

Unit-1: Group Theory

Symmetry Operations

- (1) Axis of Symmetry (AOS)
- (2) Plane of Symmetry (POS)
- (3) Centre of Symmetry (COS)
- (4) Identity (E)
- (5) Improper Axis of Symmetry (S_n)

Equivalent config. → Identical config.



Symmetry operation

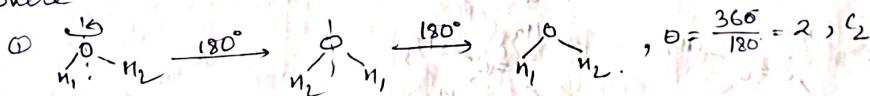
It moves a molecule about an axis, a point or a plane into a position indistinguishable from the original position. The point axis or plane w.r.t. which one or more positions can be carried out is called Symmetry element.

There are five types of elements of symmetry

- ① Axis of Symmetry (AOS), C_n
 - ② Plane of Symmetry (POS), σ
 - ③ Centre of Symmetry (COS) or Centre of Inversion, i.
 - ④ Improper Axis of Symmetry, S_n
 - ⑤ Identity, E
- Symmetry operations → ① Rotation ② Reflection ③ Inversion

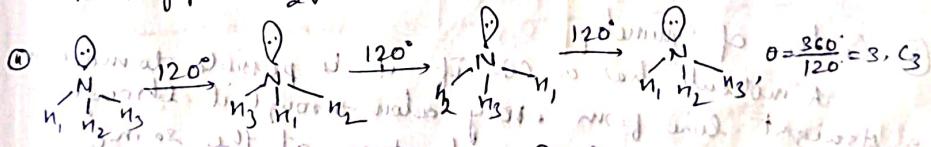
① Axis of Symmetry, C_n

It is an imaginary axis at the centre of a molecule around which, if the molecule is rotated by an angle of $\frac{360^\circ}{n}$ formed an indistinguishable orientation where n is the order of axis or degree of rotation.



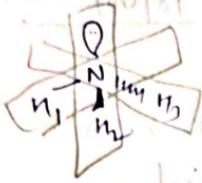
Symmetry elements → C₂, σ_v, σ_{v'}, E.

Point grp → C_{2v}



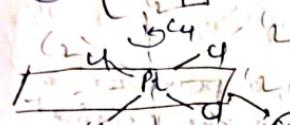
Symmetry elements → C₃, 3σ, E

Point Grp → C_{3v}



Principal Axis (C_n) → Only one type of symmetry about
 Subsidiary Axis (n_C) → more than one axis symmetry about
 (H2 picture)

(iii) $[PCl_4]^{2-}$



Principal axis = C_4

Subsidiary axis = C_2

symmetry with C_4 , C_{2v} , E, D_{4h} & D_{2h}

point GRP → Dihedral angle of 90°

(iv) BF_3 → patterned for 2nd to 3rd orbitals with one axis.
 Principal Axis = C_3 (2nd) patterned for six A₁
 Subsidiary Axis = C_3 (3rd) patterned for three E

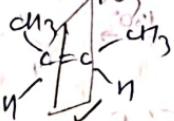
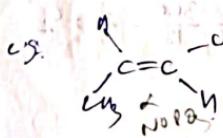
(2) Plane of Symmetry
 It is an imaginary plane which bisects the object to get two equal halves which are mirror images of each other.

There are 3 types of POS.

(i) Vertical POS, or

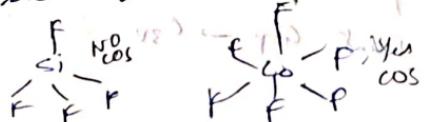
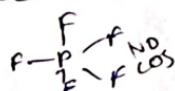
(ii) Horizontal POS, or

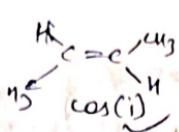
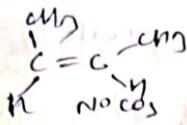
(iii) Dihedral POS, or



(3) Centre of Symmetry

A molecule has a COS if it is possible to move in a straight line from every atom through it through a single line to an individual atom at the same distance on the other side of the centre.





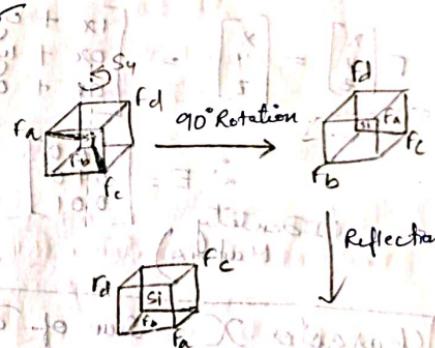
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④ Improper Axis of symmetry or Rotation - reflection Axis of Symmetry (S_n)

An improper rotation may be visualised as occurring in two steps, rotation (C_n) by $\frac{360^\circ}{n}$ followed by reflection (r) across a plane $\perp r$ to the rotational axis i.e.

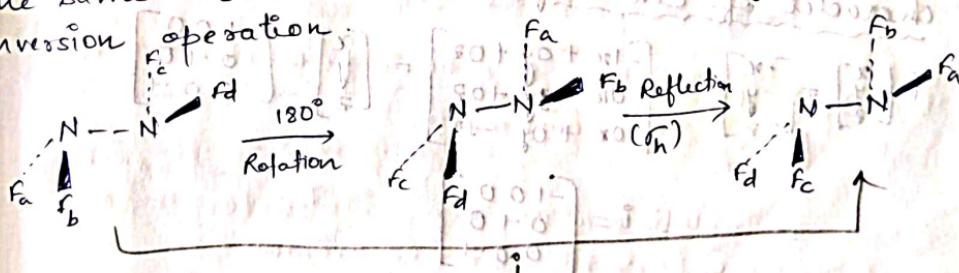
$$\text{i.e. } S_n = C_n \circ r$$

e.g. SiF_4 has three S_4 axes, one through each pair of opposite faces of the cube



Prove that S_2 is equivalent to i .

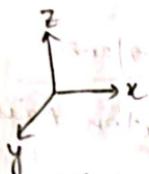
Let us consider trans configuration of dinitrogen tetrafluoride if we perform C_2 operation followed by r_h operation we will have a successful S_2 operation. However, the same result would have obtained by an inversion operation.



$S_2 \rightarrow i$

Hence Proved

Matrix Representation



$$E(x, y, z) \quad C_2(x, y, z) \quad T_{22}(x, y, z)$$

$$= x, y, z \quad = -x, -y, z \quad = x, -y, z.$$

character of trace of column matrix

$$E \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1x + 0y + 0z \\ 0x + 1y + 0z \\ 0x + 0y + 1z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\therefore E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(Identity Matrix)

Character X = sum of diagonal elts

Character (X) of identity matrix, $X_E = 3$

character of centre of inversion

$$i \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix} = \begin{bmatrix} -1x + 0y + 0z \\ 0x + -1y + 0z \\ 0x + 0y - 1z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\therefore i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Character (X) of ~~cos~~ cos matrix $X_i = -3$

Character for σ_{xz}

$$\sigma_{xz} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} zx + oy + oz \\ ox - yz + oz \\ ox + oy + lz \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\therefore \sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Character (χ) of σ_{xz} = 1 - 1 + 1 = 1

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Character of C_2^2

$$C_2^2 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix} = \begin{bmatrix} -zx + oy + oz \\ ox - yz + oz \\ ox + oy + lz \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\therefore C_2^2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Character (χ) of C_2 of $X_{C_2^2} = -1 - 1 + 1$

$$C_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\boxed{X_{C_n} = \cos\theta + \cos\theta + 1}$$

eg: $X_{C_2} = 2 \cos 180^\circ + 1$

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

$$= -1$$

$$X_{C_4} = 2 \cos 90^\circ + 1$$

$$= 1$$

$$X_{C_3} = 2 \cos 120^\circ + 1$$

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

$$= 0$$

$$S_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$S_n = 2\cos\theta - 1$$

$$\begin{aligned} X_{S_2} &= 2\cos 180^\circ - 1 & X_{S_4} &= 2\cos 90^\circ - 1 \\ &= 2(-1) - 1 & &= 2 \cdot 0 - 1 \\ &= -3 & &= -1 \end{aligned}$$

$$\begin{aligned} X_{S_3} &= 2\cos 120^\circ - 1 \\ &= 2(-\frac{1}{2}) - 1 \\ &= -1 - 1 \\ &= -2 \end{aligned}$$

Matrix Representations

Reducible representation (R.R.)

beta notation

Irreducible representation

Q Reducible matrix representation of C_{2v} point group.

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
R.R	3	-1	1	1

Reducible Representation is derived from base (x, y, z) and also from $3N$ coordinates.

Derive reducible matrix representation for water molecule w.r.t base (x, y, z) . and ammonia

Ans:

C_{3V}	E	C_3	σ_v
R.R	3	0	1

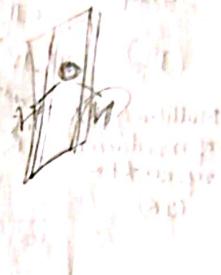
$\gamma_{RR} = \text{no. of unshifted atom } x \text{ character}$

$\text{NO USA } x \text{ change for}$

Q. Derive reducible representation of water wrt 3N coordinates.

Ans:

C_{2v}	E	C_2^2	σ_{xz}	σ_{yz}
NOUS	3	1	3	1
X	3	-1	1	1
γ_{RR}	9	-1	3	1



Q. Derive reducible representation of NH_3 wrt 3N coordinates.

Ans:

C_{3v}	E	C_3^2	σ_{xz}
NOUS	1	1	2
X	3	0	1
γ_{RR}	12	0	2

Q. Derive RRE of BF_3 wrt 3N coordinates.

Ans:

Point D_{3h} :

Symmetry elements $\rightarrow E, C_3, 3C_2, \sigma_h, \sigma_v, S_3$

D_{3h}	E	C_3	$3C_2$	σ_h	σ_v	S_3
NOUS	4	1	2	4	2	1
X	3	0	-1	1	1	-2
γ_{RR}	12	0	-2	4	2	-2

Character Table

It has two parts components -

- ① 4 columns
- ② 6 parts

Point Group	(Symmetry (I)) (II)	(III)	(IV)	(V)	(VI)
Mulliken symbol of irreducible representations (IR)	character of IR	Translation ref (yy)	Rotational axis (Rx, Ry, Rz)	Quadratic fn of x, y, z ex: xy, y^2, z^2 .	

Difference between Reducible & Irreducible representation

- ① We can reduce reducible representation into irreducible representation but we cannot reduce IR representation.
- ② We can deduce RR w.r.t to base 3N coordinate but we deduce IR by Great Orthogonality Theorem (GOT).

Great Orthogonality Theorem

From this theory we got some postulate which are applied to all the characters of a given point grp. we can also derived IR from this theorem.

- (1) No. of IR in a grp = No. of classes of the grp.

C ₁	E	C ₂	S ₂	S ₄
IR ₁				
IR ₂				
IR ₃				
IR ₄				

- (2) The sum of squares of character of the identity operation (dimension) in the IR = to the order of the grp (h).

$$\sum_{i=1}^k [x_i(E)]^2 = h$$

$$k_1^2 + k_2^2 + k_3^2 + k_4^2 = 4$$

$$k_1 = k_2 = k_3 = k_4 = 1$$

Dimension cannot be zero or one.

Orbital	E	C ₂	C _{2v}	G ₂
IR ₁	K ₁ (1)			
IR ₂	K ₂ (1)			
IR ₃	K ₃ (1)			
IR ₄	K ₄ (1)			

(3) Sum of square of characters of all the IR = Order of g.p.

$$k_1^2 + k_2^2 + m_1^2 + n_1^2 = h \quad (4)$$

Or, Over Q

$$1^2 + 1^2 + 1^2 + 1^2 = 4$$

C _{2v}	E	C ₂	C ₂ v	G ₂
IR ₁	V ₁	1	m	n ₁
IR ₂	V ₂	1	n ₂	n ₂
IR ₃	V ₃	1	m ₃	n ₃
IR ₄	V ₄	1	m ₄	n ₄

(4) The character of all the symmetry operation of two different IR is orthogonal to each other.

$$IR_1 \times IR_2 = 0 \quad IR_3 \times IR_4 = 0$$

$$IR_1 \times IR_3 = 0$$

$$IR_1 \times IR_4 = 0$$

$$IR_2 \times IR_3 = 0$$

$$IR_2 \times IR_4 = 0$$

$$IR_1 \times IR_2 = 0$$

$$k_1 k_2 + l_1 l_2 + m_1 m_2 + n_1 n_2 = 0$$

$$1 \cdot 1 + 1 \cdot 1 + 1 \cdot 1 + 1 \cdot 1 = 0$$

$$IR_1 + IR_2 + IR_3 + IR_4 = 0$$

$$l_1 = 1, m_1, n_1 = -ve$$

$$IR_3 = 1, -1, 1, -1$$

$$IR_4 = 1, -1, -1, 1$$

C _{2v}	E	C ₂	C ₂ v	G ₂
IR ₁	1	1	1	1
IR ₂	1	-1	-1	-1
IR ₃	1	-1	1	-1
IR ₄	1	1	-1	1

Now, we have to write Mulliken symbol of all IR.

* If any IR is 1D then we write A or B for that.

* If it is symmetrical wrt to Principal Axis then it is A, and if not then B.

* If subsidiary Axis is symmetry then used Subscript A'

If antisymmetry then B'

* If no subsidiary axis is present then if the molecule is symmetry wrt molecular plane then A₁ is put and if not A₂.

* If molecular plane is symmetry A' is not than A''

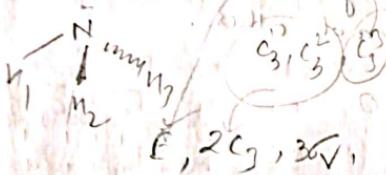
C_{3V}	E	C_2^2	σ_{xy}	γ_2
A'	1	1	1	1
A''	1	1	-1	-1
E	1	-1	1	-1
E'	1	-1	-1	1

$$C_n \rightarrow E$$

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C_2, E, A'', g_2



Character Table of NH_3

	C_{3V}	E	$2C_3$	$30V$
IR_1	1	1	1	1
IP_2				1
IR_3		1		

	C_{3V}	E	$2C_3$	$30V$
IR_1	$k_1(0)$	1	m_1	1
IP_2	$k_2(1)$	1	m_2	
IR_3	$k_3(2)$	1	m_3	

$$k_1^2 + k_2^2 + k_3^2 = 6$$

$$l^2 + m_1^2 + m_2^2 + m_3^2 = 6$$

$$(k_1^2 + k_2^2 + m_1^2) + (k_3^2 + m_2^2 + m_3^2) = 6$$

$$l^2 + (l^2 + 1)H(l^2 + f^2 + 1)^2 = 6$$

G_V	E	$2C_3$	$30V$
1	1	1	1
SP_2	1	2_2	m_2
SP_3	2	1	m_3

$$(4) IR_1 \times IR_1 = 0$$

$$k_1 k_2 + k_1 l_2 + m_1 m_2 = 0$$

$$\Rightarrow 1 + l_2 + m_2 = 0 \quad \text{but } l_2 = 1 \\ \Rightarrow m_2 = -1$$

$$\Rightarrow 1 + 2(1 \times 1) + 3[(-1) \times (-1)] = 0$$

$$IR_2 \times IR_3 = 0$$

$$k_2 k_3 + l_2 l_3 + m_2 m_3 = 0$$

$$\Rightarrow 2 + l_3 + (-1)m_3 = 0$$

$$\Rightarrow 2 + 2(1 \cdot (-1)) + 3[-1 \cdot 0] = 0 \quad l_3 = -1 \\ m_3 = 0$$

$$\Rightarrow 2 - 2 \cdot 0 = 0$$

C_{2v}	E	O_2^2	σ_{xz}	σ_{yz}
A'	1	1	1	1
A''	1	1	-1	-1
E	2	-1	0	0

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Reduction of Reducible into Irreducible Representation

We can express reducible representation into a combination of irreducible representation.

YRR w.r.t $3N$ coordinate for H_2O molecule				
C_{2v}	E	O_2^2	σ_{xz}	σ_{yz}
A'	1	1	1	1
A''	1	1	-1	-1
B _{1g}	1	-1	1	-1
B _{2g}	1	-1	-1	1

C_{2v}	E	O_2^2	σ_{xz}	σ_{yz}
NOUS	3	1	3	1
X	3	-1	1	1
Y.R.R	9	-1	3	1

Reduction formula

$$n_{IR} = \frac{1}{h} \sum_i x_i y_i z_i$$

where $h \rightarrow$ order of the group

$x_i \rightarrow$ X of RR

$y_i \rightarrow$ X of IR

$z_i \rightarrow$ coefficient of symmetry cts.

$$\begin{aligned}
 n_{A_1} &= \frac{1}{h} (x_1 y_1 z_1 + x_2 y_2 z_2 + \dots) \\
 &= \frac{1}{4} [9x_1 x_1 + (-1)x_1 x_1 + 3x_1 x_1 + 1x_1 x_1] \\
 &= \frac{1}{4} [9 - 1 + 3 + 1] \\
 &= 3
 \end{aligned}$$

$$\begin{aligned}
 n_{A_2} &= \frac{1}{h} (x_1 y_1 z_1 + x_2 y_2 z_2 + \dots) \\
 &= \frac{1}{4} [9x_1 x_1 + (-1)x_1 x_1 + 3x_1 (-1)x_1 + 1x_1 (-1)x_1] \\
 &= \frac{1}{4} (9 - 1 - 3 - 1) \\
 &= \frac{4}{4} \\
 &= 1
 \end{aligned}$$

$$\begin{aligned}
 n_{B_1} &= \frac{1}{h} (x_1 y_1 z_1 + x_2 y_2 z_2 + \dots) \\
 &= \frac{1}{4} [9x_1 x_1 + (-1)x_1 x_1 + 3x_1 x_1 + 1x_1 (-1)x_1] \\
 &= \frac{1}{4} [9 + 1 + 3 - 1] \\
 &= 3
 \end{aligned}$$

$$\begin{aligned}
 n_{B_2} &= \frac{1}{h} (x_1 y_1 z_1 + x_2 y_2 z_2 + \dots) \\
 &= \frac{1}{4} [9x_1 x_1 + (-1)x_1 (-1)x_1 + 3x_1 (-1)x_1 + 1x_1 x_1] \\
 &= \frac{1}{4} [9 + 1 - 3 + 1] \\
 &= \frac{8}{4} \\
 &= 2
 \end{aligned}$$

$$\therefore R.R = \underbrace{3A_1 + A_2 + 3B_1 + 2B_2}_{\text{Combination of IR}}$$

freq wif 3N coordinate for
NH₃ molecule.

C_{3V}	F	2G ₃	3G _V
A' ₁	1	1	1
A'' ₂	1	1	-1
E	2	-1	0

C_{3V}	F	C ₃	G _V
NOOS	4	1	2
∞	3	0	1
RR	12	0	2

$$\eta_{IR} = \frac{1}{h} \sum_i x_i y_i z_i$$

$$\begin{aligned}\eta_{A'_1} &= \frac{1}{h} (x_1 y_1 z_1 + x_2 y_2 z_2 + \dots) \\ &= \frac{1}{h} (12 \times 1 \times 1 + 0 \times 2 \times 1 + 2 \times 3 \times 1) \\ &= \frac{1}{h} (12 + 0 + 6) \\ &= \frac{18}{h} \\ &= 3\end{aligned}$$

$$\begin{aligned}\eta_{A''_2} &= \frac{1}{h} (12 \times 1 \times 1 + 0 \times 1 \times 2 + 2 \times 6 \times 3) \\ &= \frac{1}{h} (12 - 6) \\ &= \frac{6}{h} = 1\end{aligned}$$

$$\begin{aligned}\eta_E &= \frac{1}{h} (12 \times 2 \times 1 + 0 \times (-1) \times 2 + 2 \times 0 \times 3) \\ &= \frac{24}{h}\end{aligned}$$

$$RR = 3A'_1 + A''_2 + 4E$$

Ans: Linear combination of IR
Combination of 3A'

Ans: RR + (NOOS) stretching + (RR) bending

Application of Group Theory

We use reducible representation to determine the no. of vibrational active mode, translational active mode and rotational active mode and also which vibrational mode will be Raman active, which would be IR active and which will be both IR and Raman active.

C_{2v}	E	C_2^2	σ_{xz}	$\sigma_y z$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, Ry	xz
B_2	1	-1	-1	1	y, Rx	yz
VRR	9	-1	3	1		

$$\text{VRR} = \underbrace{3A_1 + A_2 + 3B_1 + 2B_2}_{\text{Total modes.}}$$

[Rotational modes of freedom (wrt R_x, R_y, R_z)] [Translational modes of freedom (wrt x, y, z)]

Rotational mode $\rightarrow A_2 + B_1 + B_2$

Translational mode $\rightarrow A_1 + B_1 + B_2$

$$\begin{aligned} \text{vibrational mode} &= \text{total modes} - \text{rotational modes} - \\ &\quad - \text{translational modes} \\ &= 3A_1 + A_2 + 3B_1 + 2B_2 - A_2 - B_1 - B_2 \\ &= A_1 + B_1 \end{aligned}$$

IR active modes of vibration (Dipole moment should be changed) = $2A_1 + B_1$

(Here we see IR active mode w.r.t x, y, z -axis)

Raman active modes of vibration (change in polarisability) = $2A_1 + B_1$, (w.r.t quadratic functn)

This vibration is both IR as well as Raman Active.

Q. C_{3v} E $2C_3$ $3\sigma_v$

	A_1	E	A_2	Σ	Translational mode of freedom transition allowed.
	1	$\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$		Σ	
	A_2	1	$\begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}$		
		E	2 -1 0 (only)		

Refer to the character table of C_{3v} point grp given above find which of the following electronic transition is forbidden?

- (i) $a_1 \leftrightarrow a_1$ (ii) $a_2 \leftrightarrow E$ (iii) $a_2 \leftrightarrow e$ (iv) $a_1 \leftrightarrow a_2$

(i) $a_1 \leftrightarrow a_1$

$$a_1 \times a_1 = 1 \ 1 \ 1$$

$$\approx A_1$$

If any one translational mode of freedom w.r.t x, y, z -axis is available in last column than transition is allowed.

(ii) $a_2 \leftrightarrow E$

$$a_2 \times E = 1 \ 1 \times 1 \ 2 \times -1 \ 0$$

$$= 2 -1 0$$

$$\approx E$$

$$\text{Allowed}$$

(iii) $a_2 \leftrightarrow e$

$\approx E$
Allowed.

(iv) $a_1 \leftrightarrow a_2$

$$a_1 \times a_2 = 1 \ 1 -1$$

$$\approx A_2$$

forbidden.

$$\gamma_{A_2} = \frac{1}{2} [6 \times 1 \times 1 + 0 \times 1 \times 2 + 2 \times 1 \times 3]$$

Q. C_{3v} E $2C_3$ $3\sigma_v$

$$A_2 \quad 1 \quad 1 \quad 1$$

$$A_L \quad 1 \quad -1 \quad -1$$

$$E \quad 2 \quad -1 \quad 0$$

$$\text{RR} \quad 6 \quad 0 \quad 2$$

$$\gamma_{IR} = \frac{1}{h} \sum_i x_i y_i z_i$$

$$\gamma_{A_1} = \frac{1}{6} [6 \times 1 \times 1 + 0 \times 2 \times 1 + 2 \times 1 \times 3]$$

$$= \frac{1}{6} [6 + 0 + 6]$$

$$= \frac{12}{6} = 2$$

$$= \frac{1}{6} [6 + 0 - 6]$$

$$= 0$$

$$\gamma_E = \frac{1}{6} [6 \times 2 \times 1 + 0 \times 1 \times 2 + 2 \times 0 \times 3]$$

$$= \frac{1}{6} (12 + 0 + 0)$$

$$= \frac{12}{6}$$

$$= 2$$

$$\therefore \text{RR} = 2A_1 + 2E$$

Direct Prod

The direct prod of two matrices

$$A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \quad \& \quad B = \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix}$$

$$A \otimes B = \begin{bmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{bmatrix}$$

it is 4×4 matrix

$$X_{AB} = a_{11}b_{11} + a_{11}b_{22} + a_{22}b_{11} + a_{22}b_{22}$$

Product of $X_A \times X_B$, $X_A \cdot X_B = (a_{11} + a_{22}) \cdot (b_{11} + b_{22})$

$$= a_{11}b_{11} + a_{11}b_{22} + a_{22}b_{11} + a_{22}b_{22}$$

$$= X_{AB}$$

$$\text{i.e. } X_{AB} = X_A \cdot X_B$$

The character of the direct prod of the two matrices is equal to the prod of the character of two matrices and we use this in group theory.

$$\text{Q. } A = \begin{bmatrix} 4 & 3 \\ 2 & 1 \end{bmatrix}, \quad B = \begin{bmatrix} 3 & 1 \\ 2 & 1 \end{bmatrix}$$

$$\text{Show that } X_{AB} = X_A \cdot X_B.$$

$$\rightarrow A \times B = \begin{bmatrix} 4 & 3 \\ 2 & 1 \end{bmatrix} \begin{bmatrix} 3 & 1 \\ 2 & 1 \end{bmatrix}$$

$$\begin{aligned} &= 12 + 4 + 6 + 3 \\ &= 8 + 4 + 9 + 1 \\ &= 6 + 2 + 9 + 1 \\ &= 4 + 2 + 3 + 1 \end{aligned}$$

$$X_A = (4+1) \quad X_B = 3+1$$

$$= 5 \quad = 4$$

$$= 20 \quad = 8$$

$$= 12 \quad = 12$$

$$(2 \times 1 \times 3 + 6 \times 1 \times 2 + 1 \times 2 \times 3) \quad 12 = 12$$

Features of IR: Some important features about IR and their direct product are given as:-

(1) If all the IR are one dimensional or non-degenerate, the product representation will be one dimensional

$$\text{eg: } A_1 \times A_2 = 1 \ 1 \ -1 = A_2$$

C_{3v}	E	$2C_3$	$3G_v$
	A_1	1	1
	A_2	1	-1

(2) The product of a non-degenerate IR with a degenerate IR (E, T etc) is a degenerate representation (multi-dimension) $\therefore A_1 \times E = 2 -1 \ 0 = E$

(3) The direct product of any representation with a totally symmetric IR will result in same representation.

$$\text{eg: } A_1 \times E = 2 - 10 = E$$

(4) The direct product of two or more degenerate representations is a reducible representation.

$$E \times E = 4 - 10 \Rightarrow \text{Reducible representation.}$$

Thus it can be reduced into IR with the help of reduction formula.

$$\frac{1}{h} \sum x_i y_i z_i$$

$$n_{A_1} = \frac{1}{6} [(1 \times 1 \times 1) + (1 \times 1 \times 2) + (0 \times 1 \times 3)] = 1$$

$$n_{A_2} = \frac{1}{6} (4 + 2 + (-0)) = 1$$

$$n_E = \frac{1}{6} (8 - 2 + 0) = 1$$

$$R \cdot R = A_1 + A_2 + E$$

Symmetry Adapted Linear Combination (SALC)

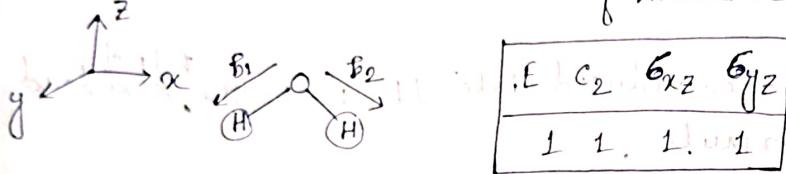
For a linear combination of atomic orbital, atomic orbital linearly combined to form molecular orbital.

Not all atomic orbital combined to form molecular orbital because there should be a proper symmetry. This is done by two methods -

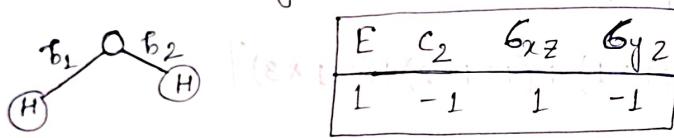
(1) Through known symmetries of the stretching mode of the molecule. This method is rarely used because we do not know all the stretching frequency modes of most of the molecules.

(2) Projection operator method - This method is applicable to all the molecules.

(1) We know vibrational mode of water molecule.



Symmetric stretching A₁



Asymmetric stretching

$$\phi_{A_1} = b_1 + b_2$$

$$\text{After normalisation} = \frac{1}{\sqrt{2}} (b_1 + b_2)$$

$$\phi_{B_1} = (b_1 - b_2)$$

$$\text{After normalisation} = \frac{1}{\sqrt{2}} (b_1 - b_2)$$

$\phi_{A_1} = \frac{1}{\sqrt{2}} (b_1 + b_2)$ and $\phi_{B_1} = \frac{1}{\sqrt{2}} (b_1 - b_2)$ are SALC for symmetric and asymmetric stretching of H₂O molecule.

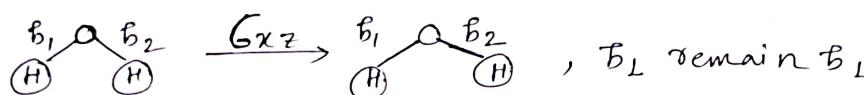
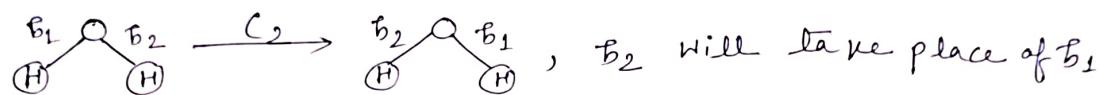
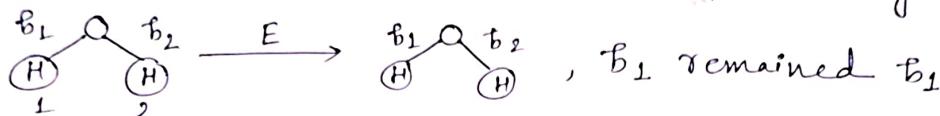
For more information, please refer to the following video:

$$② \quad \Phi_i = \sum_{j=1}^n x_i(j) T_j$$

Where Φ_i = Basis set

$x_i \rightarrow$ character of i th irreducible representation
and the j th symmetry operation.

Basis set (b_1) \rightarrow we will look upon changes on b_1



Basis set

$$\begin{array}{ccccc} & E & C_2 & G_{xz} & G_{yz} \\ b_1 & b_1 & b_2 & b_1 & b_2 \end{array}$$

$$T_J = 4$$

character table for C_{2v} point group

C_{2v}	E	C_2	G_{xz}	G_{yz}
A_1	$1 \times b_1$	$1 \times b_2$	$1 \times b_1$	$1 \times b_2$
A_2	$1 \times b_1$	$1 \times b_2$	$-1 \times b_1$	$-1 \times b_2$
B_1	$1 \times b_1$	$-1 \times b_2$	$1 \times b_1$	$-1 \times b_2$
B_2	$1 \times b_1$	$-1 \times b_2$	$-1 \times b_1$	$1 \times b_2$
$T_J(b_1)$				
	= 4			

$$\Rightarrow b_1 + b_2 + b_1 + b_2 = 2b_1 +$$

$$2b_2 = 2(b_1 + b_2)$$

After normalization = $\frac{1}{\sqrt{2}}(b_1 + b_2)$

$$\Rightarrow b_1 + b_2 - b_1 - b_2 = 0$$

$$\Rightarrow b_1 - b_2 + b_1 - b_2 = 2b_1 - 2b_2$$

$$\text{After normalization} = \frac{1}{\sqrt{2}}(b_1 - b_2) = 2(b_1 - b_2)$$

$$\Rightarrow b_1 - b_2 - b_1 + b_2 = 0$$

In both the methods we found the same LCAO but the second method is dynamic. Therefore, wave function

$$\phi_1(b_1) = \frac{1}{\sqrt{2}} (b_1 + b_2)$$

$$\phi_1(b_2) = \frac{1}{\sqrt{2}} (b_1 - b_2)$$

Unit-2

spectroscopic states -

→ crystal field theory

spectroscopic states refer

→ High spin Low spin

to the specific electronic

→ octahedral & tetrahedral

quantum states of atoms and

molecules, which are described using spectroscopic

notation. State of an atom or energy of an atom

is denoted by certain term symbol $2S+L$

where,

$2S+1$ = Spin multiplicity.

L = Total orientation

angular momentum.

J = Resultant orbital angular momentum.

$$L = 0, 1, 2, 3$$

$$S P D F$$

There are 5 types of microstates for different electronic states.

Type I

$$\frac{n!}{\sigma_1!(n-\sigma_1)!}$$

where,

$n \rightarrow$ is therefore the no of orbitals

$\sigma_1 \rightarrow$ no of given electrons.

For P^2 ,

$$n = 6$$

$$\sigma_1 = 2$$

$$\text{microstate} = \frac{6!}{2!(6-2)!} = 15$$

Type II $P^1 d^1$

$$\frac{n!}{\sigma_1!(n-\sigma_1)!} \times \frac{n!}{\sigma_1!(n-\sigma_1)!}$$

$p^1 \uparrow$

$d^1 \uparrow$

$$= \frac{6!}{2(6-2)!} \\ = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 4 \times 3 \times 2 \times 1} \\ = 15$$

$$P^1 = \frac{6!}{1(6-1)!} = \frac{6 \times 5!}{5!} = 6$$

$$d^1 = \frac{10!}{1(10-1)!} = \frac{10 \times 9!}{9!} = 10$$

$$P^1 d^1 = 6 \times 10 = 60$$

Type III 2D ,

$$\text{microstates} = (2s+1)(2L+1) \\ = 2 \times (2 \times 2 + 1) \\ = 2 \times 5 \\ = 10$$

Type IV 2P_4 ${}^{2J+1}L_J$.

$$= (2J+1) \\ = 2 \times 4 + 1 \\ = 9$$

Type V

A E. IT

Singlet
degenerate

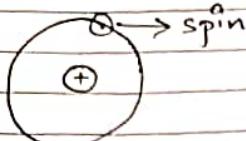
${}^2T_{1g}$

${}^3A_{1g}$
microstate = $(2s+1)$ degeneracy
 $= 2 \times 3$

$$\text{Microstate} = (2s+1) \times \text{degeneracy} \\ = 2 \times 3 \\ = 6$$

ϵ_{1g}

Russel - saunders coupling or L-S coupling



orbital angular momentum (L)

spin angular momentum of individual electron at 2 posm resulted spin angular momentum (\vec{s}). like wise orbital angular momentum of individual electron couple to produce resultant orbital angular momentum (\vec{l}). Then, $\vec{l} \& \vec{s}$ combine to form total angular momentum.

This type of coupling is called Russel-Saunder coupling. only orbital electron (outer shell electrons) take part as coupling.

There are 3 types of interaction:-

- (a) Spin-Spin interaction.
- (b) spin-orbit-orbit interaction.
- (c) spin-orbit interaction.

Step I To determine the total spin angular momentum \rightarrow It is obtained vectorial representation of different orbital spin angular momentum of electrons.

Eg: P^2

$ 1\rangle$	$ \uparrow\rangle$
+1	0
-1	

$$\mathcal{S} = (s_1 + s_2) (s_1 + s_2 - 1) \dots (s_1 - s_2)$$

$s_1 = +\frac{1}{2}, \quad l_2 = +\frac{1}{2}$

$s = 1, 0$

Step II To determine the total spin-orbital angular momentum \rightarrow it is obtained vectorial representation of different orbital angular momentum of electron.

$$\sum \vec{l} =$$

$$L = (l_1 + s_1) (l_1 + l_2 - 1) \dots (l_1 - l_2)$$

$$l_1 = -1, l_2 = 0$$

$$L = -1, 0$$

Step III

$$J = (L+S) (L+S-1) \dots (L-S)$$

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

$$= 2, 1, 0$$

Term symbol $2S+1$
 L_J

$$^3P_2, ^3P_1, ^3P_0$$

$$^2P, ^1P, ^3P$$

Ground state term symbol:-

Rules for determining ground state term symbol

Rule I The lowest Energy term will be S with highest multiplicity i.e. with maximum number of electron.

$$^2P, ^1P, ^3P$$

Lowest state.

(Ground state).

Rule II If there are more than one term of the same multiplicity then the term largest value of the L .

$^2P, ^2D$ (Ground state)

Rule III For half filled or less then half filled term ground state term is of the lowest J value and more than half filled term the ground

state, has the highest J value.

$$\frac{3}{\text{BP}_2} \quad \frac{3}{\text{P}_1} \quad \frac{3}{\text{BP}_3} \quad \boxed{14} \quad \boxed{11} \quad \boxed{1}$$

(Giornale, slate)

d^2 term symbol.

$$\frac{2s+1}{L}$$

$$\therefore \beta f$$

$$d^2 \quad \boxed{\uparrow \uparrow} \quad | \quad |$$

-2 -1 0 +1 +2

S = 1

$$2S+1=3$$

$$\therefore L = 3$$

0	1	2	3
S	P	D	F

$$(z+1) \cdot \dots \cdot (z+n) \cdot (z+1) \cdot (z+1) = 0$$

$$(1+1) \dots (1+1+1) (1+1) \dots$$

Q u i t s e

1

1 - 2 -

1. *Leucosia* 2. *Leucosia*

On 1st, 1967, the
1st Inf. Div.

~~→ ist abwegig, wenn es nicht explizit als konzeptiv benutzt wird~~

• state domain merupakan = neg. aktif
• ad. nilai untuk mencari bentuk suatu objek
• menggunakan teknik \exists dan \forall
• teknik yang pertama menggunakan fungsi

Term Symbol $2S+1$ L_J

$3P_2$, $3P_1$, $3P_0$ levels. In addition to the

Rules for determining Ground state Term symbol:

Rule ① : The lowest energy term will be 1 with highest multiplicity i.e. with maximum no. of $e\Theta$.

e.g.;- $2p, 1p, 3p \rightarrow$ lowest ground state

Rule ②: If there are more than 1 term of some multiplicity than the term with largest value of L will be ground state term.

eg; $2p$, $2d$

$$(e=1) \quad (\text{Ground state}) \quad (e=2) \quad \frac{1}{\sqrt{2}} \quad (e=3)$$

Rule ③: For half filled or less than half filled term ground state term is of lowest J value and for more than half filled term the ground state term has the highest J value.

eg:- p^{\sim}

3P_2 , 3P_1 , 3P_0 (Ground state)

p⁵

↑↓	↑↓	↑
----	----	---

$3P_2$, $3P_1$, $3P_0$
(Ground state)

d^2
Term symbol = ?

Q:- Predict whether electronic transition in
(1) d^8 (octahedral) and (2) d^5 (octahedral) high spin are allowed or not.

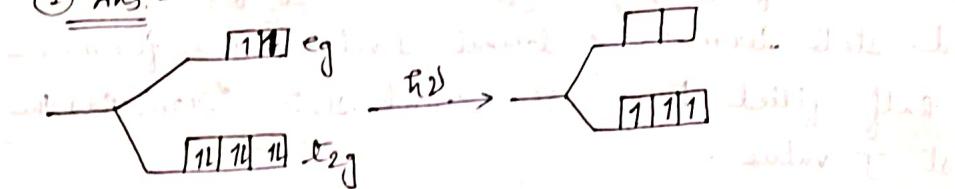
F:- The electric dipole allowed transition in a d^2 atomic system is
(a) ${}^3F \rightarrow {}^1D$ (b) ${}^3F \rightarrow {}^1P$ (c) ${}^3F \rightarrow {}^3D$ (d) ${}^3F \rightarrow {}^3P$

Q:- (a) ${}^1E_g^+ \rightarrow {}^3E_g$ (b) ${}^1E_u^+ \rightarrow {}^1E_g^+$ (c) ${}^1A_u \rightarrow {}^1E_g^+$
(d) ${}^1A_g \rightarrow {}^1E_g$ Allowed $4l=1, 2s=0$

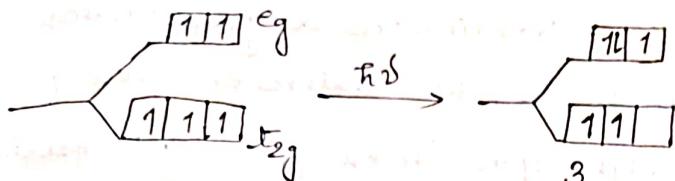
The allowed transition are (a) A & C (b) B

(c) A_u , E_g^+ ($l=0$), $\frac{1}{1}E_g$ ($l=1$), E_u^+ ($l=0$)

① Ans:-



(2) d⁵



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

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

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

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

$\Delta S \neq 0$, Spin is not allowed

Q: (a) $^3F \rightarrow ^1D$
 $l=3 \quad l=2$
 $\Delta l=2$

(b) $^3F \rightarrow ^1P$
 $l=3 \quad l=1$
 $\Delta l=2$

(c) $^3F \rightarrow ^3D$
 $l=3 \quad l=2$
 $\Delta l=2$
 $\Delta S=0$



Selection rule of degenerate levels

Energy levels are in and between the two manifolds

but not between them

The transitions

of non-degenerate levels

selection rule is the same

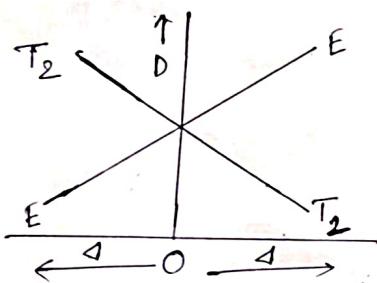
as for non-degenerate levels

transitions between levels

Leslie Orgel:-

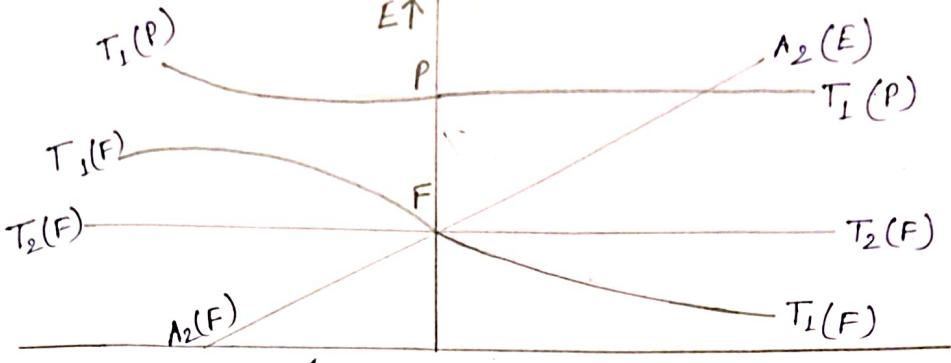
Orgel Diagram is a coordinative diagram created by Leslie Orgel, that shows the relative energies of electronic terms of high spin (weak field) transition metal complexes as the strength of the ligand field increases. It illustrates how the free ion electronic terms split in an octahedral and tetrahedral ligand environment helping to predict the number and types of spin allowed electronic transition.

<u>Configuration</u>	<u>Energy Terms</u>	
d^1, d^9	$\underline{2D}$	$\begin{matrix} -2 & 1 & 0 & 1 & 2 \\ \boxed{1} & 1 & 1 \\ \end{matrix}$
d^2, d^8	$\underline{3F}, 3P$	$\begin{matrix} 2S+1=3 \\ \boxed{1} & 1 & 1 & 1 & 1 \\ \end{matrix}$
d^3, d^7	$\underline{4F}, 4P$	$\begin{matrix} 1 & 1 & 1 & 1 \\ \end{matrix}$
d^4, d^6	$\underline{5D}$	$-2-1012$



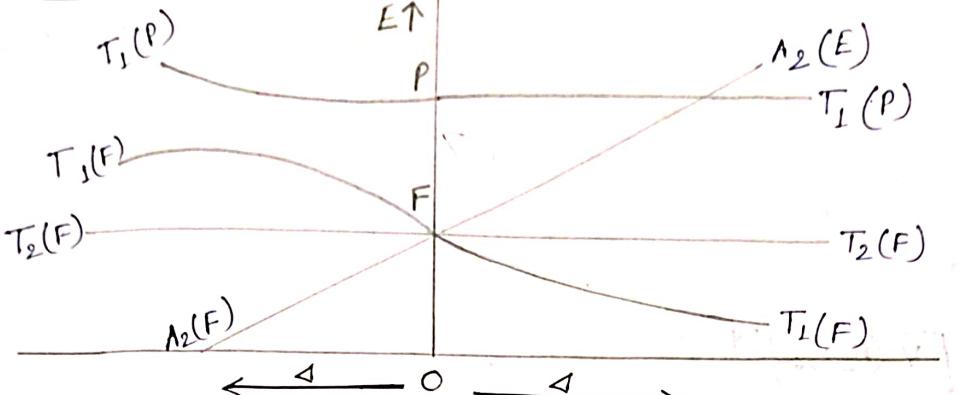
Orgel diagram for d^4, d^6 metal ion in octahedral ligand environment & d^1, d^9 metal ion in tetrahedral ligand environment.

Orgel diagram for d^1, d^9 metal ion in octahedral ligand environment & d^4, d^6 metal ion in tetrahedral ligand environment.



Organic Diagram for d^9, d^8
metal ion in octahedral
ligand environment &
 d^2, d^7 metal ion in
tetrahedral ligand environment.

Organic Diagram for d^2, d^7 metal
ion in octahedral ligand environ-
ment and d^3, d^8 metal ion in
tetrahedral ligand environment

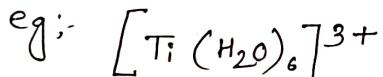


Orgel Diagram for d^5, d^8 metal ion in octahedral ligand environment & d^2, d^7 metal ion in tetrahedral ligand environment.

Orgel Diagram for d^2, d^7 metal ion in octahedral ligand environment and d^3, d^8 metal ion in tetrahedral ligand environment.

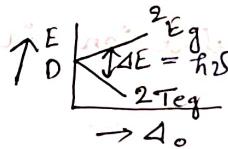
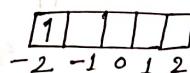
Application of orgel diagram to electronic spectra of transition metal complexes:-

d^1 metal ion in octahedral ligand environment

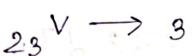
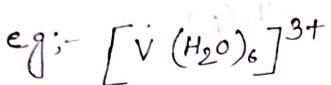
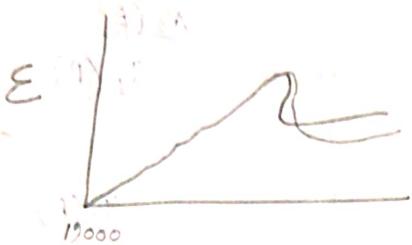


Term symbol $\rightarrow ^2D$

1	1		
-2	-1	0	1
2			

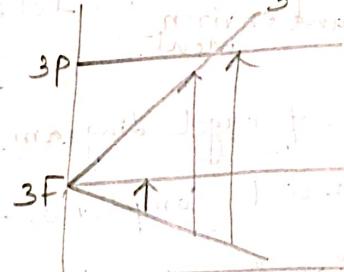
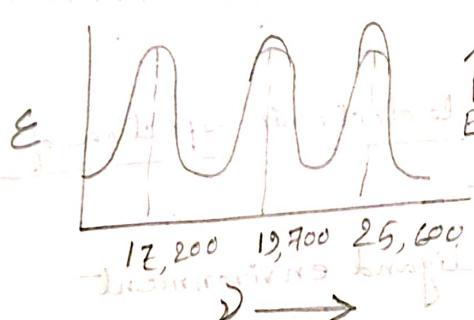


For absorption of radiation of frequency ν , the electrons get excited to one of the e_g orbital. The absorption band at $20,400\ cm^{-1}$ of crystal field origin can be assigned to $^2T_{2g} \rightarrow ^2E_g$

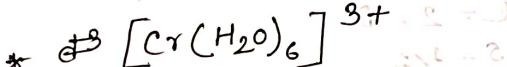


∴ Term symbol = $3F, 3P$

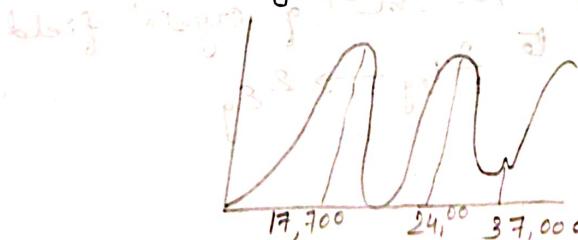
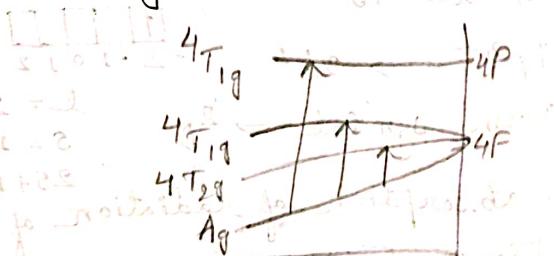
1	1	1	1
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1st metal ion in octahedral ligand



∴ Term symbol = $4F, 4P$



Tanabe Sugano diagram :-

This diagram is used in coordination chemist predict the absorption spectra of metal complexes particularly in the UV- range. Here ground state is taken as constant reference and energies of all other terms are plotted w.r.t ground state.

is expressed in terms of ligand field splitting parameter is divided by Racah parameter (B). The y-axis is in terms of energy also scaled by B .

* Difference between Tanabe sugano and orgal diagram:

Orgal Diagram

- 1) qualitative result
- 2) Applicable in high spin complexes.
- 3) only terms of same multiplicity is used
- 4) Ground term have ^{zero} drawn on same energy level _{x-axis}.
- 5) Racah parameter is not considered.
- 6) It does not depend upon ligand field strength.

Tanabe Sugano

- 1) quantitative result
- 2) Applicable in high spin as well in low spin complexes.
- 3) Terms of different multiplicity is used.
- 4) Ground term have different energy level value same.
- 5) Racah parameter is considered.

Splitting of terms in octahedral complex :-

Term splitting

$$S_0 \rightarrow A_{1g} + 2H \rightarrow E_g, T_{1g}, T_{2g}$$

$E_{\text{g}} + T_{1g} \rightarrow E_{\text{g}}, T_{1g}, T_{2g}$

and the D - ratio is T_{2g}, E_g

F T_{1g} , T_{2g} , A_{2g}

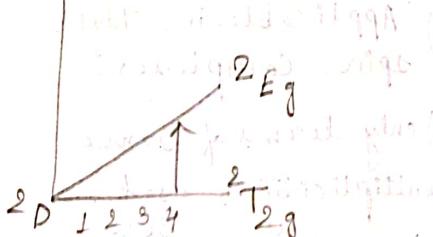
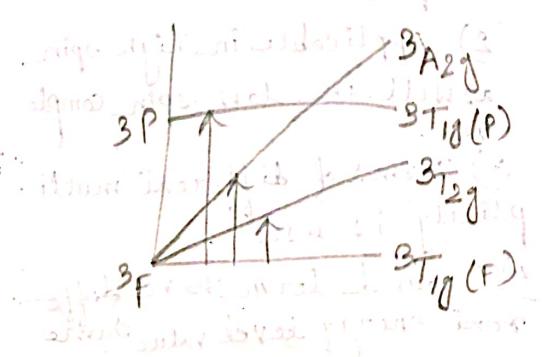
$$G_L A_{1g}, E_g, T_{1g}, T_{2g}$$

H E_g , T_{1g} , T_{2g}

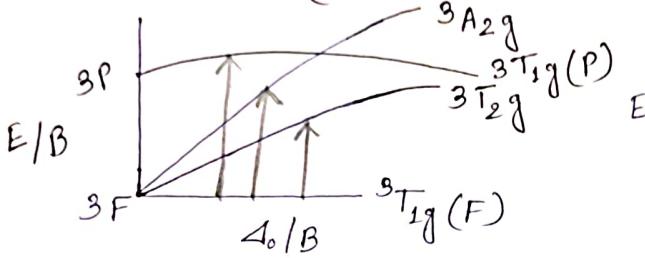
1A_1g , $^1T_{1g}$, $^1T_{2g}$, 1E_g , $^1A_{2g}$

2I \rightarrow 2S , 2P , 2D , 2F , 2G , 2H , $^2I'$

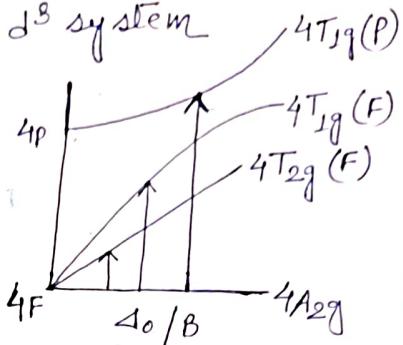
* $d_2 \rightarrow ^3F_3$, $^3P_{\text{up}}$ (t)



* d³ system (3F, 3P)



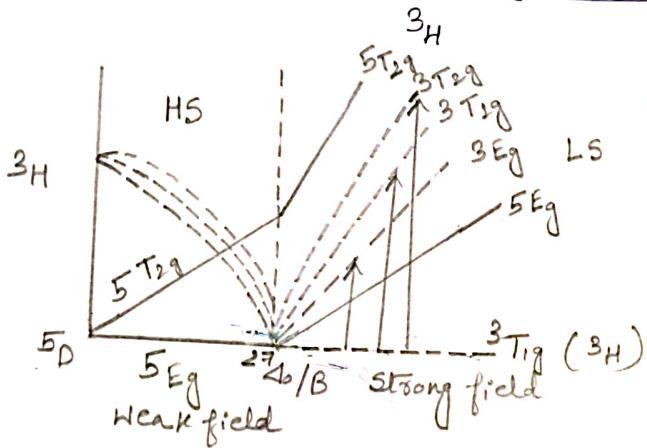
* d³ system



* d⁴ system

weak field ligand (H.S.)

5D₀



1	1	1	
-2	-1	0	+1 +2

strong field ligand (L.S.)

In H.S. → 1 transition

In L.S. → 3 transition

transition point 27