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# Electronic (Absorption) Spectra of 3d Transition Metal Complexes

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/50128>

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## 1. Introduction

### 1.1. Types of spectra

Spectra are broadly classified into two groups (i) emission spectra and (ii) absorption spectra

- i. *Emission spectra* Emission spectra are of three kinds (a) continuous spectra, (b) band spectra and (c) line spectra.

*Continuous spectra:* Solids like iron or carbon emit continuous spectra when they are heated until they glow. Continuous spectrum is due to the thermal excitation of the molecules of the substance.

*Band spectra:* The band spectrum consists of a number of bands of different colours separated by dark regions. The bands are sharply defined at one edge called the head of the band and shade off gradually at the other edge. Band spectrum is emitted by substances in the molecular state when the thermal excitement of the substance is not quite sufficient to break the molecules into continuous atoms.

*Line spectra:* A line spectrum consists of bright lines in different regions of the visible spectrum against a dark background. All the lines do not have the same intensity. The number of lines, their nature and arrangement depends on the nature of the substance excited. Line spectra are emitted by vapours of elements. No two elements do ever produce similar line spectra.

- ii. *Absorption spectra:* When a substance is placed between a light source and a spectrometer, the substance absorbs certain part of the spectrum. This spectrum is called the absorption spectrum of the substance.

Electronic absorption spectrum is of two types. d-d spectrum and charge transfer spectrum. d-d spectrum deals with the electronic transitions within the d-orbitals. In the charge – transfer spectrum, electronic transitions occur from metal to ligand or vice-versa.

## 2. Electronic spectra of transitions metal complexes

Electronic absorption spectroscopy requires consideration of the following principles:

- Franck-Condon Principle*: Electronic transitions occur in a very short time (about  $10^{-15}$  sec.) and hence the atoms in a molecule do not have time to change position appreciably during electronic transition. So the molecule will find itself with the same molecular configuration and hence the vibrational kinetic energy in the excited state remains the same as it had in the ground state at the moment of absorption.
- Electronic transitions between vibrational states*: Frequently, transitions occur from the ground vibrational level of the ground electronic state to many different vibrational levels of particular excited electronic states. Such transitions may give rise to vibrational fine structure in the main peak of the electronic transition. Since all the molecules are present in the ground vibrational level, nearly all transitions that give rise to a peak in the absorption spectrum will arise from the ground electronic state. If the different excited vibrational levels are represented as  $\nu_1, \nu_2$ , etc., and the ground state as  $\nu_0$ , the fine structure in the main peak of the spectrum is assigned to  $\nu_0 \rightarrow \nu_0, \nu_0 \rightarrow \nu_1, \nu_0 \rightarrow \nu_2$  etc., vibrational states. The  $\nu_0 \rightarrow \nu_0$  transition is the lowest energy (longest wave length) transition.
- Symmetry requirement*: This requirement is to be satisfied for the transitions discussed above.

Electronic transitions occur between split 'd' levels of the central atom giving rise to so called d-d or ligand field spectra. The spectral region where these occur spans the near infrared, visible and U.V. region.

Ultraviolet (UV)	Visible (Vis)	Near infrared (NIR)	
50,000 - 26300	26300 - 12800	12800 - 5000	cm <sup>-1</sup>
200 - 380	380 - 780	780 - 2000	nm

## 3. Russel-Saunders or L-S coupling scheme

An orbiting electronic charge produces magnetic field perpendicular to the plane of the orbit. Hence the orbital angular momentum and spin angular momentum have corresponding magnetic vectors. As a result, both of these momenta couple magnetically to give rise to total orbital angular momentum. There are two schemes of coupling: Russel-Saunders or L-S coupling and j-j coupling.

- The individual spin angular momenta of the electrons,  $s_i$ , each of which has a value of  $\pm \frac{1}{2}$ , combine to give a resultant spin angular momentum (individual spin angular momentum is represented by a lower case symbol whereas the total resultant value is given by an upper case symbol).

$$\sum s_i = S$$

Two spins of each  $\pm \frac{1}{2}$  could give a resultant value of  $S=1$  or  $S=0$ ; similarly a resultant of three electrons is  $1\frac{1}{2}$  or  $\frac{1}{2}$ . The resultant is expressed in units of  $\frac{h}{2\pi}$ . The spin multiplicity is given by  $(2S+1)$ . Hence, If  $n$  is the number of unpaired electrons, spin multiplicity is given by  $n+1$ .

- b. The individual orbital angular momenta of electrons,  $l_i$ , each of which may be 0, 1, 2, 3, 4, ..... in units of  $\frac{h}{2\pi}$  for s, p, d, f, g, ..... orbitals respectively, combine to give a resultant orbital angular momentum,  $L$  in units of  $\frac{h}{2\pi}$ .  $\sum l_i = L$

The resultant  $L$  may be once again 0, 1, 2, 3, 4, .... which are referred to as S, P, D, F, G, ... respectively in units of  $\frac{h}{2\pi}$ . The orbital multiplicity is given by  $(2L+1)$ .

0	1	2	3	4	5
S	P	D	F	G	H

- c. Now the resultant  $S$  and  $L$  couple to give a total angular momentum,  $J$ . Hence, it is not surprising that  $J$  is also quantized in units of  $\frac{h}{2\pi}$ . The possible values of  $J$  quantum number are given as

$$J = (L + S), (L + S - 1), (L + S - 2), (L + S - 3), \dots, |L - S|$$

The symbol  $| |$  indicates that the absolute value  $(L - S)$  is employed, i.e., no regard is paid to  $\pm$  sign. Thus for  $L = 2$  and  $S = 1$ , the possible  $J$  states are 3, 2 and 1 in units of  $\frac{h}{2\pi}$ .

The individual spin angular momentum,  $s_i$  and the individual orbital angular momentum,  $l_i$ , couple to give total individual angular momentum,  $j_i$ . This scheme of coupling is known as spin-orbit coupling or  $j-j$  coupling.

## 4. Term symbols

### 4.1. Spectroscopic terms for free ion ground states

The rules governing the term symbol for the ground state according to L-S coupling scheme are given below:

- The spin multiplicity is maximized i.e., the electrons occupy degenerate orbitals so as to retain parallel spins as long as possible (Hund's rule).
- The orbital angular momentum is also maximized i.e., the orbitals are filled with highest positive  $m$  values first.
- If the sub-shell is less than half-filled,  $J = L - S$  and if the sub-shell is more than half-filled,  $J = L + S$ .

The term symbol is given by  $^{2S+1}L_J$ . The left-hand superscript of the term is the spin multiplicity, given by  $2S+1$  and the right-hand subscript is given by  $J$ . It should be noted that  $S$  is used to represent two things- (a) total spin angular momentum and (b) and total angular momentum when  $L = 0$ . The above rules are illustrated with examples.

For  $d^4$  configuration:

	↑	↑	↑	↑	
$m_l$	+2	+1	0	-1	-2

Hence,  $L = 3 - 1 = 2$  i.e., D;  $S = 2$ ;  $2S+1 = 5$ ; and  $J = L - S = 0$ ; Term symbol =  $^5D_0$

For  $d^9$  configuration:

	↓↑	↓↑	↓↑	↓↑	↑
$m_l$	+2	+1	0	-1	-2

Hence,  $L = +2+1+0-1 = 2$  i.e., D;  $S = 1/2$ ;  $2S+1 = 2$ ; and  $J = L + S = 3/2$ ; Term symbol =  $^2D_{5/2}$

Spin multiplicity indicates the number of orientations in the external field. If the spin multiplicity is three, there will be three orientations in the magnetic field.- parallel, perpendicular and opposed. There are similar orientations in the angular momentum in an external field.

The spectroscopic term symbols for  $d^n$  configurations are given in the Table-1. The terms are read as follows: The left-hand superscript of the term symbol is read as singlet, doublet, triplet, quartet, quintet, sextet, septet, octet, etc., for spin multiplicity values of 1, 2, 3, 4, 5, 6, 7, 8, etc., respectively.  $^1S_0$  (singlet S nought);  $^2S_{1/2}$  (doublet S one-half);  $^3P_2$  (triplet P two );  $^5I_8$  (quintet I eight). It is seen from the Table-1 that  $d^n$  and  $d^{10-n}$  have same term symbols, if we ignore J values. Here n stands for the number of electrons in  $d^n$  configuration.

$d^n$	Term	$d^n$	Term
$d^0$	$^1S_0$	$d^{10}$	$^1S_0$
$d^1$	$^2D_{3/2}$	$d^9$	$^2D_{5/2}$
$d^2$	$^3F_2$	$d^8$	$^3F_4$
$d^4$	$^5D_0$	$d^6$	$^5D_4$
$d^5$	$^6S_{5/2}$		

**Table 1.** Term symbols

It is also found that empty sub-shell configurations such as  $p^0$ ,  $d^0$ ,  $f^0$ , etc., and full filled sub-shell configurations such as  $p^6$ ,  $d^{10}$ ,  $f^{14}$ , etc., have always the term symbol  $^1S_0$  since the resultant spin and angular momenta are equal to zero. All the inert gases have term symbols for their ground state  $^1S_0$ . Similarly all alkali metals reduce to one electron problems since closed shell core contributes nothing to L, S and J; their ground state term symbol is given by  $^2S_{1/2}$ . Hence d electrons are only of importance in deciding term symbols of transition metals.

## 5. Total degeneracy

We have seen that the degeneracy with regard to spin is its multiplicity which is given by  $(2S+1)$ . The total spin multiplicity is denoted by  $M_s$  running from S to -S. Similarly orbital

degeneracy,  $M_L$ , is given by  $(2L+1)$  running from  $L$  to  $-L$ . For example,  $L=2$  for D state and so the orbital degeneracy is  $(2 \times 2 + 1) = 5$  fold. Similarly, for F state, the orbital degeneracy is seven fold. Since there are  $(2L+1)$  values of  $M_L$ , and  $(2S+1)$  values of  $M_S$  in each term, the total degeneracy of the term is given by:  $2(L+1)(2S+1)$ .

Each value of  $M_L$  occurs  $(2S+1)$  times and each value of  $M_S$  occurs  $(2L+1)$  times in the term. For  $^3F$  state, the total degeneracy is  $3 \times 7 = 21$  fold and for the terms  $^3P$ ,  $^1G$ ,  $^1D$ ,  $^1S$ , the total degeneracy is 9,9,5,1 fold respectively. Each fold of degeneracy represents one microstate.

## 6. Number of microstates

The electrons may be filled in orbitals by different arrangements since the orbitals have different  $m_l$  values and electrons may also occupy singly or get paired. Each different type of electronic arrangement gives rise to a microstate. Thus each electronic configuration will have a fixed number of microstates. The numbers of microstates for  $p^2$  configuration are given in Table-2 (for both excited and ground states).

$m_l$		$\uparrow$	$\uparrow$		$\downarrow$	$\downarrow$		$\downarrow$	$\downarrow$			$\uparrow$			$\uparrow\downarrow$
0	$\uparrow$		$\uparrow$	$\downarrow$		$\downarrow$	$\downarrow$		$\uparrow$	$\uparrow$	$\uparrow$	$\downarrow$		$\uparrow\downarrow$	
+1	$\uparrow$	$\uparrow$		$\downarrow$	$\downarrow$		$\uparrow$	$\uparrow$		$\downarrow$	$\downarrow$		$\uparrow\downarrow$		
$m_L$	+1	0	-1	+1	0	-1	+1	0	-1	+1	+1	-1	+2	0	

**Table 2.** Number of microstates for  $p^2$  configuration

Each vertical column is one micro state. Thus for  $p^2$  configuration, there are 15 microstates. In the above diagram, the arrangement of singlet states of paired configurations given in A (see below) is not different from that given in B and hence only one arrangement for each  $m_l$  value.

$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\downarrow$	$\downarrow\uparrow$
A	B	A	B

The number of microstates possible for any electronic configuration may be calculated from the formula,

$$\text{Number of microstates} = n! / r! (n - r)!$$

Where  $n$  is the twice the number of orbitals,  $r$  is the number of electrons and  $!$  is the factorial.

For  $p^2$  configuration,  $n = 3 \times 2 = 6$ ;  $r = 2$ ;  $n - r = 4$

$$6! = 6 \times 5 \times 4 \times 3 \times 2 \times 1 = 720; 2! = 2 \times 1 = 2; 4! = 4 \times 3 \times 2 \times 1 = 24$$

Substituting in the formula, the number of microstates is 15.

Similarly for a d<sup>2</sup> configuration, the number of microstates is given by 10! / 2! (10 – 2)!

$$\frac{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1 (8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1)} = 45$$

Thus a d<sup>2</sup> configuration will have 45 microstates. Microstates of different d<sup>n</sup> configuration are given in Table-3.

d <sup>n</sup> configuration	d <sup>1</sup> ,d <sup>9</sup>	d <sup>2</sup> ,d <sup>8</sup>	d <sup>3</sup> ,d <sup>7</sup>	d <sup>4</sup> ,d <sup>6</sup>	d <sup>5</sup>	d <sup>10</sup>
No.of microstates	10	45	120	210	252	1

**Table 3.** Microstates of different d<sup>n</sup> configuration

**7. Multiple term symbols of excited states**

The terms arising from d<sup>n</sup> configuration for 3d metal ions are given Table-4.

Configuration	Ion	Term symbol
d <sup>1</sup> d <sup>9</sup>	Ti <sup>3+</sup> ,V <sup>4+</sup> Cu <sup>2+</sup>	<sup>2</sup> D
d <sup>2</sup> d <sup>8</sup>	Ti <sup>2+</sup> ,V <sup>3+</sup> ,Cr <sup>4+</sup> Ni <sup>2+</sup>	<sup>3</sup> F, <sup>3</sup> P, <sup>1</sup> G, <sup>1</sup> D, <sup>1</sup> S
d <sup>3</sup> d <sup>7</sup>	Cr <sup>3+</sup> ,V <sup>2+</sup> ,Mn <sup>4+</sup> Ni <sup>3+</sup> ,Co <sup>2+</sup>	<sup>4</sup> F, <sup>4</sup> P, <sup>2</sup> ( H, G, F, D, D, P)
d <sup>4</sup> d <sup>6</sup>	Cr <sup>2+</sup> ,Mn <sup>3+</sup> Fe <sup>2+</sup> ,Co <sup>3+</sup>	<sup>5</sup> D , <sup>3</sup> ( H, G, F, F, , D, P, P ), <sup>1</sup> (I ,G, G, F, D, D, S,S)
d <sup>5</sup> d <sup>10</sup>	Mn <sup>2+</sup> , Fe <sup>3+</sup> Zn <sup>2+</sup>	<sup>6</sup> S, <sup>4</sup> (G, F, D, P), <sup>2</sup> (I, H, G, G, F, F), <sup>2</sup> (D, D, D, P, S) <sup>6</sup> S

**Table 4.** Terms arising from d<sup>n</sup> configuration for 3d ions (n=1 to10)

## 8. Selection rules

### 8.1. La Porte selection rule

This rule says that transitions between the orbitals of the same sub shell are forbidden. In other words, the for total orbital angular momentum is  $\Delta L = \pm 1$ . This is La Porte allowed transitions. Thus transition such as  $^1S \rightarrow ^1P$  and  $^2D \rightarrow ^2P$  are allowed but transition such as  $^3D \rightarrow ^3S$  is forbidden since  $\Delta L = -2$ . That is, transition should involve a change of one unit of angular momentum. Hence transitions from *gerade* to *ungerade* (*g* to *u*) or vice versa are allowed, i.e.,  $u \rightarrow g$  or  $g \rightarrow u$  but not  $u \rightarrow u$  or  $g \rightarrow g$ . In the case of p sub shell, both ground and excited states are odd and in the case of d sub shell both ground and excited states are even. As a rule transition should be from even to odd or vice versa.

The same rule is also stated in the form of a statement instead of an equation:

*Electronic transitions within the same p or d sub-shell are forbidden, if the molecule has centre of symmetry.*

### 8.2. Spin selection rule

The selection Rule for Spin Angular Momentum is

$$\Delta S = 0$$

Thus transitions such as  $^2S \rightarrow ^2P$  and  $^3D \rightarrow ^3P$  are allowed, but transition such as  $^1S \rightarrow ^3P$  is forbidden. The same rule is also stated in the form of a statement,

*Electronic Transitions between the different states of spin multiplicity are forbidden.*

The selection Rule for total angular momentum, J, is

$$\Delta J = 0 \text{ or } \pm 1$$

The transitions such as  $^2P_{1/2} \rightarrow ^2D_{3/2}$  and  $^2P_{3/2} \rightarrow ^2D_{3/2}$  are allowed, but transition such as  $^2P_{1/2} \rightarrow ^2D_{5/2}$  is forbidden since  $\Delta J = 2$ .

There is no selection rule governing the change in the value of n, the principal quantum number. Thus in hydrogen, transitions such as  $1s \rightarrow 2p$ ,  $1s \rightarrow 3p$ ,  $1s \rightarrow 4p$  are allowed.

Usually, electronic absorption is indicated by reverse arrow,  $\leftarrow$ , and emission is indicated by the forward arrow,  $\rightarrow$ , though this rule is not strictly obeyed.

### 8.3. Mechanism of breakdown of selection rules

#### 8.3.1. Spin-orbit coupling

For electronic transition to take place,  $\Delta S = 0$  and  $\Delta L = \pm 1$  in the absence of spin-orbit coupling. However, spin and orbital motions are coupled. Even, if they are coupled very weakly, a little of each spin state mixes with the other in the ground and excited states by an amount dependent

upon the energy difference in the orbital states and magnitude of spin-orbit coupling constant. Therefore electronic transitions occur between different states of spin multiplicity and also between states in which  $\Delta L$  is not equal to  $\pm 1$ . For example, if the ground state were 99% singlet and 1% triplet (due to spin-orbit coupling) and the excited state were 1% singlet and 99% triplet, then the intensity would derive from the triplet-triplet and singlet-singlet interactions. Spin-orbit coupling provides small energy differences between degenerate state.

This coupling is of two types. The single electron spin orbit coupling parameter  $\zeta$ , gives the strength of the interaction between the spin and orbital angular momenta of a single electron for a particular configuration. The other parameter,  $\lambda$ , is the property of the term. For high spin complexes,

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

Here positive sign holds for shells less than half filled and negative sign holds for more than half filled shells.  $S$  is the same as the one given for the free ion. The  $\lambda$  values in crystals are close to their free ion values.  $\lambda$  decreases in crystal with decreasing Racah parameters  $B$  and  $C$ . For high spin  $d^5$  configuration, there is no spin orbit coupling because  $^6S$  state is unaffected by the ligand fields. The  $\lambda$  and  $\zeta$  values for 3d series are given in Table-5.

Ion	Ti(II)	V(II)	Cr(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)
$\Xi$ (cm <sup>-1</sup> )	121	167	230	347	410	533	649
$\lambda$ (cm <sup>-1</sup> )	60	56	57	0	-102	-177	-325

**Table 5.**  $\lambda$  and  $\zeta$  values for 3d series

### 8.3.2. La Porte selection rule

Physically 3d (even) and 4p (odd) wave functions may be mixed, if centre of inversion (i) is removed. There are two processes by which i is removed.

- The central metal ion is placed in a distorted field (tetrahedral field, Tetragonal distortions, etc.) The most important case of distorted or asymmetric field is the case of a tetrahedral complex. Tetrahedron has no inversion centre and so d-p mixing takes place. So electronic transitions in tetrahedral complexes are much more intense, often by a factor 100, than in a analogous octahedral complexes. *Trans* isomer of  $[\text{Co(en)}_2\text{Cl}_2]^+$  in aqueous solution is three to four times less intense than the *cis* isomer because the former is centro-symmetric. Other types of distortion include Jahn-Teller distortions.
- Odd vibrations of the surrounding ligands create the distorted field for a time that is long enough compared to the time necessary for the electronic transition to occur (Franck Condon Principle). Certain vibrations will remove the centre of symmetry. Mathematically this implies coupling of vibrational and electronic wave functions. Breaking down of La Porte rule by vibronic coupling has been termed as "Intensity Stealing". If the forbidden excited term lies energetically nearby a fully allowed transition, it would produce a very intense band. Intensity Stealing by this mechanism decreases in magnitude with increasing energy separation between the excited term and the allowed level.



## 9. Splitting of energy states

The symbols **A**(or **a**) and **B** (or **b**) with any suffixes indicate wave functions which are singly degenerate. Similarly **E** (or **e**) indicates double degeneracy and **T** (or **t**) indicates triple degeneracy. Lower case symbols,  $a_{1g}$ ,  $a_{2g}$ ,  $e_g$ , etc., are used to indicate electron wave functions (orbitals) and upper case symbols are used to describe electronic energy levels. Thus  ${}^2T_g$  means an energy level which is triply degenerate with respect to orbital state and also doubly degenerate with respect to its spin state. Upper case symbols are also used without any spin multiplicity term and they then refer to symmetry (ex.,  $A_{1g}$  symmetry). The subscripts **g** and **u** indicate *gerade* (even) and *ungerade* (odd).

**d** orbitals split into two sets -  $t_{2g}$  orbitals and  $e_g$  orbitals under the influence of crystal field. These have  $T_{2g}$  and  $E_g$  symmetry respectively. Similarly **f** orbitals split into three sets -  $a_{2u}$  ( $f_{xyz}$ ),  $t_{2u}$  ( $f_x(y^2-z^2)$ ,  $f_y(z^2-x^2)$ ,  $f_z(x^2-y^2)$ ) and  $t_{1u}$  ( $f_x^3$ ,  $f_y^3$ ,  $f_z^3$ ). These have symmetries  $A_{2u}$ ,  $T_{2u}$  and  $T_{1u}$  respectively.

Splitting of **D** state parallels the splitting of **d** orbitals and splitting of **F** state parallels splitting of **f** orbitals. For example, **F** state splits into either  $T_{1u}$ ,  $T_{2u}$  and  $A_{2u}$  or  $T_{1g}$ ,  $T_{2g}$  and  $A_{2g}$  sub-sets. Which of these is correct is determined by **g** or **u** nature of the configuration from which **F** state is derived. Since **f** orbitals are **u** in character  ${}^2F$  state corresponding to  $f^1$  configuration splits into  ${}^2T_{1u}$ ,  ${}^2T_{2u}$ , and  ${}^2A_{2u}$  components; similarly  ${}^3F$  state derived from  $d^2$  configuration splits into  ${}^3T_{2g}$ ,  ${}^3T_{1g}$  and  ${}^3A_{2g}$  components because **d** orbitals are **g** in character.

### 9.1. Splitting of energy states corresponding to $d^n$ terms

These are given in Table-6.

Energy	Sub- states
S	$A_1$
P	$T_1$
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$
H	$E + T_1 + T_1 + T_2$
I	$A_1 + A_2 + E + T_1 + T_2 + T_2$

**Table 6.** Splitting of energy states corresponding to  $d^n$  terms

The d-d spectra is concerned with  $d^n$  configuration and hence the crystal field sub-states are given for all the  $d^n$  configuration in Table -7.

<i>Configuration</i>	<i>Free ion ground state</i>	<i>Crystal field substates</i>	<i>Important excited states</i>	<i>Crystal field state</i>
$d^1, d^9$	$^2D$	$^2T_{2g}, ^2E_g$		
$d^2, d^8$	$^3F$	$^3T_{1g}, ^3T_{2g}, ^3A_{2g}$	$^3P$	$^3T_{1g}$
$d^3, d^7$	$^4F$	$^4T_{1g}, ^4T_{2g}, ^4A_{2g}$	$^4P$	$^4T_{1g}$
$d^4, d^6$	$^5D$	$^5T_{2g}, ^5E_g$		
$d^5$	$^6S$	$^6A_{1g}$		

**Table 7.** Crystal field components of the ground and some excited states of  $d^n$  ( $n=1$  to  $9$ ) configuration

## 10. Energy level diagram

Energy Level Diagrams are described by two independent schemes - Orgel Diagrams which are applicable to weak field complexes and Tanabe –Sugano (or simply T-S) Diagrams which are applicable to both weak field and strong field complexes.

## 11. Inter-electronic repulsion parameters

The inter-electronic repulsions within a configuration are linear combinations of Coulombic and exchange integrals above the ground term. They are expressed by either of the two ways: Condon - Shortley parameters,  $F_0$ ,  $F_2$  and  $F_4$  and Racah parameters,  $A$ ,  $B$  and  $C$ . The magnitude of these parameters varies with the nature of metal ion.

### 11.1. Racah parameters

The Racah parameters are  $A$ ,  $B$  and  $C$ . The Racah parameter  $A$  corresponds to the partial shift of all terms of a given electronic configuration. Hence in the optical transition considerations, it is not taken into account. The parameter,  $B$  measures the inter electronic repulsion among the electrons in the  $d$ -orbitals. The decrease in the value of the interelectronic repulsion parameter,  $B$  leads to formation of partially covalent bonding. The ratio between the crystal  $B^1$  parameter and the free ion  $B$  parameter is known as nephelauxetic ratio and it is denoted by  $\beta$ . The value of  $\beta$  is a measure of covalency. The smaller the value, the greater is the covalency between the metal ion and the ligands. The  $B$  and  $C$  values are a measure of spatial arrangement of the orbitals of the ligand and the metal ion.

Racah redefined the empirical Condon –Shortley parameters so that the separation between states having the maximum multiplicity (for example, difference between is a function of  $^3F$  and  $^3P$  or  $^4F$  and  $^4P$  is a function of a single parameter,  $B$ . However, separations between terms of different multiplicity involve both  $B$  and  $C$

## 12. Tanabe –Sugano diagrams

Exact solutions for the excited state energy levels in terms of  $Dq$ ,  $B$  and  $C$  are obtained from Tanabe-Sugano matrices. However, these are very large ( $10 \times 10$ ) matrices and hand calculations are not feasible. For this reason Tanabe-Sugano have drawn energy level diagrams known as T-S diagrams or energy level diagrams. The T-S diagrams are valid only if the value of  $B$ ,  $C$  and  $Dq$  are lower for a complex than for the free ion value.

Quantitative interpretation of electronic absorption spectra is possible by using Tanabe – Sugano diagrams or simply T-S diagrams. These diagrams are widely employed to correlate and interpret spectra for ions of all types, from  $d^2$  to  $d^8$ . Orgel diagrams are useful only qualitatively for high spin complexes whereas T-S diagrams are useful both for high spin and low spin complexes. The x-axis in T-S diagrams represent the ground state term. Further, in T-S diagrams, the axes are divided by  $B$ , the interelectronic repulsion parameter or Racah Parameter. The x-axis represents the crystal field strength in terms of  $Dq/B$  or  $\Delta/B$  and the Y-axis represents the energy in terms of  $E/B$ .

The energies of the various electronic states are given in the T-S diagrams on the vertical axis and the ligand field strength increases from left to right on the horizontal axis. The symbols in the diagram omit the subscript,  $g$ , with the understanding that all states are *gerade* states. Also, in T.S. diagrams, the zero of energy for any particular  $d^n$  ion is taken to be the energy of the ground state. Regardless of the ligand field strength, then, the horizontal axis represents the energy of the ground state because the vertical axis is in units of  $E/B$  and x-axis is also in units of  $\Delta/B$ . Thus, the unit of energy in T-S diagram is  $B$ , Racah Parameter.

The values of  $B$  are different for different ions of the same  $d^n$  (or different  $d^n$  configuration) which is shown on the top of each diagram. One T-S diagram is used for all members of an isoelectronic group. Also some assumption is made about the relative value of  $C/B$ .

## 13. Electron spin resonance

Electron Spin Resonance (ESR) is a branch of spectroscopy in which radiation of microwave frequency is absorbed by molecules possessing electrons with unpaired spins. It is known by different names such as Electron Paramagnetic Resonance (EPR), Electron Spin Resonance (ESR) and Electron Magnetic Resonance (EMR). This method is an essential tool for the analysis of the structure of molecular systems or ions containing unpaired electrons, which have spin-degenerate ground states in the absence of magnetic field. In the study of solid state materials, EPR method is employed to understand the symmetry of surroundings of the paramagnetic ion and the nature of its bonding to the nearest neighbouring ligands.

When a paramagnetic substance is placed in a steady magnetic field ( $H$ ), the unpaired electron in the outer shell tends to align with the field. So the two fold spin degeneracy is

removed. Thus the two energy levels,  $E_{1/2}$  and  $E_{-1/2}$  are separated by  $g\beta H$ , where  $g$  is spectroscopic splitting factor and is called gyro magnetic ratio and  $\beta$  is the Bohr magneton. Since there is a finite probability for a transition between these two energy levels, a change in the energy state can be stimulated by an external radio frequency. When microwave frequency ( $\nu$ ) is applied perpendicular to the direction of the field, resonance absorption will occur between the two split spin levels. The resonance condition is given by,  $h\nu = g\beta H$ , where  $h$  is Planck's constant.

The resonance condition can be satisfied by varying  $\nu$  or  $H$ . However, EPR studies are carried out at a constant frequency ( $\nu$ ), by varying magnetic field ( $H$ ). For a free electron, the  $g$  value is 2.0023. Since  $h$  and  $\beta$  are constants, one can calculate the  $g$  factor. This factor determines the divergence of the Zeeman levels of the unpaired electron in a magnetic field and is characteristic of the spin system.

In the crystal systems, the electron spins couple with the orbital motions and the  $g$  value is a measure of the spin and orbital contributions to the total magnetic moment of the unpaired electron and any deviation of magnetic moment from the free spin value is due to the spin-orbit interaction. It is known that the crystal field removes only the orbital degeneracy of the ground terms of the central metal ion either partially or completely. The strong electrical fields of the surrounding ligands results in "Stark Splitting" of the energy levels of the paramagnetic ion. The nature and amount of splitting strongly depends on the symmetry of the crystalline electric field. The Stark splitting of the free ion levels in the crystal field determines the magnetic behaviour of the paramagnetic ion in a crystal. Whenever there is a contribution from the unquenched orbital angular momentum, the measured  $g$  values are isotropic as a result of the asymmetric crystal field since the contribution from the orbital motion is anisotropic. To decide the ultimate ground state of a paramagnetic ion in the crystal, the two important theorems, Kramers and Jahn-Teller, are useful. Using group theory, one can know the nature of the splitting of the free ion levels in the crystal fields of various symmetries.

Jahn-Teller theorem states that any nonlinear molecule in an electronically degenerate ground state is unstable and tends to distort in order to remove this degeneracy. The direction of distortion which results in greatest stabilization can often be deduced from EPR and other spectroscopic data.

Kramers' theorem deals with restrictions to the amount of spin degeneracy which can be removed by a purely electrostatic field. If the system contains an odd number of electrons, such an electrostatic field cannot reduce the degeneracy of any level below two. Each pair forms what is known as a Kramers' doublet, which can be separated only by a magnetic field. For example, Fe(III) and Mn(II) belonging to  $d^5$  configuration, exhibit three Kramers' doublets labeled as  $|\pm 5/2\rangle$ ,  $|\pm 3/2\rangle$  and  $|\pm 1/2\rangle$ .

If the central metal ion also possesses a non-zero nuclear spin,  $I$ , then hyperfine splitting occurs as a result of the interaction between the nuclear magnetic moment and the electronic magnetic moment. The measurement of  $g$  value and hyperfine splitting factor provides