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UNIT I

Electronic Spectra of Transition metal complexes

Spectroscopic ground states, spectral terms, R-S coupling and J-J couplings- term symbol – selection rules—microstates—Pigeon hole diagram for p² and d² configuration. Orgel and Tanabe – sugano diagrams for transition metal complexes (d¹-d⁹ states) electronic spectra of transition metal complexes— calculation of Dq values -- Racah parameters and Beta parameters, Nephelaxatic effect, charge transfer spectra.

ELECTRONIC SPECTRA OF COMPLEXES

INTRODUCTION

Spectra is due to the transition of an electron from one energy level to another.

Types:

1. Absorption Spectra : It shows the particular wavelength of light absorbed (ie) particular amount of energy required to promote an electron from one energy level to higher level.
2. Emission spectra: It shows the energy emitted when the electron falls from the excited level to the lower level.

The electronic transitions are high-energy transitions. In the course of this transition, other smaller energy (vibrational and rotational transition) also takes place. But the energy difference is small in vibrational and rotational transition. Therefore difficult to resolve.

The electronic transition is governed by selection rules. The transition which obeys the selection rules are called as the allowed transition and the transition disobeys the selection rule, are called forbidden transition

Allowed transition \longrightarrow quite common (high intensity)

Forbidden transition \longrightarrow Not common (low intensity)

d-d transitions: This actually is electron transition from t_{2g} to e_g orbital. In this, charge distribution between excited and ground states are same. These transitions occur in visible or near U.V region. This appears to be the simple explanation for the colour in the transition metal complexes.

The absorption spectra of octahedral complexes show the molar absorbance of such d-d transition are low. This is because of selection rules. The electron transition are of high energy transition. In addition much lower energy, vibrational and rotational transition always occur. The vibrational and rotational level are too close in energy, to be resolved into separate absorption bands, but

they result in considerable broadening of electronic absorption bands in d-d spectra. Band widths are commonly found to be the order of $1000 - 3000 \text{ cm}^{-1}$

Selection rules: Not all the theoretically possible transition are actually observed. The selection rule distinguish allowed and forbidden transition. Allowed transitions are common but forbidden transition less frequently occur. They are of much low intensity.

A. Laporte orbital selection rules: Transitions involving a change in subsidiary quantum number $\Delta l = \pm 1$ are, laporte allowed transition and therefore they have high absorbance.

e.g as $S^2 \rightarrow S^1 P^1$ (changes by +1) and moral absorption co-efficient is $\Sigma = 5000 - 10000 \text{ l}/\mu/\text{cm}$.

In contrast: d-d transitions are lapore forbidden transition because $\Delta l=0$ and therefore have a lower absorbance. But spectra of much lower absorbance are observed, because of slight relaxation in the laporte rule. This enable the transition metal complex to have bright coloured.

B. In cpxes with a centre of symmetry the only allowed transitions are those with a change of parity. i.e gerade to ungerade . $u \rightarrow g$ are allowed, but not $g \rightarrow g$ and $u \rightarrow u$. Since all d orbitals have gerade symmetry, all d-d transitions are forbidden. \rightarrow

Types of Relaxation:

1. A molecule with no centre of symmetry (E.g) $T_d \rightarrow [\text{CoCl}_4]^{2-}$, $[\text{MnBr}_4]^{2-}$ also unsymmetrically substituted octahedral complexes e.g. $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ are coloured, in such cases mixing of d and p ortritals may occur in which case transitions are no longer pure d-d in nature. Therefore transitions can take place between d-orbitals having different p-character and such transitions are called as partially-allowed transitions.

2. Mixing do not occur in octahedral complexes which have a centre of symmetry such as $[\text{Co}(\text{NH}_3)_6]^{3+}$ (or) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. Here the M-L bonds vibrate so that for a fraction of time, the d-p mixing will be possible. Thus, a very small amount of mixing occurs and low intensity spectra are observed. These

transitions are said to be vibrationally allowed transitions and the effect is described as vibronic coupling. The intensity of band is roughly proportional to the extent of mixing.

3. **Spin selection Rules:** During the transition between energy levels, the spin of the electrons does not change but remains the same [$\Delta S = 0$] Spin-forbidden transitions have very weak intensity ($\Delta S \neq 0$) (can be ignored). Eg. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$. So many Mn^{2+} compounds are flesh coloured or colourless. Spin-allowed transitions have very high intensity

Sl. No	Laporte orbital	Spin	Type of spectra	$\epsilon = A/\text{cl}$	Example
1	Allowed	Allowed	Charge transfer	10,000	$[\text{Ti Cl}_6]^{2-}$
2.	Partly allowed some d-p mixing	Allowed	d - d	500	$[\text{Co Cl}_4]^{2-}$
3.	Forbidden	Allowed	d - d	8 -10	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
4.	Partly allowed some d-p mixing	Forbidden	d - d	4	$[\text{Mn Br}_4]^{2-}$
5.	Forbidden	Forbidden	d-d	0.02	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

Electronic transitions in complexes:

The electron (orbital motion) revolves round the nucleus. When a charge species revolves round the nucleus, a magnetic field is produced. Also, the electron spin around its own axis. So another type of magnetic field is generated.

1. Thus, even though the p-orbitals are degenerate and have the same energy, the electrons present in them interact with each other and result in the formation of ground state (lower energy) and one (or) more excited states due to electrostatic repulsion.
2. There can be interaction (or) coupling between the magnetic field produced as a result of orbital motion.
3. There can be a coupling (or) interaction between the magnetic field produced by the spin of electrons around its own axis.

If for 1-p e⁻, there are 6 possible ways of placing e⁻s in the 'p-orbital'.

For 2p e-s, there are 15 possible ways of placing the e-s in the p orbital.

These electronic arrangement can be divided into 3 main groups of different energy called 3 energy states. They are labelled as term symbol.

Definition of term symbol:

Term symbol is an abbreviated description of the energy, angular momentum and spin multiplicity of an atom in a particular state.

Term states for d^n ion: When several electrons occupy a sub shell the energy states obtained, depends upon the result of the orbital angular quantum number of each electron. The resultant of all the l-values is demonstrated by a new quantum number 'L' which defines the energy state for the atom

$$L = 0, 1, 2, 3, 4, 5, 6, 7, 8, \dots$$

$$\text{State} = S \quad P \quad D \quad F \quad G \quad H \quad I \quad K \quad L$$

(The letter J is omitted since this is used for another quantum number)

$$\text{Spin - multiplicity value} = (2s + 1)$$

$$S \Rightarrow \text{Spin quantum number}$$

$$\text{No of e-s present} = 1 \ 2 \ 3 \ 4 \ 5 \ \dots \dots$$

$$(2s + 1) = 2 \ 3 \ 4 \ 5 \ 6 \ \dots \dots$$

$$\text{Orbital quantum number (L)} = (m_l \times l)$$

Rules for determining the term symbols:

1. The e-s should be unpaired as much as possible and occupy different orbital (ground state) of low energy.
2. The spin multiplicity value must be maximum to be stable
3. The orbital angular momentum L value should be large (or) the highest (ground state).

$$\text{Total angular momentum quantum number (J)}$$

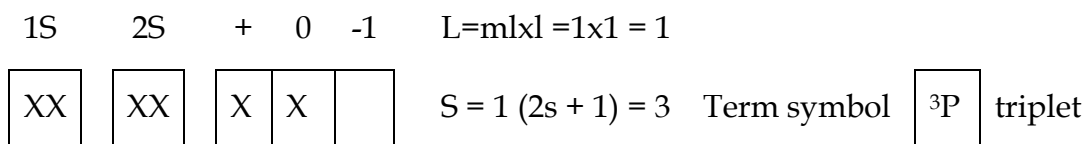
L and S values couple to give J value. Magnetic effects of L and S couple to give J value .

4. If sub shell is more than half filled - Smallest J value is more stable (L-S)

If the sub shell is less than half filled - Highest J value is more stable (L + S)

Derivation of term Symbols:

- 1 For C $1S^2 2S^2 2P^2$ (G.S)

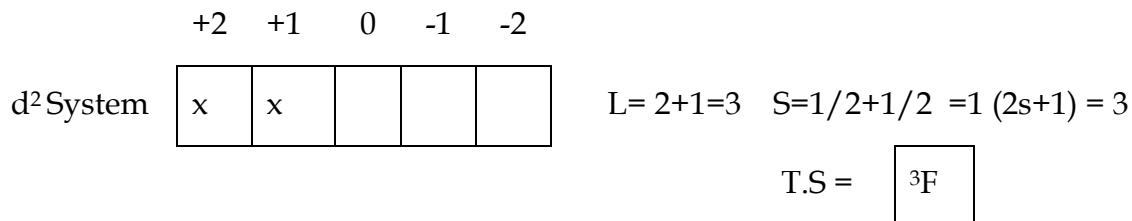
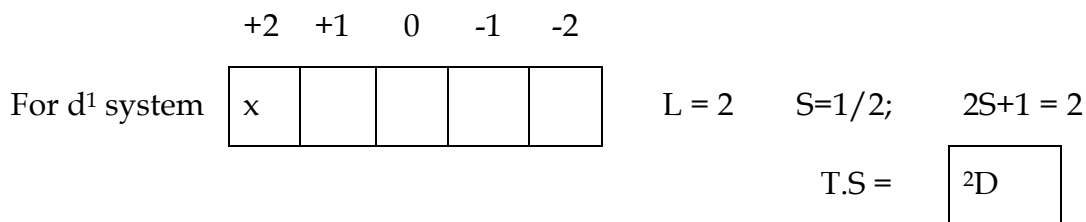


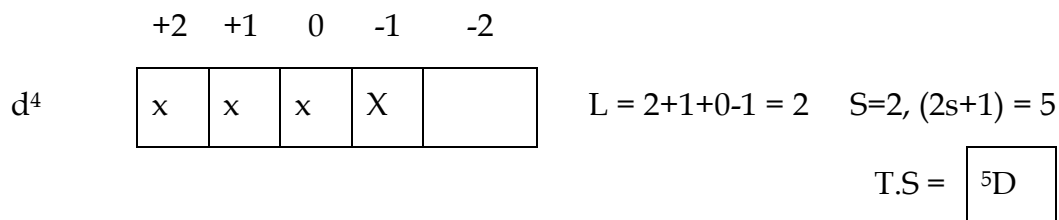
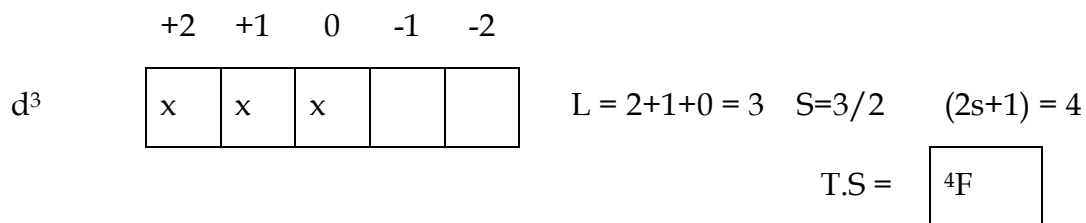
2. For B $1S^2 2S^2 2P^1$

$$L = m_l x l = 1 \times 1 = 1 \quad S = 1/2; \quad 2S + 1 = 2$$

Term symbol $\boxed{^2P}$ Doublet

For transition metals : Here the e-s go to the d orbital





Similarly for d^5 T.S = $6S$, $d^6 = 5D$ $d^7 = 4F$, $d^8 = 3F$

$d^9 = 2D$

$d^{10} = 1S$

Note: According to CFT

s orbital is completely symmetric and so does not split

p orbital all interact equally and so does not split

d orbital is split by oh field into t_{2g} and e_g orbital

f orbital is split by oh field into t_{1g} , t_{2g} and a_{2g}

Orgel diagram:

The Orgel diagram is the quantum mechanically calculated energy of the term level (as ordinate) against an increasing value of field strength, the ligand field splitting parameter.

Octahedral field	Tetrahedral field
d^1 system Ex - $[TiCl_6]^{3-}$, $[Ti(H_2O)_6]^{3+}$ here the ground state of the free ion is described by the term symbol $2D$. The degenerate 'd' orbitals or levels are	d^1 system: Here also the ground state of the free ion is described by the term symbol $2D$. The degenerate d orbitals are split

split into T_{2g} and e_g in the presence of octahedral field	into doublet e_g and triplet t_{2g} in the presence of a tetrahedral field.
The lower T_{2g} state corresponds to the single d electron occupying one of the T_{2g} orbital and 2e_g state corresponds to the electron occupying one of the e_g orbitals.	The lower E corresponds to the single d electron occupying one of the e_g orbital and ${}^2T_{2g}$ state corresponds to the electron occupying one of the t_{2g} orbital.

Note:

The magnitude of splitting Δ_o depends on the nature of the ligand and hence affects the energy of transition. As the ligand is changed, Dq varies and the colour of the complex also varies.

Note:

In d^1 case, there is a single electron in the lower t_{2g} level while in the d^9 case there is a single hole in the upper e_g level.

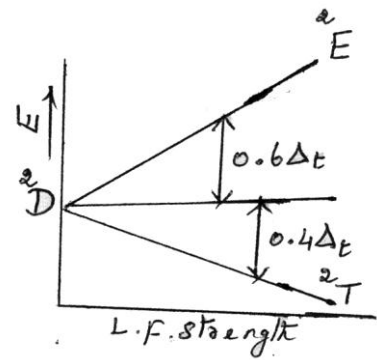
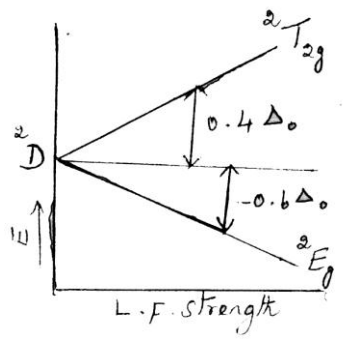
Thus, the transition of the d^1 case is the promotion of an electron from t_{2g} to e_g level, while in d^9 ion, it is simpler to consider as the transfer of a hole from e_g to t_{2g} . Thus the energy level diagram for d^9 is therefore the inverse of that for a d configuration.

For d^9 system (octahedral)

For d^9 system tetrahedral

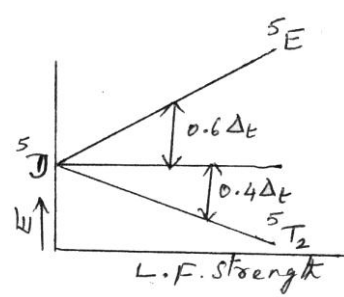
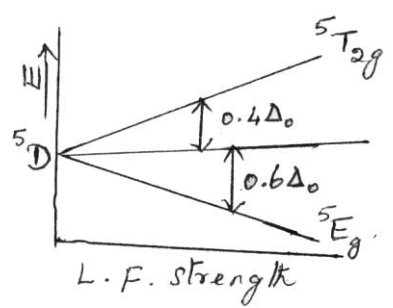
In the octahedral field the term symbol 2D is split as 2E_g and ${}^2T_{2g}$ 2D is split as 2E_g and ${}^2T_{2g}$.
 $0.6\Delta_o$ below and $0.4 \Delta_o$ above degenerate states

In the tetrahedral field the term symbol 2D is split as 2E and 2T_2 .



For d^4 system term symbol 5D is split into 5E_g & ${}^5T_{2g}$.

For d^4 system, term symbol 2D is split into 5T_2 and 5E

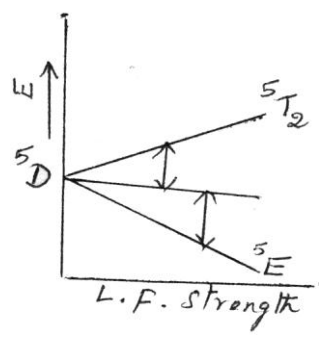
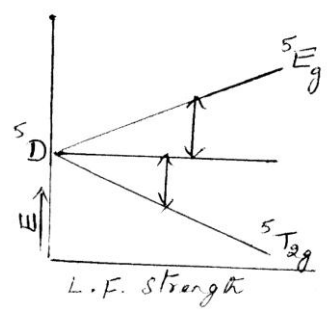


For d^6 system

For d^6 system

Here in the octahedral field, the term symbol 5D is split as ${}^5T_{2g}$ and 5E_g

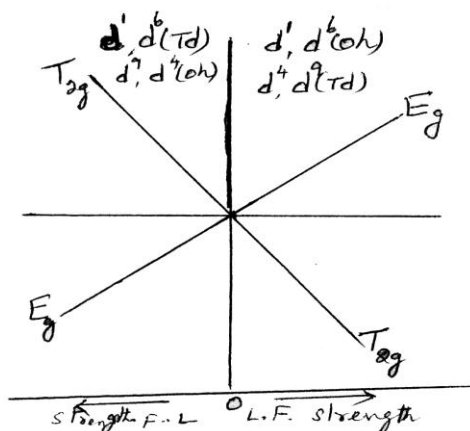
5D is split as 5E and 5T_2



Note: d^6 is inverse of that for d^4 configuration. From the above energy diagrams we can come to conclusion that d^1 and d^9 are inverse. Similarly d^4 and d^6 are inverse (or) we can say that d^1 is similar to d^6 and d^9 is similar to d^4 .

We can also state that d^1 (T_d) and d^9 (o_h) complexes have similar Orgel diagram.

So d^1 , d^9 , d^4 and d^6 diagrams can be combined to a single Orgel diagram. (fig 4)



The spectra of these complexes have only one band due to the single d-d transition, that occur is assigned as $E \rightarrow T_2$.

Hole Formalism: When a subshell is more than half filled it is simpler and more convenient to work out the terms by considering the holes (ie the vacancies) rather than considering the large number of electrons actually present.

By considering the holes, the terms which arises for pairs of atom with p^n and p^{6-n} and d^n and d^{10-n} give rise to identical terms.

Electronic configuration	G.S terms	Other term
1) p^1, p^5	$2P$	$1S, 1D$
2) p^2, p^4	$3P$	$2P, 2D$
3) p^3	$4S$	
4) p^6	$1S$	
5) d^1, d^9	$2D$	
d^2, d^8	$3F$	$3P, 1G, 1D, 1S$

d^3, d^7	$4F$	$4p, 2H, 2G, 2F, 3G, 3H, 3F,$
d^4, d^6	$5D$	$3P, 1F, 1D, 1S$
d^5	$6S$	$4G, 4F, 4D, 4P,$
d^{10}	$1S$	$2G, 2F, 2D, 2P$

Transformation of Spectroscopic symbols into mulliken symbols

Splitting of d terms in an octahedral and Tetrahedral field

Spectroscopic terms	Mulliken Symbols	
	Octahedral field	Tetrahedral field
(1) S	A_{1g}	A_1
(2) P	T_{1g}	T_1
(3) D	E_g, T_{2g}	E, T_2
(4) F	A_{2g}, T_{1g}, T_{2g}	A_2, T_1, T_2
(9) G	$A_{1g}, E_g, T_{1g}, T_{2g}$	A_1, E_1, T_1, T_2
(11) H	$T_{1g}, T_{1g}, T_{2g}, E_g$	T_1, T_2, T_2, E
(13) I	$A_{1g}, A_{2g}, E_g, T_{1g}, T_{2g}, T_{2g}$	A_1, T_1, T_2, T_2, T_1

d^2, d^7, d^3, d^8 configuration

+2 +1 0 -1 -2

$L=3, S=1, 2S+1 = 3$

d2 case

1	1			
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Term Symbol

3F

Here We have two possibilities

- 1) Parallel Spin
- 2) Anti Parallel Spin

For parallel spin $(2S+1) = 3$ (Triplet)

For anti parallel spin $(2S+1) = 1$ (Singlet)

So, the ground state $\rightarrow {}^3F$

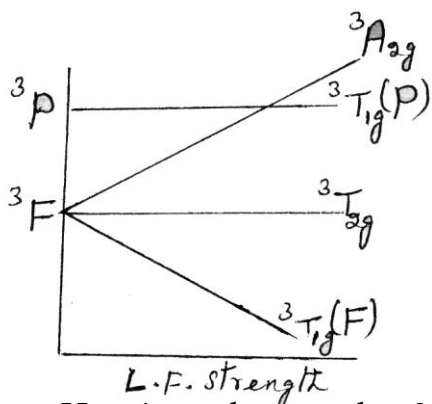
Excited State $\rightarrow {}^3P, {}^1G, {}^1D, {}^1S$

Here ${}^1G, {}^1D, {}^1S$ states contain electrons with opposite spin. The transition from the ground state to ${}^1G, {}^1D, {}^1S$ are spin-forbidden and will be very weak and can be ignored.

So, the only important transition is from 3F to 3P

In the octahedral ligand field, the P state, transforms into a T_{1g} Mulliken term and the F state splits into 3 terms, namely, A_{2g}, T_{1g} and T_{2g} .

The energy level diagram of d^2 complex ion. $[V(H_2O)_6]^{3+}$ can be shown in the figure (5).



Here it can be seen that 3 transitions are possible from the ground states, hence three peaks should occur in the spectrum.

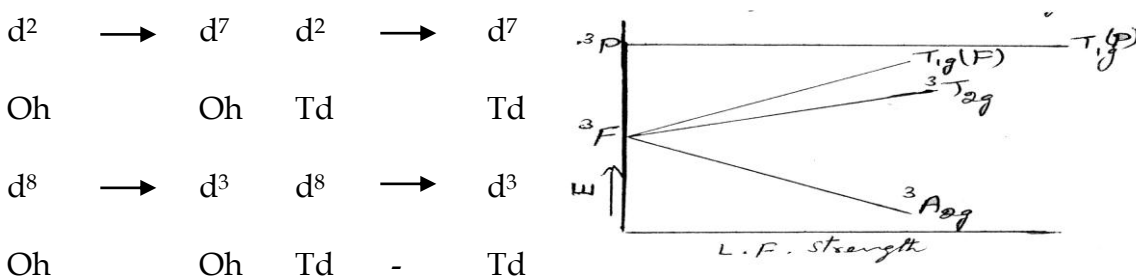
Note: 1) In d^1, d^4, d^6, d^9 system only one transition occurs (because there are only 2 energy levels)

2) In d^2 systems, nothing common. So energy can cross (ie) Crossing is allowed also spin allowed transition.

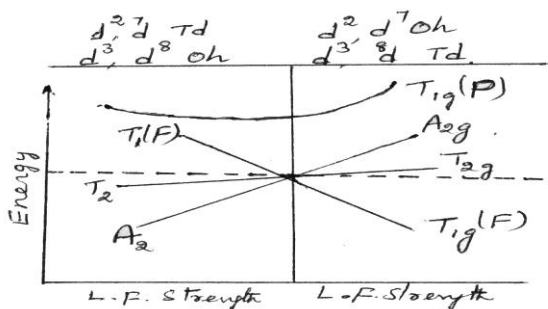
The first excited state ${}^3T_{2g} + {}^3T_{1g}(p)$ if the second electron also excited ${}^3A_{2g}$

d^8 System E_g $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$

The complex with d^8 configuration in an octahedral field may be regarded as having two holes in the e_g level hence promotion of an electron from the lower t_{2g} level to the e_g level is similar to transfer of a hole from e_g to t_{2g} . So this is inverse of d^2 case. Using the same arrangement applied to d^1 case, we can say that



So combined Orgel diagram for 2 electron and 2 hole configuration is shown Fig(7).



d^5 system Ex $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$

In Orgel diagram d^5 configuration is left out because of the following reason.

- i) It is spin forbidden transition. The compound is almost colourless. So weak intensity is observed in the spectra.

Orgel diagram for low spin complex

Orgel diagram can be modified to take into account low spin complex also. But generally Orgel diagram treats only the weak field (or) high spin case. So in these cases the excited state is not included.

Example

For d^6 system : Ex Co^{3+} for the free ion ${}^1\text{I}$ has higher energy compared to quintet ${}^5\text{D}$. So ${}^1\text{I}$ (one of the excited state) is least important.

But in the presence of ligand a ligand field or crystal field the state ${}^1\text{I}$ split into several terms. Out of these several terms ${}^1\text{A}_{1g}$ drops in energy as the strength of the field increases and at a certain stage (critical point) A_{1g} cross over (get stabilised) ${}^5\text{T}_{2g}$ and becomes the ground state.

Note : After the critical point the complex would be low spin. For low spin complex theoretically 5 transitions are possible, but we observe only two transition in spectra.

For d^5 system

Here ${}^2\text{I}$ is of higher energy compared to sextet S . For the free ion ${}^2\text{I}$ is not important. But in the presence of ligand (or) crystal field the ${}^2\text{I}$ state splits into several terms. Out of these ${}^2\text{T}_{2g}$ drops in as the strength of the field increases and at a certain stage (critical pts) ${}^2\text{T}_{2g}$ cross over. So becomes ground state

Evaluation of Dq and B value for octahedral cpx of Nickel

For high spin octahedral cpx of Nickel, the energies of the states are given by equations

$$\text{For } {}^3\text{T}_{2g} \quad E = -2Dq$$

$$\text{For } {}^3\text{A}_{2g} \quad E = -12Dq$$

$$\text{For } {}^3\text{T}_{1g} (\text{F}) \text{ and } {}^3\text{t}_{1g} (\text{P})$$

$$[6 Dq p - 16 (Dq)^2] + [-6 Dq - P] E + E^2 = 0$$

$$v_1 = \text{A}_{2g} \rightarrow \text{T}_{2g} = 10Dq$$

$$v_2 = \text{A}_{2g} \rightarrow \text{T}_{1g} (\text{F}) = 7.5 B' + 15 Dq - \frac{1}{2} [225B^2 + 100Dq^2 - 180B'Dq]^{1/2}$$

$$v_3 = \text{A}_{2g} \rightarrow \text{T}_{1g} (\text{P}) = 7.5 B' + 15Dq - \frac{1}{2} [225 B^2 + 100 Dq^2 - 180 B' Dq]^2$$

1) Ni II Epx $[\text{Ni}(\text{NH}_3)_6]^{2+}$ show the following transition.

ν_1	ν_2	ν_3
10750 cm^{-1}	17500 cm^{-1}	28200 cm^{-1}

Calculate the value of $10 Dq$ and B ?

$$\gamma = 10 Dq = 10750 \text{ cm}^{-1} \quad Dq = 1075 \text{ cm}^{-1}$$

$$B = (\nu_2 + \nu_3 - 3\nu_1) / 15.$$

$$= (17500 + 28200 - 3 \times 10750) / 15 = 896.7$$

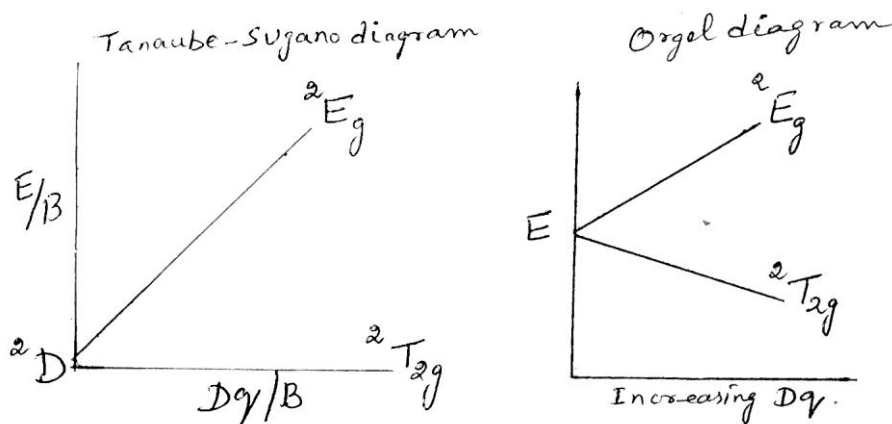
Tanaube - Sugano diagram

The tanaube and sugano diagrams are plots of the energies of the levels in a d^n system in units of B (ie) E/B (as ordinate) against the ligand field strength, in units of Dq/B (as abscissa). The ground state of the metal ion is always plotted as the abscissa, in the diagram.

For systems having more than 3 electrons and less than 8 electrons, a change in ground state can occur as we progress from weak to strong fields.

In order to treat fully the problem of interpretation of spectra including both H. Spin complex and L.spin complex.

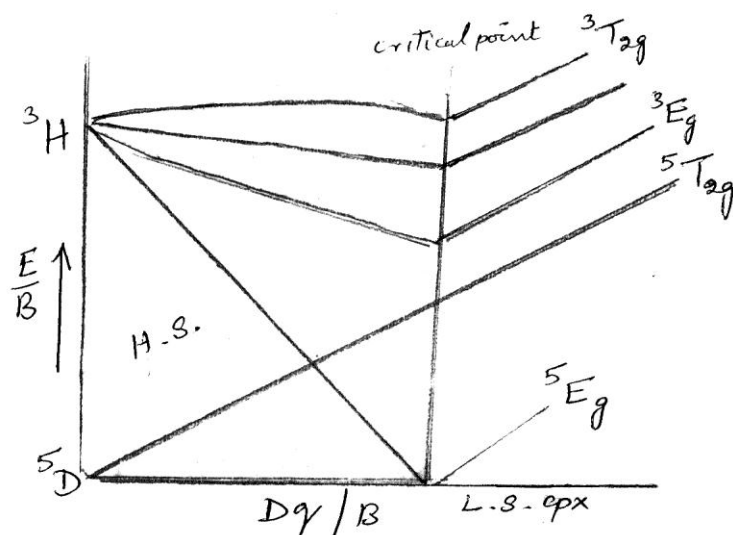
For d^1 system fig (8)



For d^4 system

There will be a considerable difference between the spectra of low spin and of high spin d^4 complexes. In high spin complexes, we expect only one spin allowed band and a series of forbidden quintet \rightarrow Triplet transition of low intensity. In low spin complexes, the transition to the triplet levels become spin allowed and a rich spectrum is expected.

So the combined diagram (both low and high spin) can be drawn as follows.

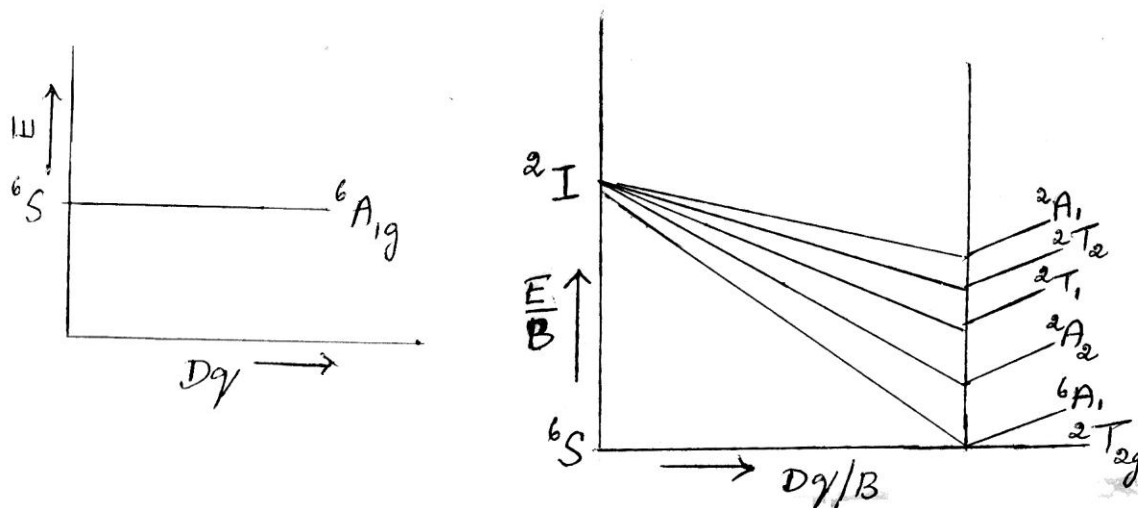


Theoretically 4 transitions are possible but in practice 2 or 3 are observed.

Note: Where there is a crossing in Orgel diagram, there will be a change in direction of Tanabe-Sugano diagram.

After the critical point we observe generally low spin complexes.

For d^5 system fig(10)



For d^6 system

Eg. $\text{Co}^{2+} \rightarrow d^7$

$\text{Co}^{3+} \rightarrow d^6$ Eg. $[\text{CoF}_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$

Here the 5D split by the increasing octahedral field strength into $^5T_{2g}$ in G.S and an excited state 5E_g .

The next excited state as 1I (singlet I) which is very high energy in the free ion is split by the application of the ligand field into several terms. Only one of which is important. The term A_{1g} is greatly stabilized by the ligand field and drops rapidly becoming the ground state at $10Dq/B = 20$. At this point spin pairing takes place and hence there is a discontinuity in the diagram showing by a vertical line. Beyond this point, the low spin A_{1g} term is the ground state.

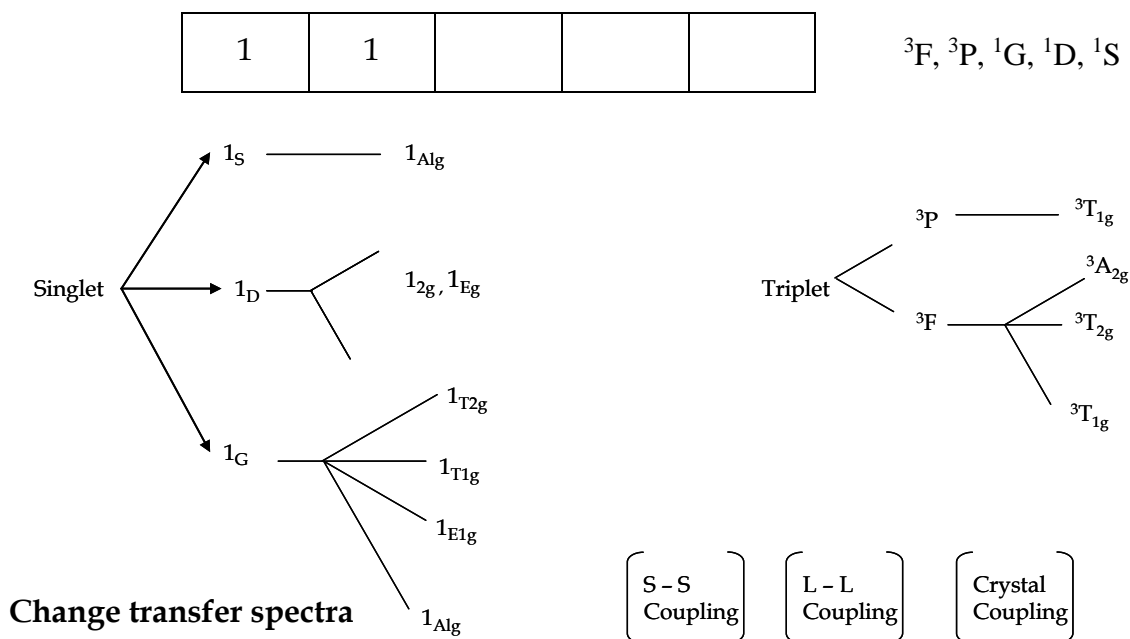
Weak and Strong Field

When the crystal field is fairly weak, it may be combined as a perturbation of the free ion levels. It is justifiable to calculate the free ion energy levels, and then to consider how these will be affected by the crystal field. This method is known as weak field approach. [Effectively the inter electronic repulsion is considered first and then the crystal field is super imposed on the levels so produced].

If the crystal field is fairly strong, it may induce electron pairing (spin paired complexes). Under such conditions, the field is important than the inter electronic repulsion since it over-rides the correlation forces trying to maintain maximum spin. [Therefore it is reasonable to consider the energy level in the crystal field environment first and then to super impose the effect of inter electronic repulsion.

1) Weak field approach

In the weak field approach we assume that the effect of the crystal field is less than inter electronic repulsion. The electron couple together to give the various spectroscopic terms of the free ion. If the free ion is now placed into a crystal field, the degeneracy of the spectroscopic terms may be partially or wholly lifted, to give a new terms which are described by group theoretical representation.

Eg. d^2 

The absorption of light is to cause an electronic transition within an atom or molecule. It is essential that the absorption results in a charge density displacement. This displacement may be localized on one atom (as it is, to first approximation, in the d-d spectra) or it may be the displacement of charge from one atom to another, so in electronic transition electrons move between orbitals that have predominantly metal d-orbital character. Thus the charge distribution is about the same in the ground state and excited state. There is another important class of transition in which the electron moves from a M.O centered mainly on the ligand to one centered mainly on the metal atom and vice versa. In these the charge distribution is different, considerably from ground state and excited state and so they are called as charge transfer transition.

Differences between d-d and charger-transfer transition

d-d transition	Charge-Transfer-Transistion
1. Here electron moves from one d-	This arises when an electron from

orbitals to another results in the d-d transition. It is forbidden transition against selection rule g-g (forbidden)	one atom goes into another atom within the same molecule. The transition is not against any selection rule ($g \rightarrow u$) allowed.
2. The Charge distribution between the ground state and excited state remains the same.	The charge distribution between the ground state and excited state different because of this we say this is as charge transfer spectra.
3. Intensity (ϵ) value is normally below 100 and have weak intensity.	ϵ value is high 10,000 [Eg] $[\text{Ti Cl}_4]^{2-}$
4. Mostly they occur in the visible and near uv region.	The bands are usually obtained is near uv region and often overlap with d-d transition because of this we do not get full d-d spectrum of complex.

There are two possibilities of charge transfer process in metal complexes. Electron from metal goes to ligand (ie) $M \rightarrow L$ transition (oxidation) electron from ligand goes to metal (ie) $L \rightarrow M$ transition (reduction).

[I] **Metal \rightarrow Ligand (oxidation)**

Here the electron from t_{2g} (or) e_g orbital of metal may go to the π^* of ligand. The direction of transition depends on the energy of the ligand and metal orbital and also on the occupancy of orbital.

- (i) $M \rightarrow L$ transition will occur when the metal is in the lower oxidation state.
- (ii) The ligand orbitals should be empty and also of lower energy.
- (iii) More the reducing power of the metal the lower will be the energy of

transition.

The energy of this type of transition probably occurs in the aqua ions of divalent metal of the first transition series (first half) because they have valency ions and reducing power. So they give deeply coloured complex with electron acceptor ligand like o-phenanthrene, pyridine (neutral) due to delocalized π electrons they are of intense colour. Intense colour is absent in Ni^{2+} and Co^{3+} (Higher oxdn state). (Here the metal has more reducing property and more the oxidizing ligand- lower the energy of transition).

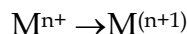
(II) Ligand \rightarrow metal (reduction)

Here the electrons from π orbital of ligand may go to t_{2g} or e_g . (Note: Electron from $\pi-\pi$ transition is intra ligand transition)

- (i) $L \rightarrow M$ transition will occur when the metals are in the higher oxidation states.
- (ii) The ligand orbital should be filled and also of higher energy.
- (iii) Higher the oxidizing power of the metal lower will be the energy of transition.

Thus charge transfer absorption in the visible spectrum is more common in complexes of Iron (III) than in those of Cr (III). This accounts for the use of iron (III) in colour tests in organic chemistry. Eg. Phenols and hydroxamic acid gives neutral FeCl_3 test.

Metal - Metal Charge transfer



1. A number of inorganic compounds contain a metal in two valence states. Eg. (i) Prussina blue $\text{K}(\text{Fe}(\text{III}) \{ \text{Fe}(\text{II}) \} (\text{CN})_6)$. Here Fe (III) is high spin and Fe(II) is low spin as shown by the study of mosbauier effect. Here the charge transfer occurs from the t_{2g} orbitals of Fe (III) to Fe (II) via interfering CN

Ligand - Ligand Charge transfer

A ligand such as SCN^- has internal charge transfer transition usually located in the u-v region of the spectrum, corresponding transition occur in co-

ordinated ligand, but can be usually identified by comparison with spectra of the free ligand.

1) M- L (oxidation) Charge transfer transition

This type of transition can only be expected when ligands possess low-lying empty orbitals and the metal ion has filled orbitals lying higher than the highest filled ligand orbitals. The best examples are provided by complexes containing CO, CN⁻ or aromatic amines (pyridine, or phenanthroline) as ligands. In the case of octahedral metal carbonyls Cr(CO)₆ and Mo (CO)₆ pairs of intense bands at 35,800 and 44,500 cm⁻¹ for the former and 35,000 and 43,000 cm⁻¹ for the latter have been assigned to transition from the bonding to the anti bonding (Ligand π*) components due to metal-ligand π bonding interaction.

For [Ni(CN)₄]²⁻ there are 3 medium to strong bands at 32,000, 35,200 and 37,600 cm⁻¹ which have been assigned as transition from the three types of filled metal d-orbitals [d_{xy}, and (d_{xz}, d_{yz})] to the lowest energy orbitals formed from the π* orbitals of the set of CN⁻ groups.

SPIN - ORBIT COUPLING

There is a magnetic interaction between the electron spin magnetic moment ($m_s = + 1/2$) and the magnetic moment due to the orbital motion of an electron. The charged electron circles the nucleus and this is equivalent in effect to placing the electron in the middle of a coil of wire carrying current. As moving charge in a circle creates a magnetic field in the centre, the orbital motion causes a magnetic field at the electronic position. This magnetic field can interact with the spin magnetic moment of the electron giving rise to spin-orbit interaction. For two electrons the various type of interactions possible are between

- i) The two spins (s_1, s_2)
- ii) The orbital moment (l_1, l_2)
- iii) The spin of the e⁻ and the orbital moment of the same e⁻ (termed spin-orbit coupling s_1, l_1)
- iv) The spin of the one e⁻ and orbital moment of the other (S_1, S_2) normally the last one is negligible.

The two extreme situations are,

- i) $s_1, s_2 > l_1, l_2 > s_1, l_1 =$ for lighter elements up to 1st row transition series
- ii) $s_1 l_1 > s_2 l_2, l_1 : l_2 =$ for heavier elements (j-j coupling)

The energy difference between adjacent J values

$$J' \text{ and } J'+1 \text{ is } (J'+1) \lambda - J' \lambda = \lambda$$

Where λ is the spin-orbit coupling constant

$$\lambda = \pm \frac{L}{2S}$$

Example 1). For p¹ ion

$$L = 1, S = \frac{1}{2}, T.S = {}^2P$$

Here L & S couple, they give rise to 2 levels corresponding to

$$J = L + S \dots L - S$$

$$J = 3/2 \text{ and } 1/2$$

Thus 2P term split into ${}^2P_{3/2}$ and ${}^2P_{1/2}$ level under the influence of magnetic field. J split into (2J+1) levels

The magnitude of splitting between two 2p states depends upon the strength of L-S coupling. It may be represented in terms of spin-orbit coupling parameter (ζ) zeta. The value of zeta is expressed in cm^{-1} .

2) For d¹ ion

$$L = 2, S = \frac{1}{2}, T.S = {}^2D$$

$$J = 5/2 \dots\dots\dots 3/2$$

Note

ζ value increases with oxidation number but not very sensitive to change in oxidation state so the impact of S.O.C on spectra is very small

The effect of Spin orbit coupling

The spin allowed d-d bands dominate the visible spectrum of complex of many transition metal. It should be pointed that S.O.C treats the phenomenon as one of the coupling of two angular momentum rather than bar magnet. It causes the splitting of degeneracies in the orbital energy level diagram. For eg ${}^4T_{1g}$ state split into the 12 fold degenerate levels. Some spin orbit arrangements are stable than the other. It is more important in the assignment of weak spin forbidden transition.

Magnetic Properties of Complexes

When an atom or molecule is placed in a magnetic field any spin degeneracy and orbital degeneracy may be removed. So a level which is orbitally non-degenerate but which is a spin doublet maybe split. The splitting produced are very small which is directly proportional to the magnetic field.

Molecules with closed shell are therefore repelled by a magnetic field and said to be diamagnetic. If an e⁻n is considered as a hard sphere carrying a negative charge and involve orbital rotation around nucleus in a closed path, it will generate a spin moment and an orbital moment which continue to give paramagnetism. It is expressed in bohr magneton (B.M)

Paramagenetic Behaviour

Free radicals or ionic system which contain one or more unpaired e⁻ns will possess a permanent magnetic moment that arises from the residual spin and angular momentum of the unpaired e⁻n. When a paramagnetic substance is placed in a external magnetic field it will be attracted and there will be negative increase in magnetic susceptibility which is independent of the applied field, but dependent on temperature. (Since as the temperature is increased there is opposition to the proper alignment because of thermal agitation which results in the decrease in the effectiveness of attraction). Hence the effectiveness of the magnetic field will diminish with increasing temperature.

Mathematically, this dependence has been expressed by the curie's law:

$$\chi = C/T$$

(or) Curie - Weiss law : $\chi = C/(T-\theta)$

C = Curie Constant, θ = Weiss Constant

Factors affecting the paramagnetic behaviour of complexes:

1. Number of unpaired electrons
2. The spectroscopic ground state and the next high excited state
3. Ligand field strength

Types of paramagnetic behaviour:

1. Large multiplet separation: (Energy difference is large)
2. Small multiplet separation: (Energy difference is small)

Large multiplet separation

Eg : Lanthanides : The paramagnetic character is due to the unpaired e⁻s in f-shell. Here the unpaired e⁻s are well shielded from external ligand field (not exposed to environment) or covalent bonding forces, and the S.O.C is very large. The ground state is very well separated from the next excited state, by an energy difference which is large, compared to KT (200cm^{-1}). Therefore only ground state is populated and not the excited state (because thermal energy cannot promote the e⁻ to excited state)

Under these circumstances S.O.C is significant and for a given state of $L+S$, J -will take all values from $L+S$ to $L-S$.

The magnetic moment in this case is given by

$$\mu = g\sqrt{J(J+1)} \text{ B.M, } g = \text{Gyro magnetic ratio}$$

In lanthanides:

This sort of behavior is met when there is a well defined single J value.

In Actinides:

1. R-S coupling or L-S coupling is inadequate for actinides, so we have to go for j-j coupling

2. In the case of actinides the 5f e-ns are not deeply seated but to some extent affected by the external field. So it is difficult to explain.

Small multiplet separation:

Eg: d-block elements

Here the 4s and the next orbitals lie close in energy and the difference in energy is comparable with kT at room temperature. Therefore both levels are equally populated therefore the effect of S.O.C is small, So one can ignore the coupling and treat L&S as to interact independently with external field and the wave mechanics shows that,

$$\mu = \mu_{S+L} = \sqrt{4S(S+1)+L(L+1)} \text{ B.M}$$

In transition metals:-

Here we find that the orbital contribution is quenched with the result of spin contribution. Thus only the spin angular momentum determines the magnetic moment.

$$\mu = \mu_S = \sqrt{4S(S+1)} \text{ B.M} \rightarrow \text{spin only formula}$$

Spin only formula hold good only for I-row of transition series.