

B.Sc. SEM-VI

US06CCHE22 INORGANIC CHEMISTRY

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

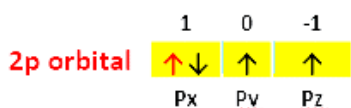
QUANTUM NUMBER: To completely describe an electron in an atom, four quantum numbers are needed: energy (n), angular momentum (ℓ), magnetic moment (m_ℓ), and spin (m_s).

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

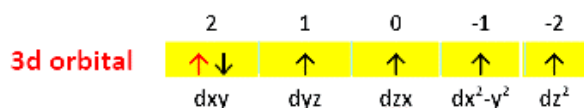
Number	Symbol	Possible Values
Principle Quantum Number	N	1, 2, 3, 4,
Angular Momentum Quantum Number	L	0, 1, 2, 3, ..., (n-1)
Magnetic Quantum Number	m_l	-l, ..., -1, 0, +1, ..., +l
Spin Quantum Number	m_s	+1/2, -1/2

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

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



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



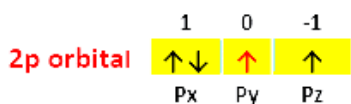
$$n = 3, l = 2, m_l = +2, m_s = +1/2$$



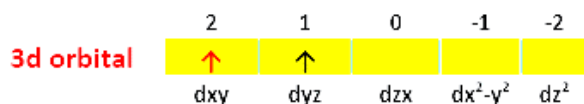
$$n = 2, l = 1, m_l = +1, m_s = -1/2$$



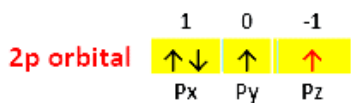
$$n = 3, l = 2, m_l = +2, m_s = -1/2$$



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



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



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

Term Symbols

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

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

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

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

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

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

Where, $2S + 1$ is spin multiplicity

L is orbital angular momentum

J is total angular momentum

All above terms are determined by calculating

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

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

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

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

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

Example: P^3

↑	↑	↑
+1	0	-1

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

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

Using value of S, spin multiplicity can be dermine as

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

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

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

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

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

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

Example: For d^7

↑↓	↑↓	↑	↑	↑
ml = +2	+1	0	-1	-2

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

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

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

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

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

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

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

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

$$= 2 \dots 0$$

$$= 2, 1, 0$$

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

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

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

↑	↑	↑
+1	0	-1

L = orbital quantum number

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

S = total spin quantum number

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

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

J = total angular momentum quantum number

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

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

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

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

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

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

↑	↑	
+1	0	-1

L = orbital quantum number

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

S = total spin quantum number

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

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

J = total angular momentum quantum number

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

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

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

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

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

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



L = orbital quantum number

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

S = total spin quantum number

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

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

J = total angular momentum quantum number

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

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

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

$$= 4, 3, 2$$

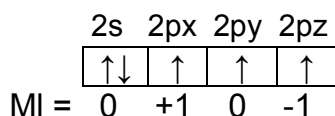
\therefore The possible term for d^3 configuration is $^{2S+1}F_J = {}^3F_2, {}^3F_3, {}^3F_4$

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

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

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

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



L = orbital quantum number

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

S = total spin quantum number

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

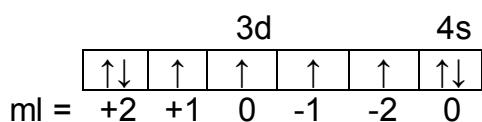
$$\therefore 2S + 1 = 2(\frac{3}{2}) + 1 = 4$$

J = total angular momentum quantum number

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

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

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



L = orbital quantum number

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

S = total spin quantum number

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

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

J = total angular momentum quantum number

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

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

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

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

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



L = orbital quantum number

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

S = total spin quantum number

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

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

J = total angular momentum quantum number

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

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

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

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

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

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

For 3F :

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

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

$$\therefore 2S = 2$$

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

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

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

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

For 1S :

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

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

$$\therefore 2S = 0$$

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

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

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

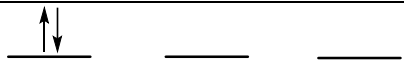
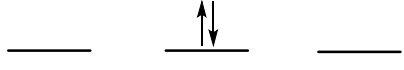
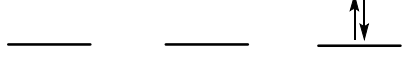
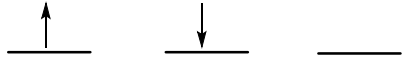
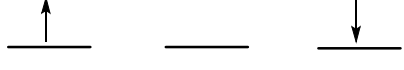
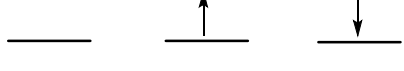
$$\begin{aligned} J &= (L + S) \dots\dots (L - S) \\ &= (0 + 0) \dots\dots (0 - 0) \\ &= \mathbf{0} \end{aligned}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Hund's rule:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

To arrange the J energy levels of p² configuration in the increasing order of their energy

The energy levels for p² configuration are ³P₂, ³P₁, ³P₀, ¹D₂ and ¹S₀.

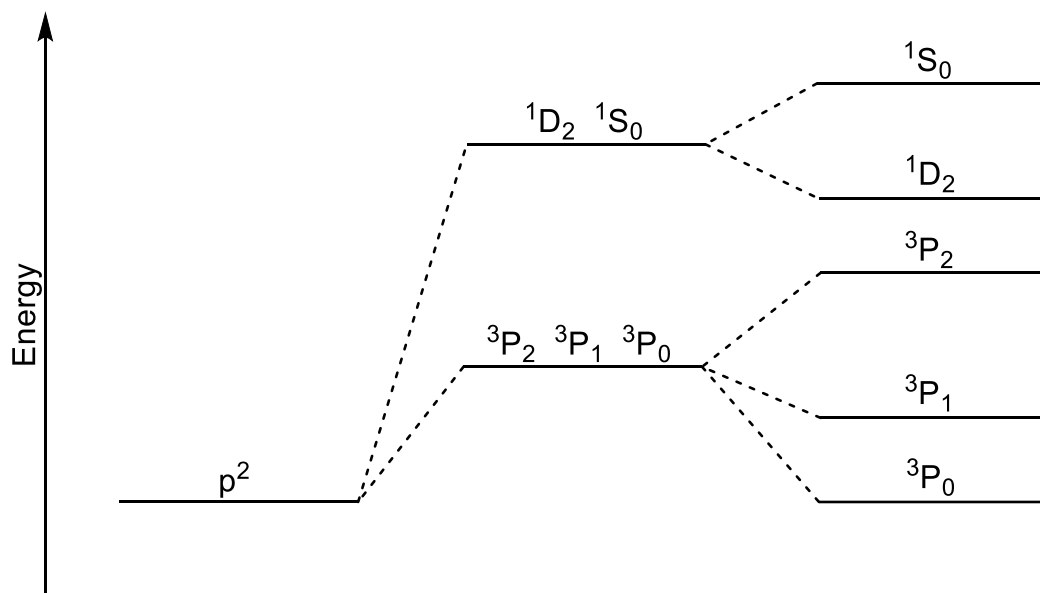
³P₂, ³P₁, ³P₀ are J energy level of ³P term, which has same value of spin multiplicity (2S+1=3). So, their energy depends on their J value. With increase of J value, energy also increase (Hund's rule).

Thus, the energy is given as: ³P₀ < ³P₁ < ³P₂ -----(2)

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

$$^3P_0 < ^3P_1 < ^3P_2 < ^1D < ^1S$$

Since ³P₀ has the lowest energy, it is Russel-Saunders term for p² configuration.



MICROSTATE:

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

Microstates are determined by following different ways.

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

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

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

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

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

r = number of electrons in the given configuration

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

Example: Calculate the number of microstates in the configurations:

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

(i) p^2 configuration:

This configuration has $r = 2$.

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

Thus,

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

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

(iii) d^1 configuration:

This configuration has $r = 1$.

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

Thus,

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

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

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

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

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

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

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

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

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

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

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

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

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

Example: To calculate microstates of 2D

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

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

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

$$= 2 (5)$$

$$= 10$$

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

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

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

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

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

$$= (3) (3)$$

$$= 9$$

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

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

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

$$= 5$$

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

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

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

$$= (1) (1)$$

$$= 1$$

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

Pigeonhole diagram for p^2 configuration:

Microstates of p^2 are 15

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

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

$\therefore L = 2$, hence D term

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

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

$= 2$

\therefore Five 1D_2

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

$\therefore L = 1$, hence P term

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

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

$= 2, 1, 0$

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

(C) $M_L = 0$

$\therefore L = 0$, hence S term

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

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

$= 0$

\therefore One 1S_0

Number of microstates for d^2

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

Thus,

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

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

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

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

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

$$= 45$$

Pigeonhole diagram for d^2 configuration:

Microstates of d^2 are 45

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

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

$\therefore L = 4$, hence G term

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

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

$= 4$

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

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

$\therefore L = 3$, hence F term

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

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

$= 4, 3, 2$

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

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

$\therefore L = 2$, hence D term

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

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

$$= 2$$

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

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

$\therefore L = 1$, hence P term

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

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

$$= 2, 1, 0$$

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

(E) $M_L = 0$

$\therefore L = 0$, hence S term

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

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

$$= 0$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

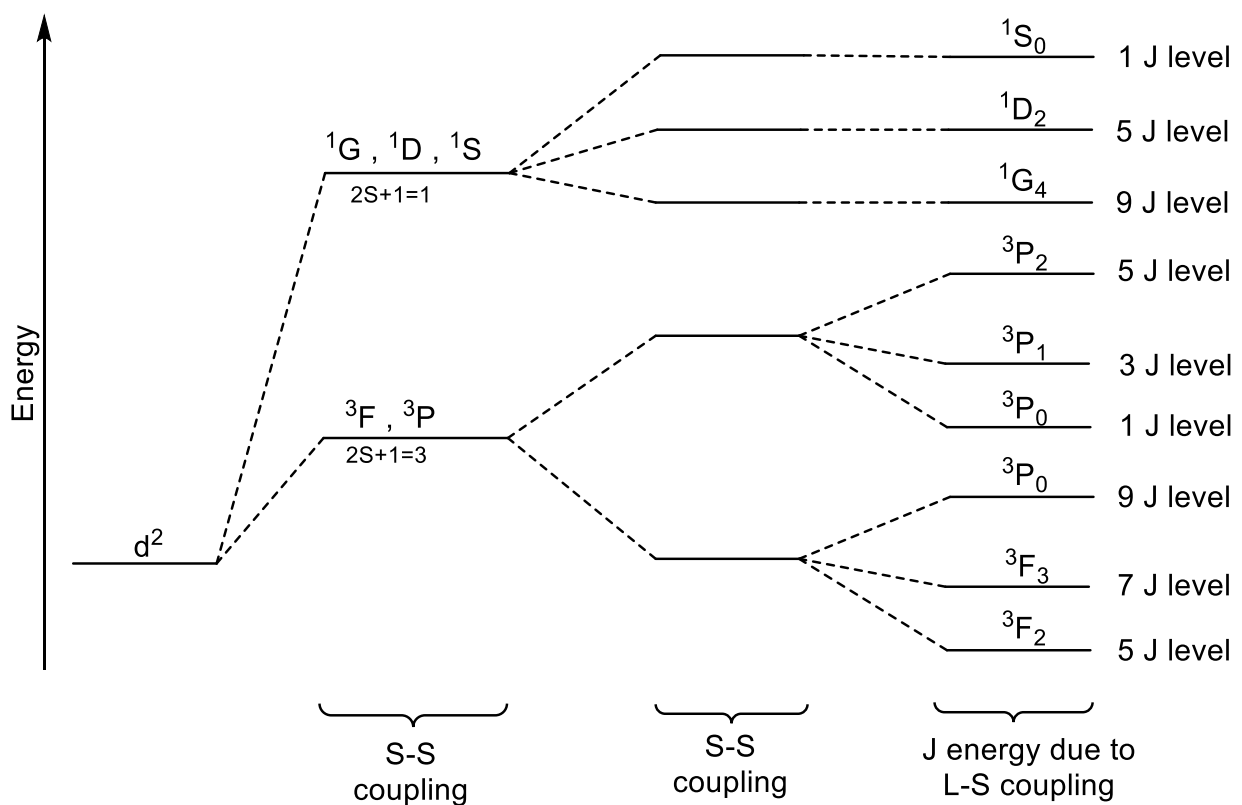
For 1D term, $(2S + 1)$ is 1 and L is 2

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

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

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

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



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

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

Example: To calculate microstates of 2P_4

For 2P_4 term, J is 4

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

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

$$= 9$$

ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES:

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

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

Selection rule:

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

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

There are two rules to decide allowed or forbidden transition.

(1) Spin selection rule:

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

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

This rule is known as rule of spin multiplicity.

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

(2) Laporte orbital selection rule:

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

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

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

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

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

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

Intensity of different types of electronic transition:

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

Splitting of d^n term:

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

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

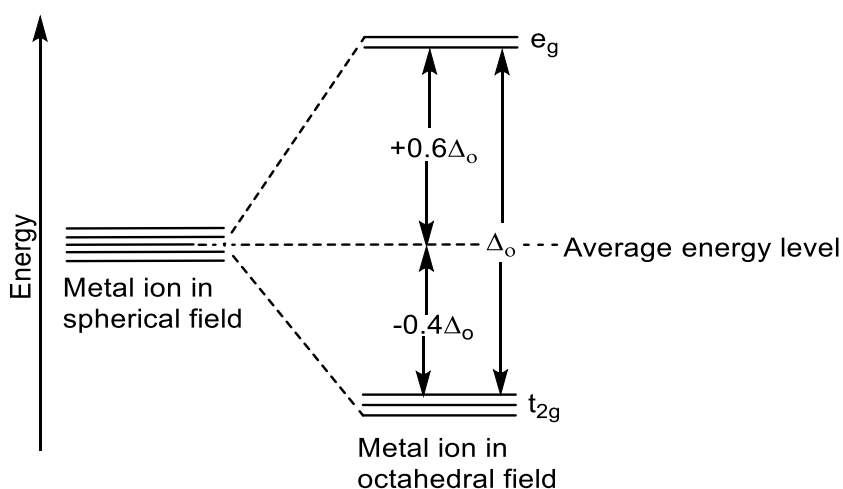
Transforming spectroscopic term in to Muliken symbol:

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

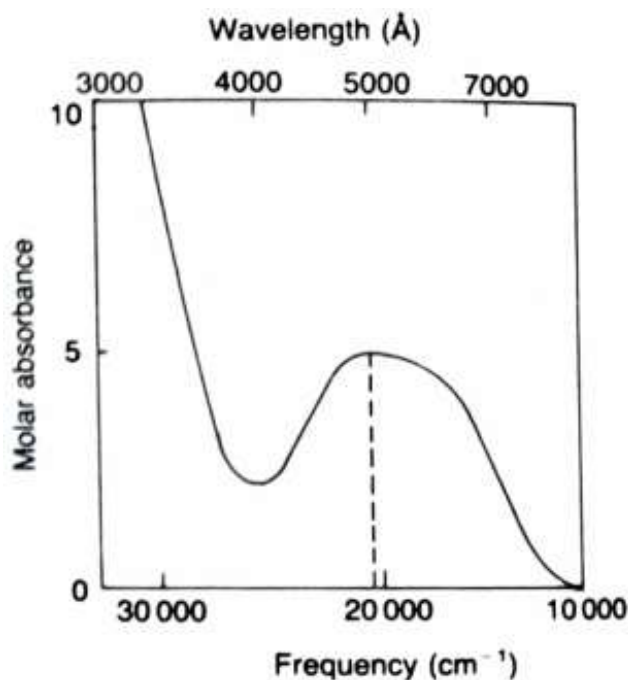
Electronic spectra of d^1 system:

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

In octahedral complex of Ti(III), $[\text{TiCl}_6]^{-3}$ and $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ (d^1 system), d-orbital splits and one electron occupies lower t_{2g} level and only one transition is possible to e_g level.



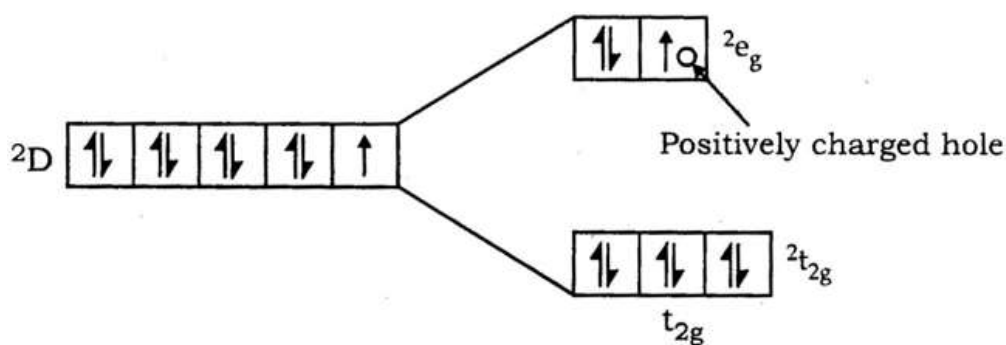
Consequently the absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{+2}$ shows only one band with a peak at 20300 cm^{-1} . The magnitude of splitting of Δ_o depends on nature of ligands and affect the energy of transition and hence the frequency of maximum absorption in the spectrum.



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

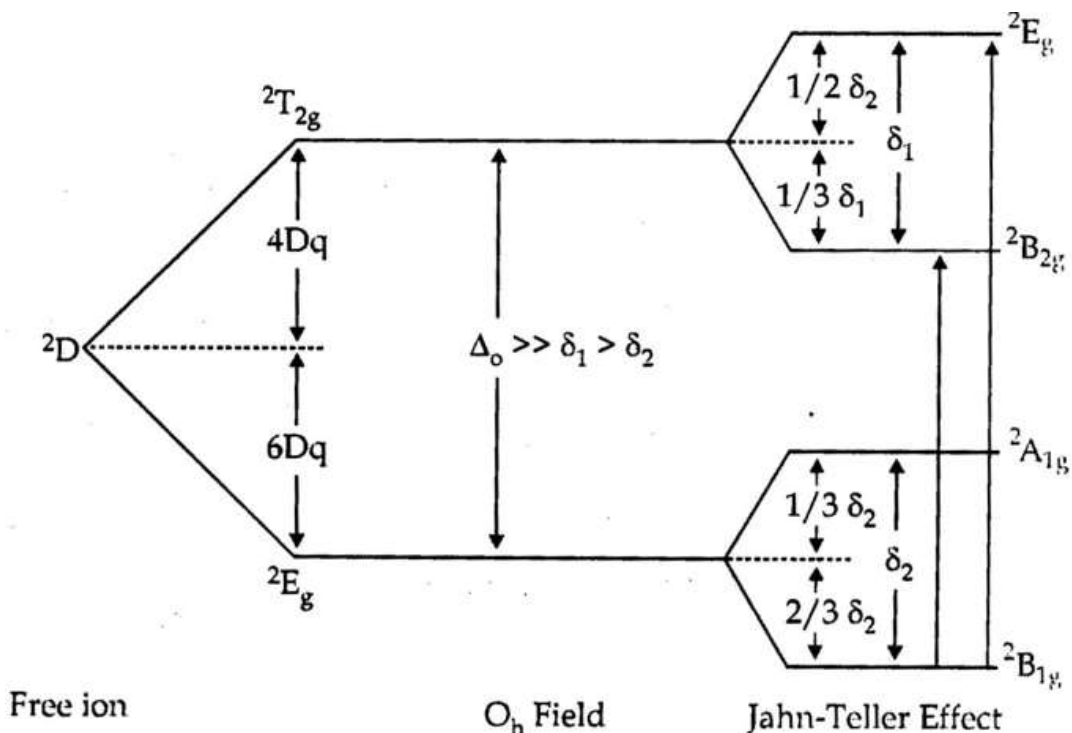
Electronic spectra of d^9 system:

Cu^{+2} ($z = 29$): $[\text{Ar}] 3d^9 4s^0$ is a d^9 system. The term symbol is 2D . In $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$, according to CFT all five orbitals do not remain equivalent. Due to octahedral field effect of H_2O ligand, the degenerate d-orbitals of Cu^{+2} splits and produces two energy levels such as lower energetic $^2t_{2g}$ (d_{xy}, d_{yz}, d_{xz}) and higher energetic 2e_g ($d_{x^2-y^2}, d_{z^2}$).



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

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

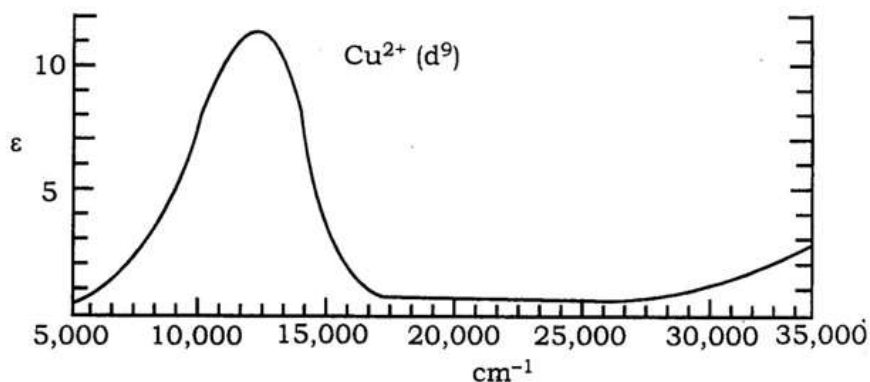


Electronic spectra of d⁹ system

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

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

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

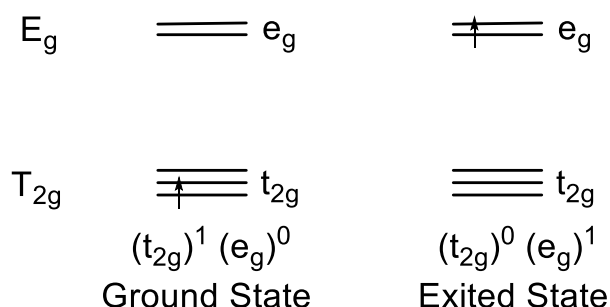


The energy difference between transition (i) and (ii) is very low, so their bands are obtained closer to each other as a big peak along with a shoulder peak. Due to Jahn-Teller effect the ground state and excited state split into many energy levels. Therefore instead of one transition, many transitions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

d¹ Correlation diagram:

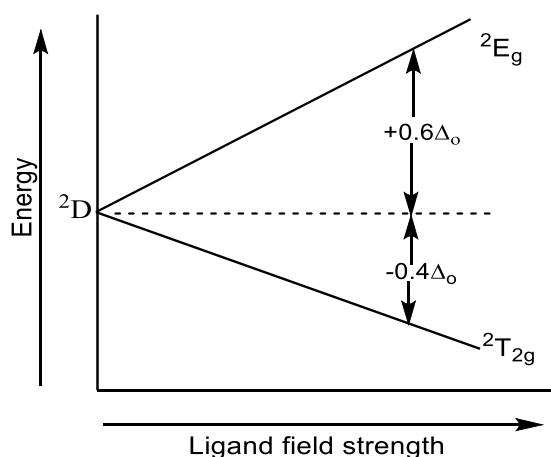
The ground term ²D arise in d¹ system.

The ground state configuration is t_{2g}¹ e_g⁰, in excited state the configuration is t_{2g}⁰ e_g¹. It means electron shift to e_g orbital. Thus, transition is from ²T_{2g} → ²E_g.



The separation is numerically equal to Δ_o, the magnitude of the field.

Relative to the energy of the ²D free ion term, the ²T_{2g} term will be stabilized by -0.4Δ_o and the ²E_g term will be destabilised by +0.6Δ_o.

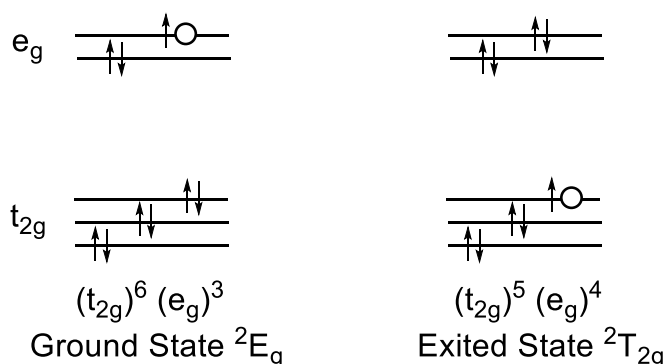


Splitting of energy levels for d¹ configuration in Oh field

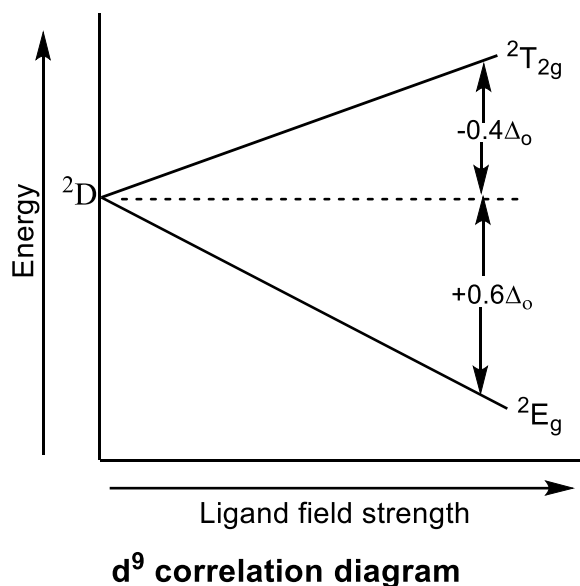
d⁹ Correlation diagram:

The same ground term ²D arise in d⁹ system.

The ground state configuration is t_{2g}⁶ e_g³, means hole is in e_g orbital. In excited state the configuration is t_{2g}⁵ e_g⁴. It means hole (positron) transition occur is from ²E_g → ²T_{2g}.

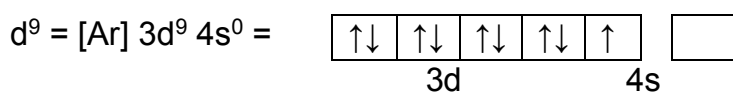
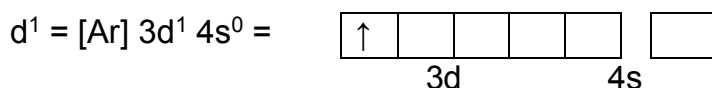


Thus, the energy ordering of the terms for d⁹ is the reverse of d¹ case. For the d⁹ (Oh) case the ²E_g is stabilised by -0.4Δ_o and the ²T_{2g} term will be destabilised by +0.6Δ_o.



Orgel diagram of d¹ – d⁹:

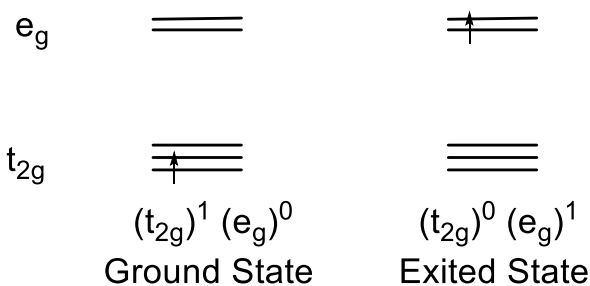
Electronic configuration of d¹ and d⁹ are as follow:



Here, in electronic configuration of d¹, there is only one electron exist in d-orbital while in d⁹ system, only one space is empty in d-orbital as 'hole' position.

The ground state term symbol of both d¹ and d⁹ is ²D. According to CFT, ²D term split in to ²T_{2g} and ²E_g. in composition to d¹, d⁹ has opposite splitting.

In splitted energy levels of d¹ system, electron is filled as follow.



Here in ground state (t_{2g})¹, electron arrangement has three probable arrangements.

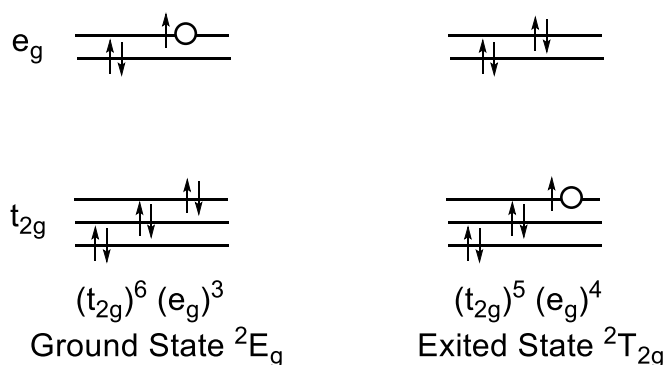
- (i) dxy¹, dyz⁰, dxz⁰
- (ii) dxy⁰, dyz¹, dxz⁰
- (iii) dxy⁰, dyz⁰, dxz¹

while in exited state (eg)¹ has two possibility

- (i) (dz²)¹ (dx²-y²)⁰
- (ii) (dz²)⁰ (dx²-y²)¹

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

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



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

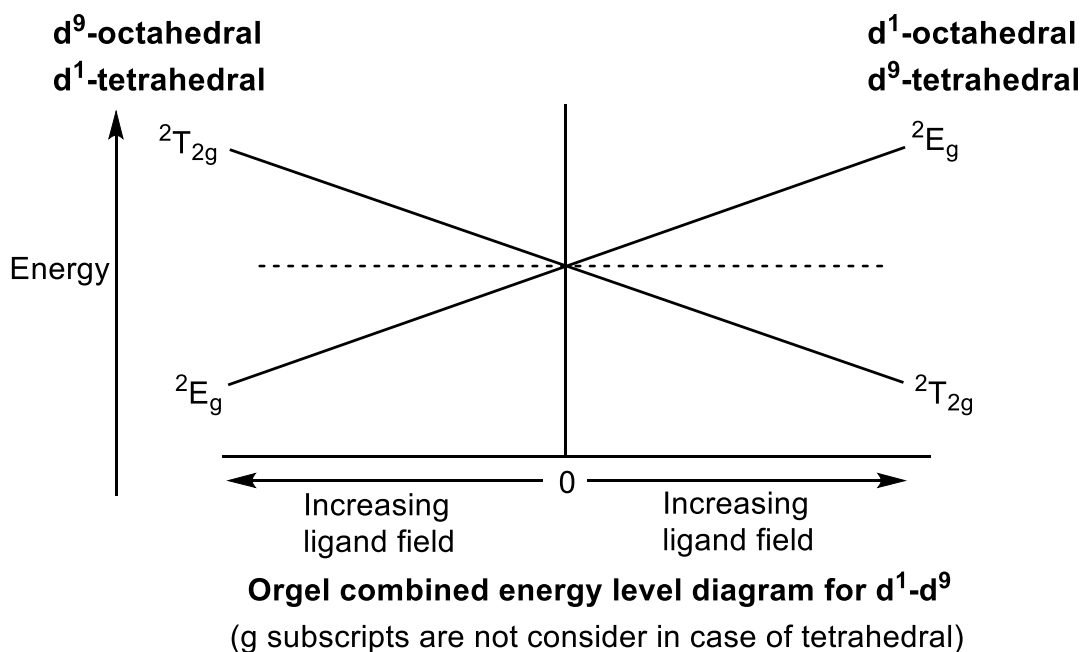
- (i) $(t_{2g})^6 (dz^2)^2 (dx^2-y^2)^1$
- (ii) $(t_{2g})^6 (dz^2)^1 (dx^2-y^2)^2$

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

- (i) $dxy^2, dyz^2, dxz^1 (e_g)^4$
- (ii) $dxy^2, dyz^1, dxz^2 (e_g)^4$ or
- (iii) $dxy^1, dyz^2, dxz^2 (e_g)^4$

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

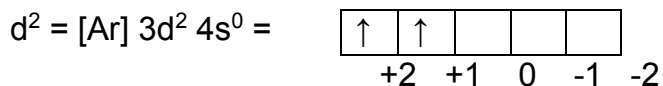
Thus, in d^1 transition, electron transition takes place while in d^9 , positron (hole) transition takes place. So, the bands of both d^1 and d^9 obtained at equal frequency.



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

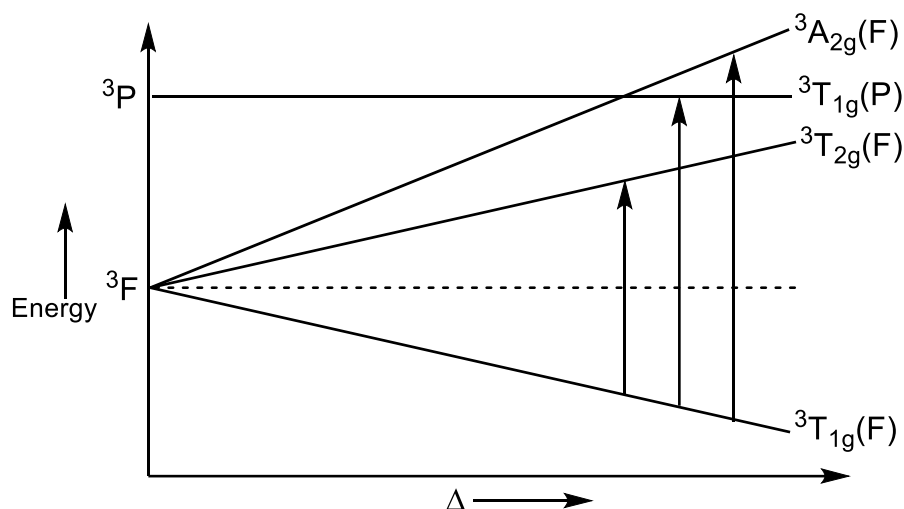
d² corelation diagram:

The V(III) octahedral complexes have the d² configuration



The ground state term symbol for d² is ³F. The excited states are ³P, ¹G, ¹D and ¹S. According to spin selection rule, ³F to ³P is allowed transition, whereas ¹G, ¹D and ¹S are forbidden transition. As per multiplicity rule, triplet → singlet is forbidden transition, therefore not shown in the Orgel diagram.

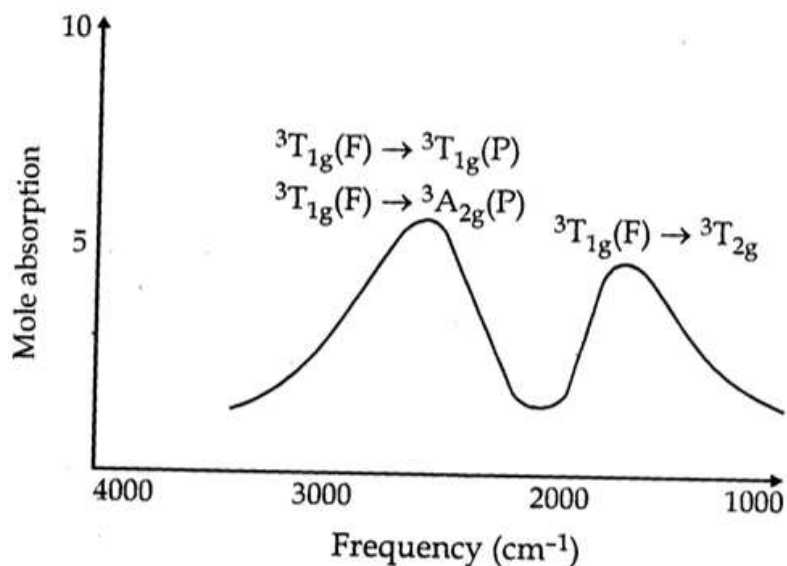
The spectra of vanadium complexes would be expected to show three absorption bands from the ground state ³T_{1g}(F) → ³T_{2g}(F), ³T_{1g}(F) → ³T_{1g}(P) and ³T_{1g}(F) → ³A_{2g}(F).



Thus, in [V(H₂O)₆] three transitions are possible:

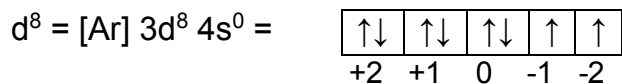
- | | |
|---|--------------------------|
| (i) ³ T _{1g} (F) → ³ T _{2g} (F) | 17200 cm ⁻¹ |
| (ii) ³ T _{1g} (F) → ³ T _{1g} (P) | } 25600 cm ⁻¹ |
| (iii) ³ T _{1g} (F) → ³ A _{2g} (F) | |

Thus, the visible spectra of [V(H₂O)₆]³⁺ should contain three peaks, but the energy difference between ³T_{1g}(F) → ³T_{1g}(P) and ³T_{1g}(F) → ³A_{2g}(F) transition is such small that it gives overtone and a single peak appear. While ³T_{1g}(F) → ³T_{2g} gives another peak. Thus, only two peaks appear.



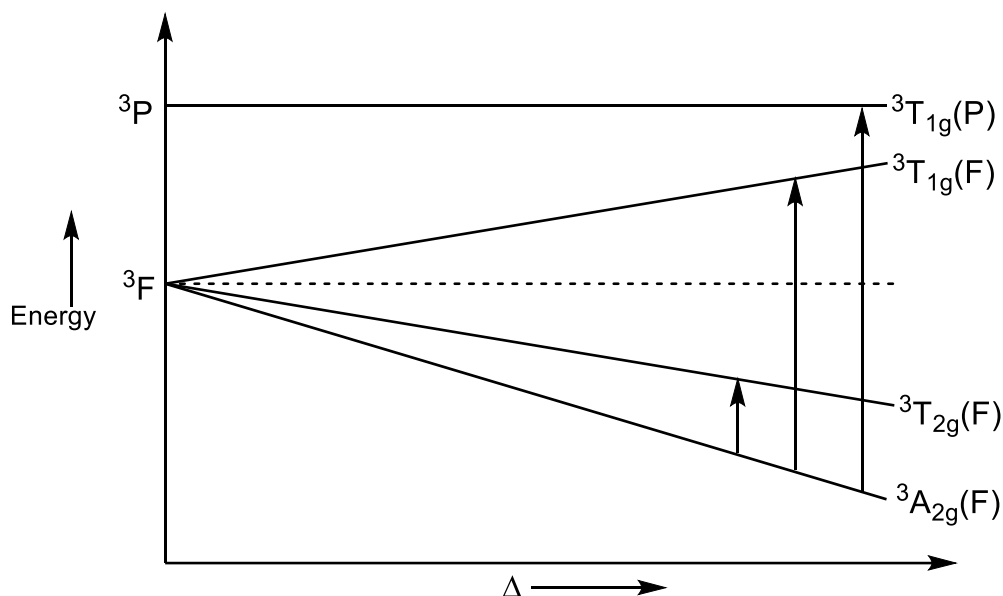
d⁸ corelation diagram:

The Ni(II) octahedral complexes have the d⁸ configuration.



The ground state term symbol for d⁸ is ³F. The excited states are ³P, ¹G, ¹D and ¹S. According to spin selection rule, ³F to ³P is allowed transition, whereas ¹G, ¹D and ¹S are forbidden transition. As per multiplicity rule, triplet→singlet is forbidden transition, therefore not shown in the Orgel diagram.

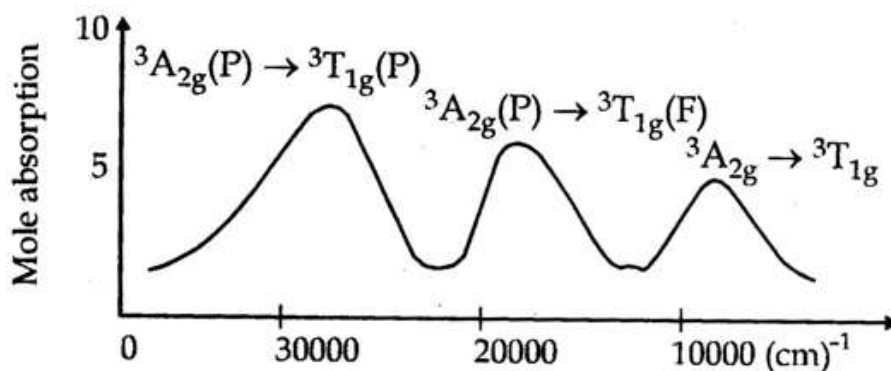
According to CFT, in octahedral field ³F term splits into lower energy ³A_{2g} and higher energy containing ³T_{2g} and ³T_{1g}(P) levels. Splitting of d⁸ system [Ni(H₂O)₆]⁺² in octahedra; field is given below.



Thus, in [Ni(H₂O)₆]⁺² three transitions take place.

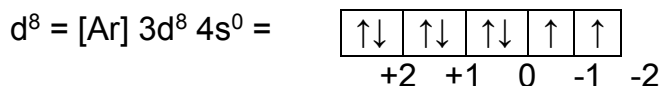
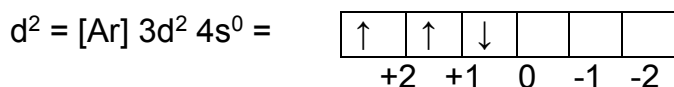
Transition	$\nu \text{ cm}^{-1}$
(i) ³ A _{2g} → ³ T _{2g} (F)	8700 cm ⁻¹
(ii) ³ A _{2g} → ³ T _{1g} (F)	14500 cm ⁻¹
(iii) ³ A _{2g} → ³ T _{1g} (P)	25300 cm ⁻¹

The required energy for all three transitions are enough so visible spectra of [Ni(H₂O)₆]⁺² contains three peaks as under.



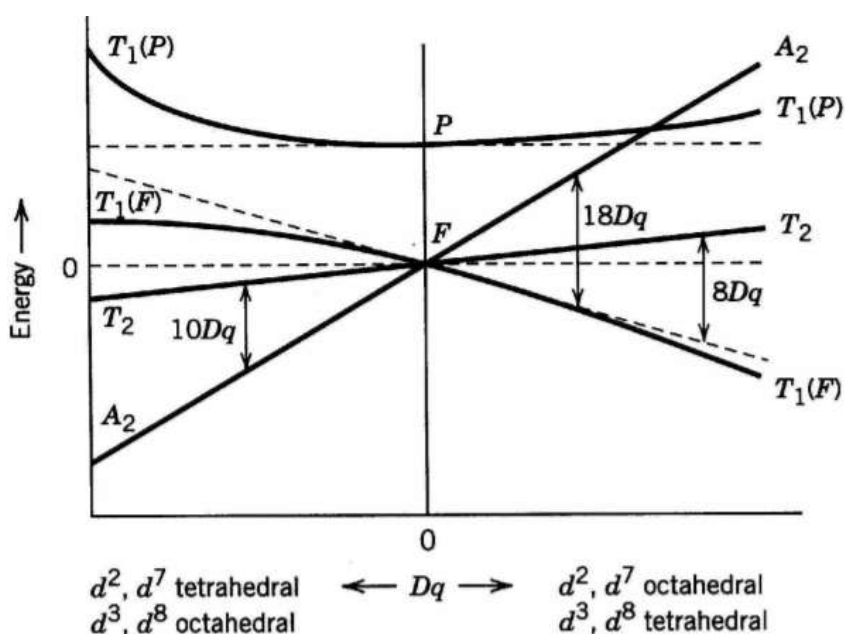
d²-d⁸ Orgel diagram:

The V(III) octahedral complexes have the d² configuration and Ni(II) octahedral complexes have the d⁸ configuration.



The ground state term symbol for d² and d⁸ is ³F. The excited states are ³P, ¹D and ¹S. According to the spin selection rule, ³F to ³P is an allowed transition, whereas ¹G, ¹D and ¹S are forbidden transitions. As per the multiplicity rule, triplet → singlet is a forbidden transition, therefore not shown in the Orgel diagram.

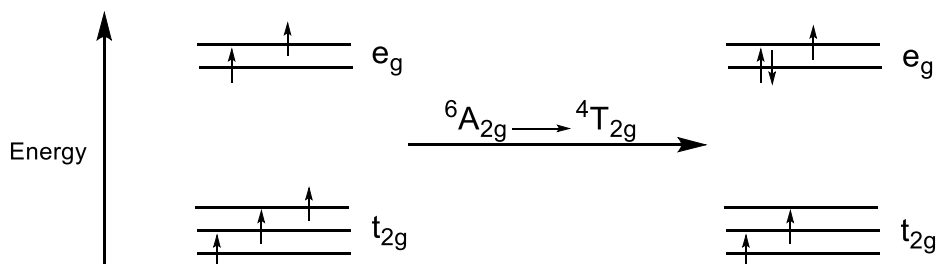
According to CFT, d² and d⁸ systems split in octahedral and tetrahedral fields respectively as shown below.



The splitting of d² in octahedral field and of d⁸ in tetrahedral field is equal. While splitting of d² in tetrahedral field and of d⁸ in octahedral field is equal.

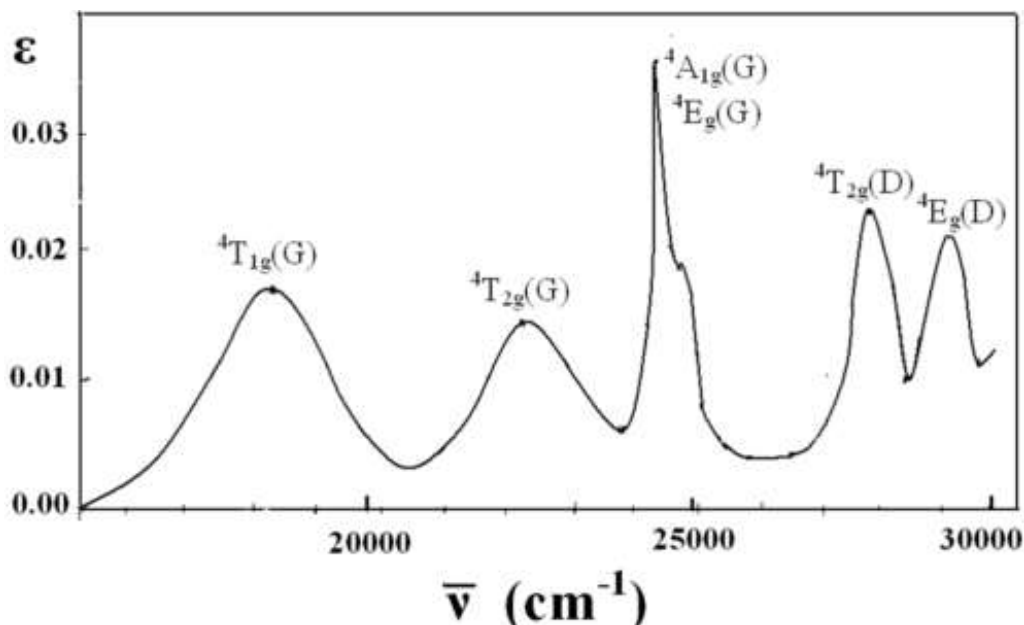
The electronic spectra of high-spin d⁵ ions:

For high-spin d⁵ ions, all possible d-d transitions are spin-forbidden. As a result, the bands in spectra of high-spin complexes of Mn(III) and Fe(III) are very weak and the compounds are nearly colourless. Below is shown a d-d transition for a high-spin d⁵ ion, showing that it is spin-forbidden.

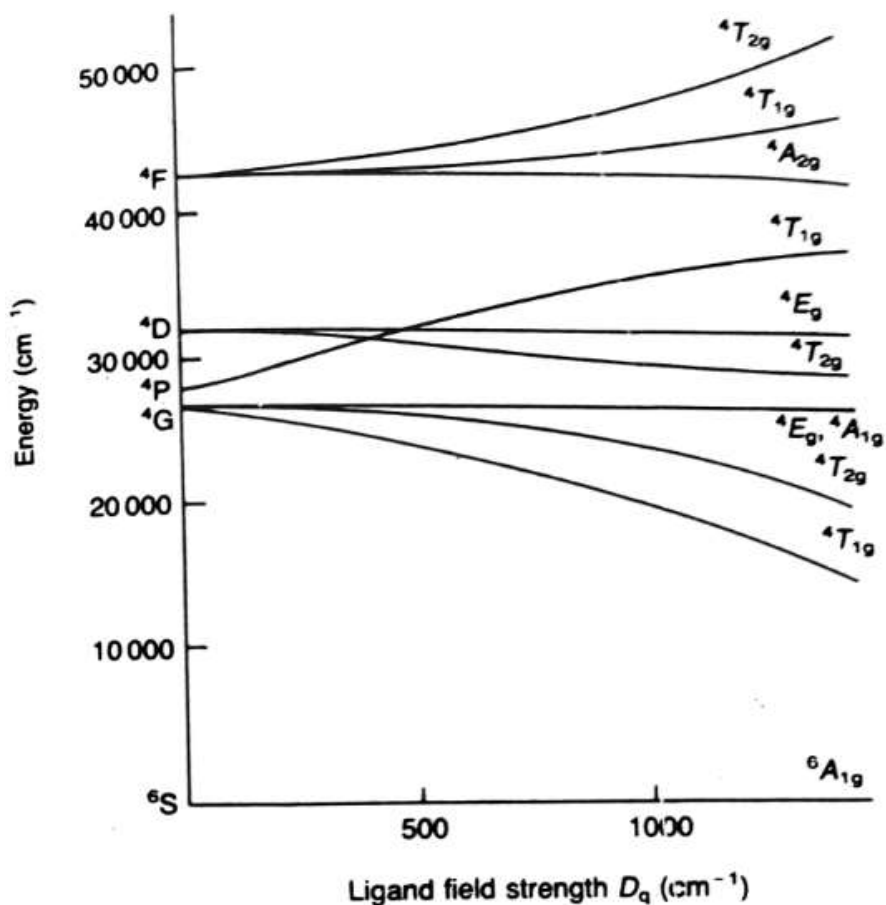


There are five unpaired electrons with parallel spin. Any electronic transition within the d-level must involve a reverse of spin, therefore it is spin forbidden transition and absorption bands will be extremely weak.

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

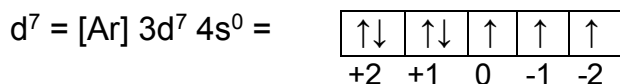
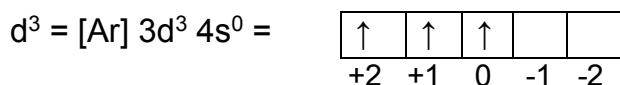


Electronic spectra of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$



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

d^3 - d^7 Orgel diagram:



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

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

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

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

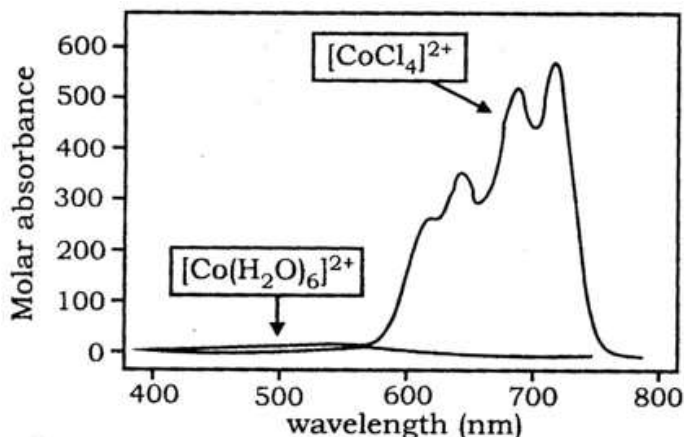
Tetrahedral complexes of Co(II) such as $[\text{CoCl}_4]^{2-}$ show intensely blue colour. There are possible transitions as follows.

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

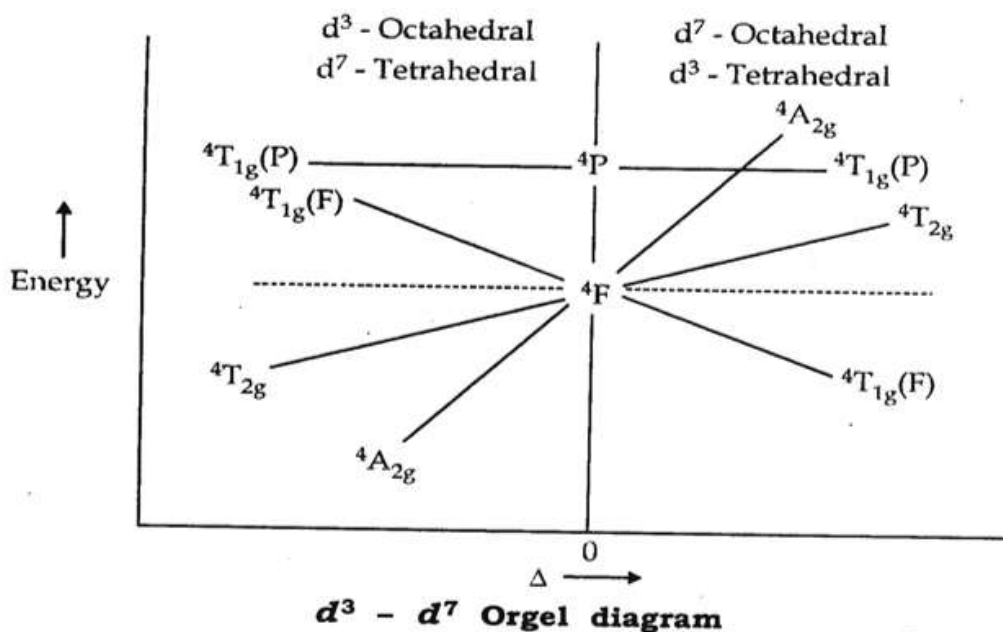
Thus, dissolving CoCl_2 in water produces a pale pink solution of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, but in alcohol tetrahedral $[\text{CoCl}_2(\text{CH}_3\text{CH}_2\text{OH})_2]$ form gives intense blue colour.

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

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

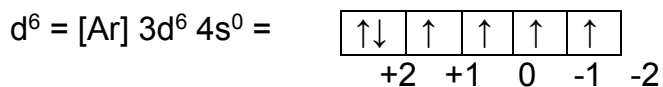
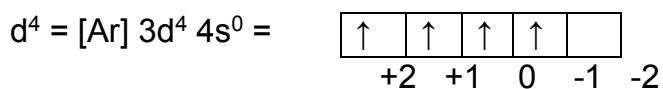


The term of d^3 and d^7 system is equal (same). Their ground state term would be 4F and 4P . The Orgel diagram of d^3 and d^7 is similar with d^2 and d^8 only terms are different instead of 3F and 3P , they contain 4F and 4P .

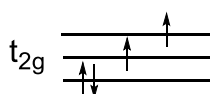
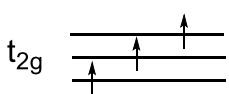
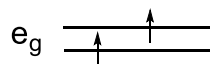
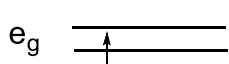


Orgel diagram of d^4 - d^6 :

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

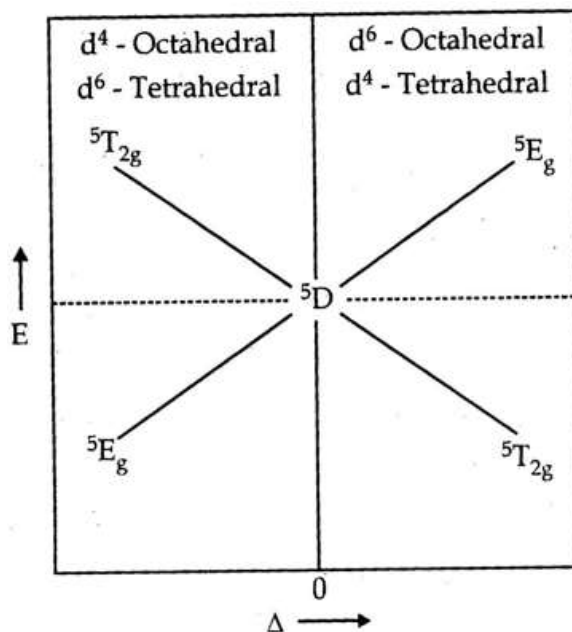


The ground state term symbol for d^4 and d^6 is 5D .



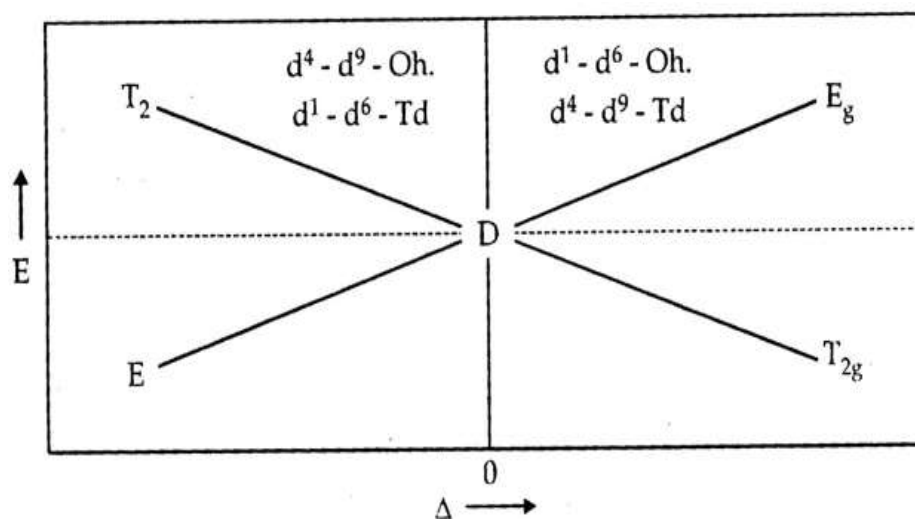
The ground state term symbol for d^4 and d^6 is 5D . In excited state 3h , 3G , 3F , 3D , 3P , 1I , 1D , 1S .

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



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

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



John-Teller effect:

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

According to this theorem:

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

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

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

Explanation:

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

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

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

For example,

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

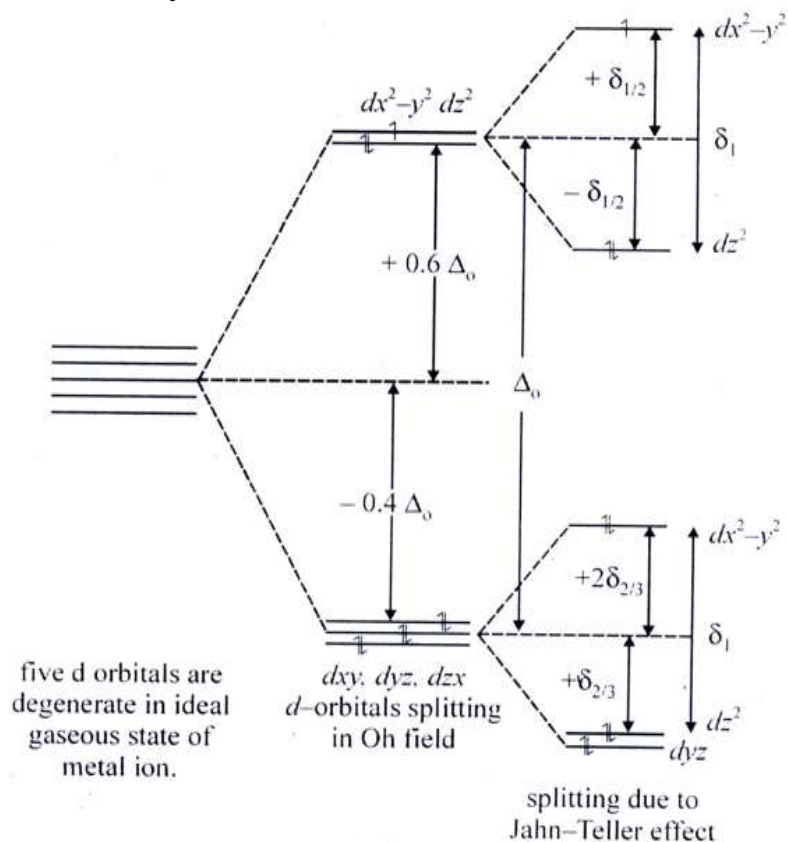


Fig. : Jahn-Teller effect in Cu^{+2} ion complexes

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

In the figure give above, splitting of the more stable octahedral distortion corresponding to configuration (i) $t_{2g}^6 (dz^2)^2, (dx^2-y^2)^1$ is being consider δ_1 and δ_2 are much smaller than as compared with Δ_o and also 2 is much smaller than, i.e. $\Delta_o \gg \delta_1 > \delta_2$.

Spectrochemical Series:

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

i.e. In $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ under the effect of the ligand, the absorption band of d-d transition is obtained in green field of visible region. So, $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ complex is green coloured. But when in that salt if ethylene diamine (en) is added, it forms $[\text{Ni}(\text{en})_3]^{+2}$ complex. Here, en ligand is stronger than H_2O . So the energy required for d-d transition increase and as a result of this the peak is obtained at low wavelength. Thus, the three peaks are obtained in spectra of $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ shift towards low wavelength in $[\text{Ni}(\text{en})_3]^{+2}$. Thus, with help of electronic spectra, the relative strength of different ligands is known.

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

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

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

This series is called spectrochemical series.

ASSIGNMENT

Short questions

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

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

Long Questions

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