

## ELECTRONIC SPECTRA

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### (1) Electronic Angular Momentum

#### Orbital Angular Momentum

An electron moving in its orbital about a nucleus possesses orbital angular momentum, a measure of which is given by  $l$  values corresponding to the orbital. This momentum is quantized and it is usually expressed in terms of the unit  $\frac{h}{2\pi}$ , where  $h$  is Plank's constant.

$$\text{Orbital Angular Momentum} = \sqrt{l(l+1)} \cdot \frac{h}{2\pi} \text{ or } \sqrt{\ell(\ell+1)} \hbar$$

$$l = \sqrt{l(l+1)} \text{ units}$$

Angular momentum is a vector quantity, by which we mean that its direction is important as well as its magnitude.

$l$  is always zero or positive and hence so is  $l$ .

Once a reference direction is specified, the angular momentum vector can point only so that its component along the reference direction are integral multiples of  $\frac{h}{2\pi}$ . The reference direction is taken vertical z-axis and so we can write the components of  $l$  in this direction as  $l_z$ . Alternatively, since we know that the  $l_z$  are integral multiples of  $\frac{h}{2\pi}$ , we can represent the components in terms of an integral number  $l_z$ .

$$l_z = l_z \cdot \frac{h}{2\pi}$$

For any value of  $l$ ,  $l_z$  has values

$$l_z = l, l-1, l-2, \dots, 0, \dots, -(l-1), -l$$

There are ' $2l + 1$ ' values of  $l_z$  for a given value of  $l$ .  $l_z$  is to be identified with the magnetic quantum number ' $m$ '.

$$l_z \equiv m$$

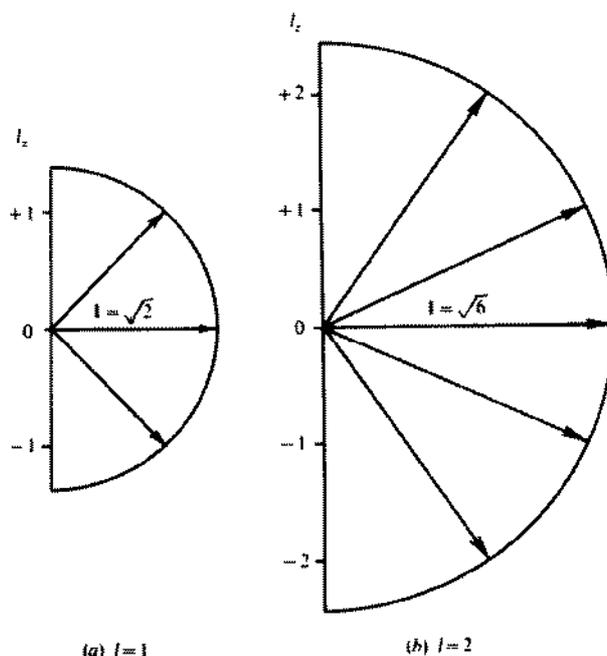
$m$  specifies the direction of an orbital.

$$\text{For } l = 1, l_z \text{ (or } m) = +1, 0, -1$$

$$\text{For } l = 2, l_z \text{ (or } m) = +2, +1, +0, -1, -2$$

The components of  $l$  for  $l = 1$  and  $l = 2$  are shown in the following figures.

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$l$  = azimuthal quantum number or subsidiary quantum number  
 = An integer (positive or zero)  
 = 0, 1, 2, 3, .....

It represents the state of an electron in the atom and determines the orbital angular momentum.

$l$  = designates the magnitude and direction of orbital angular momentum. It is expressed in the unit of  $\frac{h}{2\pi}$

$$= \sqrt{l(l+1)} \cdot \frac{h}{2\pi} = \sqrt{l(l+1)} \text{ units}$$

$l_z$  = components of  $l$  along the reference direction (z-axis, arbitrary)

$$= l_z \frac{h}{2\pi}$$

$l_z$  = An integer or zero

=  $m$  (magnetic quantum number)

There are ' $2l + 1$ ' values of  $l_z$  for a given value of  $l$ . All these values are degenerate.

## Electron Spin Angular Momentum

Every electron in an atom can be considered to be spinning about an axis as well as motion in orbit about the nucleus. Its spin motion is designated by the spin quantum number  $s$  which can have a value of  $1/2$  only. Thus the spin angular momentum is given by

$$s = \sqrt{s(s+1)} \cdot \frac{h}{2\pi} \quad \text{or} \quad s = \sqrt{s(s+1)} \hbar$$

$$s = \sqrt{s(s+1)} \text{ units}$$

$$= \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \frac{1}{2}\sqrt{3} \text{ units}$$

Spin angular momentum is a vector quantity by which we mean that its direction is important as well as its magnitude. Once a reference direction is specified, the spin angular momentum vector can point only so that its component along the reference direction are half integral multiples of  $\frac{h}{2\pi}$ .



The reference direction is taken vertical z-axis (arbitrary) and so we can write the components of  $s$  in this direction as  $s_z$ . Alternatively, since we know that the  $s_z$  are half integral multiples of  $\frac{h}{2\pi}$ , we can represent the components in terms of an half integral number of  $s_z$ .

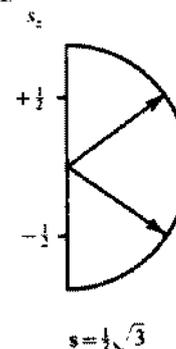
$$s_z = s \cdot \frac{h}{2\pi}$$

$$s_z = \pm \frac{1}{2}$$

There are '2s + 1' values of  $s_z$  for a given value of  $s$ .  $s_z$  is to be identified with the spin quantum no.  $m_s$

$$s_z = m_s = \pm \frac{1}{2}$$

The components of  $s$  i.e.,  $s_z$  are shown in the following figure



### Total Electronic Angular Momentum

It is the sum of orbital angular momentum and spin angular momentum

$$j = l + s \quad \dots(1)$$

$j$  is the total angular momentum. Since  $l$  and  $s$  are vectors. The equation (1) must be a vector addition.

$j$  can be expressed in terms of total angular momentum quantum number  $j$ .

$$j = \sqrt{j(j+1)} \cdot \frac{h}{2\pi} = \sqrt{j(j+1)} \text{ units} \quad \dots(2)$$

where  $j$  is half integral (since  $s$  is half integral for one electron atom) similar to  $l$  and  $s$ ,  $j$  can have  $z$ -components which are half integral only i.e.,

$$j_z = \pm j, \mp (j-1), \pm (j-2), \dots, \frac{1}{2}$$

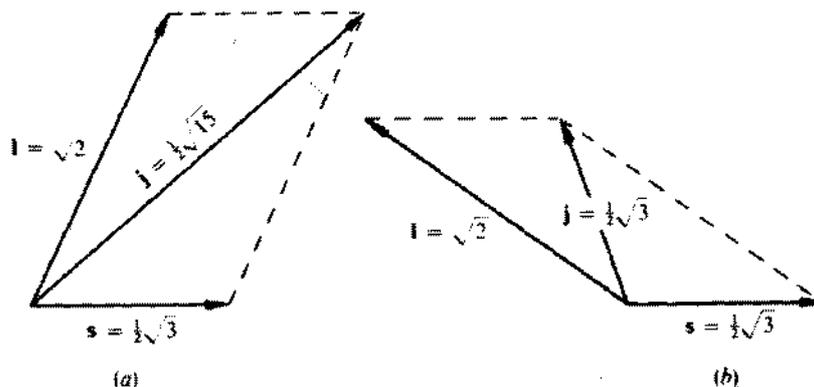
### Summation of $l$ and $s$ values for allowed values of $j$

Two methods:

- (1) **Vector Summation:** Two forces in different directions may be added by a graphical method in which vector arrows are drawn to represent magnitude and direction of the forces, the parallelogram is completed, and the magnitude and direction of the resultant given by the diagonal of the parallelogram.

Exactly the same method can be used to find the resultant ( $j$ ) of the vectors  $l$  and  $s$ . The angle b/w  $l$  and  $s$  is such that the value of  $j$  should half integral as given by equation (2). Thus  $j$  can take values

$$\frac{1}{2}\sqrt{3}, \frac{1}{2}\sqrt{15}, \frac{1}{2}\sqrt{35} \dots \text{corresponding to } j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \dots$$



$$l = 1, l = \sqrt{2}$$

$$s = \frac{1}{2}, s = \frac{1}{2}\sqrt{3}$$

$$j = \frac{3}{2}, j = \frac{1}{2}\sqrt{15}$$

$$s = \frac{1}{2}, s = \frac{1}{2}\sqrt{3}$$

$$j = \frac{1}{2}, j = \frac{1}{2}\sqrt{3}$$

Some results are obtained by summing the quantum numbers  $l$  and  $s$  to get the quantum number  $j$ .

In this example  $l = 1, s = \frac{1}{2}$ .

$$j = l + s = 1 + \frac{1}{2} = \frac{3}{2}$$

$$j = l - s = 1 - \frac{1}{2} = \frac{1}{2}$$

$$l = 1, l = \sqrt{2}$$

- (2) **Summation of z-components:** If the components along a common direction of two vectors are added, the summation yields the components in that direction of their resultant. The z-components of  $l = 1$  are  $+1, 0, -1$  while those of  $s = \frac{1}{2}$  are  $+\frac{1}{2}$  and  $-\frac{1}{2}$  only. Taking all possible sums of these quantities we have

$$j_z = l_z + s_z$$

Therefore,

$$\begin{aligned} j_z &= 1 + \frac{1}{2}, 1 - \frac{1}{2}, 0 + \frac{1}{2}, 0 - \frac{1}{2}, -1 + \frac{1}{2}, -1 - \frac{1}{2} \\ &= \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \end{aligned}$$

From these values, it is obvious that the maximum value of  $j_z$  is  $\frac{3}{2}$  which belongs to  $j = \frac{3}{2}$  (cf equation (3)). other components are  $\frac{1}{2}, -\frac{1}{2}$  and  $-\frac{3}{2}$ . We are left with  $j_z = +\frac{1}{2}$  and  $-\frac{1}{2}$  because these values are consistent with  $j = \frac{1}{2}$ .

## Many Electron Atoms

If two or more electrons are present in a sub-shell of an atom, these electrons are not independent of each other but these electrons interact with each other and result in the formation of a ground state (lowest energy state) and one or more excited states for the atom or ion. In addition to the electrostatic repulsion b/w electrons, they influence each other (1) by interaction or coupling of the magnetic fields produced by their spins and (2) by interaction or coupling of the magnetic field produced by the orbital motion of the electrons (orbital angular momentum).



There are two different ways in which we might sum the orbital and spin angular momentum of several electrons.

- (1) First sum the orbital angular momenta of electrons, then the spin angular momenta of electrons separately and finally add the total orbital and total spin angular momenta to reach the grand total

$$\sum l_i = L, \quad \sum s_i = S$$

$$L + S = J$$

Such type of coupling or interaction is called as Russel-Saunders Coupling or LS coupling. The LS coupling takes place in light atoms.

- (2) Sum the orbital and spin momenta of each electron separately, finally summing the individual totals to form the grand total

$$l_i + s_i = j_i$$

$$\sum j_i = J$$

Such type of coupling is called as j-j coupling. The j-j coupling takes place in heavy atoms.

### The Total Orbital Angular Momentum

The total orbital angular momentum is given by

$$\begin{aligned} L &= \sqrt{L(L+1)} \cdot \frac{h}{2\pi} \\ &= \sqrt{L(L+1)} \hbar \quad \left( \hbar = \frac{h}{2\pi} \right) \quad \hbar \text{ is called } h \text{ bar} \\ &= \sqrt{L(L+1)} \text{ units} \end{aligned}$$

$L$  = Total orbital angular momentum

$L$  = Total orbital angular momentum quantum number

The value of  $L$  (a non negative integer) is obtained by coupling the individual orbital angular momentum quantum numbers by using the Clebsch-Gordan Series:

If the quantum numbers of two electrons are  $l_1$  and  $l_2$  we can obtain the total orbital angular momentum quantum no.  $L$  as:

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

The modulus signs are attached to  $l_1 - l_2$  because  $L$  is non negative.

The maximum value  $L = l_1 + l_2$  is obtained when the two orbital angular momenta are in the same direction. The lowest value  $L = |l_1 - l_2|$  is obtained when they are in opposite directions. The intermediate value represent possible intermediate relative orientations of the two momenta, for two  $p$ -electrons (for which  $l_1 = l_2 = 1$ ),  $L = 2, 1, 0$ . The code for converting the value of  $L$  into a letter is same as for the  $s, p, d, f, \dots$  designation of orbitals but uses uppercase Roman letters

$L$	0	1	2	3	4	5	6	7	8.....
	S	P	D	F	G	H	I	K	L.....

Thus a  $p^2$  configuration ( $L = 2, 1, 0$ ) can give rise to D, P and S terms. The terms differ in energy on account of the different spatial distribution of the electrons and the consequent differences in repulsion between them.

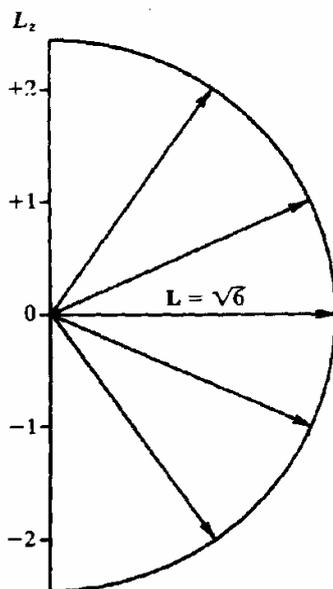
We can also define the component of the total angular momentum along a given axis ( $z$ -axis, arbitrary).

$$L_z \text{ or } M_L = L, L-1, L-2, \dots, 0, \dots, -L$$

The number of possible value of  $M_L$  is given by ' $2L + 1$ '  $M_L$  is also given by

$$M_L = m_{l_1} + m_{l_2} + \dots + m_{l_n} = \sum m_l$$

The z-components of total angular momentum for  $L = 2$  are shown the following figure.

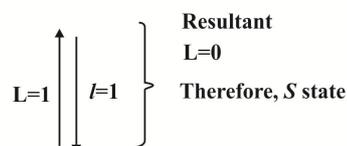
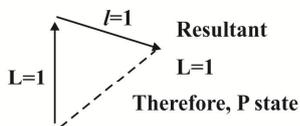
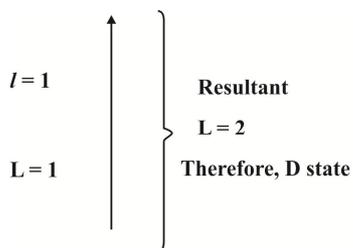


(a)  $L = 2$

### Pictorial Representation of Total Orbital Angular Momentum

For  $p^2$ -configuration:

$$l_1 = 1, l_2 = 1$$

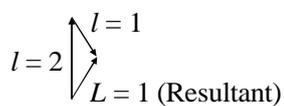
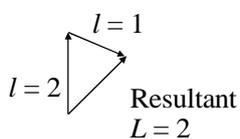
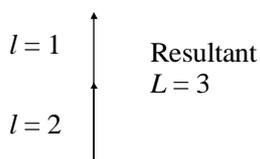


For  $p^1d^1$ -configuration:

$$l_1 = 1, l_2 = 2$$

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

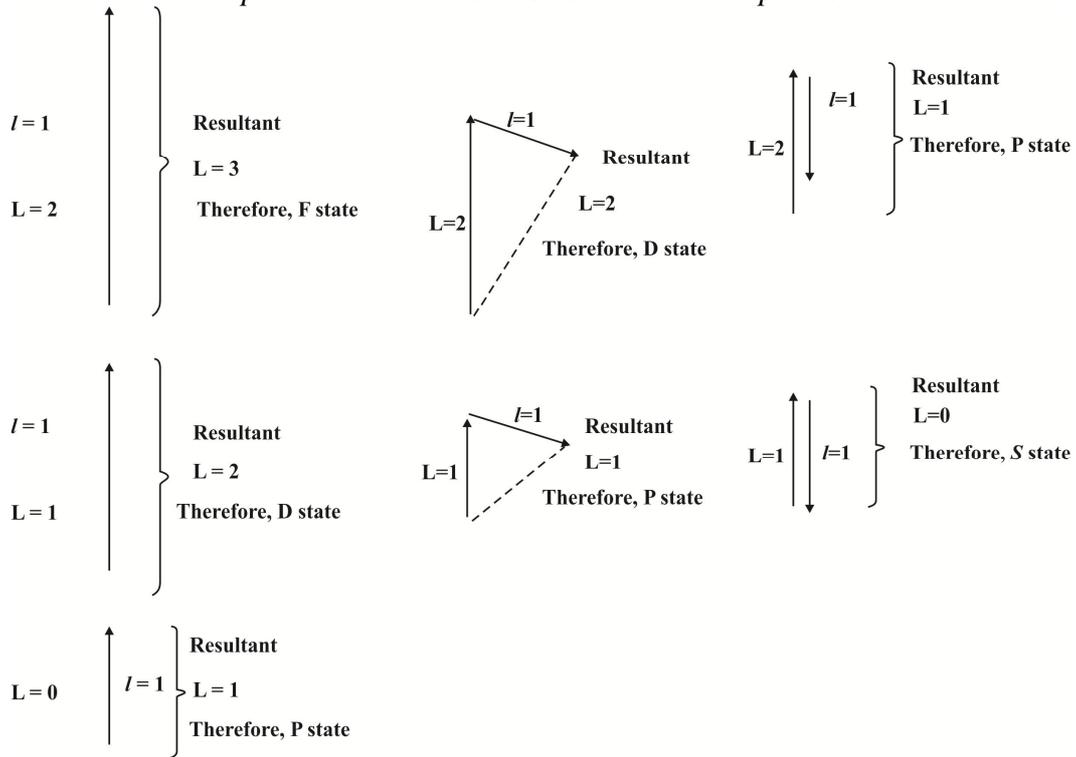
$$= 3, 2, 1$$





**For  $p^3$ -configuration:**

There is interaction of a third  $p$ -electron on the states obtained for the  $p^2$ -case.



**Total Spin Angular Momentum**

The total spin angular momentum is given by

$$S = \sqrt{S(S+1)} \cdot \frac{h}{2\pi} = \sqrt{S(S+1)} \text{ units}$$

$S$  = Total spin angular quantum number

$S$  is either integral or zero, if the no. of contributing spins is even.

$S$  is half integral, if the number is odd.

The value of  $S$  (non negative) can be obtained by using Clebsch-Gordan series. If we have two electrons with spin quantum no  $s_1$  and  $s_2$ , then

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$$

For each electron  $s = \frac{1}{2}$

$\therefore S = 1, 0$  (for two electrons)

We can also define the component of the total spin angular momentum along a given axis.

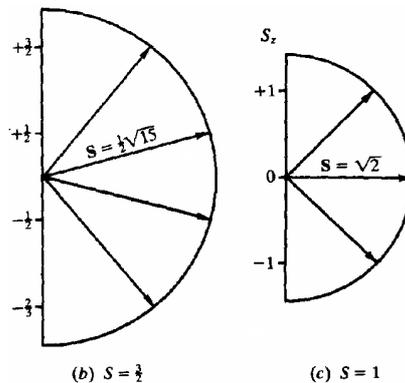
$$S_z \text{ or } M_s = S, S-1, S-2, \dots, -S$$

$$M_S = m_{s_1} + m_{s_2} + \dots + m_{s_n} = \sum m_{sn}$$

There will be  $2S + 1$  values of  $M_S$  for given value of  $S$ .



The z-components of total spin angular momentum ( $S$ ) i.e.,  $M_S$  for  $S = \frac{3}{2}$  and  $S = 1$  are shown in the following figure:



### Coupling of Spin Angular Momenta

For a single electron, the spin quantum no.  $m_s$  has a value of  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . If two or more electrons are present in a subshell, the magnetic fields produced interact with each other i.e., couple, giving a resultant spin quantum number  $S$ .

For two electrons  $p^2$  or  $d^2$ :

$$\left. \begin{array}{l} m_s = +\frac{1}{2} \uparrow \\ m_s = +\frac{1}{2} \uparrow \end{array} \right\} \text{Resultant } S = 1
 \qquad
 \left. \begin{array}{l} m_s = +\frac{1}{2} \uparrow \\ m_s = -\frac{1}{2} \downarrow \end{array} \right\} \text{Resultant } S = 0$$

### Spin Multiplicity:

The quantity  $2S + 1$  is called the multiplicity of the system.

Spin multiplicity =  $2S + 1$

### Total Angular Momentum ( $J$ ):

It is the sum of total orbital angular momentum ( $L$ ) and the total spin momentum ( $S$ )

$$J = L + S$$

and  $J = \sqrt{J(J+1)} \cdot \frac{h}{2\pi}$ ;

$$J = \sqrt{J(J+1)} \text{ units}$$

$J$  = Total angular momentum quantum number

(Non negative integer or half integer)

The permitted values of  $J$  are given by the Clebsch-Gordan Series

$$J = L + S, L + S - 1, \dots, |L - S|$$

If there is a single electron outside a closed shell,  $J = j$ , with  $j$  either  $l + \frac{1}{2}$  or  $l - \frac{1}{2}$ .

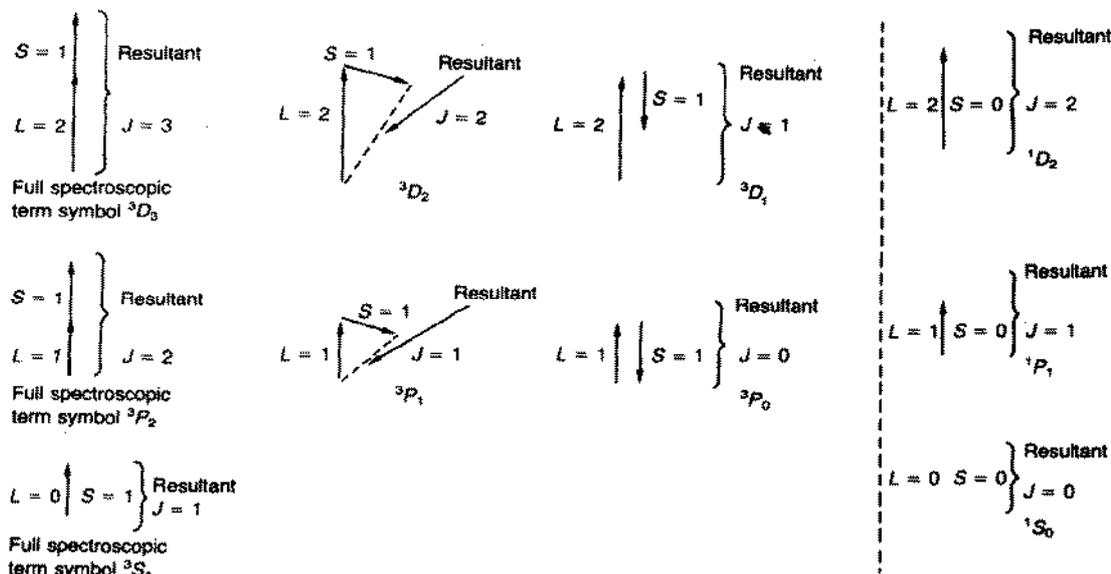
### Spin Orbit Coupling

When several electrons are presents in a subshell, the overall effect of the individual angular momenta  $l$  is given by the resultant angular quantum no.  $L$  and the overall effect of individual spins  $m_s$  is given by the resultant spin quantum no.  $S$ . In an atom, the magnetic effect of  $L$  and  $S$  may interact or couple, giving a new quantum no.  $J$  called the total angular momentum quantum no. which results from the vectorial combination of  $L$  and  $S$ . This coupling of  $S$  and  $L$  is called Russel-Saunders Coupling.

For  $p^2$ :

$$l_1 = l_2 = 1 \quad s_1 = s_2 = \frac{1}{2}$$

$$L = 2, 1, 0 \quad s = 1, 0$$



This helps to identify the term symbol for a particular electronic configuration.

## Microstates

The electronic configuration of an atom, ion or molecule is an incomplete description of the arrangement of electrons in atoms. In the configuration  $p^2$ , for instance, the two electrons might occupy orbitals with different orientations of their orbital angular momenta (i.e., with different values of  $m_l$  from among the possibilities  $+1, 0, -1$  that are available when  $l = 1$ ). Similarly, the designation  $p^2$  tells us nothing about the spin orientations of the two electrons ( $m_s = +\frac{1}{2}$  or  $-\frac{1}{2}$ ). The atom may in fact have several different states of total orbital and spin angular momenta, each one corresponding to the occupation of orbital with different values of  $m_l$  by electrons with different values of  $m_s$ . The different ways in which the electrons can occupy the orbitals specified in the configuration are called **microstates** of the configuration.

## Calculations of number of Microstates

Each different arrangement of electrons in a set of orbitals has a slightly different energy and is called a microstate.

$$\text{No. of microstates} = \frac{N!}{x!(N-x)!}$$

$N = 2(2l + 1) =$  Twice the no. of orbitals

$x =$  Number of electrons.

**Example :**

$$p^2, \quad N = 6, x = 2$$

$$\text{No. of Microstates} = \frac{6!}{2!(6-2)!} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1 \times 4 \times 3 \times 2 \times 1} = 15$$



## Spectroscopic Terms

The microstates of a given configuration have the same energy only if interelectronic repulsions are negligible. However, because atoms and most molecules are compact, interelectronic repulsions are strong and can not always be ignored. As a result, microstates that correspond to different relative spatial distributions of electrons have different energies. If we group together the microstates that have the same energy when electron repulsions are taken into account, we obtain the spectroscopically distinguishable energy levels called **Terms**.

The values of  $L$  correspond to **atomic states** described as S, P, D, F .....in a manner similar to the designation of atomic orbitals  $s, p, d, f$ ..... .

$L = 0$	S state
$L = 1$	P state
$L = 2$	D state
$L = 3$	F state
$L = 4$	G state
$L = 5$	H state
$L = 6$	I state

The values of  $S$  are used to calculate the spin multiplicity  $2S + 1$ , the spin multiplicity. The term is obtained by writing spin multiplicity as superscript to the state  
 Term =  $^{2S+1}L$

The state having multiplicity of 1, 2, 3 or 4 are described as singlet, doublet, triplet or quartet states respectively.

### Relation between number of unpaired electron and spin multiplicity.

Number of unpaired electron	S	Spin multiplicity	State
0	0	1	Singlet
1	1/2	2	Doublet
2	1	3	Triplet
3	3/2	4	Quartet
4	2	5	Quintet
5	5/2	6	Sextet

In above calculation we have taken  $n$  and  $l$  quantum number to be constant.

### Term Symbols:

The term symbol for a particular **atomic state** is written as follows:

$$\text{Term symbol} = ^{2S+1}L_J$$

Where the numerical superscript gives the multiplicity of state, the numerical subscript gives the total angular momentum quantum number  $J$  and the value of orbital quantum no.  $L$  is expressed by a letter.

For  $L = 0, 1, 2, 3, 4, \dots$  symbol are S, P, D, F, G .....respectively.

The fifteen microstates and resultant value of  $M_L$  and  $M_S$  for  $p^2$  are given in the following table:

	$m = +1, 0, -1$	$M_s$	$M_L$
1	$\uparrow\downarrow$	0	2
2	$\uparrow\downarrow$	0	-2
3	$\uparrow\downarrow$	0	0
4	$\uparrow$     $\downarrow$	0	0
5	$\downarrow$     $\uparrow$	0	0
6	$\uparrow$   $\downarrow$	0	1
7	$\downarrow$   $\uparrow$	0	1
8	$\uparrow$   $\downarrow$	0	-1
9	$\downarrow$   $\uparrow$	0	-1
10	$\uparrow$   $\uparrow$	1	1
11	$\uparrow$     $\uparrow$	1	0
12	$\uparrow$   $\uparrow$	1	-1
13	$\downarrow$   $\downarrow$	-1	1
14	$\downarrow$     $\downarrow$	-1	0
15	$\downarrow$   $\downarrow$	-1	-1

Figure (a)

**To calculate spectroscopic term for a particular configuration:**

Suppose we have to calculate term symbol arising for  $p^2$  configuration.

As we discussed on page 122 that for  $p^2$  configuration possible L value will be

$L = 2$ ; corresponds to D state

$L = 1$ ; corresponds to P state

$L = 0$ ; corresponds to S state

Since,  $M_s = +1/2, -1/2$

Either  $S = \uparrow\uparrow = 1$  or  $S = \uparrow\downarrow = 0$

Thus for  $p^2$  case

$L = 2, 1, 0, S = 1, 0$

Thus term arising from  $p^2$  configuration will be  $^3D, ^1D, ^3P, ^1P, ^3S, ^1S$ ,

To write energy state:

1. Write number of possible state using Pauli's exclusion principle:

Figure (a)

2. Find the energy state

(a) Took the configuration having maximum  $M_L$

From table it is clear that  $M_L = 2$

Maximum  $M_L$  value is 2,  $M_L = 2$  comes from  $L = 2$ . Thus we got D state.

Now took  $M_s$  value corresponding to this maximum  $M_L$  which is 0, Thus  $S = 0$

Thus spin multiplicity =  $2S + 1 = 2 \times 0 + 1 = 1$

$D^1$  state results. Since  $L = 2$  here

Thus  $M_L = 2, 1, 0, -1, -2$  and  $S = 0$



Number of microstate =  $(2L + 1)(2S + 1) = 5$

Thus (2, 0); (1, 0); (0, 0); (-1, 0); (-2, 0) in the table belongs to  $D^1$  state.

Now, next possible  $M_L$  value is  $M_L = 1$

$M_L = 1$  comes from  $L = 1$  which corresponds to P state

Corresponding maximum  $M_S$  value = 1

Thus spin multiplicity will be  $2S + 1 = 3$

Hence energy state corresponding to this particular  $M_L$  value =  $^3P$

Number of microstate corresponding to  $P^3$  state =  $(2L + 1)(2S + 1) = 9$

Hence, (1, 1), (1, 0), (1, -1), (0, 1), (0, 0), (0, -1), (-1, 1), (-1, 0) and (-1, -1) belong to  $^3P$  state.

Next  $M_L$  value = 0  $\Rightarrow$   $L = 0$  which corresponds to S state

Now took  $M_S$  value corresponding to this  $M_L$  value, which is found to be zero.

$S = 0$

Spin multiplicity will be  $(2S + 1) = 1$

Hence energy state corresponds to this value is  $^1S$

Number of microstate corresponds to  $^1S$  state =  $(2L + 1)(2S + 1) = 1$

(0, 0) belongs to  $^1S$  state.

From above it is clear that the term arising from  $p^2$  configuration.

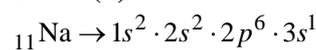
i.e.  $^3D, ^1D, ^3P, ^1P, ^3S, ^1S$  reduces to  $^1D, ^3P$  and  $^1S$  in accordance to Pauli's exclusion principle.

Thus for  $p^2$  configuration energy state are  $^1D, ^3P$  and  $^1S$ .

Similarly we can calculate term symbol arising from any configuration.

**Problem:** Find the term symbols arising from the ground state configuration of (a) Na (b) F and (c) the excited configuration  $1s^2 \cdot 2s^2 \cdot 2p^1 3p^1$  of carbon.

**Soln: (a) For Na:**



Ignore the inner closed shells and consider only incomplete shell i.e.,  $3s^1$

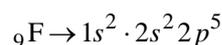
$$L = l = 0, \quad S = s = \frac{1}{2}, \quad \text{spin multiplicity} = 2S + 1 = 2 \times \frac{1}{2} + 1 = 2$$

S state

$$J = |L + S| \dots \dots \dots |L - S| = |0 + \frac{1}{2}| \dots \dots \dots |0 - \frac{1}{2}| = \frac{1}{2}$$

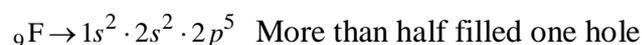
Term symbol =  $^2S_{1/2}$

**(b) F-atom:**



If a subshell is more than half filled, it is easy to find out the terms by considering the holes i.e., vacancies in the orbitals rather than considering the large no. of electrons. For example  $\text{Cu}^{2+}$  ion with  $(\text{Ar})3d^9$  configuration may be treated as one hole. Similarly F-atom with  $1s^2 \cdot 3s^2 \cdot 2p^5$  configuration may be treated as considering one hole. Also in case of oxygen with electronic configuration  $1s^2 \cdot 2s^2 \cdot 2p^4$  there would be two holes.

**For F-atom**





$$L = 1, \quad S = s = \frac{1}{2}, \quad 2S + 1 = 2 \times \frac{1}{2} + 1 = 2$$

∴ P state

$$J = |L + S| \dots \dots \dots |L - S| = |1 + \frac{1}{2}| \dots \dots \dots |1 - \frac{1}{2}| = \frac{3}{2}, \frac{1}{2}$$

Term symbols =  ${}^2P_{3/2}$   ${}^2P_{1/2}$

According to Hund's third rule

Ground state Term symbol =  ${}^2P_{3/2}$  (Because p is more than half filled)

**(c)  $2p^1 3p^1$  configuration :**

$$l_1 = l_2 = 1 \qquad s_1 = s_2 = \frac{1}{2}$$

$$L = |l_1 + l_2| \dots \dots \dots |l_1 - l_2| \qquad S = \frac{1}{2} + \frac{1}{2} \dots \dots \dots |\frac{1}{2} - \frac{1}{2}|$$

$$L = 1 + 1, 1 + 1 - 1, \dots \dots \dots |1 - 1| = 1, 0$$

$$= 2, 1, 0 \qquad \text{For } S = 1, \quad 2S + 1 = 2 \times 1 + 1 = 3$$

$$\text{States} = D, P \text{ and } S \qquad \text{For } S = 0, \quad 2S + 1 = 1$$

Thus terms are  $\underbrace{3D, 3P, 3S}_{\text{For } S=1}$   $\underbrace{1D, 1P \text{ and } 1S}_{\text{For } S=0}$

**For  $3D$  :**  $L = 2, S = 1$   
 $J = L + S, L + S - 1, \dots \dots \dots |L - S|$   
 $= 2 + 1, 2 + 1 - 1, \dots \dots \dots 2 - 1$   
 $= 3, 2, 1$

Energy Levels =  $3D_3, 3D_2, 3D_1$

**For  $1D$  :**  $L = 2, S = 0; \quad J = 2$   
 Energy level =  $1D_2$

**For  $3P$  :**  $L = 1, S = 1$   
 $J = 1 + 1, 1 + 1 - 1, \dots \dots \dots |1 - 1|$   
 $= 2, 1, 0$   
 Energy levels =  $3P_2, 3P_1, 3P_0$

**For  $1P$  :**  $L = 1, S = 0$   
 $J = 1$   
 Energy level =  $1P_1$

**For  $3S$  Term :**  $L = 0, S = 1$   
 $J = 0 + 1, \dots \dots \dots |0 - 1|$   
 $= 1$

Energy level =  $3S_1$

For  $1S$  Term :  $L = 0, S = 0; \quad J = 0$

Energy level =  $1S_0$

Thus total term symbols are

${}^3D_3, {}^3D_2, {}^3D_1, {}^3P_2, {}^3P_1, {}^3P_0, {}^3S_1, {}^1D_2, {}^1P_1, {}^1S_0$

## Ground State Term : Hund's Rule

The term derived for a given configuration possess different energies. For example the term derived for

$p^2$  configuration are  $^3P, ^1D$  and  $^1S$ . These three term possess different energies.

Provided that Russell-Saunders coupling is applicable, the lowest energy term i.e. ground state is summarized in a set of rules known as Hund's Rule. This rule is different what we learnt in chemical bonding earlier.

1. When there is more than one energy state, the energy state having the maximum multiplicity or having most unpaired electron (parallel spins) will have lowest energy i.e. that will be the ground state.

For example among  $^3P, ^1D$  and  $^1S$ , which are the three term derived from  $p^2$  configuration,  $^3P$  term has highest multiplicity, thus it will be the ground state.

2. In the case of more than one term having the highest multiplicity, then the one with greatest value of L is the most stable.

For example, in  $d^2$  configuration case out of  $F^3$  and  $P^3$ ,  $F^3$  will be the ground state.

3. For all terms having a given multiplicity and L value, the sequence of energy of the components which have different value of J follows the numerical value of J.

(a) If the subshell is less than half filled. The terms which has lowest J value is the ground state.

(b) If the subshell is more than half filled. The term which have highest J value will be the ground state.

**Note:** Hund's Rule can not be used to predict the energy of excited term. Their order can be predicted by quantum mechanical calculation method.

### Interpretation of Hund's Rule:

We can focus and understand Hund's first rule. The maximum multiplicity corresponds to the maximum value of S, and this in turn corresponds to the electron spins being preferentially aligned parallel, so favouring a distribution in which the electrons are well separated from one another leading to a low potential energy.

The way in which the second rule arises is perhaps less easy to visualize; it requires that for the term having the same value of S, the one having the greatest value of L has the lowest energy. This is clear that, the maximum value having connection with the maximum orbital angular momentum, which arises when the orbital angular momenta of the individual electrons reinforce each other to the greatest extent. This clearly indicates that the electrons are tending to move in the same direction. One result of this is that they will be in close proximity less often, and will on the whole experience a smaller electrostatic repulsion. The alignment of magnetic moments is a principal factor in the operation of third rule. Where the subshell is less than half filled, the state of lowest energy corresponds to the alignment of the orbital magnetic moment antiparallel with the spin magnetic moment so that the value of J given by (L-S) has the lowest value. On the other hand parallel alignment ( $J = L + S$ ) is the most unfavourable arrangement.

As we importantly mentioned earlier that Hund's Rule can not be used satisfactorily to predict the order of excited terms. To know which energy state lies above the ground state or what is the sequence of energy of energy state, we have to consider two interaction parameter, which is briefly discussed here.

- (a) **Inter electron repulsion parameter:** When the interaction between two or more electrons are considered theoretically, it is possible to write down the energy for each term, which arises as an expression involving several parameters, labelled as  $F_0, F_2, F_4$  etc.



- (i) For  $p^n$  configuration the two parameter  $F_0$  and  $F_2$  are required for  $d^n$ ,  $F_0$ ,  $F_2$  and  $F_4$  and so on.
- (ii)  $F_0$  takes account of spherically symmetrical part of electron repulsion, i.e., it involves only the radial functions of the electrons.
- (iii)  $F_2$  and  $F_4$  are connected with the angular dependent electron repulsion.
- (iv) Racah recommended the use of two alternative parameters known as Racah B and C parameters, which are related to F parameters by  $B = F_2 - 5F_4$ ,  $C = 35F_4$

By doing this he got the energy difference between two energy terms having same multiplicity in the terms of single inter electron repulsion parameter B.

#### For Example:

$d^2, d^8$  ; energy difference between  $F^3$  and  $P^3$  is  $15B$

$d^3, d^7$  ;  $F^4 \longrightarrow P^4 \approx 15B$

$d^4, d^6$  ;  $D^3 \longrightarrow H^3 \approx 12B$

Later it was found that roughly  $C \approx 4B$

- (v) If in the whole energy level scheme of an atom, we find two terms having identical L and S value e.g. two  $^2P$  terms, then the actual energy of the lower one will be depressed and the higher one raised, from their simply calculated values. This is known as **configuration interaction**.

#### (b) Spin orbital coupling parameters:

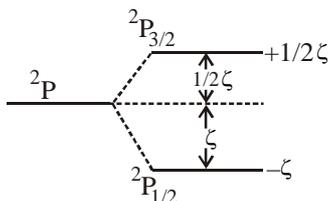
When spin-orbital coupling is considered, the degeneracy of a given free ion energy term is partly removed, and the energy state is split into two or more components. Consider first a one electron case for example  $p^1$  which of course, gives rise to the term  $^2P$ . Through spin orbital coupling, two components arise, having  $J = 3/2$  and  $J = 1/2$ . The energy of each component and the separation between them is expressed in terms of one electron spin-orbital coupling parameter  $\zeta$  (Zeta).

Energy has calculated quantum mechanically and have been found that

$$E(^2P_{3/2}) = 1/2\zeta$$

$$E(^2P_{1/2}) = -\zeta$$

The separation between them is therefore  $3/2\zeta$



This result may be derived from two general rules applicable to spin orbital coupling for a single electron.

- (i) The energy of the component having the maximum value of J is given by  $1/2L\zeta$  , where L is the value of the orbital angular momentum quantum number for the electron under consideration.
- (ii) The separation in energy between the two components is  $J_i\zeta$  where  $J_i$  is the J value for the higher component.



Now turning towards many electron configuration. Here, Zeta ( $\zeta$ ) factor has been replaced by  $\lambda$ .

Both  $\zeta$  and  $\lambda$  are related by  $\zeta / 2S = \lambda$

In this case energy of the highest J component will be  $LS\lambda$

$$\Rightarrow E(J_{\max}) = LS\lambda$$

The separation of a given component (having  $J = J_i$ ) from the next component ( $J = J_i - 1$ ) is given by

$$\Delta E = J_i \lambda, \text{ where } J_i \text{ is the J value for higher component.}$$

This is the famous Lande Interval Rule.

Now consider the case of  $d^2$  system for  $F^3$  case

$$L = 3, S = 1$$

$$\Rightarrow J = 4, 3, 2$$

Thus according to Hund's Rule  ${}^3F_2$  will be of lowest energy

$$\text{Now, } E_{J_{\max}} = LS\lambda = 3\lambda$$

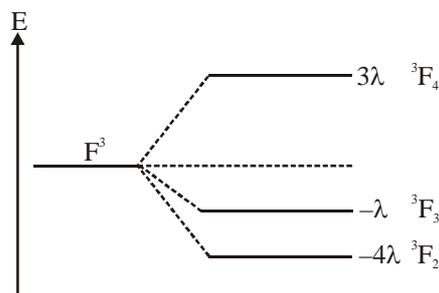
$$\text{Energy separation between } {}^3F_4 \text{ and } {}^3F_3 = J_i \lambda = 4\lambda$$

$$\text{Thus } E({}^3F_3) = 3\lambda - x = 4\lambda = -\lambda$$

$$\text{Again energy separation between } {}^3F_3 \text{ and } {}^3F_2$$

$$= J_i \lambda = 3\lambda$$

$$\text{Thus, } E({}^3F_2) = -4\lambda$$



Spin orbital splitting for the  ${}^3F$  ground term of  $d^2$

### Term Symbol for Closed Subshell Configuration: ( $s^2, p^2, d^{10}$ )

If a subshell is completely filled, such as  $s^2, p^6$  or  $d^{10}$  configurations both  $L$  and  $S$  are zero. Thus closed shell always give  $1s_0$  term symbol.

### Calculation of Ground State Term and Ground State Term Symbol:

Following steps are used for determining the ground state.

1. Write the electronic configuration.
2. Determine the spin multiplicity ( $2S + 1$ )
3. Determine the maximum possible value  $M_L (= \sum ml) \sum m_e$
4. Select maximum value of  $J$  for more than half filled subshell and minimum  $J$  value for less than half filled subshell.

### $p^2$ -configuration:

$m_l$	+1	0	-1	$M_L = 1$	State P
	↑	↑	□		



Since both the electrons have parallel spins

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

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

Ground state term =  $3P$

For  $3P$ ,  $L = 1$ ,  $S = 1$

$$J = |L + S| \dots \dots \dots |L - S| = 2, 1, 0$$

$\therefore$  Ground state term symbol =  $3P_0$  (Less than half filled subshell  $p^2$ )

**$p^3$ -configuration (N-atom  $\rightarrow 1s^2 \cdot 2s^2 \cdot 2p^3$ )**

$m_l$     +1    0    -1             $M_L = 0$     S state

↑	↑	↑
---	---	---

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

$$2S + 1 = 2 \times \frac{3}{2} + 1 = 4$$

Term =  $4S$

For  $L = 0$ ,  $S = 3/2$ ,  $J = 3/2$

Term symbol  $4S_{3/2}$

**Ground state term for  $V^{3+}$  for ( $d^2$ -configuration) (Gate 2007)**

$m_l$     +2    +1    0    -1    -2             $M_L = +2 + 1 = 3$

↑	↑				
---	---	--	--	--	--

$\therefore F$  state

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

Spin multiplicity  $(2S + 1) = 2 \times 1 + 1 = 3$

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

$$= |3 + 1| \dots \dots \dots 3 - 1$$

$$= 4, 3, 2$$

Ground state term symbol =  $3F_2$  (for less than half filled subshell  $d^2$ )

**Ground state term symbols for high spin  $d^5s^1$  and  $d^5$  configuration (Gate 2004)**

**High spin  $d^5s^1$**

$m_l$     +2    +1    0    -1    -2            0     $M_L = 2 + 1 + 0 - 1 - 2 + 0 = 0$

↑	↑	↑	↑	↑		↑
---	---	---	---	---	--	---

$\therefore S$  state

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

$$2S + 1 = 2 \times 3 + 1 = 7$$

Ground state term =  $7S$

For  $L = 0$  and  $S = 3$

$$J = 3$$

Therefore, ground State Term Symbol  $7S_3$

**High spin  $d^5$** 

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

$$= \frac{5}{2}$$

$$M_L = 2 + 1 + 0 - 1 - 2 = 0$$

$$\therefore S \text{ state}$$

$$2S + 1 = 2 \times \frac{5}{2} + 1 = 6$$

Ground State term =  $6S$

$J$  value for  $L = 0$  and  $S = 5/2$  is  $5/2$

Ground state term symbol  ${}^6S_{5/2}$

**Ground State Terms for High Spin and Low Spin  $d^6$ -octahedral Complex:****High spin  $d^6$ :**

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

Spin multiplicity =  $2S + 1 = 2 \times 2 + 1 = 5$

Maximum value of  $M_L = 2 + 2 + 1 + 0 - 1 - 2 = 2$

$\therefore L = 2$ ,  $D$  state

Therefore, ground state Term =  $5D$

**Low spin  $d^6$ :**

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

Spin multiplicity =  $2S + 1 = 2 \times 0 + 1 = 1$

Maximum value of  $M_L = 2 + 2 + 1 + 1 + 0 + 0 = 6$

$\therefore L = 6$ ,  $I$  state

$\therefore$  Ground state term =  $1I$

**Ground State Terms for High Spin and Low Spin  $d^4$  Octahedral Complex  $d^4$  (High spin):**

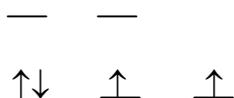
$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 2$$

Spin multiplicity =  $2 \times 2 + 1 = 5$

Maximum value of  $M_L = 2 + 1 + 0 - 1 = 2$

$\therefore D$  state

Ground state term =  $5D$

 **$d^4$  (Low spin):**

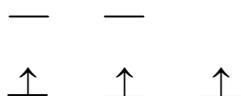
$$S = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 1$$

$$\text{Spin multiplicity} = 2S + 1 = 2 \times 1 + 1 = 3$$

$$\text{Maximum value of } M_L = 2 + 2 + 1 + 0 = 5$$

$$\therefore L = 5, \quad \text{H state}$$

$$\text{Ground state term} = {}^3H$$

 **$d^3$ -configuration in Octahedral Symmetry:**

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

$$\text{Spin multiplicity} = 2S + 1 = 2 \times \frac{3}{2} + 1 = 4$$

$$\text{Maximum value of } M_L = 2 + 1 + 0 = 3$$

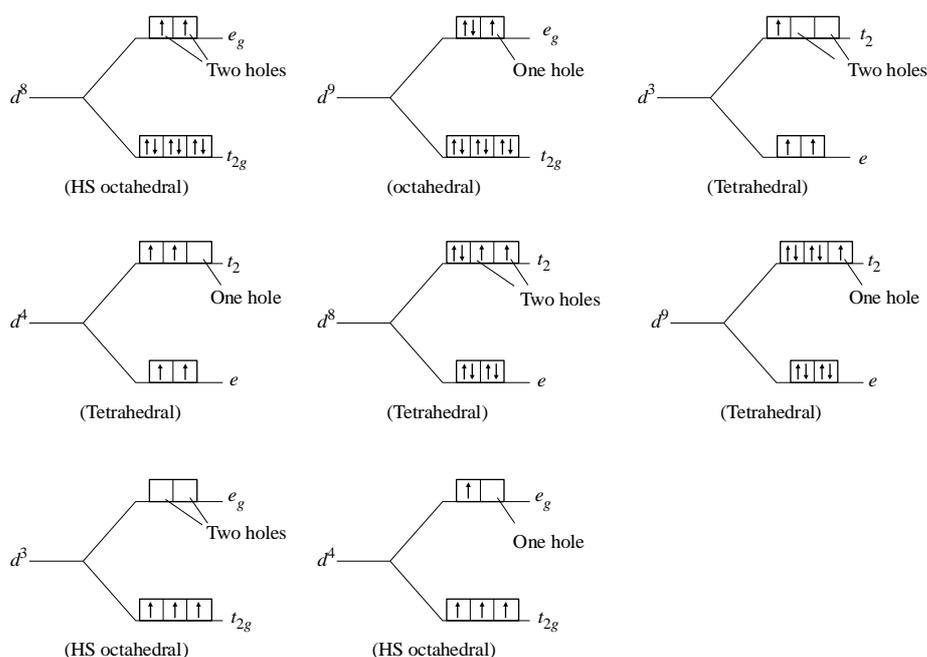
$$\therefore L = 3, \quad \text{F state}$$

$$\therefore \text{Ground state term} = {}^4F$$

**(2) Hole Formulation**

When a subshell is more than half filled, it is simpler and more convenient to work out the terms by considering the 'holes'—that is the vacancies in the various orbitals – rather than the larger number of electrons actually present. In octahedral (HS) or Tetrahedral complexes of transition elements, if  $t_{2g}$  orbitals (octahedral) or  $e$  orbitals (tetrahedral) are symmetrically filled and  $e_g$  orbitals (octahedral) or  $t_2$  orbitals (tetrahedral) have one electron less than the any of the lower energy state orbitals, then these orbitals having one electron less than any  $d$  orbitals of the lower energy state is called hole.

Note that number of holes in the upper energy state should be lower than or equal to the electrons in the lower energy state. The terms derived in this way for the ground state of oxygen which has a  $p^4$  configuration and hence two 'holes' are the same as for carbon with a  $p^2$  configuration, that is  ${}^1S$ ,  ${}^1D$  and  ${}^3P$ . However, oxygen has a more than half filled subshell, and hence when applying Hund's third rule, the energy of the triplet  $P$  states for oxygen are  ${}^3P_2 < {}^3P_1 < {}^3P_0$ , making  ${}^3P_2$  the ground state. In a similar way, by considering 'holes', the terms which arise for pairs of atoms with  $p^n$  and  $p^{6-n}$  arrangements, and also  $d^n$  and  $d^{10-n}$ , give rise to identical terms.

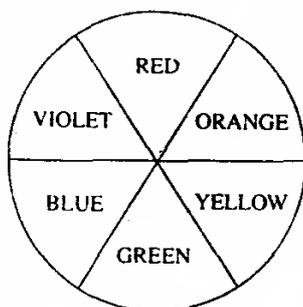


**Table :** Terms arising for  $p$  and  $d$  configurations:

Electronic configuration	Ground state term	Other term
$p^1, p^5$	$^2P$	
$p^2, p^4$	$^3P$	$^1S, ^1D$
$p^3$	$^4S$	$^2P, ^2D$
$p^6$	$^1S$	
$d^1, d^9$	$^2D$	
$d^2, d^8$	$^3F$	$^3P, ^1G, ^1D, ^1S$
$d^3, d^7$	$^4F$	$^4P, ^2H, ^2G, ^2F, ^2D, ^2P$
$d^4, d^6$	$^5D$	$^3H, ^3G, ^3F, ^3D, ^3P, ^1I, ^1G, ^1F, ^1D, ^1S$
$d^5$	$^6S$	$^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2F, ^2D, ^2P, ^2S$

### (3) Absorption of Light

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

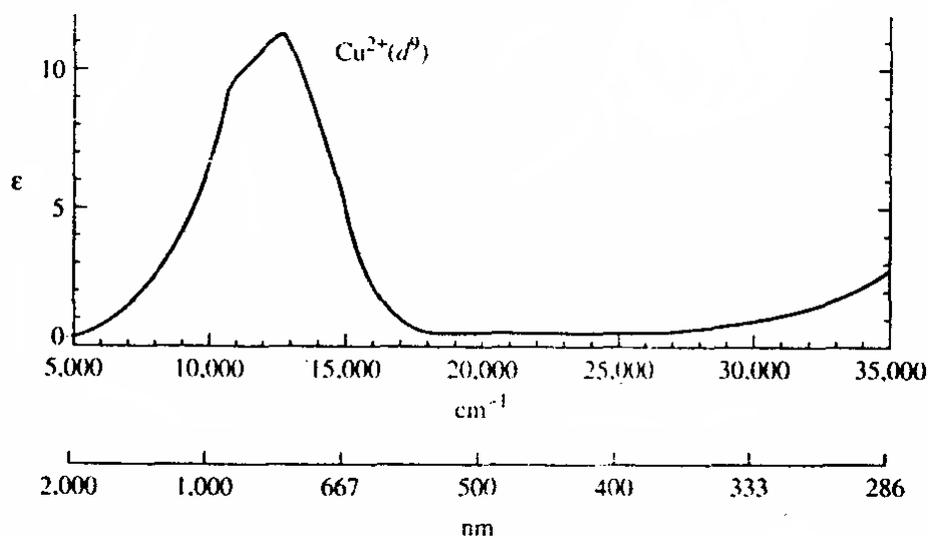


An example from coordination chemistry is the deep blue color of aqueous solutions of copper (II) compounds, containing the ion  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . The blue color is a consequence of the absorption of light between approximately 600 and 1000 nm (maximum near 800 nm;), in the yellow to infrared region of the spectrum. The color observed, blue, is the average complementary color of the light absorbed.

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

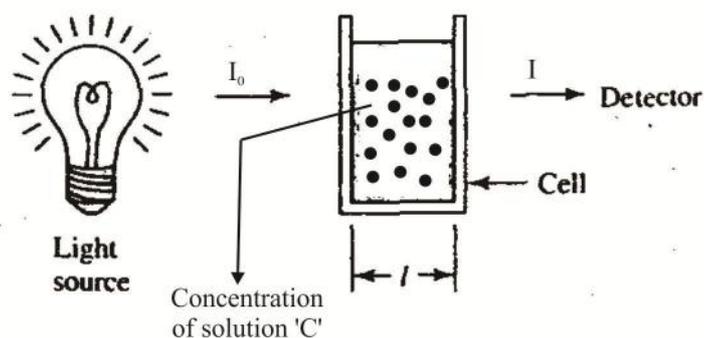
### Beer-Lambert Absorption Law

If light of intensity  $I_0$  at a given wavelength passes through a solution containing a species that absorbs light, the light emerges with intensity  $I$ , which may be measured by a suitable detector.



### Visible Light and Complementary Colors

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



The Beer-Lambert law may be used to describe the absorption of light (ignoring scattering and reflection of light from cell surfaces) at a given wavelength by an absorbing species in solution:

$$\log \frac{I_0}{I} = A = \epsilon l c$$

where  $A$  = absorbance

$\epsilon$  = molar absorptivity ( $\text{L mol}^{-1} \text{cm}^{-1}$ ) (also known as molar extinction coefficient)

$l$  = path length through solution (cm)

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

Absorbance is a dimensionless quantity. An absorbance of 1.0 corresponds to 90% absorption at a given wavelength, an absorbance of 2.0 corresponds to 99% absorption and so on.

Spectrophotometers commonly obtain spectrum as plots of absorbance versus wavelength. The molar absorptivity is a characteristic of the species that is absorbing the light and is highly dependent on wavelength. A plot of molar absorptivity versus wavelength gives a spectrum characteristic of the molecule or ion in question, figure. As we will see, this spectrum is a consequence of transitions between states of different energies and can provide valuable information about those states and in turn, about the structure and bonding of the molecule or ion.

Although the quantity most commonly used to describe absorbed light is the wavelength, energy and frequency are also used. In addition, the wave number the number of waves per centimeter, a quantity proportional to the energy, is frequently used. For reference, the relations between these quantities are given by the equations.

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

where

$\Delta E$  = energy

$h$  = Planck's constant =  $6.626 \times 10^{-34} \text{ J s}$

$c$  = speed of light =  $2.998 \times 10^8 \text{ ms}^{-1}$

$\nu$  = frequency ( $\text{s}^{-1}$ )

$\lambda$  = wavelength (often reported in nm)

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

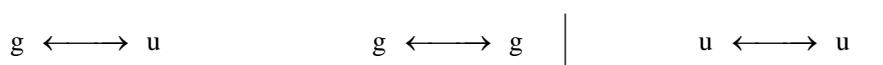
#### (4) Selection Rules:

##### (a) Laporte 'Orbital' Selection Rule

Transitions which involve a change in the subsidiary quantum number  $\Delta l = \pm 1$  are 'Laporte allowed' and therefore have a high absorbance. If  $\Delta l = 0$  i.e., there is no change in subsidiary quantum number, then transitions are said to be forbidden. Laporte selection rule may also be given as follows:



Transitions between g (gerade) and u (ungerade) orbitals are permitted and the transition between g orbitals or u orbitals are not permitted.

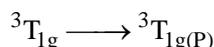
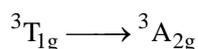


Thus for Ca,  $s^2 \rightarrow s^1 p^1$ ,  $l$  changes by + 1 and the molar absorption coefficient  $\epsilon$  is 5000–10,000 litres per mol per centimetre. In contrast  $d-d$  transition are ‘Laporte forbidden’, since the change in  $l = 0$ , but spectra of much lower absorbance are absorbed ( $\epsilon = 5 - 10 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) because of slight relaxation in the Laporte rule. When the transition metal ion forms a complex it is surrounded by ligands, and some mixing of  $d$  and  $p$  orbitals may occur, in which case transitions are no longer pure  $d-d$  in nature. Mixing of this kind occurs in complexes which do not possess a centre of symmetry, for example tetrahedral complexes, or asymmetrically substituted octahedral complexes. Thus  $[\text{MnBr}_4]^{2-}$  which is tetrahedral and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  which is octahedral but non-centrosymmetric are both coloured. Mixing of  $p$  and  $d$  orbitals does not occur in octahedral complexes which have a centre of symmetry such as  $[\text{Co}(\text{NH}_3)_6]^{3+}$  or  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . However, in these cases the metal-ligands bonds vibrate so that the ligands spend an appreciable amount of time out of their centro-symmetric equilibrium position. Thus a very small amount of mixing occurs and low-intensity spectra are observed. Thus Laporte allowed transitions are very intense, whilst Laporte forbidden transitions vary from weak intensity if the complex is non-centrosymmetric to very weak if it is centrosymmetric. Since  $p-d$  mixing is much more pronounced in tetrahedral complexes (non-centro symmetric) than octahedral complexes (centro symmetric). Thus tetrahedral complexes give more intense colour than octahedral complexes.

### (b) Spin Selection Rule

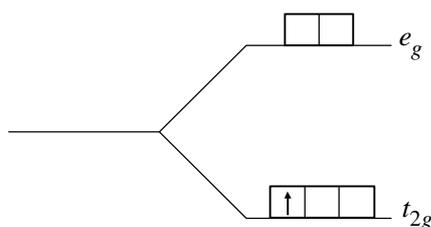
During transitions between energy levels, an electron does not change its spin, that is  $\Delta S = 0$  i.e., any transition for which  $\Delta S = 0$  (no change in spin state) is allowed. If  $\Delta S \neq 0$  (change in spin state) transition is forbidden. In other words, for allowed transitions spin multiplicity does not change.

e.g.,

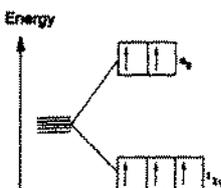


Here, there are fewer exceptions than for the Laporte selection rule. Thus in the case of  $\text{Mn}^{2+}$  in a weak octahedral field such as  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  the  $d-d$  transitions are spin forbidden because each of the  $d$  orbitals is singly occupied. Many  $\text{Mn}^{2+}$  compounds are off white or pale flesh coloured, but the intensity is only about one hundredth of that for a spin allowed transition. Since the spin forbidden transitions are very weak, analysis of the spectra of transition metal complexes can be greatly simplified by ignoring all spin forbidden transitions and considering only those excited states which have the same multiplicity as the ground state. Thus for a  $d^2$  configuration the only terms which need to be considered are the ground state  ${}^3F$  and the excited state  ${}^3P$ .

$\text{Ti}^{3+}$  in weak octahedral field (spin allowed), if electron in  $t_{2g}$  level is excited to  $e_g$  level then spin state will not change. Thus this transition is spin allowed.



$\text{Mn}^{2+}$  in weak octahedral field (spin forbidden transition), if one of the electrons in  $t_{2g}$  level is excited to  $e_g$  state then spin state is changed (from clockwise to anticlockwise) thus this electronic transition is spin forbidden.

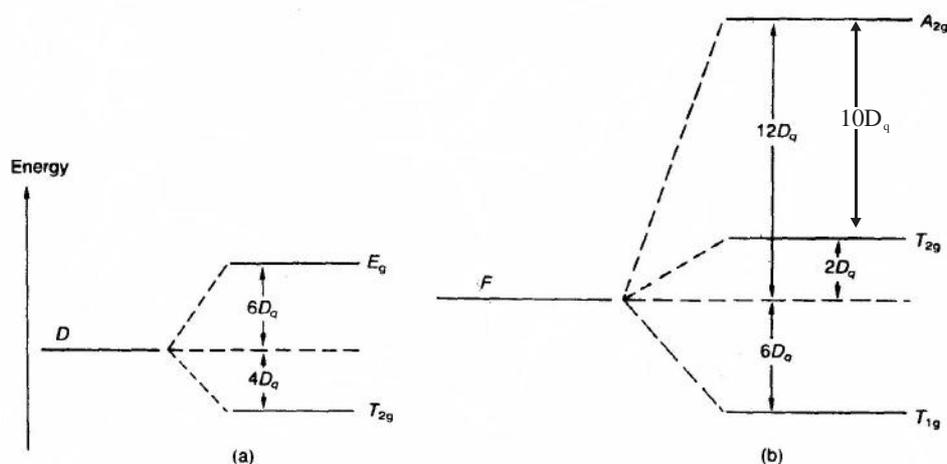


Molar absorption coefficient for different types of transition are given in the following table:

Laporte (orbital)	Spin	Type of Spectra	$\epsilon$ ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	Example
Allowed	Allowed	Charge transfer	10000	$[\text{TiCl}_6]^{2-}$
Partly allowed, some $p$ - $d$ mixing	Allowed	$d$ - $d$	500	$[\text{CoBr}_4]^{2-} \cdot [\text{CoCl}_4]^{2-}$
Forbidden	Allowed	$d$ - $d$	8–10	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} \cdot [\text{V}(\text{H}_2\text{O})_6]^{3+}$
Partly allowed, some $p$ - $d$ mixing	Forbidden	$d$ - $d$	4	$[\text{MnBr}_4]^{2-}$
Forbidden	Forbidden	$d$ - $d$	0.02	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

### (5) Splitting of Electronic Energy Levels and Spectroscopic States

$s$  orbital is spherically symmetrical and is unaffected by an octahedral (or any other) field,  $p$  orbitals are directional, and  $p$  orbitals are affected by an octahedral field. However, since a set of three  $p$  orbitals are all affected equally, their energy levels remain equal, and no splitting occurs. A set of  $d$  orbitals is split by an octahedral field into two level  $t_{2g}$  and  $e_g$ . The difference in energy between these may be written as  $\Delta_0$  or  $10D_q$ . The  $t_{2g}$  level is triply degenerate and is  $4D_q$  below the barycentre and the  $e_g$  level is doubly degenerate and is  $6D_q$  above the barycentre. For a  $d^1$  configuration, the ground state is a  $2D$  state, and the  $t_{2g}$  and  $e_g$  electronic energy levels correspond with the  $T_{2g}$  and  $E_g$  spectroscopic states. A set of  $f$  orbitals is split by an octahedral field into three levels. For an  $f^1$  arrangement the ground state is a  $^3F$  state and is split into a triply degenerate  $T_{1g}$  state which is  $6D_q$  below the barycentre, a triply degenerate  $T_{2g}$  level which is  $2D_q$  above the barycentre and a single  $A_{2g}$  state which is  $12D_q$  above the barycentre.



In the one electron cases  $s^1, p^1, d^1$  and  $f^1$  there is a direct correspondence between the splitting of electronic energy levels which occurs in a crystal field and the splitting of spectroscopic states. Thus in an octahedral field the  $S$  and  $P$  states are not split.  $D$  states are split into two states and  $F$  states are split into three states.

**Table :** Transforming spectroscopic terms into Mulliken symbols

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

### (6) Table

Ground and excited terms having the same spin multiplicities for weak field octahedral (oct) and tetrahedral (tet) complexes

Configuration	Ground term	Excited terms with the same spin multiplicity as the ground term
$d^1$ oct, $d^9$ tet	${}^2T_{2(g)}$	${}^2E_{2(g)}$
$d^2$ oct, $d^8$ tet	${}^3T_{1(g)}F$	${}^3T_{2(g)}, {}^3A_{2(g)}, {}^3T_{1(g)}(P)$
$d^3$ oct, $d^7$ tet	${}^4A_{2(g)}$	${}^4T_{2(g)}, {}^4T_{1(g)}(F), {}^4T_{1(g)}(P)$
$d^4$ oct, $d^6$ tet	${}^5E_{2(g)}$	${}^2T_{2(g)}$
$d^5$ oct, $d^5$ tet	${}^6A_{1(g)}$	None
$d^6$ oct, $d^4$ tet	${}^5T_{2(g)}$	${}^5E_{2(g)}$
$d^7$ oct, $d^3$ tet	${}^4T_{1(g)}(F)$	${}^4T_{2(g)}, {}^4A_{2(g)}, {}^4T_{1(g)}(P)$
$d^8$ oct, $d^2$ tet	${}^3A_{2(g)}$	${}^3T_{2(g)}, {}^3A_{1(g)}(F), {}^3T_{1(g)}(P)$
$d^9$ oct, $d^1$ tet	${}^2E_{2(g)}$	${}^2T_{2(g)}$

## Configuration                      Correlation of Spectroscopic Ground Term

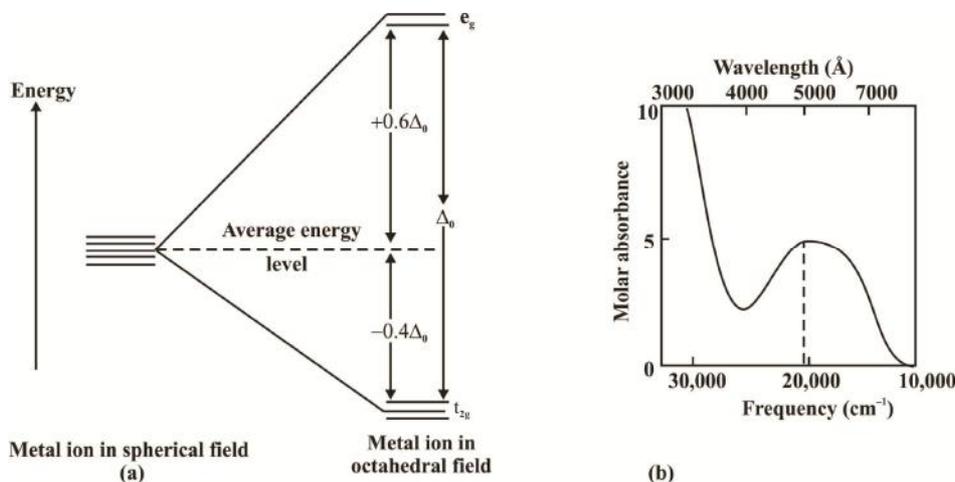
1. $d^1$	
2. $d^2$	$3P \dots\dots\dots 3T_1 \quad t_2^1 e^1$ 
3. $d^3$	$4P \dots\dots\dots 4T_1 \quad t_2^1 e^1$ 
4. $d^4$	
5. $d^5$	$6S \dots\dots\dots 6A_1 \quad t_2^3 e^2$ 
6. $d^6$	
7. $d^7$	$4P \quad 4T_1$

### (1) Spectra of $d^1$ :

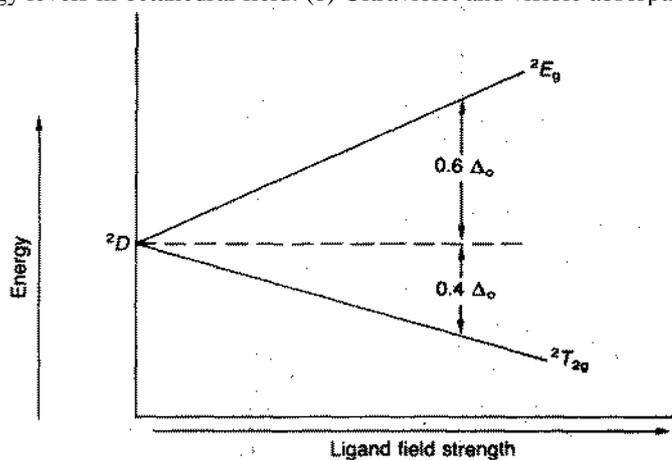
In a free gaseous metal ion the  $d$  orbitals are degenerate, and hence there will be no spectra from  $d-d$  transitions. When a complex is formed, the electrostatic field from the ligands splits the  $d$  orbitals into two groups  $t_{2g}$  and  $e_g$ . The simplest example of a  $d^1$  complex is Ti(III) in octahedral complexes such as  $[\text{TiCl}_6]^{3-}$  or  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . The splitting of the  $d$  orbitals is shown in the following figure (a). In the ground state the single electron occupies the lower  $t_{2g}$  level, and only one transition is possible to the  $e_g$  level.

Consequently the absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  which is shown in figure (b) shows only one band with a peak at  $20300 \text{ cm}^{-1}$ . The magnitude of the splitting  $\Delta_0$  depends on the nature of the ligands, and affects the energy of the transition, and hence the frequency of maximum absorption in the spectrum. Thus the peak occurs at  $13000 \text{ cm}^{-1}$  in  $[\text{TiCl}_6]^{3-}$ ,  $18900 \text{ cm}^{-1}$  in  $[\text{TiF}_6]^{3-}$ ,  $20300 \text{ cm}^{-1}$  in  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  and  $22300 \text{ cm}^{-1}$  in  $[\text{Ti}(\text{CN})_6]^{3-}$ . The amount of splitting caused by various ligands is related to their position in the spectrochemical series. The symbol  ${}^2D$  at the left is the ground state term for a free ion with a  $d^1$  configuration. Under the influence of a ligand field this splits into two states which are described by the

Mulliken symbols  ${}^2E_g$  and  ${}^2T_{2g}$ . The lower  ${}^2T_{2g}$  state corresponds to the single  $d$  electron occupying one of the  $t_{2g}$  orbitals, and the  ${}^2E_g$  state corresponds to the electron occupying one of the  $e_g$  orbitals. The two states are separated more widely as the strength of the ligand field increases.



(a) Diagram of energy levels in octahedral field. (b) Ultraviolet and visible absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



Splitting of energy levels for  $d^1$  configuration in octahedral field.

**Orgel Diagrams:** If the assumption is made that the Racah parameter  $B$  has the same value in complex that it has in the free ion, then the energy of the each level may be plotted out for various value of  $\Delta_0$  as the variable. This was first done by Orgel in 1955 and weak field method type of energy level diagrams constructed in this way are usually referred to as Orgel diagram.

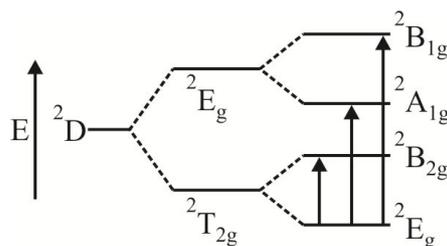
Orgel diagrams are used for interpretation of electron spin absorption bands of crystal field of d-d origin in electronic spectra of tetrahedral and octahedral transition metal complexes. The energy level order of states arising from splitting of a state for a particular ion in an octahedral field is opposite of that for ion in a tetrahedral field.

Orgel diagrams are particularly useful in interpretation of spin allowed electronic transitions of tetrahedral and high spin octahedral complexes but not for low spin octahedral complexes. The spin allowed electronic transitions occur between the two energy states that have same spin multiplicity. In all  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$  metal ions octahedral complexes, Orgel diagrams can be used as they give identical energy states.

**Some feature of this diagram may be stated as follows:**

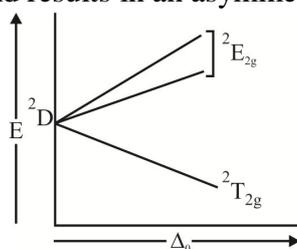
- For the  $d^1$  configuration note that the energy levels diverge linearly, as they must do since the energy gap is a function of only the one parameter  $\Delta_0$ .
- In the other diagram only some of the levels diverge linearly,
- Those levels which do not diverge linearly are the ones involved in configuration interaction.

**Spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  :** The absorption band in spectra of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is broad because of **John-Teller Distortion** which splits  ${}^2E_g$  state into  ${}^2A_{1g}$  and  ${}^2B_{1g}$ . This splits ground state  ${}^2T_{2g}$  into  ${}^2E_g$  and  ${}^2B_{2g}$  also in some extent.

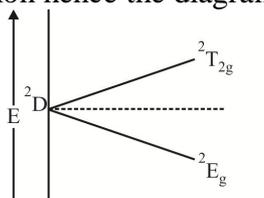


In complex ion  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  absorption maximum observed at  $20300\text{ cm}^{-1}$  and also the absorption maximum has a shoulder at  $17400\text{ cm}^{-1}$  because of John-Teller Distortion. The shoulder is responsible for broad band.

It has also been suggested that the electronic excited state of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  has the configuration  $t_{2g}^0 e_g^1$  and so in the excited state of complex  $e_g$  orbitals are electronically degenerate. Therefore the single electronic transition is really the superposition of two transitions, one from an octahedral ground state ion to an octahedral excited state ion and a lower energy transition from an octahedral ground state ion to a lower energy tetragonally distorted excited state ion. Since these transitions have slightly different energies, therefore the bands overlap one another and can not be resolved. Thus unresolved superimposed band results in an asymmetric broad band.

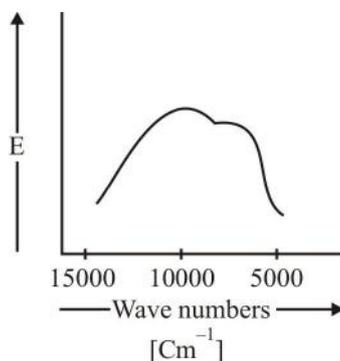


**Spectra of  $d^9$  octahedral Complex:** In octahedral  $d^9$  complexes the term  ${}^2D$  splitted into  ${}^2E_g$  and  ${}^2T_{2g}$ . In  $d^9$  octahedral a hole may be considered in  $e_g$  orbital. When transition takes place hole moves from  $e_g$  to  $t_{2g}$ . This is similar to electron transition i.e.  ${}^2T_{2g} \leftarrow {}^2E_g$ . However hole and electron as moves in opposite direction hence the diagram of  $d^9$  will be inverse of  $d^1$ .

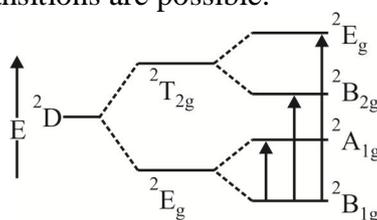


**Note:** Hence it can be concluded that the Orgel diagrams of  $d^n$  and  $d^{10-n}$  are inversely related.

**Spectra of  $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$**  : The  $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$  complex show absorption in visible region at  $12000 \text{ cm}^{-1}$  and complex is of blue coloured.

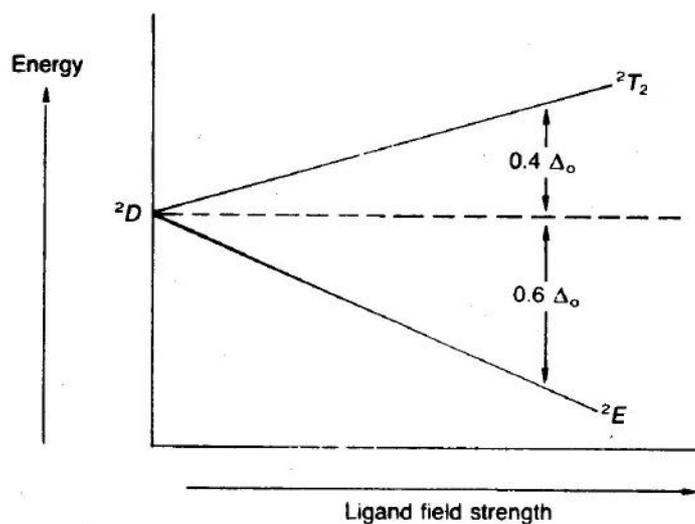


The complex show, intact a broad band, not sharp. This broadening can be explained on the basis that in  $d^9$  system John-Teller splitting takes place. Due to distortion  ${}^2E_g$  states splits into lower energy  ${}^2B_{1g}$  and higher energy  ${}^2A_{1g}$ . Same time  ${}^2T_{2g}$  state splits into lower energy  ${}^2B_{2g}$  and higher energy  ${}^2E_g$ . Hence now three transitions are possible.



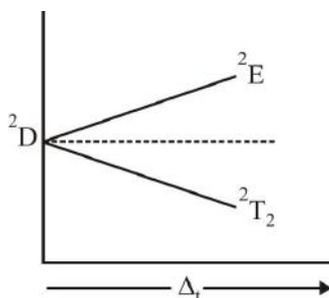
As the splitting is poor, the three absorption bands overlap together showing broad band.

The effect of a tetrahedral ligand field is now considered, the degenerate  $d$  orbitals split into two  $e_g$  orbitals of lower energy and three  $t_{2g}$  orbitals of higher energy. The energy level diagram for  $d^1$  complexes in a tetrahedral field is the inverse of that in an octahedral field, and is similar to the  $d^9$  octahedral case, except that the amount of splitting in a tetrahedral field is only about  $\frac{4}{9}$  of that in an octahedral field. There is only one possible transition i.e.  ${}^2T_2 \leftarrow {}^2E$



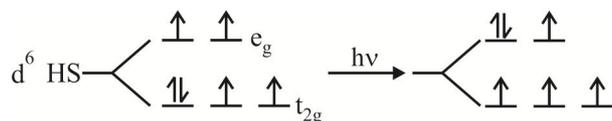
Splitting of energy levels for  $d^1$  configuration in tetrahedral field

**Spectra of  $d^9$  in Tetrahedral:** In tetrahedral complex of  $d^9$ , the splitting is reverse of  $d^9$  octahedral. The ground state term is  ${}^2D$  which splits into lower  ${}^2T_2$  and higher  ${}^2E$ . Only one transition is possible.

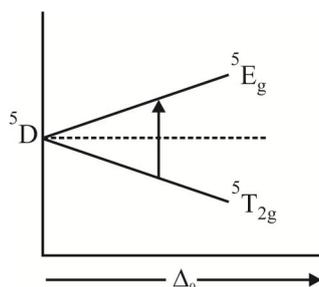


**Spectra of HS  $d^6$  Octahedral Complexes:** The ground state term for  $d^6$  is  ${}^5D$ . The  $d^6$  has configuration  $t_{2g}^4 e_g^2$ .

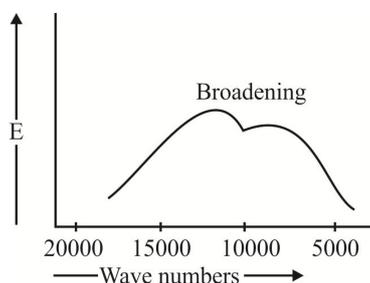
According to selection rule, transition of electron which is paired in  $t_{2g}$  will take place (spin allowed).



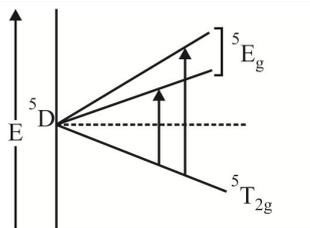
From this it is clear that this transition is similar to  $d^1$ . Now  ${}^5D$  splits into  ${}^5T_{2g}$  and  ${}^5E_g$ . Thus there must be only one sharp transition band observed. However, broadening of band takes place.



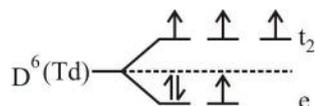
**Note:** The absorption band is  $[\text{Fe}(\text{H}_2\text{O})_6]^{++}$  is usually found in between 10000 to 11000  $\text{cm}^{-1}$ . i.e. broadening takes place.



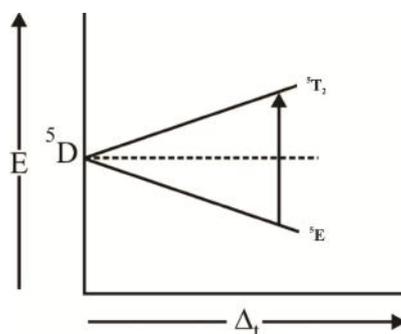
This broadening takes place due to Jahn-Teller distortion.



**Electronic Spectra of  $d^6$  – tetrahedral complex:** Fe(II) forms many tetrahedral complex of formula  $[Fe X_4]^{2-}$  where  $X = Cl^-, Br^-, I^-, NCS^-$ . The ground state term symbol is  $^5D$  and ‘d’ splitting is

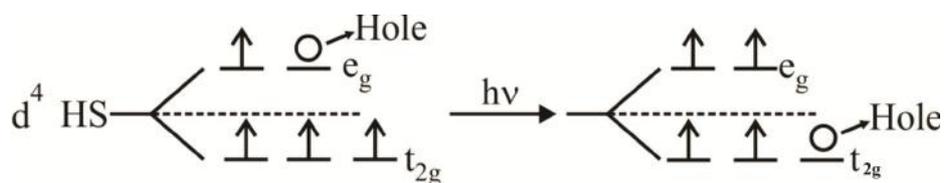


Transition of paired electron can only take place (spin selection rule). In  $[FeCl_4]^{2-}$  only single absorption band appears at  $4000\text{ cm}^{-1}$  (near IR region) which is due to  $^5T_2 \leftarrow ^5E$ .

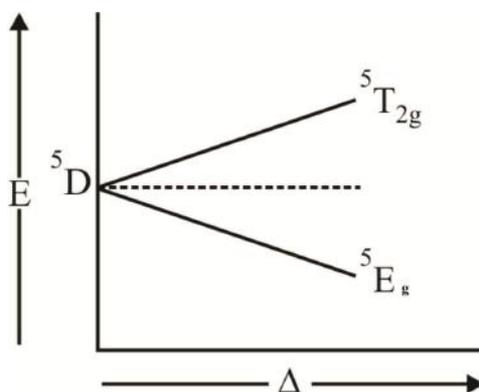


Transition  $[FeCl_4]^{2-}$  is hence colourless as absorption takes place in near IR region.

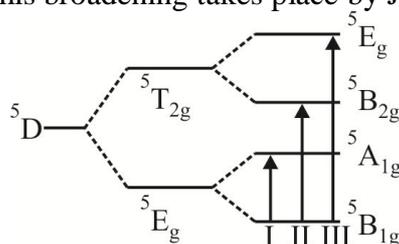
**Spectra of HS  $d^4$  Octahedral Complex:** In HS  $d^4$  on the transition of hole takes place.



This is similar to  $d^9$  octahedral.

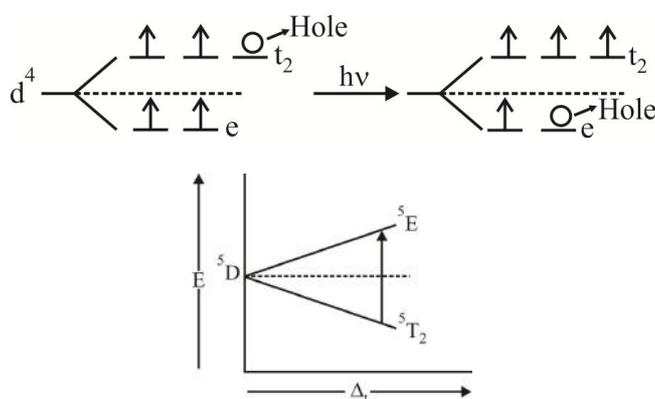


**Example:** The absorption band for  $\text{Cr}^{++}$  HS is typically a broad band in region of  $16000 \text{ cm}^{-1}$  with another band at  $10000 \text{ cm}^{-1}$ . This broadening takes place by John-Teller Distortion.

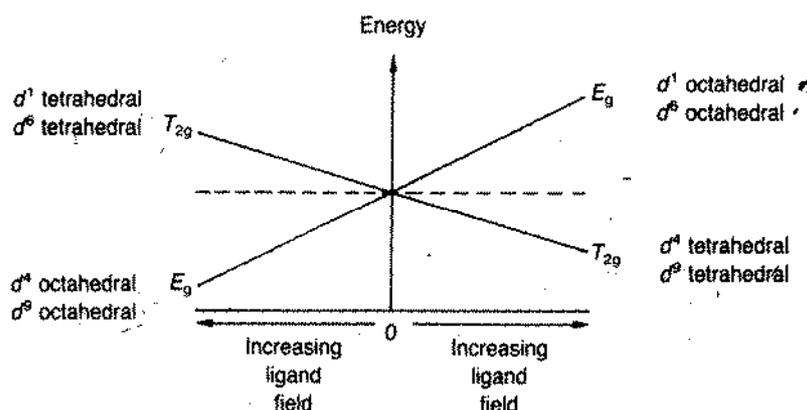


The two bands II and III i.e.  ${}^5\text{B}_{2g} \leftarrow {}^5\text{B}_{1g}$  and  ${}^5\text{E}_g \leftarrow {}^5\text{B}_{1g}$  are superimposed giving broadening.

**Spectra of  $d^4$  Tetrahedral Complex:** In Td  $d^4$  splits into  $e$  and  $t_2$  but the splitting is reverse of  $d^4$  HS On.



Above figures can be combined into a single diagram called an Orgel diagram, which describes in a qualitative way the effect of electron configurations with one electron, one electron more than a half filled level, one electron less than a full shell, and one electron less than a half filled shell.



### Electronic spectra of $d^2$ – octahedral complexes:

Before discussing the detailed description of Orgel diagram for many electron system, it is important to note some more concept about the Orgel diagram.

After quantum mechanical calculation, it has been found that

$$E({}^3T_{1g}(F)) = -0.6\Delta_0$$

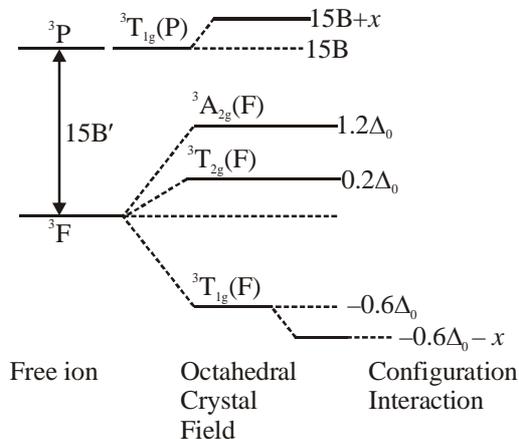
$$E({}^3T_{2g}(F)) = 0.2\Delta_0$$

$$E({}^3A_{2g}(F)) = 1.2\Delta_0$$

Remember that the energy in each case measured relative to the unsplit term.

It is already known to us from previous discussion that the energy difference between the state of same multiplicity in most of the cases will be  $15B$ .

Based on these energies, the energy levels at this stage of weak field are those indicated in the following figure.



Splitting of  ${}^3F$  and  ${}^3P$  terms of the configuration  $d^2$  in a weak octahedral crystal field, and effect of configuration interaction on the  ${}^3T_{1g}$  levels.

Here  $x$  is the term arises due to the phenomenon of configuration interaction.

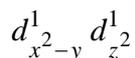
In octahedral complexes (whether the ligand is weak or strong) of  $d^2$ - metal ion like  $[V(H_2O)_6]^{3+}$  the  $d$ -orbitals split into  $t_{2g}$  (lower energy) and  $e_g$  (higher energy) orbitals. The ground state of  $d^2$ -metal ion in octahedral complex have two electrons with parallel spin in any two of the three lower energy orbitals:  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ . The ground state, based on the  $t_{2g}^2$  configuration is triply degenerate ( ${}^3T_{1g}$  state) because there are three ways of arrangement of the electrons with parallel spins in  $t_{2g}$  orbitals:  $d_{xy}^1 d_{yz}^1$  or  $d_{yz}^1 d_{zx}^1$  or  $d_{xy}^1 d_{zx}^1$ . If one electron is excited to a  $e_g$  orbital, the electronic configuration becomes  $t_{2g}^1 e_g^1$ , then the most stable (lowest energy) arrangement of electrons for this configuration will be when the two electron are present in orbitals as far apart as possible i.e., at right angle to each other. For example if one electron is present in  $d_{xy}$  orbital, the other electron will be in the  $d_{z^2}$  orbital rather than in the  $d_{x^2-y^2}$  orbital. There are three ways of

arranging these two electrons in orbitals perpendicular to each other:  $d_{xy}^1 d_{z^2}^1, d_{zx}^1 d_{x^2-y^2}^1, d_{yz}^1 d_{x^2-y^2}^1$

Thus this state is triply degenerate and is represented as  ${}^3T_{2g}$ . This state have lowest energy because two electrons occupy more space in all the three directions and causes less electron-electron repulsion.

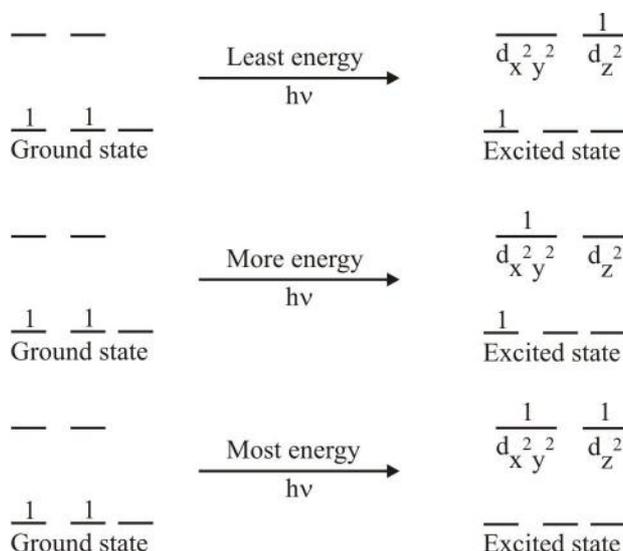
There is an another triply degenerate arrangements of the two electrons in which two electrons occupy the orbitals which are relatively closer together i.e., the orbitals are at  $45^\circ$  to each other  $d_{xy}^1 d_{x^2-y^2}^1, d_{zx}^1 d_{z^2}^1, d_{yz}^1 d_{z^2}^1$ . This arrangement is represented by  ${}^3T_{2g}$  state. This state will be higher in energy because both electrons occupy space only in one plane.

If both the electrons are excited to  $e_g$  orbitals, there is only one arrangement of two electrons with parallel spins.

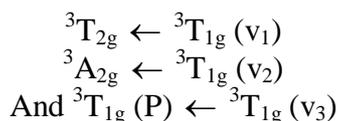


This state is electronically non degenerate and can be represented as  ${}^3A_{2g}$ .

Thus there are three transitions from ground state to excited states of the same multiplicity. The three electronic transitions for  $d^2$ -octahedral complex are shown in figure.

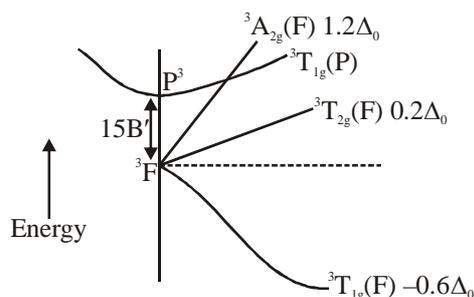


The terms arising for  $d^2$  configuration are  ${}^3F$ ,  ${}^3P$ ,  ${}^1S$ ,  ${}^1D$  and  ${}^1G$  out of which  ${}^3F$  is the ground state term. The excited state of maximum multiplicity ( $= 3$ ) is only  ${}^3P$ . In octahedral complexes  ${}^3F$  term splits into  ${}^3T_{1g}(F)$ ,  ${}^3T_{2g}(F)$  and  ${}^3A_{2g}(F)$ . the term  ${}^3P$  does not split in octahedral complexes but it transforms into  ${}^3T_{1g}(P)$  term and energy of the terms varies as the ligand field strength is changed as shown in figure. The two  ${}^3T_{1g}$  states are distinguished by adding the symbol (F) or (P) after  ${}^3T_{1g}$  term as  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$ . The ground state term of  $d^2$ -in octahedral complex is  ${}^3T_{1g}(F)$  and excited states are  ${}^3T_{2g}$ ,  ${}^3A_{2g}$  and  ${}^3T_{1g}(P)$ . Three spin allowed transitions are possible as shown below:



Transitions from  ${}^3T_{1g}$  ground state to any of the singlet states are spin forbidden. Therefore only three absorption bands may appear in spectrum of  $[V(H_2O)_6]^{3+}$ .

The separation between the ground state  ${}^3T_{1g}(F)$  and the excited states  ${}^3T_{2g}$ ,  ${}^3A_{2g}$  and  ${}^3T_{1g}(P)$  increase with increase in ligand field strength. Thus as the ligand field strength increases, the transitions require higher energies and the absorption bands shift towards the UV region.



Orgel diagram for  $d^2$  octahedral complexes

For  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  which is a  $d^2$  complex shows only two absorption bands in the visible region corresponding to  ${}^3T_{2g} \leftarrow {}^3T_{1g}$  and  ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}$  at  $17200 \text{ cm}^{-1}$  and  $25700 \text{ cm}^{-1}$  respectively.

Theoretically three transition are possible, then why are we getting only two?

This behaviour can be explained by taking into account the concept of cross over point. At or near the cross over point two bands viz  ${}^3A_{2g} \leftarrow {}^3T_{1g}$  and  ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}$  can overlap each other and thus only two bands are observed. Here  $\nu_1$  corresponds to  ${}^3T_{2g} \leftarrow {}^3T_{1g} = 17200 \text{ cm}^{-1}$

Energy of  ${}^3T_{2g} \leftarrow {}^3T_{1g} = 17200 \text{ cm}^{-1}$

$$0.2\Delta_0 - (-0.6\Delta_0) = 17200 \text{ cm}^{-1}$$

$$0.8\Delta_0 = 17200$$

$$\Delta_0 = \frac{17200}{0.8} = 21500 \text{ cm}^{-1}$$

**Note:** In many cases it has been found that the energy of  ${}^3T_{1g}(F)$  is not equal to  $-0.6\Delta_0$ ; it further reduces due to phenomenon of configuration interaction. In such case we can do our calculation by putting.

$$E({}^3T_{1g}(F)) = -0.6\Delta_0 - x$$

Similarly,  $\nu_2 = 25200 \text{ cm}^{-1}$ ; which corresponds to the transition between  ${}^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$

Unfortunately when third band can not be observed, in such cases a more complicated analysis is required, which will be discussed in Tanabe-Sugano diagram.

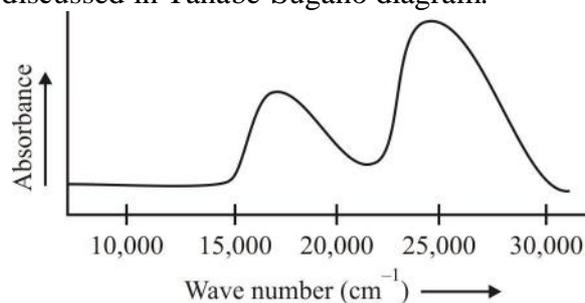


Fig. Absorption spectra for  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$

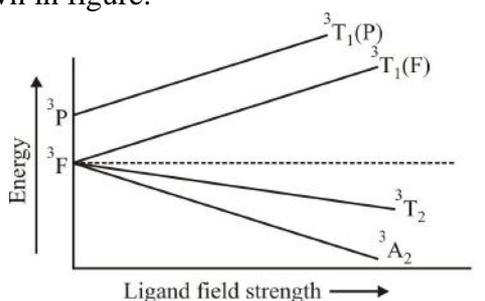
**Electronic spectra of  $d^2$ -tetrahedral complexes:** In tetrahedral complexes of  $d^2$ -metals ions like  $[\text{VCl}_4]^-$  and  $[\text{VBr}_4]^-$  the d-orbitals split into  $e$  (lower energy) and  $t_2$  (higher energy) orbitals giving rise to electronic configuration  $e^2 t_2^0$ . In ground state there is only one arrangement of two electrons with parallel spins  $d_{x^2-y^2}^1 d_{z^2}^1$ . Thus this state is electronically non degenerate and is represented as  ${}^3A_2$ . If one of the two electrons is excited to a  $t_2$  orbital, the electronic configuration becomes  $e^1 t_2^1$ . Corresponding to this electronic configuration, the lower energy state will be that when the two electrons are present in orbitals as far apart as possible. The two electrons can be arranged in either of the three ways:  $d_{z^2}^1 d_{xy}^1, d_{x^2-y^2}^1 d_{zx}^1$  and  $d_{x^2-y^2}^1 d_{yz}^1$ .

Therefore this state is triply degenerate and is represented as  ${}^3T_2$ . There is another triplet state corresponding to  $e^1 t_2^1$  configuration in which the two electrons occupy the orbitals which are relatively closer together:  $d_{x^2-y^2}^1 d_{xy}^1, d_{z^2}^1 d_{xz}^1$  and  $d_{z^2}^1 d_{yz}^1$ . This state is of higher energy and is represented as  ${}^3T_1$ . If both the electrons are excited to  $t_2$  orbitals, the electronic configuration

becomes  $e^0 t_2^2$ . Corresponding to this electronic configuration, there are three ways of arrangement of two electrons in any of the three orbitals of  $t_2$  orbitals:  $d_{xy}^1 d_{yz}^1$  or  $d_{yz}^1 d_{zx}^1$  or  $d_{xy}^1 d_{zx}^1$ . Therefore this state is once again is triply degenerate and is represented as  ${}^3T_1(P)$ . This state is of highest energy.

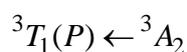
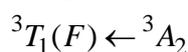
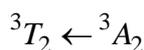
It has been seen that the order of energies of these states  ${}^3A_2$ ,  ${}^3T_2$ ,  ${}^3T_1$  is reverse of the energies of  ${}^3A_{2g}$ ,  ${}^3T_{2g}$  and  ${}^3T_{1g}$  for  $d^2$ - octahedral complexes.

The terms having same spin multiplicity arising for  $d^2$ -configuration are  ${}^3F$  and  ${}^3P$ .  ${}^3F$  is the ground state term. The P state does not split in a complex but  ${}^3F$  state splits into  ${}^3A_2$ ,  ${}^3T_2$  and  ${}^3T_1$  states in tetrahedral complex as shown in figure.



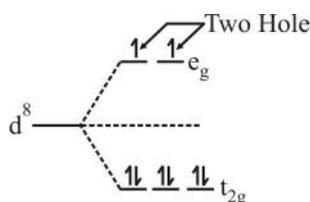
Orgel diagram for  $d^2$ -tetrahedral complex

Three possible transitions are:



**Electronic spectra of  $d^8$  – octahedral complexes:** In  $d^8$ - octahedral complexes, the d-orbitals split into  $t_{2g}$  (lower energy) and  $e_g$  (higher energy) orbitals. Thus in ground state the electronic configuration is  $t_{2g}^6 e_g^2$ . There is only one electronic arrangement for this electronic configuration i.e.  $t_{2g}^6 d_{x^2-y^2}^1 d_{z^2}^1$  and the ground state term corresponding to this configuration is represented as  ${}^3A_{2g}$ .

In a  $d^8$ - octahedral complex two holes may be considered in  $e_g$  orbitals as shown in figure.

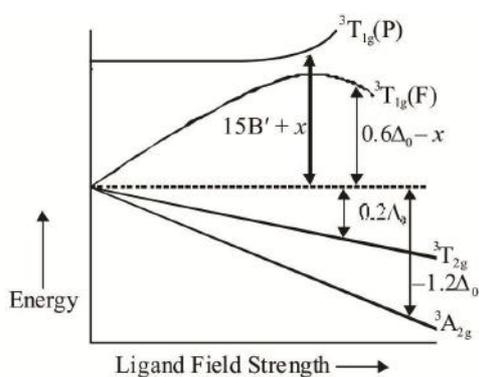


When an electron from any of the  $t_{2g}$  orbitals is excited to any one of the  $e_g$  orbitals, the electronic configuration becomes  $t_{2g}^5 e_g^3$ . Now there will be two holes one in  $t_{2g}$  and one in  $e_g$  orbitals. Corresponding to this electronic configuration, there are two triply degenerate states. The lower energy state will arise when two holes occupy the orbitals as far apart as possible. This state is represented as  ${}^3T_{2g}$ . The holes may be present either in  $d_{xy} d_{z^2}$  or  $d_{yz} d_{x^2-y^2}$  or  $d_{zx} d_{x^2-y^2}$  orbitals giving rise to lesser repulsions between two holes because two holes occupy more space in x, y and z-directions. Holes are effected in the opposite way as compared to electros. There is an

another triply degenerate arrangement of two holes in which the two holes occupy the orbitals which are closer together. The holes may be presented in either  $d_{xy} d_{x^2-y^2}$  or  $d_{yz} d_{z^2}$  or  $d_{zx} d_{z^2}$  orbitals. This is of higher energy and is represented as  ${}^3T_{1g}$ .

When both the electrons are excited, the electronic configuration becomes  $t_{2g}^4 e_g^4$ . Now two holes are present in any of the two  $t_{2g}$  orbitals either in  $d_{xy} d_{yz}$  or  $d_{yz} d_{zx}$  or  $d_{xy} d_{zx}$  orbitals. Therefore this state is triply degenerate and is represented as  ${}^3T_{1g}(P)$ . Since double excitation requires higher energy therefore  ${}^3T_{1g}$  state is of highest energy state. There are four energy states including ground state. Thus there are three transitions. The transitions of holes is similar to electronic transitions.

The terms having same multiplicity arising for  $d^8$  – configuration are  ${}^3F$ ,  ${}^3P$ . The  ${}^3F$  state is the ground state. In octahedral complex  ${}^3F$  term splits into  ${}^3A_{2g}$ ,  ${}^3T_{2g}$  and  ${}^3T_{1g}$  as shown in figure. The term  ${}^3P$  does not split but it transforms into  ${}^3T_{1g}(P)$  state.



Orgel diagram of  $d^8$  octahedral complex

When ligand field strength increases, there will be bending of  ${}^3T_{1g}(F)$  and  ${}^3T_{1g}(P)$  line because these states are of same symmetry and there is inter electronic repulsion (or mixing of two  $T_{1g}$  states). This electronic repulsion lowers the energy of lower state and increases energy of the higher state. Thus due to inter electronic repulsion the two  $T_{1g}$  states do not cross. This is called non crossing rule.

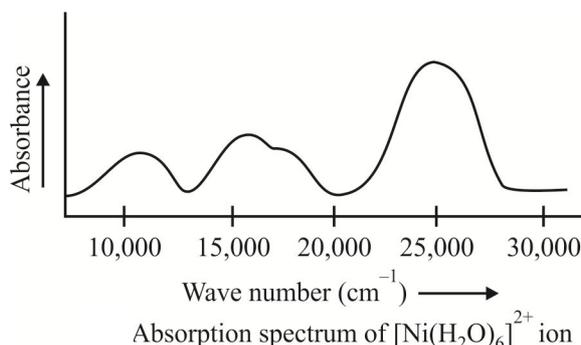
Electronic spectra of octahedral Ni(II),  $d^8$  complexes usually consist of three bands according to the following transitions:

$${}^3T_{2g} \leftarrow {}^3A_{2g} = \nu_1$$

$${}^3T_{1g}(F) \leftarrow {}^3A_{2g} = \nu_2$$

$${}^3T_{1g}(P) \leftarrow {}^3A_{2g} = \nu_3$$

The lowest energy transition i.e.  ${}^3T_{2g} \leftarrow {}^3A_{2g}$  gives the value of  $\Delta_0$ .





**Problem :** For complex  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  three absorption bands are observed at  $8700 \text{ cm}^{-1}$ ,  $14500 \text{ cm}^{-1}$  and  $25300 \text{ cm}^{-1}$ . Calculate the value of  $\Delta_0$ , Racah parameter  $B'$  and configuration interaction parameter  $x$ .

**Soln.** In the complex  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  Ni metal is +2 state i.e. is in  $d^8$  configuration. Thus we can use the Orgel diagram of  $d^8$ -octahedral complex as drawn above.

It is given that  $\nu_1 = 8700 \text{ cm}^{-1}$ ,  $\nu_2 = 14500 \text{ cm}^{-1}$ ,  $\nu_3 = 25300 \text{ cm}^{-1}$

Energy corresponding to lowest transition i.e. for  ${}^3T_{2g} \leftarrow {}^3A_{2g}$

$$\Rightarrow E({}^3T_{2g} \leftarrow {}^3A_{2g}) = 8700 \text{ cm}^{-1}$$

$$\Rightarrow -0.2\Delta_0 - (-1.2\Delta_0) = 8700 \text{ cm}^{-1}$$

$$\Rightarrow \Delta_0 = 8700 \text{ cm}^{-1}$$

Again  $E({}^3T_{1g}(F) \leftarrow {}^3A_{2g}) = 14500 \text{ cm}^{-1}$

$$[(0.6\Delta_0 - x) - (-1.2\Delta_0)] = 14500 \text{ cm}^{-1}$$

$$1.8\Delta_0 - x = 14500$$

$$x = 15660 - 14500$$

$$x = 1160 \text{ cm}^{-1}$$

Similarly,  $E({}^3T_{1g}(P) \leftarrow {}^3A_{2g}) = 25300 \text{ cm}^{-1}$

$$[(15B' + x) - (-1.2)] = 25300$$

$$15B' + 1160 + 1.2 \times 8700 = 25300$$

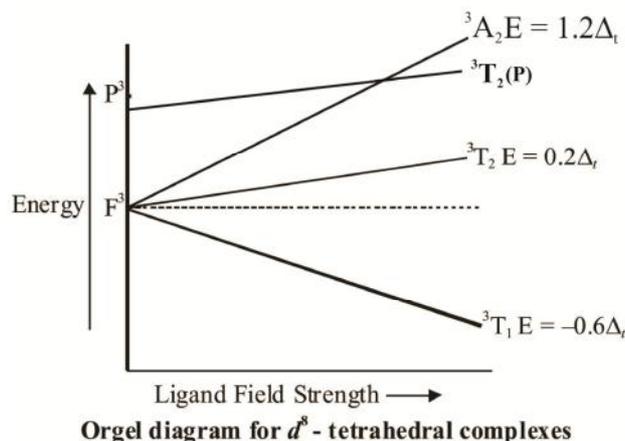
$$B' = 913 \text{ cm}^{-1}$$

Thus  $\Delta_0 = 8700 \text{ cm}^{-1}$

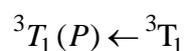
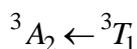
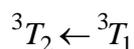
$$x = 1160 \text{ cm}^{-1}$$

$$B' = 913 \text{ cm}^{-1}$$

**Electronic spectra for  $d^8$ -tetrahedral complexes:** For  $d^8$ -metal ion in tetrahedral fields, the splitting of the free ion ground state term is the inverse of its splitting in octahedral fields as shown in the figure.



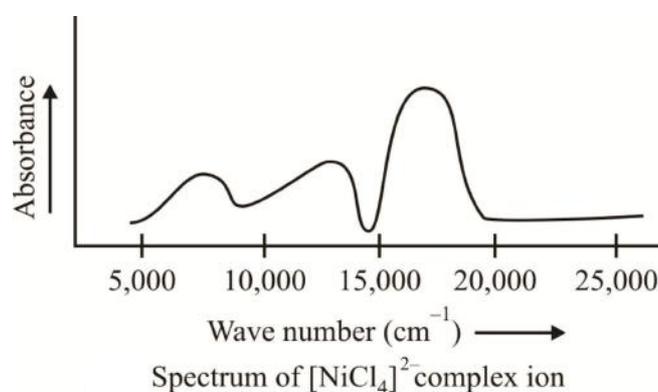
The following three transition are possible for  $d^8$ -tetrahedral complex.



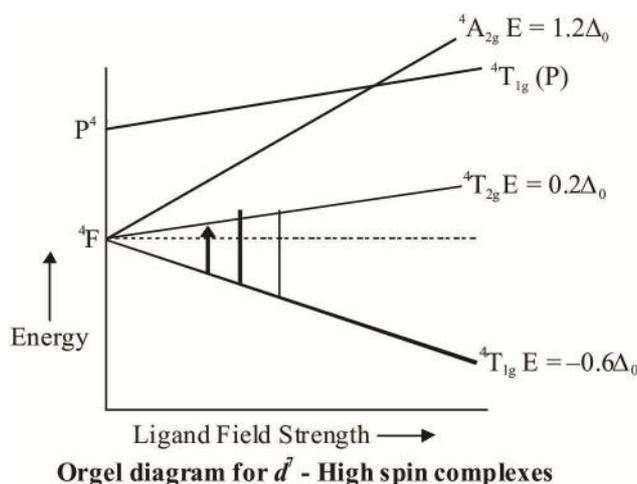
Corresponding to these transitions, three relatively intense bands are expected. For  $[\text{NiCl}_4]^{2-}$  two bands are observed at  $7549 \text{ cm}^{-1}$ ,  $14250 - 15240 \text{ cm}^{-1}$  as in figure.

The band appears at  $14250 - 15240 \text{ cm}^{-1}$  is due to Jahn Teller distortion.

The  ${}^3T_2 \leftarrow {}^3T_1$  transition shows an absorption band at  $3400 \text{ cm}^{-1}$  but it is not observed in visible region because it lies in infra red region.



**Electronic spectra of  $d^7$ -High spin octahedral complexes:** The Free ion ground state term for  $\text{Co}^{2+}$  ( $d^7$ ) is  ${}^4F$  and its other term with same spin multiplicity of higher energy is  ${}^4P$ . In high spin octahedral complexes the splitting of  ${}^4F$  state is same as for  $d^2$ -octahedral complexes. The  ${}^4F$  term splits into  ${}^4T_{1g}$ ,  ${}^4T_{2g}$  and  ${}^4A_{2g}$  states as shown in the figure.



For crystal of  $\text{KCoF}_3$  in which  $\text{Co}^{2+}$  ion is surrounded octahedrally by six  $\text{F}^-$  ligands. There are three absorption bands at  $7150 \text{ cm}^{-1}$ ,  $15200 \text{ cm}^{-1}$  and  $19200 \text{ cm}^{-1}$  corresponding to three transitions.

$${}^4T_{2g} \leftarrow {}^4T_{1g} \quad \nu_1 = 7150 \text{ cm}^{-1}$$

$${}^4A_{2g} \leftarrow {}^4T_{1g} \quad \nu_2 = 15200 \text{ cm}^{-1}$$

$${}^4T_{1g}(P) \leftarrow {}^4T_{1g} \quad \nu_3 = 19200 \text{ cm}^{-1}$$

In this case bending of lines due to configuration interaction may not be observed. Thus both  ${}^4T_{1g}$  term are far apart to undergo this repulsion.

Now,  $\nu_1 = 7150 \text{ cm}^{-1}$

$$E({}^4T_{2g} \leftarrow {}^4T_{1g}) = 7150 \text{ cm}^{-1}$$

$$0.8\Delta_0 = 7150$$

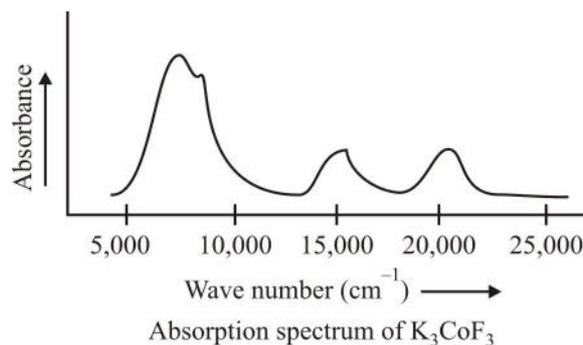
$$\Delta_0 = 8937 \text{ cm}^{-1}$$

Similarly since  $\nu_3[{}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)] = 19200$

$$15B' + 0.6\Delta_0 = 19200$$

$$B' = 922.53 \text{ cm}^{-1}$$

Absorption spectra of  $\text{K}_3\text{CoF}_3$  is shown in figure.



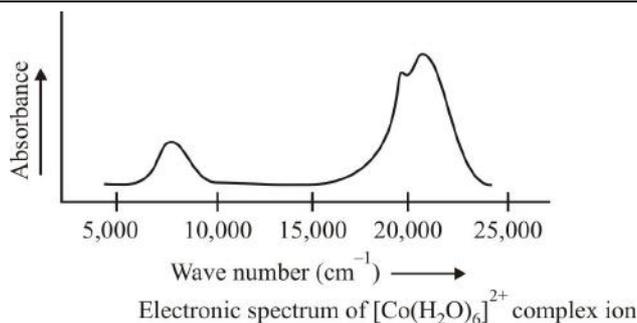
### Absorption spectrum of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ion:

In  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  complex ion, the spectrum usually consists of a weak band in near infrared region at  $8000 \text{ cm}^{-1}$ . This band is assigned as  $\nu_1 = {}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ . An another band appears at approximately  $20000 \text{ cm}^{-1}$ . This band is considered to be comprising three overlapping peaks. This band has three peaks at  $16000 \text{ cm}^{-1}$ ,  $19400 \text{ cm}^{-1}$  and  $21600 \text{ cm}^{-1}$ . Two peaks observed at  $16000 \text{ cm}^{-1}$  and  $19400 \text{ cm}^{-1}$  correspond to  ${}^4A_{2g} \leftarrow {}^4T_{1g}$  and  ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$  transitions. Since these two transitions are near the cross over point of  ${}^4A_{2g}$  and  ${}^4T_{1g}(P)$  states, therefore two peaks overlap one another forming a shoulder in the spectrum.

The extra band which appears at  $21600 \text{ cm}^{-1}$  is due to spin orbit coupling or transition to another state of lower spin multiplicity.

In some cases  $\nu_2$  is not observed but the fine peaks arise from splitting of term due to spin orbit coupling or Jahn Teller distortion in excited state.

The spectrum of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is shown in figure.



### Electronic Spectra of $d^7$ – Tetrahedral Complexes:

In a tetrahedral complex ion, say  $[\text{CoCl}_4]^{2-}$  the splitting of free ion ground term is the reverse of that in octahedral complexes so that for  $d^7$  – ion in tetrahedral complex  ${}^4A_2$  is of lowest energy. There are three possible transitions:

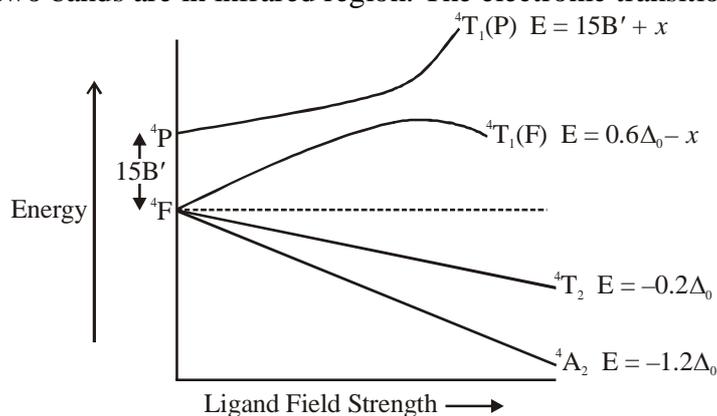
$${}^4T_2 \leftarrow {}^4A_2 \quad \nu_1 = 3300 \text{ cm}^{-1} \quad (\text{IR region})$$

$${}^4T_1(F) \leftarrow {}^4A_2 \quad \nu_2 = 5500 \text{ cm}^{-1} \quad (\text{IR region})$$

$$\text{and } {}^4T_1(P) \leftarrow {}^4A_2 \quad \nu_3 = 14700 \text{ cm}^{-1} \quad (\text{Visible region})$$

Only one band corresponding to  ${}^4T_1(P) \leftarrow {}^4A_2$  appears in visible region at  $14700 \text{ cm}^{-1}$  ( $\nu_3$ ).

Two bands corresponding to  ${}^4T_2 \leftarrow {}^4A_2$  and  ${}^4T_1(F) \leftarrow {}^4A_2$  appear at  $3300 \text{ cm}^{-1}$  ( $\nu_1$ ) and  $5500 \text{ cm}^{-1}$  ( $\nu_2$ ) respectively. These two bands are in infrared region. The electronic transition are shown in figure.

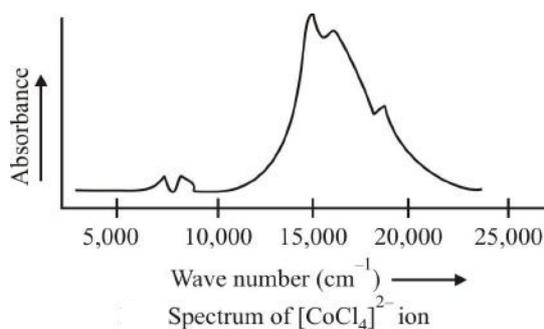


**Orgel diagram of  $d^7$  tetrahedral complexes**

Absorption spectrum of  $(\text{CoCl}_4)_2$  complex ion is shown in figure.

For  $(\text{CoCl}_4)^{2-}$  ion,  $\Delta_t$  is the energy difference between  ${}^4A_2$  and  ${}^4T_2$  states.

$$\Delta_t = [-0.2 - (-1.2)] \Delta_t = 3300 \text{ cm}^{-1}.$$





Tetrahedral complex  $[\text{CoCl}_4]^{2-}$  is more intensely blue in colour where as the high spin complexes of  $\text{Co}^{2+}$  ion are of faint colour.

The intense colour of  $[\text{CoCl}_4]^{2-}$  tetrahedral complex ion is due to:

- (i) d-d transition is laporte partly allowed i.e., there is some p-d mixing.
- (ii) d-d transitions are spin allowed.

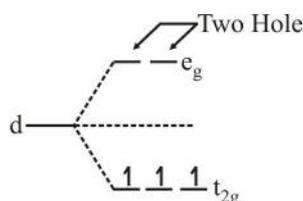
The faint colour of high spin complexes of  $\text{Co}^{2+}$  ion is due to:

- (i) d-d transition is Laporte forbidden
- (ii) d-d transitions is spin allowed.

### Electronic spectra of $d^3$ – octahedral complexes:

In  $d^3$  octahedral complexes the d-orbitals split into  $t_{2g}$  (lower energy) and  $e_g$  (higher energy) orbitals.

Therefore in ground state the electronic configuration is  $t_{2g}^3 e_g^0$  and there are two holes in  $e_g$  orbitals.



There is only one electronic arrangement corresponding to this electronic configuration i.e.  $t_{2g}^3 e_g^0$  ( $d_{xy}^1 d_{yz}^1 d_{zx}^1 e_g^0$ ). Therefore this arrangement is electronically non degenerate and can be represented as  ${}^3A_{2g}$ .

This case is similar to  $d^8$ - octahedral complex. When an electron is excited to any one of the  $e_g$  orbitals, the electronic configuration becomes  $t_{2g}^2 e_g^1$ . Now there are two holes, one in  $t_{2g}$  and one in  $e_g$  orbitals. There are two triply degenerate arrangements of holes corresponding to this electronic configuration. The lower energy state will arise when two holes occupy the orbitals as far apart as possible. Therefore the two holes may be present either in  $d_{xy} d_{z^2}$  or  $d_{yz} d_{x^2-y^2}$  or  $d_{zx} d_{x^2-y^2}$ . Thus this state is triply degenerate and is represented as  ${}^3T_{2g}$ .

There is another triply degenerate arrangement of two holes in which two holes occupy the orbitals which are closer together. The holes may be present either in  $d_{xy} d_{x^2-y^2}$  or  $d_{yz} d_{z^2}$  or  $d_{zx} d_{z^2}$  orbitals.

This state is of higher energy and is represented as  ${}^3T_{1g}$ .

When two electrons are excited to  $e_g$  orbitals the electronic configuration becomes  $t_{2g}^1 e_g^2$ . Now two holes are present in two  $t_{2g}$  orbitals either in  $d_{xy} d_{yz}$  or  $d_{yz} d_{zx}$  or  $d_{xy} d_{zx}$  orbitals. Thus this state is triply degenerate and have highest energy. This state is represented as  ${}^3T_{1g}$  (P).

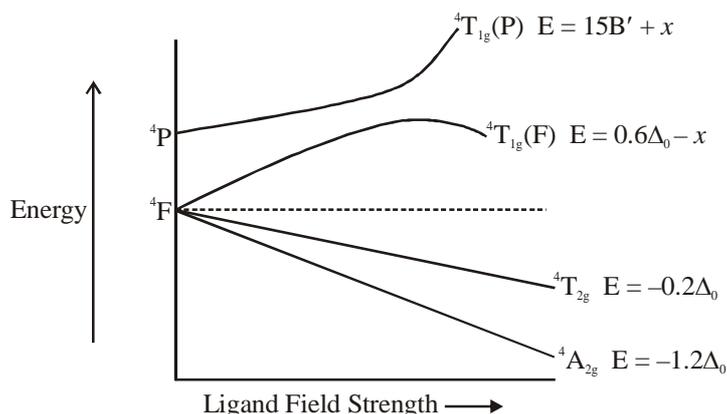
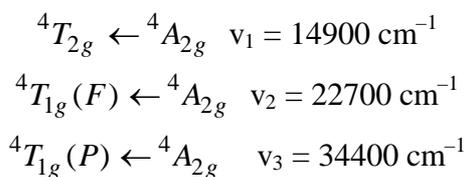
Therefore there are three transitions of holes from ground states to three other excited states. Transition of holes is similar to electronic transition.

The terms of  $d^3$ -metal cation having same spin multiplicity (= 4) are  ${}^4F$  and  ${}^4P$ . For  $d^3$ -configuration  ${}^4F$  term is the ground state and  ${}^4P$  term is of higher energy. In octahedral complex  ${}^4F$  term splits into  ${}^4T_{1g}$ ,  ${}^4T_{2g}$  and  ${}^4A_{2g}$  states as shown in figure. The  ${}^4P$  term does not split but transforms into  ${}^4T_{1g}$  (P) state.

When ligand field strength increases, there will be bending of  ${}^4T_{1g}$  (F) and  ${}^4T_{1g}$  (P) lines because these have same symmetry and there is electron repulsion (mixing of two  ${}^4T_{1g}$  states). This mixing lower the

energy of lower state,  ${}^4T_{1g}(F)$  and increase the energy of higher state,  ${}^4T_{1g}(P)$  in equal amount. Therefore due to mixing the two  $T_{1g}$  states do not cross each other.

There are three possible spin allowed d-d transitions.



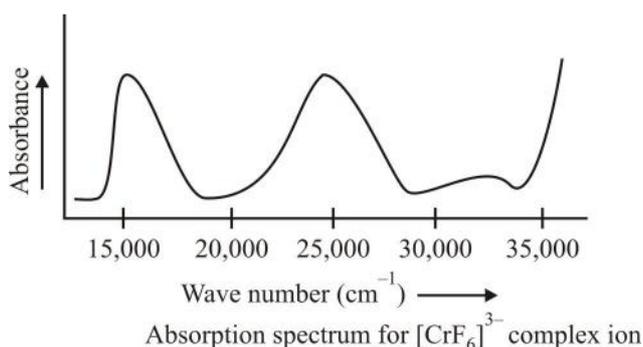
Orgel diagram of  $d^3$  octahedral complexes

These transitions are possible for three absorbance bands in electronic spectrum of  $d^3$  - octahedral complexes. For  $[\text{CrF}_6]^{3-}$  three absorption bands occur at  $14900 \text{ cm}^{-1}$ ,  $22700 \text{ cm}^{-1}$  and  $34400 \text{ cm}^{-1}$ .

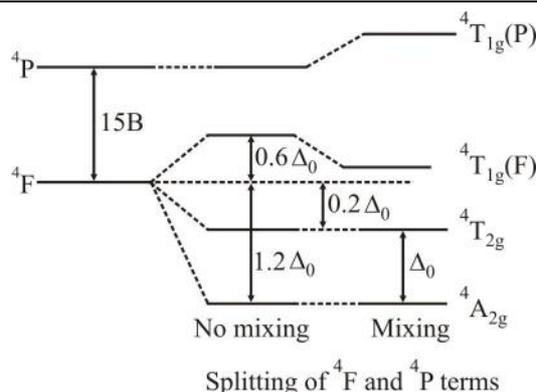
One d-d- transition with lowest energy ( ${}^4T_{2g} \leftarrow {}^4A_{2g}$ ) is a direct measure of the crystal field splitting  $\Delta_0$  or  $10 D_q$ .

$$\Delta_0 = -0.2 \Delta_0 - (-1.2 \Delta_0) = 14900 \text{ cm}^{-1} (\nu_1)$$

Two bands are observed in visible region but third band corresponding to  $\nu_3$  is weak and is observed in UV region. Electronic spectrum for  $[\text{CrF}_6]^{3-}$  is shown in figure.



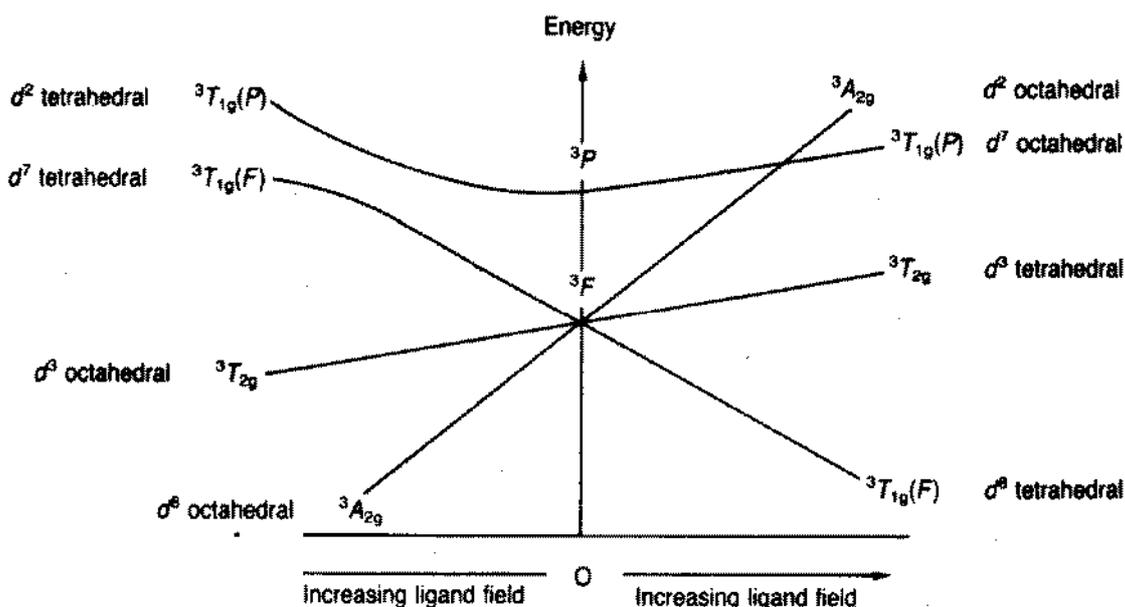
The splitting of  ${}^4F$  and  ${}^4P$  terms including mixing of two states [ ${}^4T_{1g}(F)$  and  ${}^4T_{1g}(P)$ ] is shown in figure.



In  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  complex ion three bands appear at  $17400\text{ cm}^{-1}$ ,  $24700\text{ cm}^{-1}$  and  $37800\text{ cm}^{-1}$ . The high energy band  $37800\text{ cm}^{-1}$  is weak and is assigned due to promotion of two holes and is hidden by charge transfer band.

$\text{Cr}^{3+}$  ion does not form tetrahedral complexes, therefore spectra of  $\text{Cr}^{3+}$  ion in tetrahedral complex can not be interpreted here.

Combined Orgel diagram for  $d^2$ ,  $d^3$ ,  $d^7$  and  $d^8$  octahedral and tetrahedral complex is shown in figure.

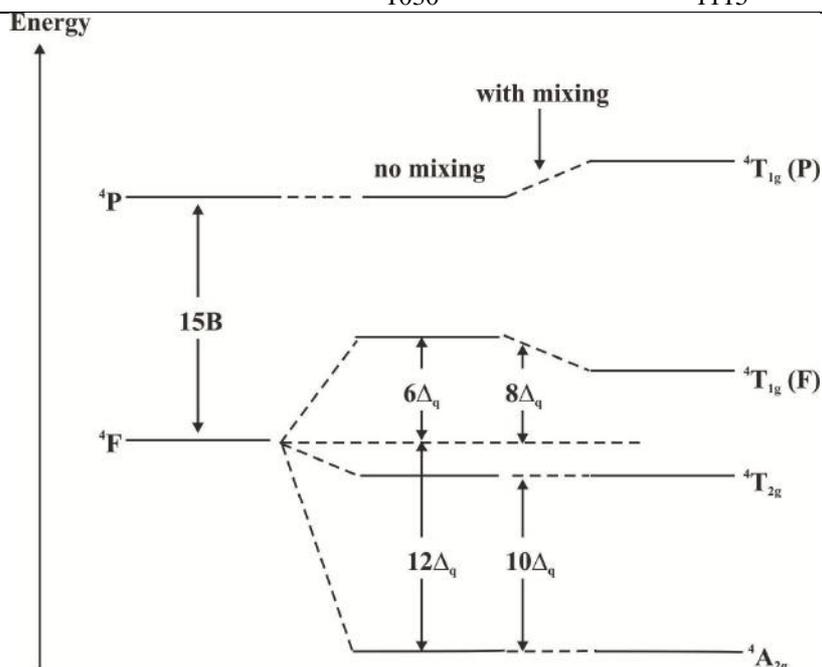


Combined Orgel energy level diagram for two-electron and two-hole configurations.

Experimentally measured spectra may be compared with those expected from theory. Consider for example the spectra of  $\text{Cr}(\text{III})$ .  $\text{Cr}^{3+}$  is a  $d^3$  ion. In the ground state, the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals each contain one electron and the two  $e_g$  orbitals are empty. The  $d^3$  arrangement gives rise to two states  $^4F$  and  $^4P$ . In an octahedral field the  $^4F$  state is split into  $^4A_{2g}(F)$ ,  $^4T_{2g}(F)$  and  $^4T_{1g}(F)$  states, and the  $^4P$  state is not split but transforms into a  $^4T_{1g}(P)$  state.

**Table :** Racah parameters  $B$  for transition metal ions in  $\text{cm}^{-1}$ .

Metal	$M^{2+}$	$M^{3+}$
Ti	695	–
V	755	861
Cr	810	918
Mn	860	965
Fe	917	1015
Co	971	1065
Ni	1030	1115

**The splitting of the  $^4F$  and  $^4P$  states in  $\text{Cr}^{3+}$** 

Three transitions are possible  $^4A_{2g} \rightarrow ^4T_{2g}$ ,  $^4A_{2g} \rightarrow ^4T_{1g}(F)$  and  $^4A_{2g} \rightarrow ^4T_{1g}(P)$ . The Racah parameters for the free  $\text{Cr}^{3+}$  ion are known exactly ( $B = 918 \text{ cm}^{-1}$  and  $C = 4133 \text{ cm}^{-1}$ ).

**Table :** Correlation of spectra for  $[\text{CrF}_6]^{3-}$  (in  $\text{cm}^{-1}$ )

	Observed spectra	Predicted
$^4A_{2g} \rightarrow ^4T_{1g}(P)$ $\nu_3$	34 400	30 700( $12D_q + 15B$ )
$^4A_{2g} \rightarrow ^4T_{1g}(F)$ $\nu_2$	22 700	26 800( $18 D_q$ )
$^4A_{2g} \rightarrow ^4T_{2g}$ $\nu_1$	14 900	14 900( $10 D_q$ )

The lowest energy transition correlates perfectly, but agreement for the other two bands is not very good. Two corrections must be made to improve the agreement.

- If some mixing of the  $P$  and  $F$  terms occurs (bending of lines on the Orgel diagram), then the energy of the  $^4T_{1g}(P)$  state is increased by an amount  $x$  and the energy of the  $^4T_{1g}(F)$  state is reduced by  $x$ .
- The value of the Racah parameter  $B$  relates to a free ion. The apparent value  $B'$  in a complex is always less than the free ion value because electrons on the metal can be delocalized into molecular orbitals covering both the metal and the ligands. As a consequence of this delocalization or cloud expanding, the average interelectronic repulsion is reduced. This is due to the fact that the delocalization



increases the average separation of electrons and have reduces their mutual repulsion. The use of adjusted  $B'$  values improves the agreement. This delocalization is called the nephelauxetic effect. The reduction of  $B'$  from its free ion value is normally reported in terms of nephelauxetic parameter,  $\beta$  and the nephelauxetic ratio  $\beta$  is given by

$$\beta = \frac{B'}{B}$$

$\beta$  decreases as delocalization increases, and is always less than one, and  $B'$  is usually  $0.7 B$  to  $0.9 B$ .

### The Nephelauxetic Series

In example we found that  $B = 657 \text{ cm}^{-1}$  for  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ . This value is only 64 per cent of the value for a free  $\text{Cr}^{3+}$  ion in the gas phase, which indicates that electron repulsions are weaker in the complex than in the free ion. This weakening occurs because the occupied molecular orbitals are delocalized over the ligands and away from the metal. The delocalization increases the average separation of the electrons and hence reduces their mutual repulsion.

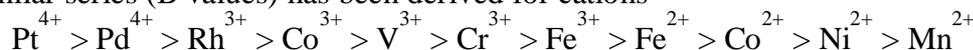
The reduction of  $B$  from its free ion value is normally reported in terms of the nephelauxetic parameter,  $\beta$ .

$$\beta = \frac{B(\text{complex})}{B(\text{free ion})}$$

The values of  $\beta$  depend on the identity of the metal ion and the ligand. They vary along the nephelauxetic series.



A similar series (B values) has been derived for cations



A small value of  $\beta$  indicates a large measure of  $d$ -electron delocalization on to the ligands and hence a significant covalent character in the complex. Thus the series shows that a  $\text{Br}^-$  ligands results in a greater reduction in electron repulsions in the ion than an  $\text{F}^-$  ion, which is consistent with a greater covalent character in bromo complexes than in analogous fluoro complexes. Another way of expressing the trend represented by the series is that, the softer the ligand, the smaller the nephelauxetic parameter.

The nephelauxetic character of a ligand is different for electrons in  $t_{2g}$  and  $e_g$  orbitals. Because the  $\sigma$  overlap of  $e_g$  is usually larger than the  $\pi$  overlap of  $t_{2g}$ , the cloud expansion is larger in the former case. The measured nephelauxetic parameter of an  $e \leftarrow t$  transition is an average of the affects on both types of orbitals.

The nephelauxetic parameter is a measure of the extent of  $d$ -electron delocalization on the ligands of a complex, the softer the ligand, the smaller the nephelauxetic parameter.

$B'$  is easily obtained if all three transitions are observed since:

$$15B' = \nu_3 + \nu_2 - 3\nu_1$$

Using both of these corrections gives much better correlation between observed and improved theoretical results

**Table :** Correlation of spectra for  $[\text{CrF}_6]^{3-}$  (using corrected constants) (in  $\text{cm}^{-1}$ )

	Observed spectra	Predicted
${}^4A_{2g} \rightarrow {}^4T_{1g}(P) \quad \nu_3$	34 400	$34\,800(12D_q + 15B' + x)$
${}^4A_{2g} \rightarrow {}^4T_{1g}(F) \quad \nu_2$	22 700	$22\,400(18 D_q - x)$
${}^4A_{2g} \rightarrow {}^4T_{2g} \quad \nu_1$	14 900	$14\,900(10 D_q)$

As a second example consider the spectrum of crystals of  $\text{KCoF}_3$ . There are three absorption bands at  $7150\text{ cm}^{-1}$ ,  $15200\text{ cm}^{-1}$  and  $19200\text{ cm}^{-1}$ . The compound contains  $\text{Co}^{2+}$  ions ( $d^7$ ) surrounded octahedrally by six  $\text{F}^-$  ions. This case should be similar to the  $d^2$  case and we would expect transitions  $\nu_1 ({}^4T_{1g} \rightarrow {}^4T_{2g})$ ,  $\nu_2 ({}^4T_{1g} \rightarrow {}^4A_{2g})$  and  $\nu_3 ({}^4T_{1g} \rightarrow {}^4T_{1g}(P))$ .  $D_q$  may be calculated from  $\nu_1$  since:

$$\nu_1 = 8D_q$$

However, this makes no allowance for the configuration interaction between the  ${}^4T_{1g}$  and  ${}^4T_{2g}$  states (i.e., bending of lines on the Orgel diagram). It is therefore better to evaluate  $D_q$  from the equation:

$$\nu_2 - \nu_1 = 10D_q$$

since this is not affected by configuration interaction. Thus:

$$15200 - 7200 = 10D_q$$

hence  $D_q = 800\text{ cm}^{-1}$

The value of the configuration interaction term  $x$  is obtained either from the equation:

$$\nu_1 = 8D_q + x$$

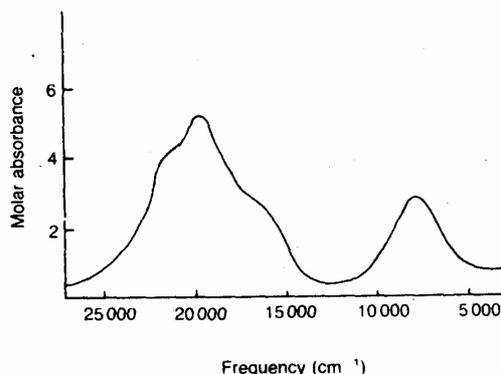
or from

$$\nu_2 = 18D_q + x$$

The Racah parameter  $B$  for a free  $\text{Co}^{2+}$  ion is  $971\text{ cm}^{-1}$ , but corrected value  $B'$  may be calculated from the equation:

$$\nu_3 = 15B' + 6D_q + 2x$$

The pale pink colour of many octahedral complexes of  $\text{Co(II)}$  are of interest. The spectrum of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is shown in figure.



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

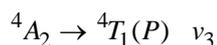
The spectrum of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is less easy to interpret. It shows a weak but well resolved absorption band at about  $8000\text{ cm}^{-1}$ , and a multiple absorption band comprising three overlapping peaks at about  $20000\text{ cm}^{-1}$ . The lowest energy band  $\nu_1$  at  $8000\text{ cm}^{-1}$  is assigned to the  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  transition. The multiple band has three peaks at about  $16000$ ,  $19400$  and  $21600\text{ cm}^{-1}$ . Two of these are the  ${}^4T_{1g} \rightarrow {}^4A_{2g}$  and  ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$  transitions, and since the peaks are close together this indicates that this complex is close to the crossover point between the  ${}^4A_{2g}$  and  ${}^4T_{1g}$  states on the energy diagram. This means that the assignments are only tentative, but the following assignments are commonly accepted:

$$\nu_2 ({}^4T_{1g} \rightarrow {}^4A_{2g}) \quad 16000\text{ cm}^{-1}$$

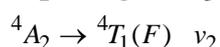
$$\text{and } \nu_3 ({}^4T_{1g} \rightarrow {}^4T_{1g}(P)) \quad 19400\text{ cm}^{-1}$$

The extra band is attributed either to spin orbit coupling effects or to transitions to doublet states.

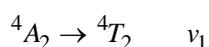
Tetrahedral complexes of  $\text{Co}^{2+}$  such as  $[\text{CoCl}_4]^{2-}$  are intensely blue in colour with an intensity  $\epsilon$  of about  $600 \text{ l mol}^{-1} \text{ cm}^{-1}$  compared with the pale pink colour of octahedral complexes with an intensity  $\epsilon$  of only about  $6 \text{ l mol}^{-1} \text{ cm}^{-1}$ ,  $\text{Co}^{2+}$  has a  $d^7$  electronic configuration, and in  $[\text{CoCl}_4]^{2-}$  the electrons are arranged  $(e_g)^4(t_{2g})^3$ . This is similar to the  $\text{Cr}^{3+}$  ( $d^3$ ) octahedral case since only two electrons can be promoted. There are three possible transitions:  ${}^4A_2(F) \rightarrow {}^4T_2(F)$ ,  ${}^4A_2(F) \rightarrow {}^4T_1(F)$  and  ${}^4A_2(F) \rightarrow {}^4T_1g(P)$ . Only one band appears in the visible region at  $15000 \text{ cm}^{-1}$ . This band is assigned  $\nu_3$ . There are two bands in the infrared region at  $5800 \text{ cm}^{-1}$  assigned  $\nu_2$  and the lowest energy transition (assigned  $\nu_1$ ) is expected at  $3300 \text{ cm}^{-1}$ .



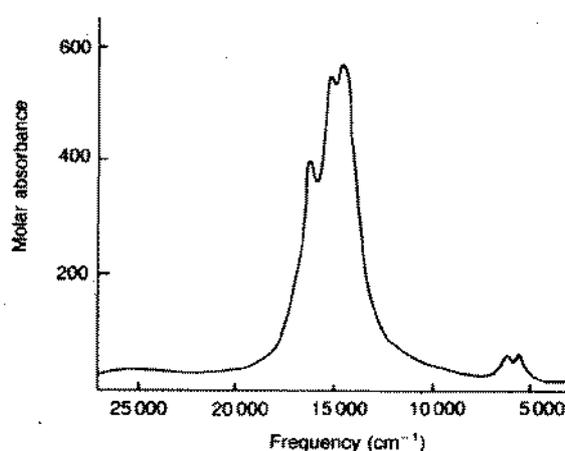
$15000 \text{ cm}^{-1}$  in the visible region



$5800 \text{ cm}^{-1}$  in the infrared region



$(3300 \text{ cm}^{-1})$  in the infrared region)

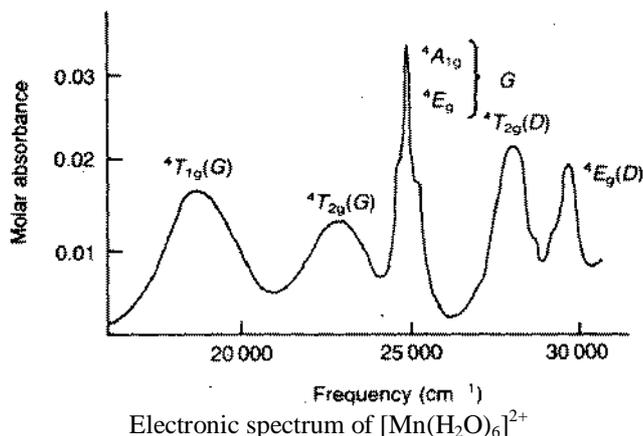


Electronic spectrum of  $[\text{CoCl}_4]^{2-}$

### Spectra of $d^5$ ions

The  $d^5$  configuration occurs with Mn(II) and Fe(III). In high-spin octahedral complexes formed with weak ligands, for example  $[\text{Mn}^{II}\text{F}_6]^{4-}$ ,  $[\text{Mn}^{II}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}^{III}\text{F}_6]^{3-}$ , there are five unpaired electrons with parallel spins. Any electronic transition within the  $d$  level must involve a reversal of spins, and in common with all other 'spin forbidden' transitions any absorption bands will be extremely weak. This accounts for the very pale pink colour of most Mn(II) salts, and the pale violet colour of iron(III) alum. The ground state term is  ${}^6S$ . None of the 11 excited states can be attained without reversing the spin of an electron, and hence the probability of such transitions is extremely low. Of the 11 excited states, the four quartets  ${}^4G$ ,  ${}^4F$ ,  ${}^4D$  and  ${}^4P$  involved the reversal of only one spin. The other seven states are doublets, are double spin forbidden, and are unlikely to be observed. In an octahedral field these four split into ten states, and hence up to ten extremely weak absorption bands may be observed. The spectrum of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  is shown in figure. Several features of this spectrum are unusual.

1. The bands are extremely weak. The molar absorption coefficient  $\epsilon$  is about  $0.02 - 0.03 \text{ l mol}^{-1} \text{ cm}^{-1}$ . Compared with  $5-10 \text{ l mol}^{-1} \text{ cm}^{-1}$  for spin allowed transitions.
2. Some of the bands are sharp and other are broad. Spin allowed bands are invariably broad.



### The Widths of Observed Bands

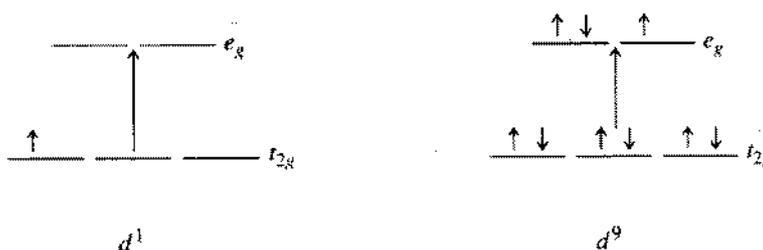
Consider again the visible spectrum for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . The single absorption band is quite broad, extending over several thousand wave numbers. The breadth of the absorption can be attributed mainly to the fact that the complex is not a rigid, static structure. Rather, the metal-ligand bonds are constantly vibrating, with the result that an absorption peak is integrated over a collection of molecules with slightly different molecular structures and  $\Delta_0$  values. Such ligand motions will be exaggerated through molecular collisions in solution. In the solid state, however, it is sometimes possible to resolve spectral bands into their vibrational components.

Sharp peaks also occur in solution spectra when the transitions involve ground and excited states that are either insensitive to changes in  $\Delta_0$  or are affected identically by the changes.

Two additional factors that can contribute to line breadth and shape are spin-orbit coupling, which is particularly prevalent in complexes of the heavier transition metals, and departures from cubic symmetry, such as through the Jahn-Teller effect or excited state Jahn-Teller distortion.

### Jahn-Teller Distortions and Spectra

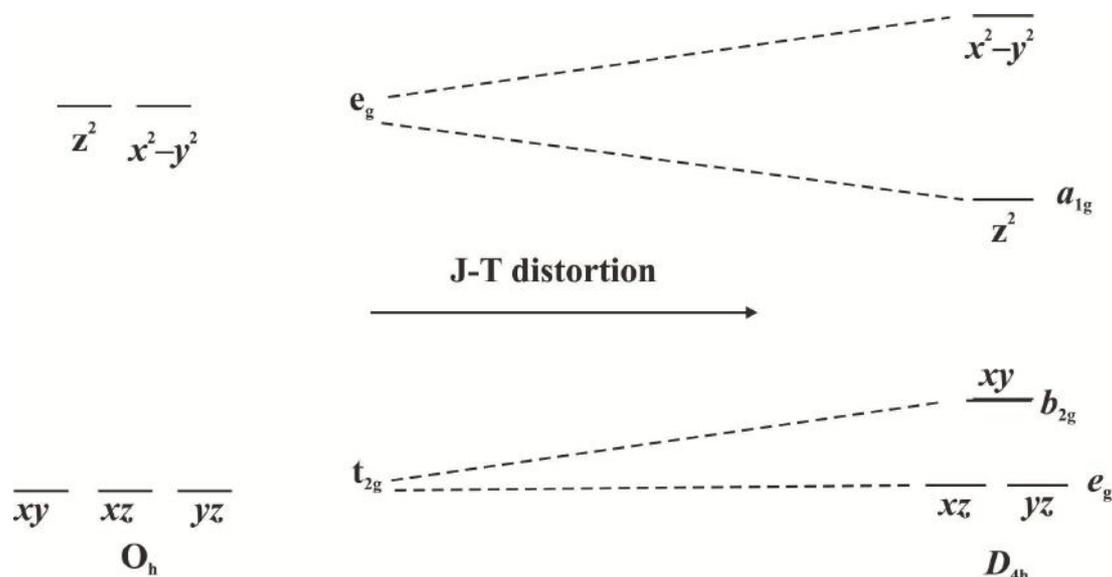
Up to this point, we have not discussed the spectra of  $d^1$  and  $d^9$  complexes. By virtue of the simple  $d$ -electron configurations for these cases, we might expect each to exhibit one absorption band corresponding to excitation of an electron from the  $t_{2g}$  to the  $e_g$  levels:



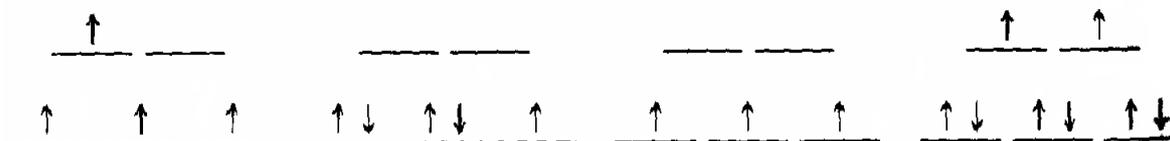
However this view must be at least a modest over simplification, because examination of the spectra of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}(d^1)$  and  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(d^9)$  shows these coordination compounds to exhibit two closely overlapping absorption bands rather than a single band.

To account for the apparent splitting of bands in these examples, it is necessary to recall that, some configurations can cause complexes to be distorted. In 1937, Jahn and Teller showed that nonlinear molecules having a degenerate electronic state should distort to lower the symmetry of the molecule and to reduce the degeneracy; this is commonly called the Jahn-Teller theorem. For example, a  $d^9$  metal in an octahedral complex has the electron configuration  $t_{2g}^6 e_g^3$ ; according to the Jahn-Teller theorem, such a complex should distort. If the distortion takes the form of an elongation along the  $z$  axis (the most

common distortion observed experimentally), the  $t_{2g}$  and  $e_g$  orbitals are affected as shown in following figure. Distortion from  $O_h$  to  $O_{4h}$  symmetry results in stabilization of the molecule: the  $e_g$  orbital is split into a lower  $a_{1g}$  level and a higher  $b_{1g}$  level.



When degenerate orbitals are symmetrically occupied, Jahn-Teller distortions are likely. For example, the first two configurations below should give distortions, but the third and fourth should not:

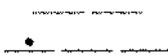
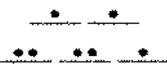
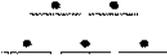


In practice, the only electron configuration for  $O_h$  symmetry that give rise to measurable Jahn-Teller distortions are those that have asymmetrically occupied  $e_g$  orbitals, such as the high spin  $d^4$  configuration. The Jahn-Teller theorem does not predict what the distortion will be; by far, the most common distortion observed is elongation along the  $z$  axis. Although the Jahn-Teller theorem predicts that configurations having asymmetrically occupied  $t_{2g}$  orbitals, such as the low-spin  $d^5$  configuration, should also be distorted, such distortions are too small to be measured in most cases.

The Jahn-Teller effect on spectra can easily be seen from the example of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , a  $d^9$  complex. From above figure, which shows the effect on  $d$  orbitals of distortion from  $O_h$  to  $D_{4h}$  geometry, we can see the additional splitting of orbitals accompanying the reduction of symmetry.

## Symmetry Labels for Configurations

Electron configurations have symmetry labels that match their degeneracies, as follows:

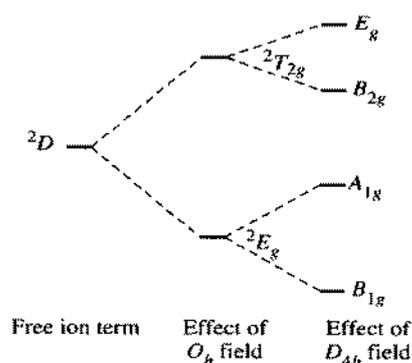
		<i>Examples</i>	
$T$	designates a triply degenerate asymmetrically occupied state.		
$E$	designates a doubly degenerate asymmetrically occupied state.		
$A$ or $B$	designate a nondegenerate state. Each set of levels in an $A$ or $B$ state is symmetrically occupied.		

When a  ${}^2D$  term for  $d^p$  is split by an octahedral ligand field, two configurations result:



The lower energy configuration is doubly degenerate in the  $e_g$  orbitals (occupation of the  $e_g$  orbitals could be  $\uparrow\uparrow \downarrow$  or  $\downarrow \uparrow\uparrow$ ) and has the designation  ${}^2E_g$ ; the higher energy configuration is triply degenerate in the  $t_{2g}$  levels (three arrangements are possible in these levels:  $\uparrow\uparrow \downarrow \downarrow$ ,  $\uparrow\uparrow \downarrow \downarrow$ ,  $\uparrow\uparrow \downarrow \downarrow$  or  $\downarrow \uparrow\uparrow \downarrow$ ) and has the designation  ${}^2T_{2g}$ . Thus, the lower energy configuration is the  ${}^2E_g$ , and the higher energy configuration  ${}^2T_{2g}$ , as in the following figure. This is the opposite of the order of energies of the orbitals ( $t_{2g}$  lower than  $e_g$ ), shown in figure.

Similarly, for distortion of  $D_{4h}$ , the order of labels of the orbitals in figure is the reverse of the order of labels of the energy configurations in figure.

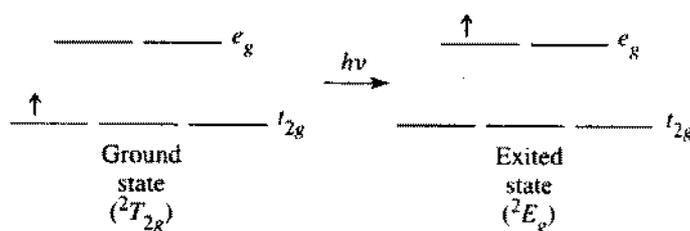


In summary, the  ${}^2D$  free ion term is split into  ${}^2E_g$  and  ${}^2T_{2g}$  by a field of  $O_h$  symmetry, and further split on distortion to  $D_{4h}$  symmetry. The labels of the states resulting from the free-ion term are in reverse order to the labels on the orbitals; for example, the  $b_{1g}$  atomic orbital is of highest energy, whereas the  $B_{1g}$  state originating from the  ${}^2D$  free-ion term is of lowest energy.

For a  $d^p$  configuration, the ground state in octahedral symmetry is a  ${}^2E_g$  term and excited state is a  ${}^2T_{2g}$  term. On distortion to  $D_{4h}$  geometry, these terms split, as shown in figure. In an octahedral  $d^p$  complex, we would expect excitation from the  ${}^2E_g$  state to the  ${}^2T_{2g}$  state and a single absorption band. Distortion

of the complex to  $D_{4h}$  geometry splits the  ${}^2T_{2g}$  levels into two levels, the  $E_g$  and the  $B_{2g}$ . Excitation can now occur from the ground state (now the  $B_{1g}$  state) to the  $A_{1g}$ , the  $E_g$ , or the  $B_{2g}$  (the splitting is exaggerated in figure). The  $B_{1g} \rightarrow A_{1g}$  transition is too low in energy to be observed in the visible spectrum. If the distortion is strong enough, therefore, two separate absorption bands may be observed in the visible region, to the  $E_g$  or the  $B_{2g}$  levels (or a broadened or narrowly split peak is found, as in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ).

For a  $d^1$  complex, a single absorption band, corresponding to excitation of a  $t_{2g}$  electron to an  $e_g$  orbital, might be expected:



However, the spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , an example of a  $d^1$  complex, shows two apparently overlapping bands rather than a single band. How is this possible?

One explanation commonly used is that the excited state can undergo Jahn-Teller distortion, as in figure. As in the examples considered previously, asymmetric occupation of the  $e_g$  orbitals can split these orbitals into two of slightly different energy (of  $A_{1g}$  and  $B_{1g}$  symmetry). Excitation can now occur from the  $t_{2g}$  level to either of these orbitals. Therefore, as in the case of the  $d^9$  configuration, there are now two excited states of slightly different energy. The consequence may be a broadening of a spectrum into a two-humped peak, as in  $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ , or in some cases into two more clearly defined separate peaks.