2 configuration, these two rules allow us to order the terms according to increasing energy: $^3F < ^3P < ^1G < ^1D < ^1S$

We need a new way of writing electron configurations that allows us to not only describe the ground state, but any possible excited states as well.

We can do this by describing the electronic state according to its orbital and spin degeneracy.

Splitting of d^n Terms

Each of these free ion terms will be affected by the ligands in a complex and this will depend upon the geometry of the complex. As an example, d orbitals will be split into t_{2g} and e_g orbitals and in the same way, ^2D terms will also be split into $^2T_{2g}$ and ^2E_g terms in an octahedral complex. In the same way, other terms arising from the free ion terms will be transformed and split as follows in an octahedral field.

Splitting of Free-Ion Terms in Octahedral Symmetry

Term	Irreducible Representations
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

If the ligands cause large splitting between the terms, it is called strong field case. If they cause small splitting between the terms, it is called weak field case. In strong field case, electrons will try to pair whenever possible and in weak field case, the electrons will try to remain unpaired.

The ground state terms obtained from d^1 and d^2 configurations are split by octahedral field and the resulting energy diagrams are shown below:
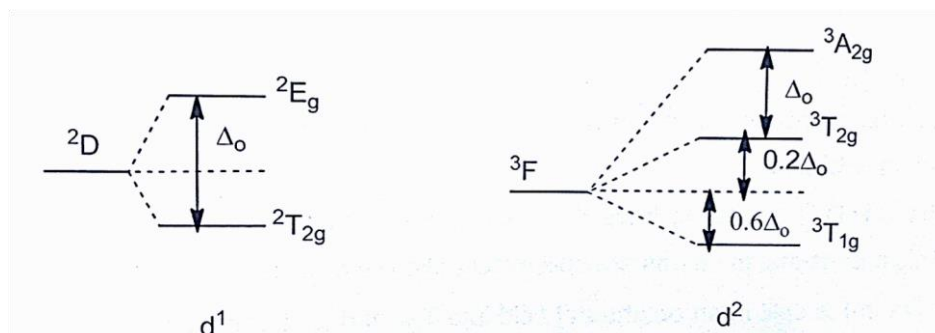
Spectra of Octahedral Complexes

Some important points shall be considered are that the electronic spectra of the complexes for the first transition series exhibit bands depending on the electron configuration (number of electrons of d orbital) as flow:

d^1, d^4, d^6, and d^9 complexes consist of one broad absorption. d^2, d^3, d^7, and d^8 complexes consist of three broad absorptions. d^5 complexes consist of a series of very weak, relatively sharp absorptions.

The d^1 electronic configuration gives rise to only one term, that of ^2D. On the other hand, d^9 configuration gives ^2D ground term. (the d^9 configuration of Cu^{2+} could be treated as an inverted d^1 configuration). Thus the spectrum of $[Ti(H_2O)_6]^{3+}$ shows a single peak corresponding to the $^2T_{2g} \rightarrow {}^2E_g$ transition.

In octahedral Cu(II) complexes we might expect a single absorption band in the visible region corresponding to $^2E_g \rightarrow {}^2T_{2g}$.

For a d^2 configuration gives ^3F ground term, the spectra show three absorption bands corresponding to the following transitions:

ν_1: $^3T_{1g}$ (F) $\rightarrow {}^3T_{2g}$(F) ν_2: $^3T_{1g}$(F) $\rightarrow {}^3T_{1g}$(P)

ν_3: $^3T_{1g}$(F) $\rightarrow {}^3A_{2g}$(F)

For a d^3 configuration the ground term is ^4F, the spectra show three bands due to the following transitions:

ν_1: $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ ν_2:
$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ ν_3:
$^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$