

## B.Sc. SEM-VI

## US06CCHE22 INORGANIC CHEMISTRY

## Unit-3(A) Term Symbol (B) Electronic spectra of metal complexes

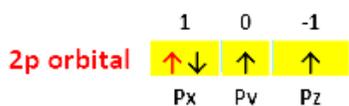
**QUANTUM NUMBER:** To completely describe an electron in an atom, four quantum numbers are needed: energy ( $n$ ), angular momentum ( $\ell$ ), magnetic moment ( $m_\ell$ ), and spin ( $m_s$ ).

The first quantum number describes the electron shell, or energy level, of an atom. The value of  $n$  ranges from 1 to the shell containing the outermost electron of that atom.

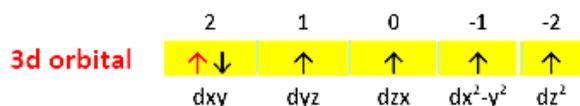
Number	Symbol	Possible Values
Principle Quantum Number	N	1, 2, 3, 4, ....
Angular Momentum Quantum Number	L	0, 1, 2, 3, ..., (n-1)
Magnetic Quantum Number	$m_l$	-l, ..., -1, 0, +1, ..., +l
Spin Quantum Number	$m_s$	+1/2, -1/2

$n$	$l$	$M_l$	Number of orbitals	Orbital Name	Number of electrons
1	0	0	1	1s	2
2	0	0	1	2s	2
	1	-1, 0, +1	3	2p	6
3	0	0	1	3s	2
	1	-1, 0, +1	3	3p	6
	2	-2, -1, 0, +1, +2	5	3d	10
4	0	0	1	4s	2
	1	-1, 0, +1	3	4p	6
	2	-2, -1, 0, +1, +2	5	4d	10
	3	-3, -2, -1, 0, +1, +2, +3	7	4f	14

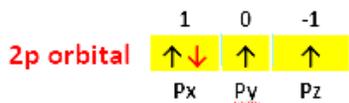
Example: To find out all the QUANTUM NO. of selected (red) electrons



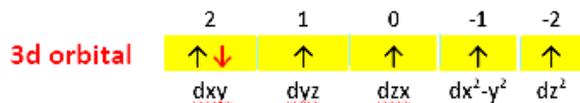
$$n = 2, l = 1, m_l = +1, m_s = +1/2$$



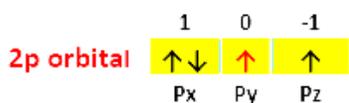
$$n = 3, l = 2, m_l = +2, m_s = +1/2$$



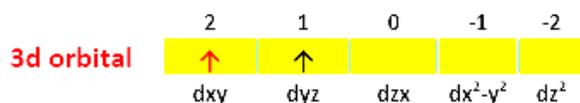
$$n = 2, l = 1, m_l = +1, m_s = -1/2$$



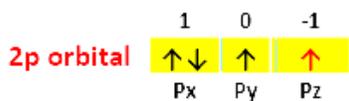
$$n = 3, l = 2, m_l = +2, m_s = -1/2$$



$$n = 2, l = 1, m_l = 0, m_s = +1/2$$



$$n = 3, l = 2, m_l = +2, m_s = +1/2$$



$$n = 2, l = 1, m_l = -1, m_s = +1/2$$

## Term Symbols

“The symbol which indicates electronic configuration & different energy states of atom is called term symbol.”

Term symbol represented as  $^{2S+1}L_J$

HN Russell and FA Saunders introduced a system to fully represent the position of electrons in an atom. According to this method, in a multi-electron system, many different arrangements of electrons is possible. Term symbol is given for ground state arrangement which follow all the law i.e. Hund, Pauli, Aufbau etc,. Term symbol is assign using R-S coupling scale or L-S coupling scale.

### The Russell-Saunders coupling scheme (or R-S coupling or L-S coupling):

It is applied to smaller atoms ( $Z < 30$ ) having less interactions between spin and orbital angular momentum.

The term symbol for ground state configuration is in the form of  $^{2S+1}L_J$

Where,  $2S + 1$  is spin multiplicity

L is orbital angular momentum

J is total angular momentum

All above terms are determined by calculating

(1) s-s coupling which give total spin angular momentum (S)

(2) l-l coupling which give total orbital angular momentum (L)

(3) L-S coupling which give total angular momentum (J)

**(1) s-s coupling (S):** The value of the resulting spin angular momentum is obtained from the unpaired electrons in the outer orbit of the atom.

Total spin angular momentum (S) = Total available spin =  $s_1 + s_2 + s_3 \dots$

Example:  $P^3$

↑	↑	↑
+1	0	-1

$$S = s_1 + s_2 + s_3 \dots$$

$$= 1/2 + 1/2 + 1/2 = 3/2$$

Using value of S, spin multiplicity can be dermine as

$$2S + 1 = 2(3/2) + 1 = 3$$

Hence spin angular momentum is sum of spin of each unpaired electron. (Paired electrons spins are cancel due to the opposite spin).

**(2) l-l coupling (L):** It give total orbital angular momentum which is total of the orbital angular momentum l of each electron.

$$L = ml_1 + ml_2 + ml_3 \dots$$

Value of L is assigned by term given below in term symbol.

<b>L</b>	0	1	2	3	4	5	6
<b>Term</b>	S	P	D	F	G	H	I

Example: For  $d^7$

↑↓	↑↓	↑	↑	↑
ml = +2	+1	0	-1	-2

$$L = \text{number of electron} \times \text{angular momentum} = n \times ml$$

$$= 2(+2) + 2(+1) + 1(0) + 1(-1) + 1(-2)$$

$$= 4 + 2 + 0 - 1 - 2 = 3 = f$$

**(3) L-S coupling:** The total orbital angular momentum (L) is coupled with the total spin angular momentum (S) to give total angular momentum (J). Hence value of J are range from L+S to L-S.

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

Example: For  $P^2$  we have value of S =1 and L =1

$$\therefore J = (L + S) \dots \dots (L - S)$$

$$= (1 + 1) \dots \dots (1 - 1)$$

$$= 2 \dots 0$$

$$= 2, 1, 0$$

For less than half-filled orbital, minimum value of J will be used and for more than half-filled orbital, maximum value of J is used.

$$\therefore J = 0 \text{ for } P^2$$

**The ground state term for free ion with  $P^3$  configuration:**

↑	↑	↑
+1	0	-1

L = orbital quantum number

$$= 1(+1) + 1(0) + 1(-1) = 0, \therefore S \text{ term}$$

S = total spin quantum number

$$= \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$\therefore 2S + 1 = 4$$

J = total angular momentum quantum number

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

$$= (0 + \frac{3}{2}) \dots \dots \dots (0 - \frac{3}{2})$$

$$= \frac{3}{2} \dots \dots \dots \frac{3}{2}$$

$$= \frac{3}{2}$$

$\therefore$  The ground state term for a free ion with  $P^3$  configuration is  $^{2S+1}S_J = ^4S_{3/2}$

**The ground state term for free ion with  $P^2$  configuration:**

↑	↑	
+1	0	-1

L = orbital quantum number

$$= 1(+1) + 1(0) + 0(-1) = 1, \therefore S \text{ term}$$

S = total spin quantum number

$$= \frac{1}{2} + \frac{1}{2} = 1$$

$$\therefore 2S + 1 = 3$$

J = total angular momentum quantum number

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

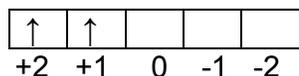
$$= (1 + 1) \dots \dots \dots (1 - 1)$$

$$= \frac{3}{2} \dots \dots \dots \frac{3}{2}$$

$$= \frac{3}{2}$$

$\therefore$  The ground state term for a free ion with  $P^2$  configuration is  $^{2S+1}S_J = ^4S_{3/2}$

The ground state term for free ion with  $d^2$  configuration:



$L$  = orbital quantum number

$$= 1(+2) + 1(+1) + 0(0) + 0(-1) + 0(-2) = 3, \therefore F \text{ term}$$

$S$  = total spin quantum number

$$= \frac{1}{2} + \frac{1}{2} = 1$$

$$\therefore 2S + 1 = 3$$

$J$  = total angular momentum quantum number

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

$$= (3 + 1) \dots \dots \dots (3 - 1)$$

$$= 4 \dots \dots \dots 2$$

$$= 4, 3, 2$$

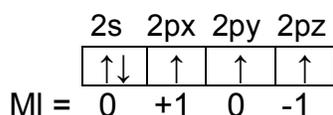
$\therefore$  The possible term for  $d^3$  configuration is  $^{2S+1}F_J = {}^3F_2, {}^3F_3, {}^3F_4$

Now, for less than half-filled orbital, minimum value of  $J$  will be used.

$\therefore$  The ground state term for a free ion with  $d^3$  configuration is  ${}^3F_2$

**QUE: Determined the ground state from term symbol for (1)  ${}^7N$  and (2)  ${}^{26}Fe$**

(1)  ${}^7N : 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$



$L$  = orbital quantum number

$$= 2(0) + 1(+1) + 1(0) + 1(-1) = 0, \therefore S \text{ term}$$

$S$  = total spin quantum number

$$= \frac{1}{2} + (-\frac{1}{2}) + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

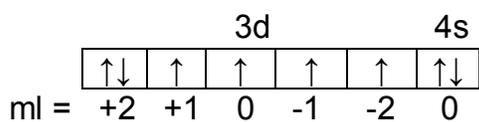
$$\therefore 2S + 1 = 2(\frac{3}{2}) + 1 = 4$$

$J$  = total angular momentum quantum number

$$= |0 + \frac{3}{2}| \dots \dots \dots |0 - \frac{3}{2}|$$

$$= \frac{3}{2}$$

$\therefore$  The term symbol is  ${}^4S_{3/2}$  (quartet S three by two)



L = orbital quantum number

$$= 2(2) + 1(+1) + 1(0) + 1(-1) = 1(-2) + 2(0) = 2, \therefore \text{D term}$$

S = total spin quantum number

$$= 0 + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + 0 = 2$$

$$\therefore 2S + 1 = 2(2) + 1 = 5$$

J = total angular momentum quantum number

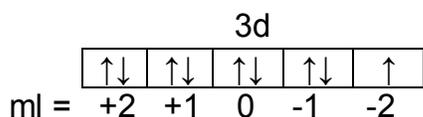
$$= |2 + 2| \dots \dots \dots |2 - 2|$$

$$= 4, 3, 2, 1, 0$$

Now for more than half-filled orbital, maximum value of J is used.

$\therefore$  The term symbol is  $^5D_4$  (quintet D four)

**QUE: Derive the ground state term for free ion with  $d^9$ .**



L = orbital quantum number

$$= 2(2) + 2(+1) + 2(0) + 2(-1) = 1(-2) = 2, \therefore \text{D term}$$

S = total spin quantum number

$$= 0 + 0 + 0 + 0 + \frac{1}{2} = 1/2$$

$$\therefore 2S + 1 = 2(1/2) + 1 = 2$$

J = total angular momentum quantum number

$$= (2 + \frac{1}{2}) \dots \dots \dots (2 - \frac{1}{2})$$

$$= (5/2) \dots \dots \dots (3/2)$$

$$= 5/2, 4/2, 3/2$$

Now for more than half-filled orbital, maximum value of J is used.

$\therefore$  The term symbol is  $^2D_{5/2}$

**QUE: Find L, S and J value of  $^3F$  and  $^1S$ .**

**For  $^3F$ :**

$$^{2S+1}L_J = ^3F$$

$$\therefore 2S + 1 = 3$$

$$\therefore 2S = 2$$

$$\therefore \mathbf{S = 1}$$

$$\therefore \text{no. of unpaired electrons} = 2$$

Now, term symbol is F. Therefore  $\mathbf{L = 3}$ .

$$\begin{aligned} J &= (L + S) \dots\dots (L - S) \\ &= (3 + 1) \dots\dots (3 - 1) \\ &= \mathbf{4, 3, 2} \end{aligned}$$

**For  $^1S$ :**

$$^{2S+1}L_J = ^1S$$

$$\therefore 2S + 1 = 1$$

$$\therefore 2S = 0$$

$$\therefore \mathbf{S = 0}$$

$$\therefore \text{no. of unpaired electrons} = 0$$

Now, term symbol is S. Therefore  $\mathbf{L = 0}$ .

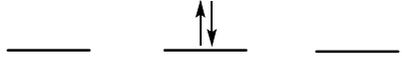
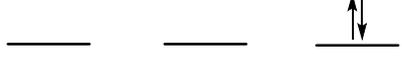
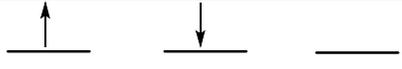
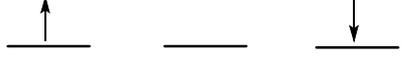
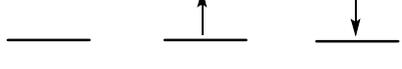
$$\begin{aligned} J &= (L + S) \dots\dots (L - S) \\ &= (0 + 0) \dots\dots (0 - 0) \\ &= \mathbf{0} \end{aligned}$$

**Determination of term symbols for  $p^2$  configuration (of carbon atom):**

(The electronic configuration of C is  $1s^2 2s^2 2p^2$  in ground state. Since 2s and 2p orbital are full-filled, the electrons of these orbital do not contribute anything for determination of term symbols for C. Thus, we consider two electrons of  $2p^2$  configuration only).

The two electrons of  $p^2$  configuration (of carbon) can be arranged in three p orbitals in following different ways.

<b>Fig: 1 Electron with parallel spins</b>				
	$L = +1$	$0$	$-1$	
<b>(a)</b>	↑ —	↑ —	—	$L = 1(+1) + 1(0) + 0(-1) = +1$ $S = \frac{1}{2} + \frac{1}{2} = 1$ $2S + 1 = 3$
<b>(b)</b>	↑ —	—	↑ —	$L = 1(+1) + 0(0) + 1(-1) = 0$ $S = \frac{1}{2} + \frac{1}{2} = 1$ $2S + 1 = 3$
<b>(c)</b>	—	↑ —	↑ —	$L = 0(+1) + 1(0) + 1(-1) = -1$ $S = \frac{1}{2} + \frac{1}{2} = 1$ $2S + 1 = 3$

Fig: 2 Electron with opposite spins		
(a)		$L = 2(+1) + 0(0) + 0(-1) = +2$ $S = \frac{1}{2} + (-\frac{1}{2}) = 0$ $2S + 1 = 1$
(b)		$L = 0(+1) + 2(0) + 0(-1) = 0$ $S = \frac{1}{2} + (-\frac{1}{2}) = 0$ $2S + 1 = 1$
(c)		$L = 0(+1) + 0(0) + 2(-1) = -2$ $S = \frac{1}{2} + (-\frac{1}{2}) = 0$ $2S + 1 = 1$
Fig: 3 Electron with opposite spins		
(a)		$L = 1(+1) + 1(0) + 0(-1) = +1$ $S = \frac{1}{2} + (-\frac{1}{2}) = 0$ $2S + 1 = 1$
(b)		$L = 1(+1) + 0(0) + 1(-1) = 0$ $S = \frac{1}{2} + (-\frac{1}{2}) = 0$ $2S + 1 = 1$
(c)		$L = 0(+1) + 1(0) + 1(-1) = -1$ $S = \frac{1}{2} + (-\frac{1}{2}) = 0$ $2S + 1 = 1$

It may be seen from the above figure-1 that the three value of L for the three arrangement (a), (b) and (c) are +1, 0 and -1 respectively. For these values, L=1 which stands for P term. The values of 2S+1 for each arrangement is 3.

Hence, term =  $^{2S+1}L = ^3P$

It may be seen from the figure-2 that three values of L are +2, 0 and -2 while three values of L from figure-3 are +1, 0 and -1. The value of 2S+1 for all six arrangements is equal to 1. All six values (+2, 0, -1, +1, 0, -1) of L can be arranged systematically in to following two groups.

**Group(a):** Contains +2, +1, 0, -1, -2 values of L. For these values L = 2 which stands for D term and S=0 hence 2S+1=1.

Hence, term =  $^{2S+1}L = ^1D$

**Group(b):** This group has only one L value which is 0. For L=0 which stands for S term and 2S+1=1.

Hence, term =  $^{2S+1}L = ^1S$ .

Above discussion shows that for  $p^2$  configuration the terms are  $^3P$ ,  $^1D$  and  $^1S$  which are triplet P, singlet D and singlet S respectively.

**To arrange  $^1S$ ,  $^1D$  and  $^3P$  term in increasing order of their energy with the help of Hund's rule:**

**Hund's rule:**

- (1) The terms having highest value of spin multiplicity ( $2S+1$ ) is the most stable and has lowest energy. Since  $^3P$  term has highest value of ( $2S+1$ ) which is 3, is the most stable hence lowest energy.
- (2) The stability of terms having the same value of  $2S+1$  depends on their  $L$  values. The term having higher value of  $L$  is more stable hence has lowest energy. Since  $^1D$  and  $^1S$  terms have the same value of  $2S+1$ ,  $^1D$  ( $L=2$ ) which has higher value of  $L$  is more stable than  $^1S$  ( $L=1$ ) term. Hence  $^1D$  has lower energy than  $^1S$ .

The increasing order of energy of term is  $^3P < ^1D < ^1S$  -----(1)

Since  $^3D$  term has the lowest energy, this term is ground state term of  $p^2$  configuration.

**To determined J energy levels (J states) for the term symbols for  $p^2$  configuration:**

Term symbols which have J values are represented as  $^{2S+1}L_J$ . The energy levels for  $p^2$  configuration, we should find out values of J for  $^3P$ ,  $^1D$  and  $^1S$ .

**For  $^3P$ :** For this term,  $L = 1$  and  $2S+1 = 3$  or  $S=1$ . Hence J values for  $^3P$  term are given by

$$\begin{aligned} J &= (L+S)\dots\dots(L-S) \\ &= (1+1)\dots\dots(1-1) \\ &= 2, 1, 0 \end{aligned}$$

Thus, J energy level for  $^3P$  term are:  $^3P_2$ ,  $^3P_1$  and  $^3P_0$

**For  $^1D$ :** For this term,  $L = 2$  and  $2S+1 = 1$  or  $S=0$ . Hence J value for  $^1D$  term is given by

$$\begin{aligned} J &= (L+S)\dots\dots(L-S) \\ &= (2+0)\dots\dots(2-0) \\ &= 2 \end{aligned}$$

Thus, J energy level for  $^1D$  term is  $^1D_2$

**For  $^1S$ :** For this term,  $L = 0$  and  $2S+1 = 1$  or  $S=0$ . Hence J value for  $^1S$  term is given by

$$\begin{aligned} J &= (L+S)\dots\dots(L-S) \\ &= (0+0)\dots\dots(0-0) \\ &= 0 \end{aligned}$$

Thus, J energy level for  $^1S$  term is  $^1S_0$

All the energy levels can be written as:  $^3P_2$ ,  $^3P_1$ ,  $^3P_0$ ,  $^1D_2$  and  $^1S_0$ .

**To arrange the J energy levels of p<sup>2</sup> configuration in the increasing order of their energy**

The energy levels for p<sup>2</sup> configuration are <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub>, <sup>1</sup>D<sub>2</sub> and <sup>1</sup>S<sub>0</sub>.

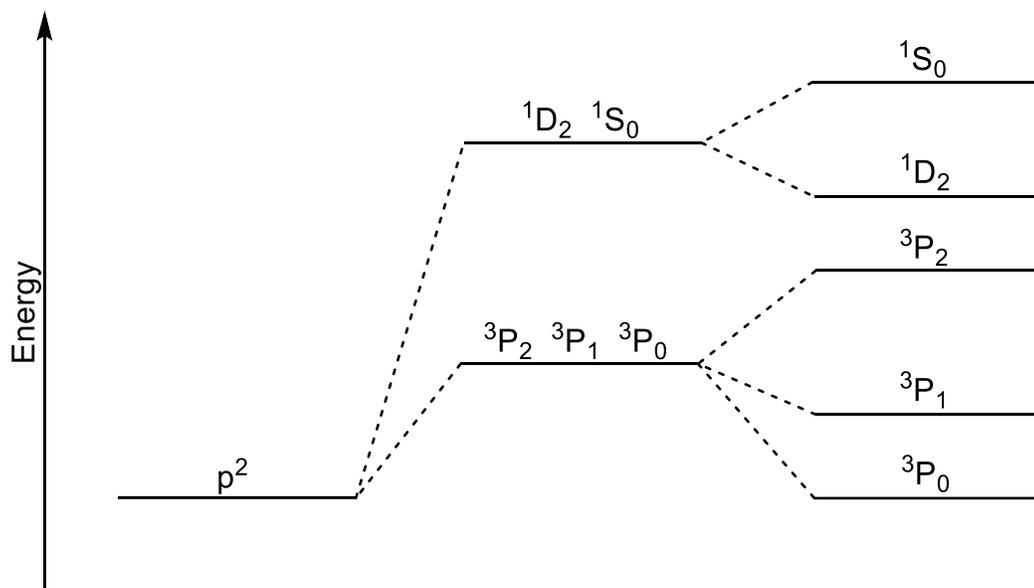
<sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub> are J energy level of <sup>3</sup>P term, which has same value of spin multiplicity (2S+1=3). So, their energy depends on their J value. With increase of J value, energy also increase (Hund's rule).

Thus, the energy is given as: <sup>3</sup>P<sub>0</sub> < <sup>3</sup>P<sub>1</sub> < <sup>3</sup>P<sub>2</sub> -----(2)

On combining energy relation (1) and (2) we get

$$^3P_0 < ^3P_1 < ^3P_2 < ^1D_2 < ^1S_0$$

Since <sup>3</sup>P<sub>0</sub> has the lowest energy, it is Russel-Saunders term for p<sup>2</sup> configuration.



**MICROSTATE:**

In a given configuration, the electrons are arrangement in many different way which have slightly different energy. These different arrangements are called microstate.

Microstates are determined by following different ways.

- (1) From electronic configuration of single sub-shell
- (2) From electronic configuration of two different sub-shell
- (3) From the term symbol without L-S coupling (J)
- (4) From the term symbol with L-S coupling (J)

**(1) To determine the microstates from electronic configuration of single sub-shell**

The total number of possible arrangements of given number of electrons are the microstate of that electronic configuration.

$$\text{No. of microstates of a given configuration} = \frac{n!}{r! (n - r)!}$$

Where n = Twice the number of orbitals in the sub shell

r = number of electrons in the given configuration

n! and r! are the factorials of n and r respectively

**Example: Calculate the number of microstates in the configurations:**

**(i)  $p^2$  (ii)  $p^3$  (iii)  $d^1$  (Answer: (i) 15 (ii) 20 (iii) 10)**

**(i)  $p^2$  configuration:**

This configuration has  $r = 2$ .

Since the number of orbitals in p sub-shell = 3,  $n = 2 \times 3 = 6$

Thus,

$$\text{No. of microstates of a given configuration} = \frac{n!}{r! (n - r)!}$$

$$\begin{aligned}\therefore \text{No. of microstates of a given configuration} &= \frac{6!}{2! (6 - 2)!} \\ &= \frac{6!}{2! \times 4!} \\ &= \frac{6 \times 5 \times 4!}{2 \times 1 \times 4!} \\ &= \frac{30}{2} \\ &= 15\end{aligned}$$

**(iii)  $d^1$  configuration:**

This configuration has  $r = 1$ .

Since the number of orbitals in d sub-shell = 5,  $n = 2 \times 5 = 10$

Thus,

$$\text{No. of microstates of a given configuration} = \frac{n!}{r! (n - r)!}$$

$$\begin{aligned}\therefore \text{No. of microstates of a given configuration} &= \frac{10!}{1! (10 - 1)!} \\ &= \frac{10!}{1! \times 9!} \\ &= \frac{10 \times 9!}{1 \times 9!} \\ &= 10\end{aligned}$$

## Number of microstates of configuration of p, d and f sub-shell

$P^n - Conf^n$	$d^n - Conf^n$	$f^n - Conf^n$
$P^1 = 6$	$d^1 = 10$	$f^1 = 14$
$P^2 = 15$	$d^2 = 45$	$f^2 = 91$
$P^3 = 20$	$d^3 = 120$	$f^3 = 364$
$P^4 = 15$	$d^4 = 210$	$f^4 = 1001$
$P^5 = 6$	$d^5 = 252$	$f^6 = 3003$
$P^6 = 1$	$d^6 = 210$	$f^7 = 3432$
	$d^7 = 120$	$f^8 = 3003$
	$d^8 = 45$	$f^9 = 2002$
	$d^9 = 10$	$f^{10} = 1001$
	$d^{10} = 1$	$f^{11} = 364$
		$f^{12} = 91$
		$f^{13} = 14$
		$f^{14} = 1$

### (2) To determine the microstates from electronic configuration of two different sub-shell

It can be calculated by multiplying microstate of one sub-shell to other sub-shell.

#### Example: To calculate the number of microstates of $p^1d^1$

For  $p^1$  term,  $n = 2 \times 3 = 6$  and  $r = 1$

For  $d^1$  term,  $n = 2 \times 5 = 10$  and  $r = 1$

$$\text{No. of microstates of a given configuration} = \frac{n!}{r! (n-r)!} \times \frac{n!}{r! (n-r)!}$$

$$\begin{aligned} \therefore \text{No. of microstates of a given configuration} &= \frac{6!}{1! (6-1)!} \times \frac{10!}{1! (10-1)!} \\ &= \frac{6!}{1! \times 5!} \times \frac{10!}{1! (9)!} \\ &= \frac{6 \times 5!}{1 \times 5!} \times \frac{10 \times 9!}{1 (9)!} \\ &= 6 \times 10 \\ &= 60 \end{aligned}$$

### (3) To determine the microstates from the term symbol without L-S coupling

Number of microstates is equal to the product of spin energy level  $(2S+1)$  and orbital energy level  $(2L+1)$  of the term. Hence, it can be calculated by the equation  $(2S+1)(2L+1)$

#### Example: To calculate microstates of $^2D$

For  $^2D$  term,  $(2S + 1)$  is 2 and  $L$  is 3

$$\therefore \text{Microstates of a given term symbol} = (2S + 1)(2L + 1)$$

$$= 2 (2 \times 2 + 1)$$

$$= 2 (5)$$

$$= 10$$

**To determine the number of microstates in term symbol of  $p^2$ :**

$^3P$ ,  $^1D$  and  $^1S$  are the term symbol of  $p^2$  configuration

No. of microstates in  $^3P$  term  $[(2S+1) = 3$  and  $L = 1]$

$$= (2S + 1) (2L + 1)$$

$$= (3) (2 \times 1 + 1)$$

$$= (3) (3)$$

$$= 9$$

No. of microstates in  $^1D$  term  $[(2S+1) = 1$  and  $L = 2]$

$$= (2S + 1) (2L + 1)$$

$$= (1) (2 \times 2 + 1)$$

$$= 5$$

No. of microstates in  $^1S$  term  $[(2S+1) = 1$  and  $L = 0]$

$$= (2S + 1) (2L + 1)$$

$$= (1) (2 \times 0 + 1)$$

$$= (1) (1)$$

$$= 1$$

Hence, total number of microstates in  $p^2$  configuration =  $9+5+1 = 15$

**Pigeonhole diagram for  $p^2$  configuration:**

Microstates of  $p^2$  are 15

L	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o
-1			↓	↓	↑↓		↑	↑		↑	↑		↓	↓	
0		↓		↑		↑		↑	↑		↓	↓		↓	↑↓
+1	↑↓	↑	↑			↑	↑		↓	↓		↓	↓		
$M_L$	+2	+1	0	-1	-2	+1	0	-1	+1	0	-1	+1	0	-1	0
$M_S$	0	0	0	0	0	+1	+1	+1	0	0	0	-1	-1	-1	0
$M_J$	+2	+1	0	-1	-2	+2	+1	0	+1	0	-1	0	-1	-2	0
	(A)					(B)					(C)				

(A)  $M_L = +2, +1, 0, -1, -2$

$\therefore L = 2$ , hence D term

$$S = 0, \therefore 2S+1 = 1$$

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

$$= 2$$

$\therefore$  Five  $^1D_2$

(B)  $M_L = +1, 0, -1$

$\therefore L = 1$ , hence P term

$$S = 1, \therefore 2S+1 = 3$$

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

$$= 2, 1, 0$$

$\therefore$  Five  $^3P_2$ , Three  $^3P_1$ , One  $^3P_0$

(C)  $M_L = 0$

$\therefore L = 0$ , hence S term

$$S = 0, \therefore 2S+1 = 1$$

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

$$= 0$$

$\therefore$  One  $^1S_0$

### Number of microstates for $d^2$

Since the number of orbitals in d sub-shell = 5,  $n = 2 \times 5 = 10$

Thus,

$$\text{No. of microstates of a given configuration} = \frac{n!}{n!(n-r)!}$$

$$\therefore \text{No. of microstates of a given configuration} = \frac{10!}{2!(10-2)!}$$

$$= \frac{10!}{2! \times 8!}$$

$$= \frac{10 \times 9 \times 8!}{2 \times 1 \times 8!}$$

$$= \frac{90}{2}$$

$$= 45$$

### Pigeonhole diagram for $d^2$ configuration:

Microstates of  $d^2$  are 45

+2	+1	0	-1	-2	$M_S$	$M_L$	J	
↑↓					0	4	4	(A)
↑	↓				0	3	3	
↑		↓			0	2	2	
↑			↓		0	1	1	
↑				↓	0	0	0	
	↑			↓	0	-1	-1	
		↑		↓	0	-2	-2	
			↑	↓	0	-3	-3	
				↑↓	0	-4	-4	
↑	↑				1	3	4	(B)
↑		↑			1	2	3	
↑			↑		1	1	2	
↑				↑	1	0	1	
	↑			↑	1	-1	0	
		↑		↑	1	-2	-1	
			↑	↑	1	-3	-2	
	↑↓				0	2	2	(C)
	↑	↓			0	1	1	
	↑		↓		0	0	0	
		↑	↓		0	-1	-1	
		↑		↓	0	-2	-2	
	↑	↑			1	1	2	(D)
	↑		↑		1	0	1	
		↑	↑		1	-1	0	
		↑↓			0	0	0	(E)

(A)  $M_L = -4$  to  $+4$

$\therefore L = 4$ , hence G term

$S = 0$ ,  $\therefore 2S+1 = 1$

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

$= 4$

$\therefore T.S. = {}^1G_4$

(B)  $M_L = -3$  to  $+3$

$\therefore L = 3$ , hence F term

$S = 1$ ,  $\therefore 2S+1 = 3$

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

$= 4, 3, 2$

$\therefore T.S. = {}^3F_4, {}^3F_3, {}^3F_2$

(C)  $M_L = -2$  to  $+2$

$\therefore L = 2$ , hence D term

$$S = 0, \therefore 2S+1 = 1$$

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

$$= 2$$

$$\therefore \text{T. S.} = {}^1D_2$$

(D)  $M_L = -1$  to  $+1$

$\therefore L = 1$ , hence P term

$$S = 1, \therefore 2S+1 = 3$$

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

$$= 2, 1, 0$$

$$\therefore \text{T. S.} = {}^3P_2, {}^3P_1, {}^3P_0$$

(E)  $M_L = 0$

$\therefore L = 0$ , hence S term

$$S = 0, \therefore 2S+1 = 1$$

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

$$= 0$$

$$\therefore \text{T. S.} = {}^1S_0$$

The two electrons in d-orbital can be arranged in 45 different ways. However, for simplicity the following method may be used to determine the term symbols. The sub levels  ${}^3P$  and  ${}^3F$  can be worked out separately by finding the compounds of 'S' quantum number.  $S=1$  can be split into 3 components  $M_S = +1, 0, -1$  giving 3 times the energy level shown in the figure for  ${}^3P$  and for  ${}^3F$  viz.  $3 \times 3 = 9$  and  $7 \times 3 = 21$  energy levels respectively.

Although one microstate may belong to 2 or more term symbol. We fix one arrangement or microstate for one particular microstate and not repeat it again for other terms in this way, we can assign the term symbols for  $d^2$  configuration. Again it is not necessary to write alternate term symbol for each and every microstates. eg for  $M_L = -4$  to  $+4$  and  $M_S = 0$  is microstate only for  ${}^1G$

According to Hund's rule, the term symbol for ground state five term symbol is

$${}^3F_{4,3,2}, {}^3P_{2,1,0}, {}^1G_4, {}^1D_2 \text{ and } {}^1S_0.$$

For  $d^2$  configuration the orbital is less than half field, hence smallest value of J is most stable term and also according to Hund's rule, the arrangement of term symbol for  $d^2$  configuration  ${}^1F_2 < {}^1F_3 < {}^1F_4 < {}^3P_0 < {}^3P_1 < {}^3P_2 < {}^1G_4 < {}^1D_2 < {}^1S_0$

**To determine the number of microstates (J levels) in term symbol of  $d^2$  configuration:**

The term symbol for  $d^2$  configuration is  ${}^3F, {}^3P, {}^1G, {}^1D$  and  ${}^1S$

Microstates of a given term symbol =  $(2S + 1)(2L + 1)$

**For  $^3F$  term,  $(2S + 1)$  is 2 and  $L$  is 3**

$\therefore$  Microstates of a given term symbol =  $3 (2 \times 3 + 1) = 3 (7) = 21$

**For  $^3P$  term,  $(2S + 1)$  is 2 and  $L$  is 1**

$\therefore$  Microstates of a given term symbol =  $3 (2 \times 1 + 1) = 3 (3) = 9$

**For  $^1G$  term,  $(2S + 1)$  is 1 and  $L$  is 4**

$\therefore$  Microstates of a given term symbol =  $1 (2 \times 4 + 1) = 1 (9) = 9$

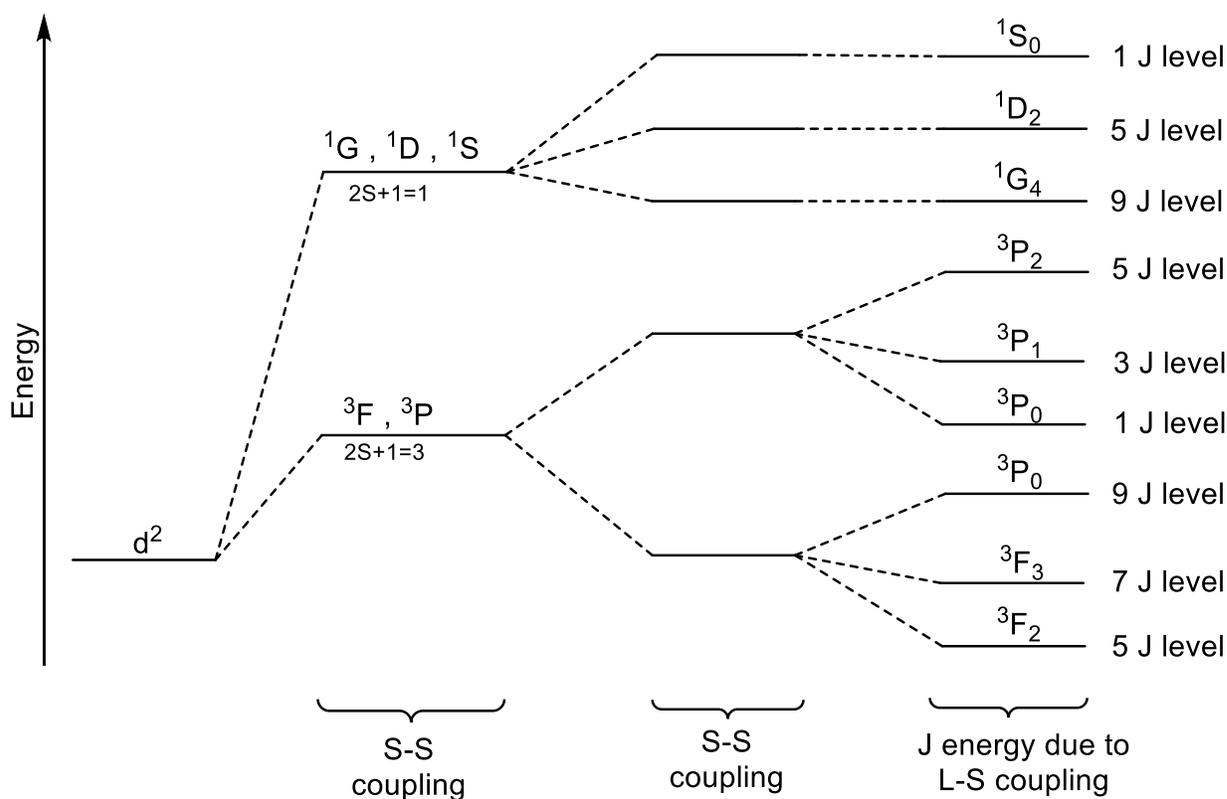
**For  $^1D$  term,  $(2S + 1)$  is 1 and  $L$  is 2**

$\therefore$  Microstates of a given term symbol =  $1 (2 \times 2 + 1) = 1 (5) = 5$

**For  $^1S$  term,  $(2S + 1)$  is 1 and  $L$  is 0**

$\therefore$  Microstates of a given term symbol =  $1 (2 \times 0 + 1) = 1 (1) = 1$

Hence total number of microstates in  $d^2$  configuration =  $21 + 9 + 9 + 5 + 1 = 45$



**(4) To determine the microstates from the term symbol without L-S coupling (J)**

It can be calculated by the equation  $(2J + 1)$

**Example: To calculate microstates of  $^2P_4$**

For  $^2P_4$  term,  $J$  is 4

$\therefore$  Microstates of a given term symbol =  $(2J + 1)$

$$= (2 \times 4 + 1)$$

$$= 9$$

## ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES:

When electrons promoted from one energy level to another, spectra arise. Such electronic transitions are high energy and in addition much lower energy vibrational and rotational transitions always occur. These vibrational and rotational levels are too close in energy to be resolved in to separate absorption bands, but they result in considerable broadening of the electronic absorption bands in d-d spectra. Band widths are commonly  $1000-3000\text{ cm}^{-1}$ .

Not all the theoretically possible electronic transitions are actually observed. The selection rules distinguish between 'allowed' and 'forbidden' transitions do occurs, but much less frequently and much lower intensity.

### Selection rule:

In intensity of hight of electronic spectra is based on the probability of electronic transition.

If there is high probability of electronic transition then more light is absorbed during transition. So, the spectra which is obtained would be more intense and high.

There are two rules to decide allowed or forbidden transition.

### (1) Spin selection rule:

During the transition the total spin of the molecule (atom or ion) should remain constant. It means electron does not change its spin.

If  $\Delta S = 0$ , such transition is allowed transition and if  $\Delta S \neq 0$ , such transition is forbidden.

This rule is known as rule of spin multiplicity.

According to this rule singlet→singlet, doublet→doublet, triplet→triplet are allowed transition whereas singlet→doublet, doublet→ triplate are forbidden transitions.

### (2) Laporte orbital selection rule:

$\Delta l = \pm 1$  is Laporte allowed transition which gives sharp band.

The subsidiary quantum number  $\Delta l \neq \pm 1$  is forbidden transition.

Each electron has finite value of its orbital angular quantum number  $l$  and its orbital has definite symmetry too.

According to this rule  $s \rightarrow p$ ,  $p \rightarrow s$ ,  $p \rightarrow d$ ,  $d \rightarrow p$ ,  $d \rightarrow f$ ,  $f \rightarrow d$  are Laporte allowed transition which gives sharp band.

$g \rightarrow u$  and  $u \rightarrow g$  allowed while  $g \rightarrow g$  and  $u \rightarrow u$  are forbidden transition. (g is gerade ie symmetrical and u is ungerade ie unsymmetrical)

Orbital	$l$	symmetry
s	0	Gerade
p	1	ungerade
d	2	gerade
f	3	ungerade

### Intensity of different types of electronic transition:

Type of transition	Approx $\epsilon$ (Molar absorption constant)
Spin forbidden, Laporte forbidden	$10^{-2}$ to 1.0
Spin allowed, Laporte forbidden	1 to 10
Spin allowed, Laporte forbidden (p & d orbitals overlaps)	10 to $10^2$
Spin allowed, Laporte forbidden (Intensity stilling effect)	$10^2$ to $10^3$
Spin allowed, Laporte allowed	$10^4$ to $10^5$

### Splitting of $d^n$ term:

Each of the free ion terms will be affected by the ligands in a complex and this will depend upon the geometry of the complex.

e.g. s-orbital is spherically symmetrical and is unaffected by an octahedral or any other field. p-orbitals are affected but set of all three orbitals are affected equally hence, their energy levels remain equal and no splitting occurs. d and f splits in to two and three states respectively.

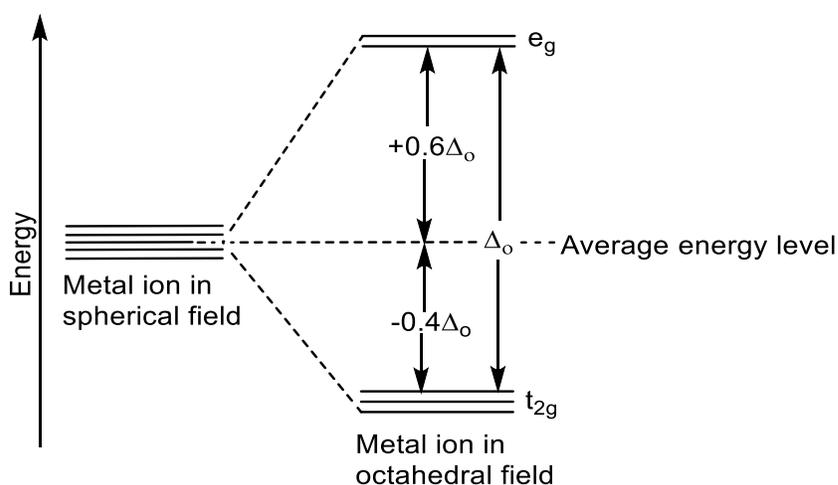
### Transforming spectroscopic term in to Muliken symbol:

Spectroscopic term	Muliken symbols	
	Octahedral field	Tetrahedral field
S	$A_{2g}$	$A_1$
P	$T_{1g}$	$T_1$
D	$E_g + T_{2g}$	$E + T_2$
F	$A_{2g} + T_{1g} + T_{2g}$	$A_2 + T_1 + T_2$

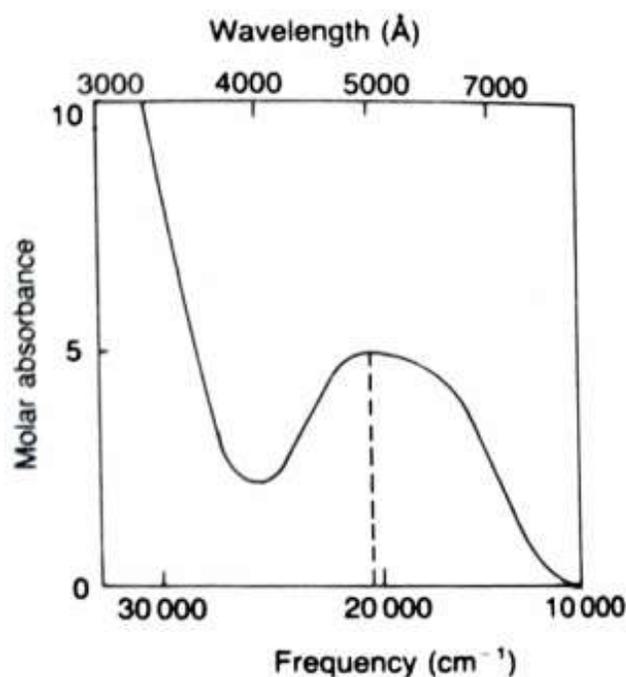
### Electronic spectra of $d^1$ system:

In the free gaseous metal ion 5d orbitals are degenerate and no spectra from d-d transitions.

In octahedral complex of Ti(III),  $[TiCl_6]^{-3}$  and  $[Ti(H_2O)_6]^{+3}$  ( $d^1$  system), d-orbital splits and one electron occupies lower  $t_{2g}$  level and only one transition is possible to  $e_g$  level.



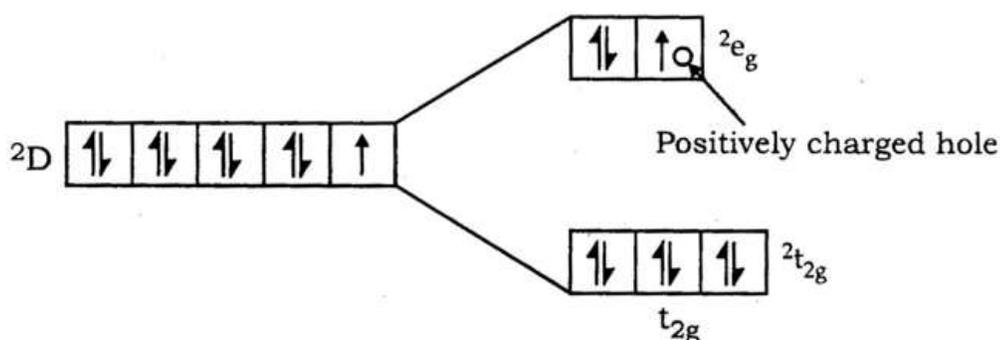
Consequently the absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{+2}$  shows only one band with a peak at  $20300\text{ cm}^{-1}$ . The magnitude of splitting of  $\Delta_o$  depends on nature of ligands and affect the energy of transition and hence the frequency of maximum absorption in the spectrum.



Thus, the peak occurs at  $13000\text{ cm}^{-1} \rightarrow [\text{TiCl}_6]^{-3}$ ,  $18900\text{ cm}^{-1} \rightarrow [\text{TiF}_6]^{-3}$ ,  $20300\text{ cm}^{-1} \rightarrow \text{Ti}(\text{H}_2\text{O})_6^{+2}$ ,  $22300\text{ cm}^{-1} \rightarrow \text{Ti}(\text{CN})_6^{-3}$ .

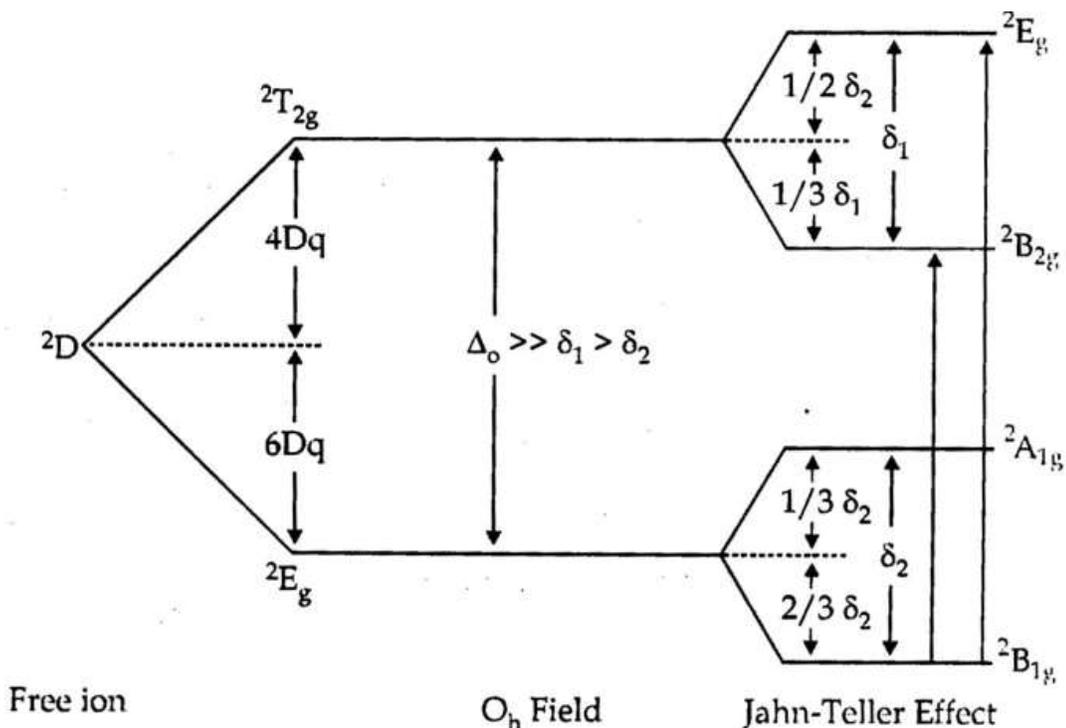
### Electronic spectra of d<sup>9</sup> system:

$\text{Cu}^{+2}$  ( $z = 29$ ):  $[\text{Ar}] 3d^9 4s^0$  is a d<sup>9</sup> system. The term symbol is  $^2D$ . In  $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$ , according to CFT all five orbitals do not remain equivalent. Due to octahedral field effect of  $\text{H}_2\text{O}$  ligand, the degenerate d-orbitals of  $\text{Cu}^{+2}$  splits and produces two energy levels such as lower energetic  $^2t_{2g}$  ( $d_{xy}, d_{yz}, d_{xz}$ ) and higher energetic  $^2e_g$  ( $d_{x^2-y^2}, d_{z^2}$ ).



Thus, according to CFT,  $^2T_{2g} \rightarrow ^2E_g$  type of only one transition takes place and only one band should be obtained. But electronic spectrum of  $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$  is of two bands, asymmetric and broad. This can be explained using Jahn-Teller theory.

According to Jahn-Teller theory, non-linear molecule containing equivalent orbitals gets distorted and in its ground state, the degeneracy also destroyed. Thus,  $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$  molecule lost its symmetry according to Jahn-Teller's effect and further split.

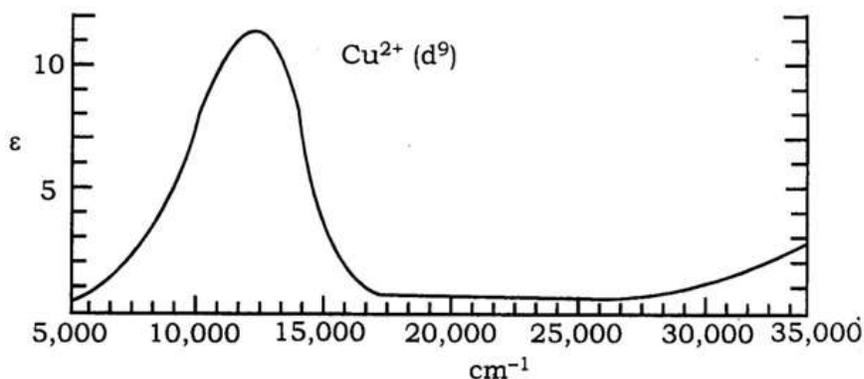


### Electronic spectra of $d^9$ system

Thus, instead of only one transition, the distorted octahedral field split and gives further three transitions:

- (i)  ${}^2B_{1g} \rightarrow {}^2E_g$ , (ii)  ${}^2A_{1g} \leftarrow {}^2E_g$  and (iii)  ${}^2B_{2g} \leftarrow {}^2E_g$

The energy of  ${}^2B_{2g} \leftarrow {}^2E_g$  transition is very low and near IR region, so it is not found in visible region therefore only two bands are obtained.

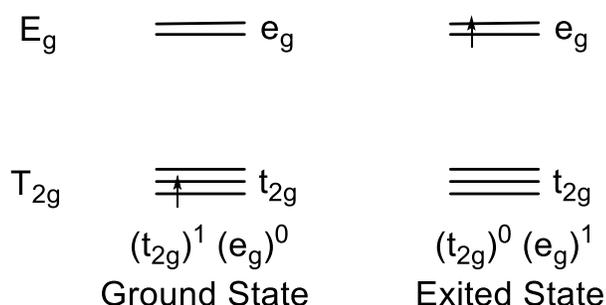


The energy difference between transition (i) and (ii) is very low, so their bands are obtained closer to each other as a big peak along with a shoulder peak. Due to Jahn-Teller effect the ground state and excited state split into many energy levels. Therefore instead of one transition, many transitions of less energy take place. These transitions have less energy difference so instead of sharp, they give a broad band, so  $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$  contains blue-green colour.

### d<sup>1</sup> Correlation diagram:

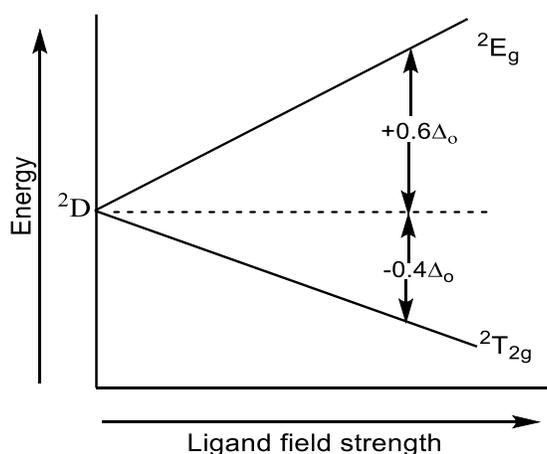
The ground term <sup>2</sup>D arise in d<sup>1</sup> system.

The ground state configuration is t<sub>2g</sub><sup>1</sup> e<sub>g</sub><sup>0</sup>, in excited state the configuration is t<sub>2g</sub><sup>0</sup> e<sub>g</sub><sup>1</sup>. It means electron shift to e<sub>g</sub> orbital. Thus, transition is from <sup>2</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>.



The separation is numerically equal to  $\Delta_o$ , the magnitude of the field.

Relative to the energy of the <sup>2</sup>D free ion term, the <sup>2</sup>T<sub>2g</sub> term will be stabilized by  $-0.4\Delta_o$  and the <sup>2</sup>E<sub>g</sub> term will be destabilised by  $+0.6\Delta_o$ .

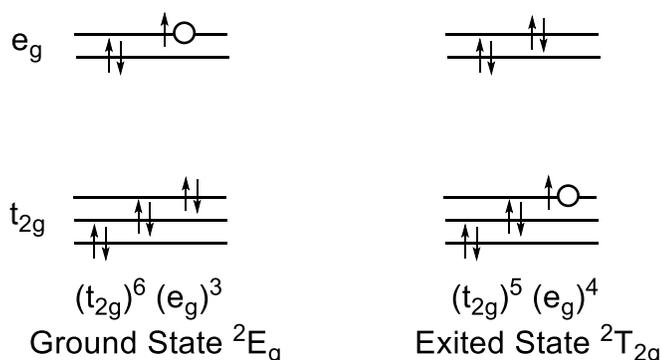


**Splitting of energy levels for d<sup>1</sup> configuration in Oh field**

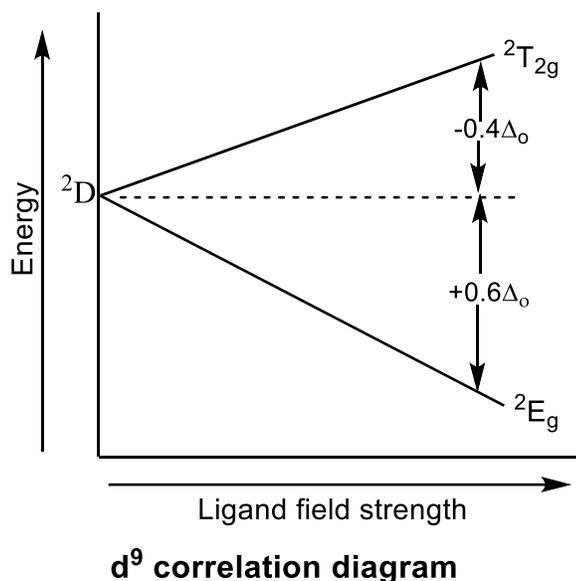
### d<sup>9</sup> Correlation diagram:

The same ground term <sup>2</sup>D arise in d<sup>9</sup> system.

The ground state configuration is t<sub>2g</sub><sup>6</sup> e<sub>g</sub><sup>3</sup>, means hole is in e<sub>g</sub> orbital. In excited state the configuration is t<sub>2g</sub><sup>5</sup> e<sub>g</sub><sup>4</sup>. It means hole (positron) transition occur is from <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub>.

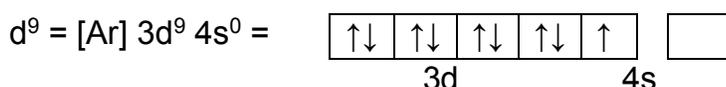
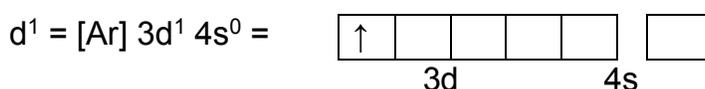


Thus, the energy ordering of the terms for d<sup>9</sup> is the reverse of d<sup>1</sup> case. For the d<sup>9</sup> (Oh) case the <sup>2</sup>E<sub>g</sub> is stabilised by  $-0.4\Delta_o$  and the <sup>2</sup>T<sub>2g</sub> term will be destabilised by  $+0.6\Delta_o$ .



### Orgel diagram of d<sup>1</sup> – d<sup>9</sup>:

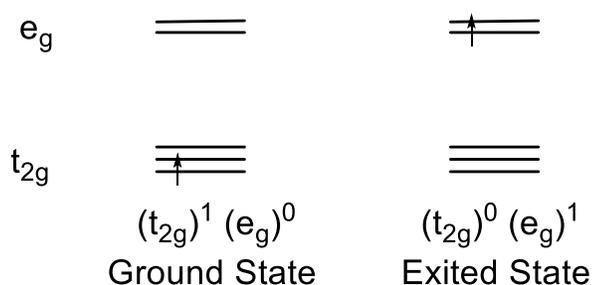
Electronic configuration of d<sup>1</sup> and d<sup>9</sup> are as follow:



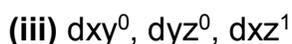
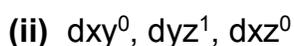
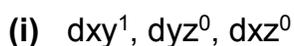
Here, in electronic configuration of d<sup>1</sup>, there is only one electron exist in d-orbital while in d<sup>9</sup> system, only one space is empty in d-orbital as 'hole' position.

The ground state term symbol of both d<sup>1</sup> and d<sup>9</sup> is <sup>2</sup>D. According to CFT, <sup>2</sup>D term split in to <sup>2</sup>T<sub>2g</sub> and <sup>2</sup>E<sub>g</sub>. in composition to d<sup>1</sup>, d<sup>9</sup> has opposite splitting.

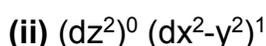
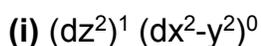
In splitted energy levels of d<sup>1</sup> system, electron is filled as follow.



Here in ground state (t<sub>2g</sub>)<sup>1</sup>, electron arrangement has three probable arrangements.

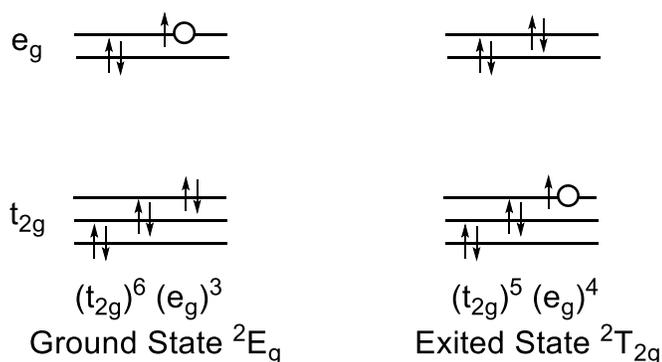


while in exited state (eg)<sup>1</sup> has two possibility

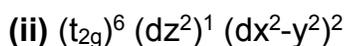
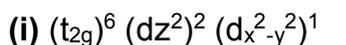


Due to this difference in probable arrangement, the  $t_{2g}$  which has three probable arrangement becomes less energetic and  $e_g$  has two probable arrangements become more energetic.

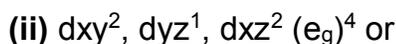
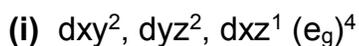
In the  $d^9$  system (i.e.  $Cu^{+2}$ ), nine electron filled as follows:



Here in ground state  $(t_{2g})^6 (e_g)^3$ , the probable arrangement of electrons is as

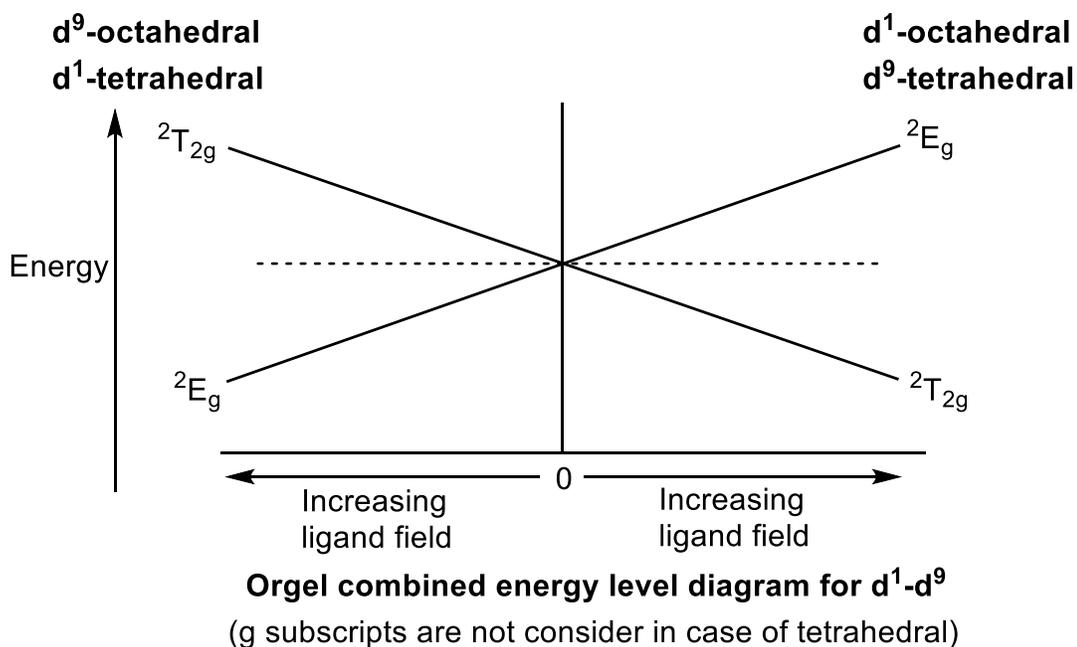


while in excited state  $(t_{2g})^5 (e_g)^4$ , the probable arrangement of electrons is as



Thus, here excited state is more stable than ground state.

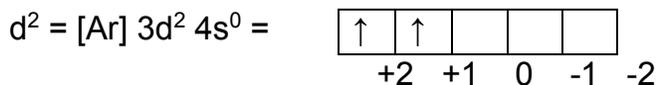
Thus, in  $d^1$  transition, electron transition takes place while in  $d^9$ , positron (hole) transition takes place. So, the bands of both  $d^1$  and  $d^9$  obtained at equal frequency.



In case of tetrahedral field, the energy level diagram for  $d^1$  complexes is inverse of that in an octahedral field and similar in case of  $d^9$  field.

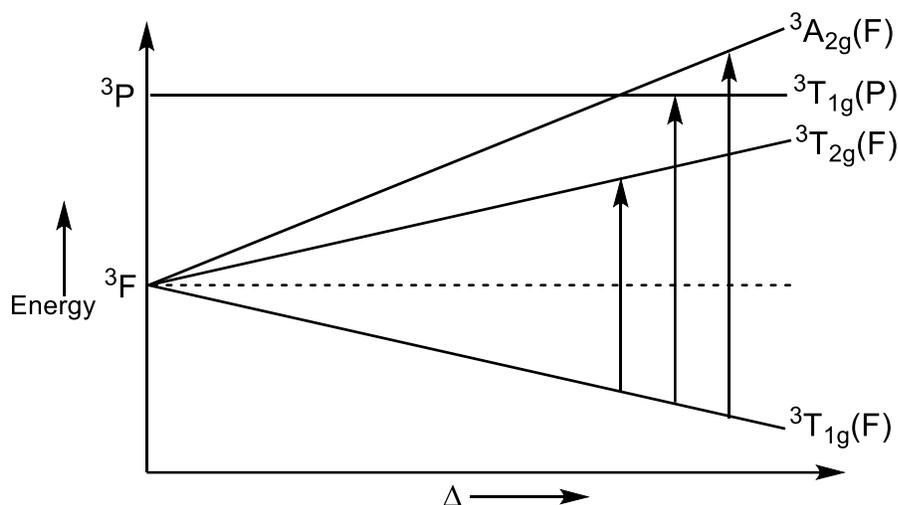
## d<sup>2</sup> corelation diagram:

The V(III) octahedral complexes have the d<sup>2</sup> configuration



The ground state term symbol for d<sup>2</sup> is <sup>3</sup>F. The excited states are <sup>3</sup>P, <sup>1</sup>G, <sup>1</sup>D and <sup>1</sup>S. According to spin selection rule, <sup>3</sup>F to <sup>3</sup>P is allowed transition, whereas <sup>1</sup>G, <sup>1</sup>D and <sup>1</sup>S are forbidden transition. As per multiplicity rule, triplet → singlet is forbidden transition, therefore not shown in the Orgel diagram.

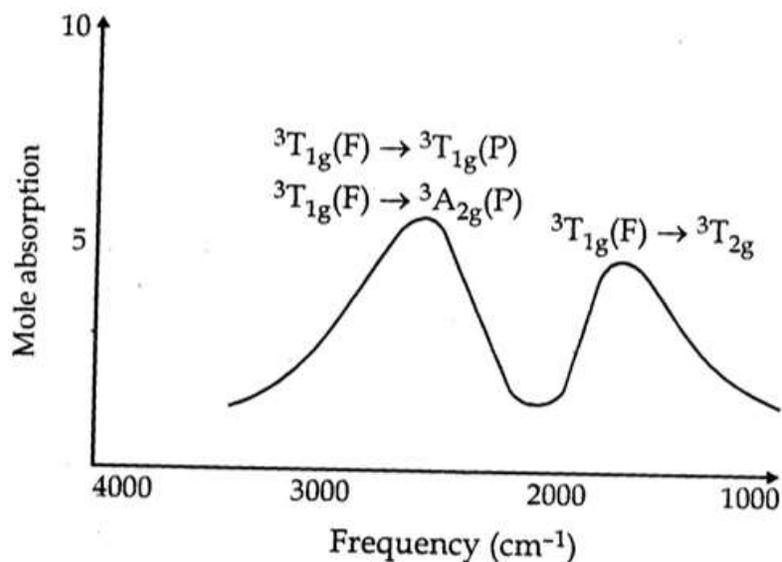
The spectra of vanadium complexes would be expected to show three absorption bands from the ground state <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) and <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>A<sub>2g</sub>(F).



Thus, in [V(H<sub>2</sub>O)<sub>6</sub>] three transitions are possible:

- (i) <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F)    17200 cm<sup>-1</sup>
- (ii) <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P)    } 25600 cm<sup>-1</sup>
- (iii) <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>A<sub>2g</sub>(F)    }

Thus, the visible spectra of [V(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> should contain three peaks, but the energy difference between <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) and <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>A<sub>2g</sub>(F) transition is such small that it gives overtone and a single peak appear. While <sup>3</sup>T<sub>1g</sub>(F) → <sup>3</sup>T<sub>2g</sub> gives another peak. Thus, only two peaks appear.



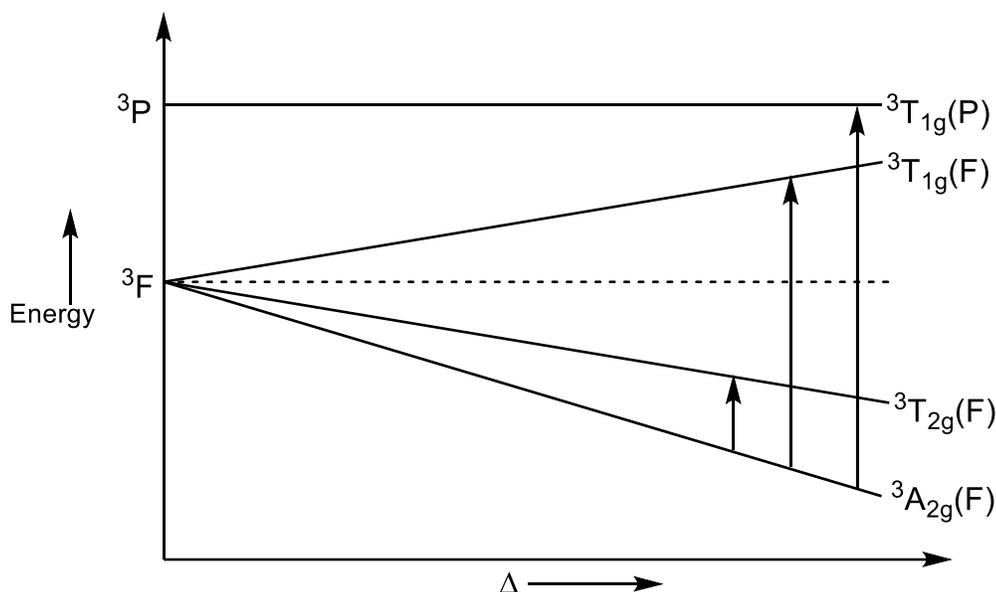
## d<sup>8</sup> corelation diagram:

The Ni(II) octahedral complexes have the d<sup>8</sup> configuration.



The ground state term symbol for d<sup>8</sup> is <sup>3</sup>F. The excited states are <sup>3</sup>P, <sup>1</sup>G, <sup>1</sup>D and <sup>1</sup>S. According to spin selection rule, <sup>3</sup>F to <sup>3</sup>P is allowed transition, whereas <sup>1</sup>G, <sup>1</sup>D and <sup>1</sup>S are forbidden transition. As per multiplicity rule, triplet→singlet is forbidden transition, therefore not shown in the Orgel diagram.

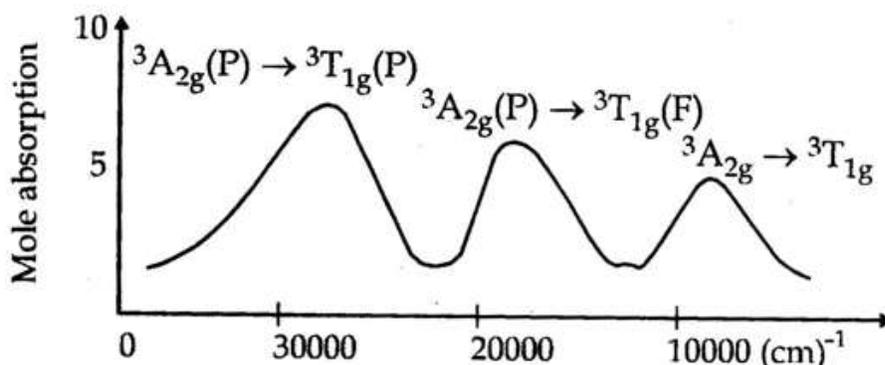
According to CFT, in octahedral field <sup>3</sup>F term splits into lower energy <sup>3</sup>A<sub>2g</sub> and higher energy containing <sup>3</sup>T<sub>2g</sub> and <sup>3</sup>T<sub>1g</sub>(P) levels. Splitting of d<sup>8</sup> system [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>+2</sup> in octahedra; field is given below.



Thus, in [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>+2</sup> three transitions take place.

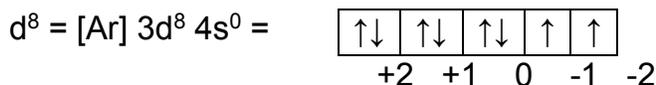
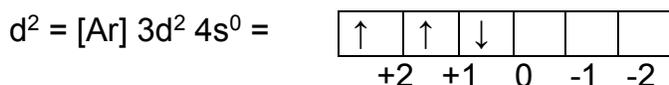
Transition	$\nu \text{ cm}^{-1}$
(i) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub> (F)	8700 cm <sup>-1</sup>
(ii) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F)	14500 cm <sup>-1</sup>
(iii) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)	25300 cm <sup>-1</sup>

The required energy for all three transitions are enough so visible spectra of [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>+2</sup> contains three peaks as under.



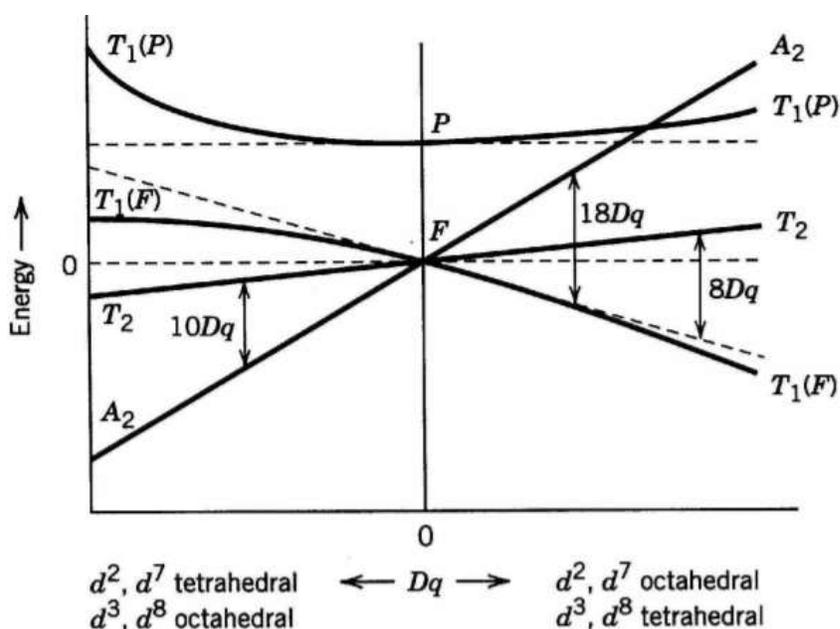
## d<sup>2</sup>-d<sup>8</sup> Orgel diagram:

The V(III) octahedral complexes have the d<sup>2</sup> configuration and Ni(II) octahedral complexes have the d<sup>8</sup> configuration.



The ground state term symbol for d<sup>2</sup> and d<sup>8</sup> is <sup>3</sup>F. The excited states are <sup>3</sup>P, <sup>1</sup>D and <sup>1</sup>S. According to the spin selection rule, <sup>3</sup>F to <sup>3</sup>P is an allowed transition, whereas <sup>1</sup>G, <sup>1</sup>D and <sup>1</sup>S are forbidden transitions. As per the multiplicity rule, triplet → singlet is a forbidden transition, therefore not shown in the Orgel diagram.

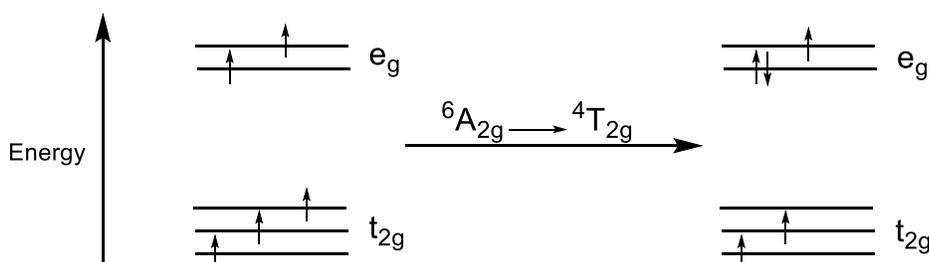
According to CFT, d<sup>2</sup> and d<sup>8</sup> systems split in octahedral and tetrahedral fields respectively as shown below.



The splitting of d<sup>2</sup> in octahedral field and of d<sup>8</sup> in tetrahedral field is equal. While splitting of d<sup>2</sup> in tetrahedral field and of d<sup>8</sup> in octahedral field is equal.

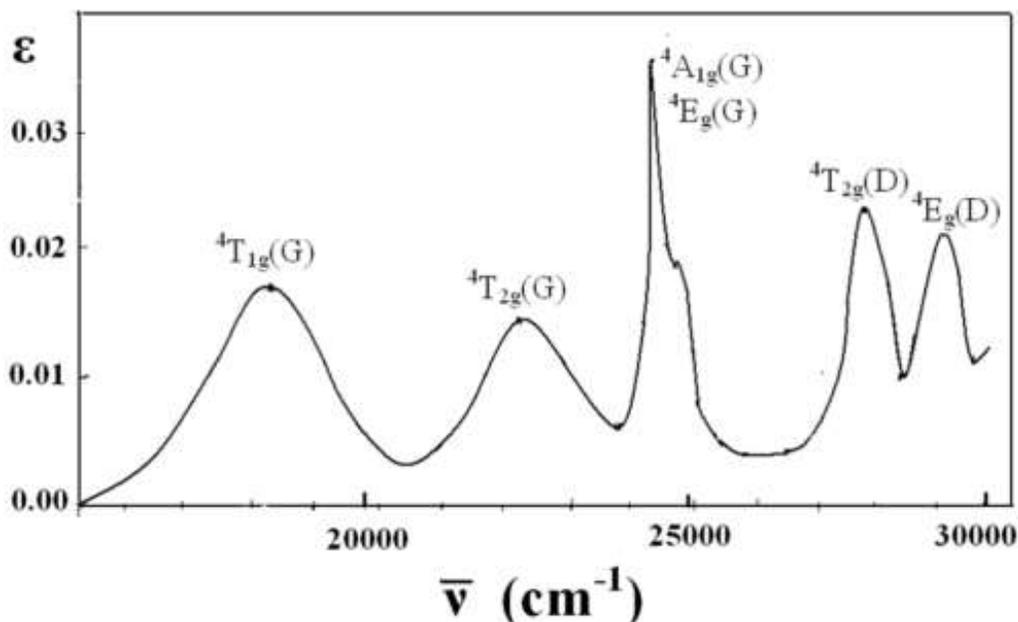
## The electronic spectra of high-spin d<sup>5</sup> ions:

For high-spin d<sup>5</sup> ion, all possible d-d transitions are spin-forbidden. As a result, the bands in spectra of high-spin complexes of Mn(III) and Fe(III) are very weak and the compounds are nearly colourless. Below is shown a d-d transition for a high-spin d<sup>5</sup> ion, showing that it is spin-forbidden.

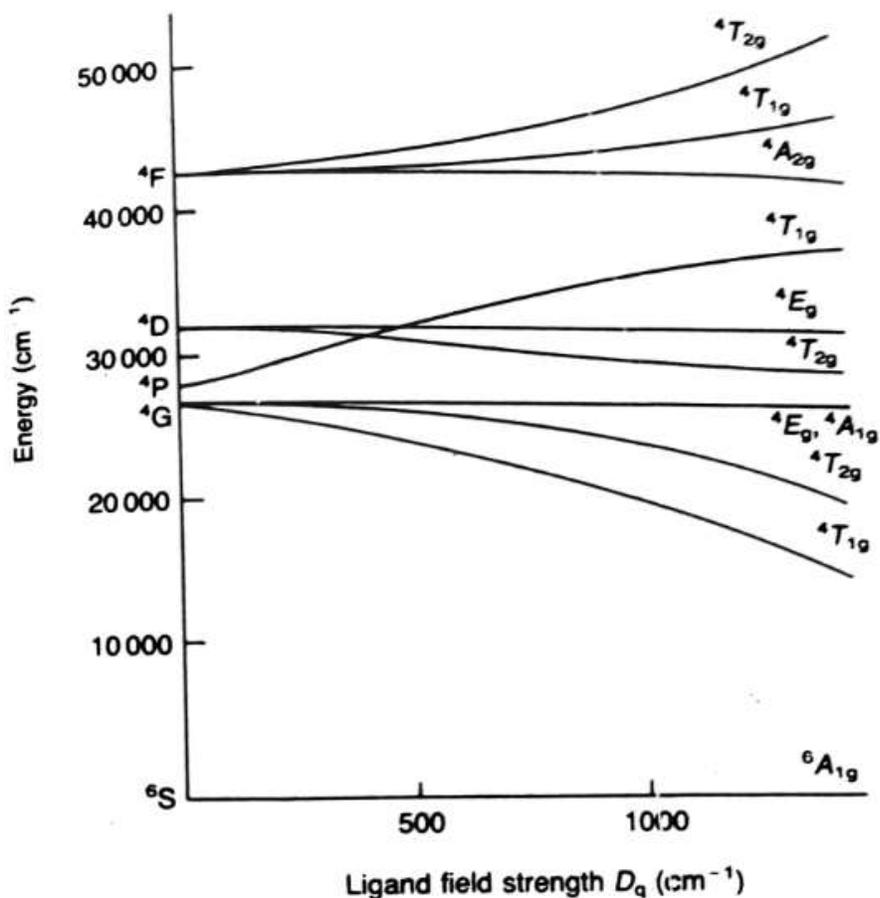


There are five unpaired electrons with parallel spin. Any electronic transition within the d-level must involve a reverse of spin, therefore it is spin forbidden transition and absorption bands will be extremely weak.

The four quartets 4G, 4F, 4D and 4P involve the reversal of only one spin, other seven states are doublet and doubly spin forbidden. In octahedral field ten extremely weak absorption bands may be observed.

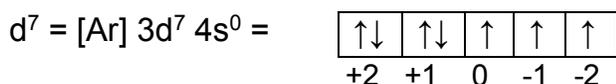
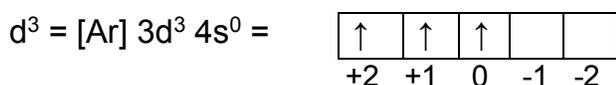


Electronic spectra of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$



Orgel energy level diagram for  $\text{Mn}^{2+}$  ( $d^5$ ) octahedral.

### $d^3$ - $d^7$ Orgel diagram:



The Cr(III) octahedral complexes have the  $d^3$  configuration and Co(III) octahedral complexes have the  $d^7$  configuration. The ground state term symbol for  $d^3$  and  $d^7$  is  $^4F$  and excited state term symbols are  $^4P$ ,  $^2G$ ,  $^2F$ ,  $^2D$  and  $^2P$ .

According to spin multiplicity rule  $^4F$  to  $^4P$  is allowed transition whereas  $^2G$ ,  $^2F$ ,  $^2D$  and  $^2P$  are forbidden transitions and not shown in the Orgel diagram.

The spectra of chromium complexes would be expected to show three absorption bands from the ground state  $^4A_{2g} \rightarrow ^4T_{1g}$  (P). Chromium(III) complexes show at least two well-defined absorption peaks in the visible region. In some cases the third band can also be seen. The spectra of cobalt complexes in octahedral field such as  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  show three absorption bands.

- (i)  $^4T_{1g}$  (F)  $\rightarrow$   $^4T_{2g}$  (F), energy band at  $8000 \text{ cm}^{-1}$
- (ii)  $^4T_{1g}$  (F)  $\rightarrow$   $^4A_{2g}$  (F), energy band at  $19600 \text{ cm}^{-1}$
- (iii)  $^4T_{1g}$  (F)  $\rightarrow$   $^4T_{1g}$  (P), energy band at  $21600 \text{ cm}^{-1}$

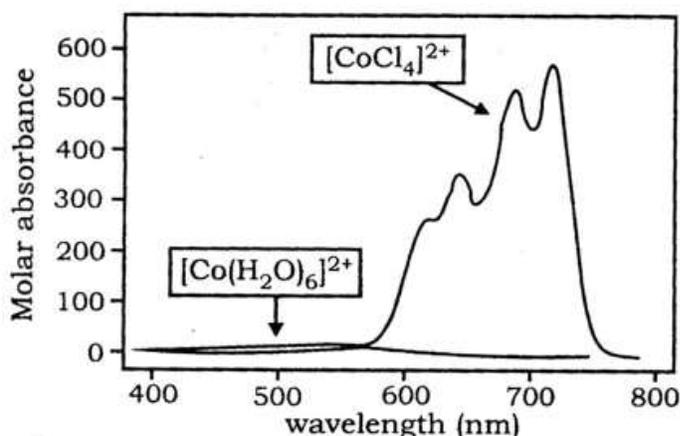
Tetrahedral complexes of Co(II) such as  $[\text{CoCl}_4]^{2-}$  show intensely blue colour. There are possible transitions as follows.

- (i)  $^4A_2$  (F)  $\rightarrow$   $^4T_1$  (P),  $15000 \text{ cm}^{-1}$  in the visible region
- (ii)  $^4A_2$  (F)  $\rightarrow$   $^4T_1$  (F),  $5800 \text{ cm}^{-1}$  in the visible region
- (iii)  $^4A_2$  (F)  $\rightarrow$   $^4T_2$  (F),  $3500 \text{ cm}^{-1}$  in the visible region

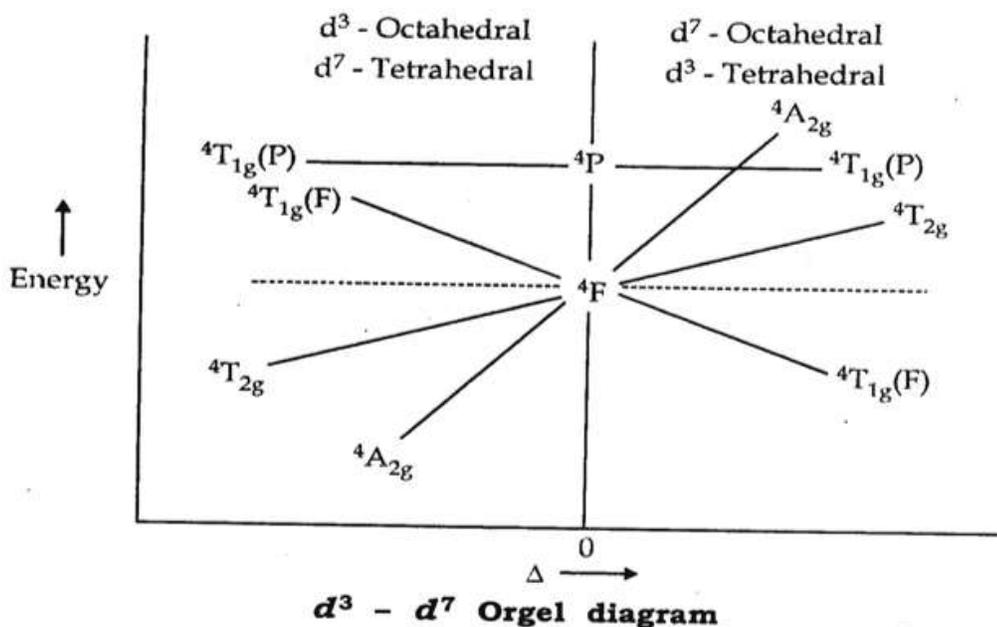
Thus, dissolving  $\text{CoCl}_2$  in water produces a pale pink solution of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , but in alcohol tetrahedral  $[\text{CoCl}_2(\text{CH}_3\text{CH}_2\text{OH})_2]$  form gives intense blue colour.

### The spectra of octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and tetrahedral $[\text{CoCl}_4]^{2-}$ ion:

The spectra at left show the very intense  $d-d$  bands in the blue tetrahedral complexes  $[\text{CoCl}_4]^{2-}$ , as compared with the much weaker band in the pink octahedral complex  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . This difference arises because the tetrahedral complex has no center of symmetry, helping to overcome the  $g \rightarrow g$  Laporte selection rule.

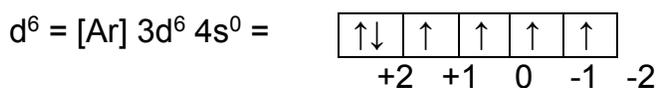
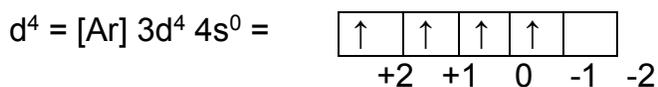


The term of  $d^3$  and  $d^7$  system is equal (same). Their ground state term would be  $^4F$  and  $^4P$ . The Orgel diagram of  $d^3$  and  $d^7$  is similar with  $d^2$  and  $d^8$  only terms are different instead of  $^3F$  and  $^3P$ , they contain  $^4F$  and  $^4P$ .

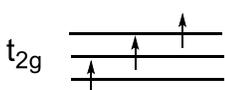
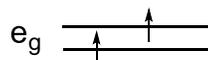


### Orgel diagram of $d^4$ - $d^6$ :

The electronic configuration of  $d^4$  and  $d^6$  are as follows:

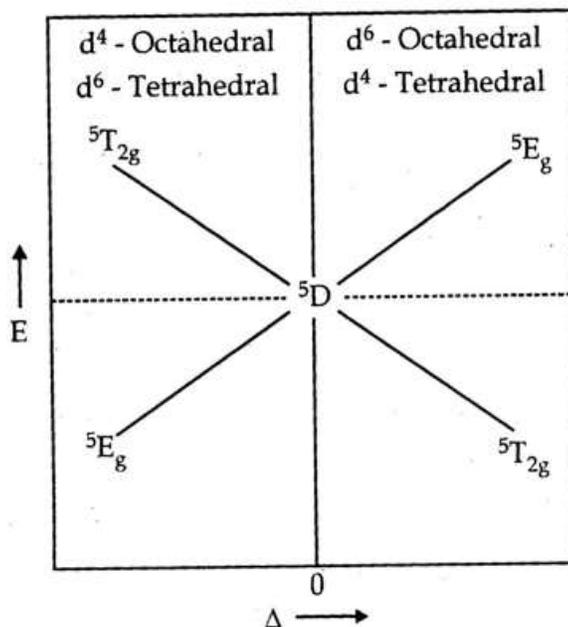


The ground state term symbol for  $d^4$  and  $d^6$  is  $^5D$ .



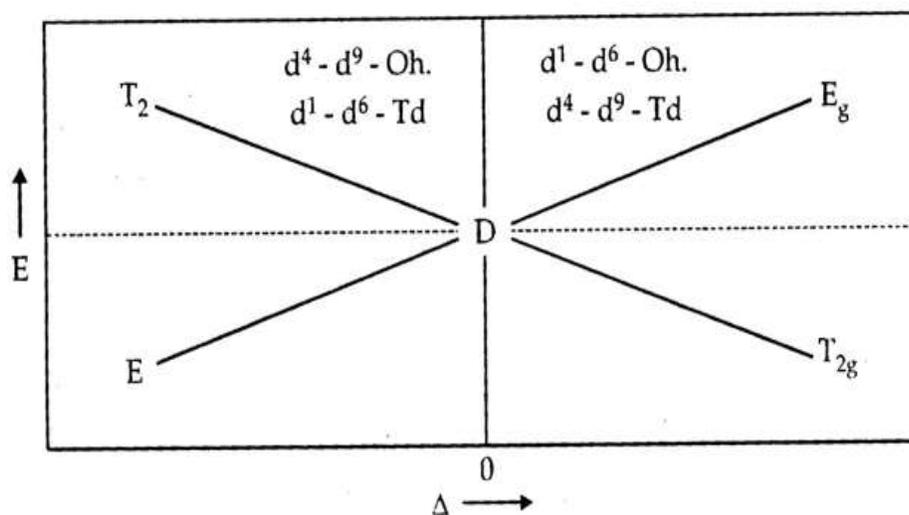
The ground state term symbol for  $d^4$  and  $d^6$  is  $^5D$ . In excited state  $^3h$ ,  $^3G$ ,  $^3F$ ,  $^3D$ ,  $^3P$ ,  $^1I$ ,  $^1D$ ,  $^1S$ .

According to spin multiplicity rule only  $^5D$  transition is possible. The  $^5D$  term is split into  $T_{2g}$  and  $E_g$ . In high spin  $d^6$  electron is promoted from  $T_{2g} \rightarrow E_g$  as same as  $d^1$  case. In  $d^4$  positron (hole) is promoted from  $E_g \rightarrow T_{2g}$  as same as  $d^9$  case.



If complex contain tetrahedral field then in orgel diagram subscript g is not written.

The above orgel diagram stated that the orgel diagrams of  $d^1$ - $d^9$  and  $d^4$ - $d^6$  are quite similar. So, the combined orgel diagram for  $d^1$ ,  $d^9$ ,  $d^4$ ,  $d^6$  system is as follows.



### John-Teller effect:

This theorem explained why certain six coordinated complexes possess distorted octahedral geometry.

According to this theorem:

- An octahedral complex is said to have a regular shape if the d-orbitals (both  $t_{2g}$  and  $e_g$  sets) are occupied symmetrically.
- When the d-orbitals or central metal ion of an octahedral complex possess  $t_{2g}$  orbitals as asymmetrical orbitals there occurs slight distortion from the regular octahedron. This distortion in octahedral complex is due to unevenly filling of these orbitals which do not point towards the ligands. The slight distortion may occur in such cases when the central metal ion contains 1, 2, 4 and 5 electrons.
- Strong distortion occurs when the  $e_g$  orbitals of an octahedral complex are asymmetrically filled because these orbitals do not point towards the ligands. Due to strong distortion, the

octahedral shapes of complexes may change to tetragonal and even to square planar complexes. The high-spin complexes of  $d^4$  and  $d^9$  and low-spin complexes of  $d^7$ ,  $d^8$  and  $d^9$  lead to strong distortion.

The above three postulates (i), (ii) and (iii) which describe the effect of asymmetrical  $t_{2g}$  or  $e_g$  orbitals on the shape of an octahedral complex is known as **John-Teller effect**.

**Explanation:**

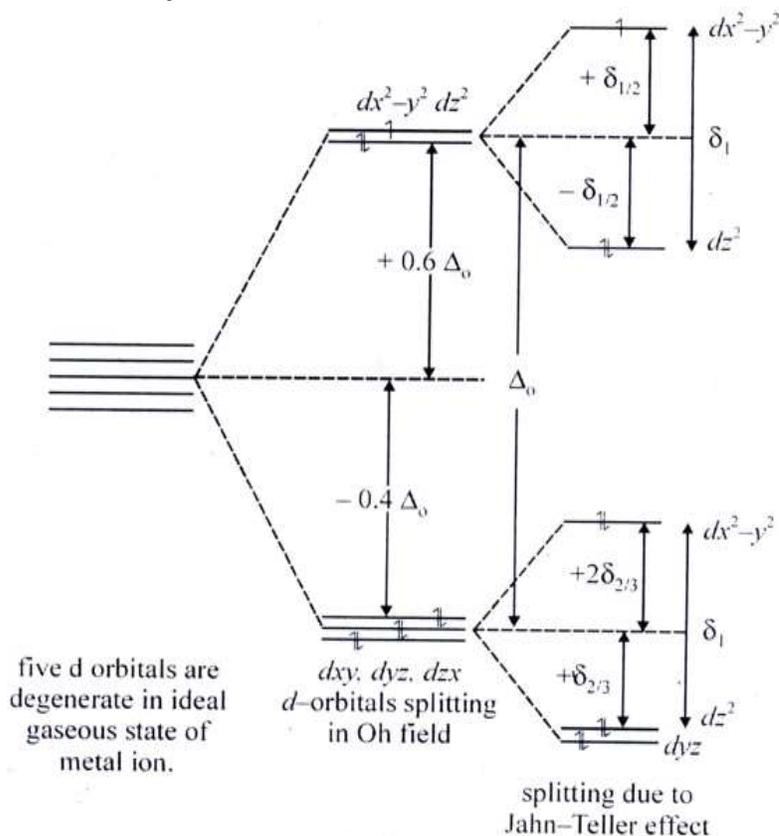
The CFT explains John-Teller effect. This can be illustrated by considering the distortion produced by the presence of  $e_g$  orbitals in a complex of  $\text{Cu}^{+2}$  ion ( $d^9$  ion). This ion of configuration  $t_{2g}^6 e_g^3$  in both the fields. Thus, there are two possible configurations.

- (i)  $t_{2g}^6 e_g^3$  or  $t_{2g}^6 (dz^2)^2 (dx^2-y^2)^1$
- (ii)  $t_{2g}^6 e_g^3$  or  $t_{2g}^6 (dz^2)^1 (dx^2-y^2)^2$

Due to unsymmetrical  $e_g$  orbital, the ligand along z axis move away from the nucleus and the ligand along x-y plane move closer to the nucleus. Therefore, complex of  $\text{Cu}^{+2}$  ion has four long two short metal ligand bonds.

For example,

- (i) In the cupric chloride crystal, each  $\text{Cu}^{+2}$  ion is surrounded by six  $\text{Cl}^-$  ions. Four of them are lying at a distance of 2.30 Å and the other two are at 2.95 Å away.
- (ii) In the cupric fluoride crystal,  $\text{F}^-$  ions are lying at a distance of 1.93 Å and the remaining two are at 2.27 Å away.



**Fig. : Jahn-Teller effect in  $\text{Cu}^{+2}$  ion complexes**

We will now consider the effect of distortion due to Jahn-Teller effect on the energy of  $\text{Cu}^{+2}$  ion ( $d^9$ ) as shown in figure given above.

In the figure give above, splitting of the more stable octahedral distortion corresponding to configuration (i)  $t_{2g}^6 (dz^2)^2, (dx^2-y^2)^1$  is being consider  $\delta_1$  and  $\delta_2$  are much smaller than as compared with  $\Delta_o$  and also 2 is much smaller than, i.e.  $\Delta_o \gg \delta_1 > \delta_2$ .

### Spectrochemical Series:

In complex salts, different ligands remain attached with metal ion. The relative strength and weakness of these ligands are different. The relative strength or weakness of ligand can be decided on the bases of electronic spectra of complex salt.

i.e. In  $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$  under the effect of the ligand, the absorption band of d-d transition is obtained in green field of visible region. So,  $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$  complex is green coloured. But when in that salt if ethylene diamine (en) is added, it forms  $[\text{Ni}(\text{en})_3]^{+2}$  complex. Here, en ligand is stronger than  $\text{H}_2\text{O}$ . So the energy required for d-d transition increase and as a result of this the peak is obtained at low wavelength. Thus, the three peaks are obtained in spectra of  $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$  shift towards low wavelength in  $[\text{Ni}(\text{en})_3]^{+2}$ . Thus, with help of electronic spectra, the relative strength of different ligands is known.

If electronic band indicates deviation towards blue field on addition of new ligand in complex, then the entering ligand is more powerful than the existing ligand and if deviate towards red wavelength (high wavelength) than the ligand is consider as a weak ligand.

Thus, on the study of absorption spectra, comparing the relative strength of ligand, the following order is obtained.

$\text{CO} \sim \text{CN} > \text{N containing ligands} > \text{NH}_3 > \text{H}_2\text{O} > \text{O containing ligands} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

This series is called spectrochemical series.

## ASSIGNMENT

### Short questions

1. Define term symbol.
2. Give the value of L for s, p, d, f and g.
3. What is spin multiplicity?
4. Give Pauli Exclusion Principle and Hund's Rule
5. Define: Total degeneracy
6. Write the rules for 'Ground state term symbol'.
7. Find Ground state term symbol for  $\text{N}(\text{P}^3)$  ( $Z=7$ ),  $\text{C}$  ( $Z=6$ ),  $\text{V}^{+3}$  ( $Z=23$ ),  $\text{Mn}^{+2}$  ( $Z=25$ ),  $\text{Ni}^{+2}$  ( $Z=28$ ),  $\text{Cu}^{+2}$  ( $Z=29$ ).
8. Find L, S, spin multiplicity, number of unpaired electrons and J values of  $^3\text{F}$ ,  $^1\text{S}$ ,  $^5\text{D}$
9. Calculate microstate for  $p^3$  and  $d^2$ .
10. Explain: Bands of d-d transition are weaker
11. Explain: Identification of octahedral and tetrahedral complexes through electronic spectra.

12. According to Leporté rule transition complexes should be colourless but it is not true. Explain.
13. Complexes of  $Zn^{+2}$  are mostly colourless.
14. Explain: Electronic absorption band of cis  $MA_4B_2$  is more intense than  $MA_4B_2$ .

### Long Questions

1. Explain R-S or L-S coupling to derive ground state term symbol.
1. What is L-S coupling? Explain with the example of  $p^2$  configuration of carbon.
2. Derive the ground state term symbol for the following  
(i) N ( $z=7$ ) (ii) S ( $z=16$ ) (iii) Ti ( $z=22$ ) (iv)  $Cr^{+3}$  ( $z=24$ ) (v)  $Fe^{+3}$  ( $z=26$ ) (vi)  $Cu^{+2}$  ( $z=29$ ) (vii)  $Co^{+2}$  ( $z=27$ ) (viii)  $Ni^{+2}$  ( $z=28$ ).
3. Identify the ground state term giving reason for the following set.  
(i)  $^1S$  (ii)  $^3F$  (iii)  $^3P$  (iv)  $^1G$  (v)  $^1D$
4. Calculate L for  $p^2$  configuration and show the energy states.
5. Draw Pigeon hole diagram for  $p^2$  configuration and arranged according to their energy level.
2. Draw Pigeon hole diagram for  $d^2$  configuration and arranged according to their energy level.
3. Discuss 'Selection Rule' for electronic Transition.
4. Explain John Teller effect in  $[Ti(H_2O)_6]^{+3}$ .
6. Discuss the electronic spectra of  $[Ti(H_2O)_6]^{+3}$  complex ion.
7. Explain John Teller effect in  $[Cu(H_2O)_6]^{+2}$
8. Explain: Orgel energy diagram of  $d^1$  and  $d^9$  are opposite of each other.
9. Write a short note on Hole formalism.
10. In  $[V(H_2O)_6]^{+3}$  three transition are possible but only two peaks are observed. Explain.
11. In  $[Ni(H_2O)_6]^{+2}$  three peaks are observed. Explain.
12. Draw and explain the combined Orgel diagram of  $d^3$  and  $d^7$