26 - Symmetry and Group Theory

INTRODUCTION

Symmetry is a very fascinating phenomenon in nature which comes from the Greek word syn-metron, that is to measure together. *Mathematical study of symmetry is called* **Group theory**. Its foundations were laid in the 19th century by E. Galois, Jordan, Sylow, Cayley and Lie etc. **Murray Geil-Mann** was awarded the 1969 Nobel prize for applying symmetry to the classification of particles and the postulation of quarks which are the constituents of baryons and hadrons.

SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

Symmetry Element. *A symmetry element is a geometrical entity such as a line or a plane or a point about which an operation of rotation or reflection or inversion is performed.*

Symmetry Operation. A symmetry operation is a movement of the molecule such that the resulting configuration of the molecule is indistinguishable from the original. The molecule may assume an equivalent configuration or an identical configuration. Symmetry operation should be performed within the molecule. There should be at least one point in the molecule which is unaffected by all the symmetry operations. All the symmetry elements intersect at this point. Thus there is no translational motion of the molecule during the course of a symmetry operation.

There are five types of symmetry elements corresponding to symmetry operations (Table 1).

Table 1. Symmetry elements and symmetry operations.

S.No.	Symmetry element	Symmetry operation
1.	Proper axis of rotation (C_n)	Rotation by an angle $\theta = 2\pi/n$ about the axis
2.	Plane of symmetry (σ)	One or more reflections in the plane
3.	Improper axis of rotation or rotation-reflection axis (S_n)	Rotation about the axis followed by reflection in a plane perpendicular to the rotation axis
4.	Centre of symmetry or inversion centre (i)	Inversion of all atoms through the centre of symmetry
5.	Identity element (E)	This operation leaves the molecule unchanged.

1. Proper Axis of Rotation (C_n). A molecule is said to possess a proper axis of rotation of the order n if rotation about the axis by an angle $\theta = 2\pi/n$ leaves the molecule in a configuration which is indistinguishable from the original one. Consider an example of BF_3 molecule (**Fig. 1**) in which there is a C_3 axis, that is, an axis of order 3 which is perpendicular to the plane

containing all the atoms and passing through the boron atom. The BF_3 molecule also possesses three C_2 axes of symmetry in addition to the C_3 axis. One such axis is shown in Fig. 1 (b). The C_3 axis is called the *principal axis*. In general if a molecule possesses C_n axes of different orders, the axis of the highest order is known as the *principal axis*. A H_2O molecule has one two-fold axis C_2 whereas an NH_3 molecule has one three-fold axis C_3 (*i.e.*, rotation axis of order 3), as shown in **Figs. 2 (a) and (b)**.

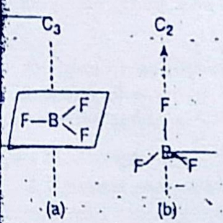

Fig. 1. (a) The C_3 and (b) C_2 axis of symmetry in BF_3 molecule.

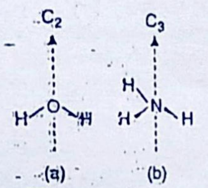

Fig. 2. (a) Two-fold axis (C_2) of H_2O molecule, (b) Three-fold axis (C_3) of NH_3 molecule.

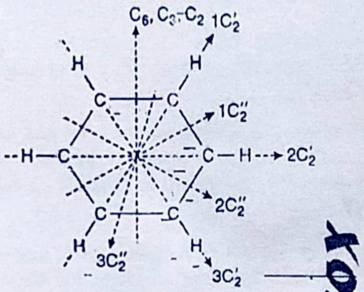

Fig. 3. C_n axis of rotation in benzene.

Note that there is only one two-fold rotation associated with a C_2 axis because clockwise and anticlockwise rotations are identical. However, with a three-fold axis C_3 two symmetry operations are associated, one being 120° rotation in a clockwise direction and the other 120° rotation in a counter clockwise direction. The principal axis of benzene molecule is the six-fold axis, C_6, perpendicular to the regular hexagonal ring. Also the C_6 axis perpendicular to the molecular plane and passing through the centre of the molecule is a C_3 axis as well as C_2 axis (**Fig. 3**). The symmetry operations associated with a C_6 axis are :

$$\begin{array}{cccccc} C_6 & C_6^2 & C_6^3 & C_6^4 & C_6^5 & C_6^6 \\ & C_3 & C_2 & C_3^2 & & E \end{array}$$

A sphere possesses an infinite number of symmetry axes (along any diameter) of all possible integral values of n.

2. Plane of Symmetry (σ). A molecule possesses a plane of symmetry if reflection through the plane leaves the molecule unchanged. The plane containing all the atoms is known as molecular plane. For instance, $[PtCl_4]^{2-}$ contains a molecular plane and four more reflection planes. BF_3 molecule possesses two planes of symmetry, the *vertical plane* (σ_v) *and the horizontal plane* (σ_h). The σ_v plane contains the highest-order rotation axis, *i.e.*, the C_3 axis; σ_h is perpendicular to the C_3 axis (**Fig. 4**).

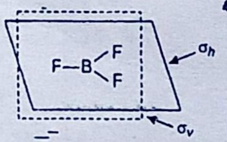

Fig. 4. The vertical and horizontal planes in BF_3 molecule.

There is the *dihedral plane* σ_d, which is a vertical plane that bisects the angle between the two C_2 axes. Dihedral planes are present only in molecules having more than one C_2 axis.

3. Improper Axis of Rotation (S_n). A molecule is said to possess an improper axis of rotation of order n if rotation about the axis by $2\pi/n$ followed by reflection in a plane

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perpendicular to the axis leaves the molecule in an indistinguishable position. Examples are allene which possesses an S_2 axis and the staggered form of ethane which possesses an S_6 axis [Figs. 5 (a) and (b)].

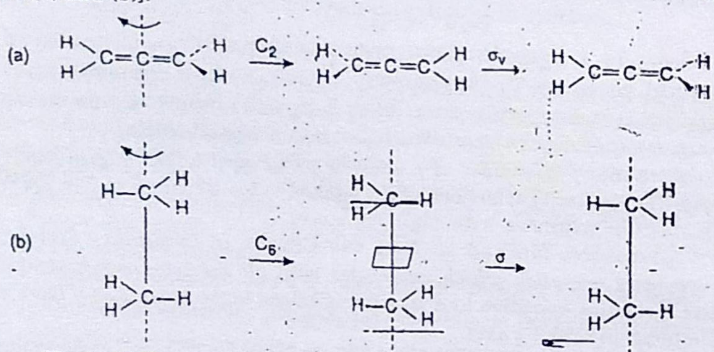

Fig. 5. (a) The S_2 axis in allene. (b) S_6 axis in staggered form of ethane.

4. Centre of Symmetry (*i*). If in a molecule the coordinates (x, y, z) of every atom are changed into $(-x, -y, -z)$ and the molecule is left in an indistinguishable position, then the point of origin, *i.e.*, (0, 0, 0) is called the centre of symmetry of the molecule. Examples are all homonuclear diatomic molecules and trans-1, 2-dichloroethylene (Fig. 6).

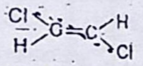

Fig. 6. Centre of symmetry in trans-1,2 dichloroethylene.

5. The Identity Element (*E*). All molecules possess an identity element which does not do anything to the molecule. A particular symmetry element generates many symmetry operations. A C_n axis generates a set of operations $C_n^1, C_n^2, C_n^3 \ldots C_n^n$. The C_n^n operation is equivalent to the identity operation.

Note that $[PtCl_4]^{2-}$, which has S_4 axis as well as C_2 axis, possesses all the five elements of symmetry. A square planar AB_4 type molecule has 13 elements of symmetry $(E, C_4, S_4, 4C_2, 4\sigma_v, \sigma_h$ and $i)$ and 16 symmetry operations $[E, C_4^1, C_4^2, C_4^3, S_4^1, S_4^3, 4C_2^1, 4\sigma_v, \sigma_h$ and $i]$.

DEFINITION OF A GROUP

A **group** *is a collection or set of elements which together with some well defined combining law obey certain rules.* It should denote numbers, matrices, vectors and symmetry operations. It could be ordinary or vector addition, ordinary or matrix multiplication and symmetry operation etc. Group was defined first by **Arthur Cayley** in 1854.

Group Postulates.

The complete set of operations forms a mathematical group. In order that the symmetry elements $A, B, C, \ldots$, form a mathematical group G, the following conditions must be satisfied :

1. Ring Closure. *Two elements A and B of a group combine to give the third element C, which is also an element of the group.*

$$AB = C$$

It means that the application of *B* followed by *A* is equivalent to the application of C. If $AB = BA$, the elements *A* and *B* are said *to commute*.

2. *An element combines with itself to form another element of the group.*

3. Identity. *The group must contain the identity element E which commutes with all the elements and leaves them unchanged* :

$$EA = AE = A$$

$$EB = BE = B, \text{ etc.}$$

4. Associativity. *Every element of the group obeys the associative law of combination.*

$$A(BC) = (AB)C$$

5. Inverse Element. Every element *A* of a group has an inverse A^{-1} which is also an element of the group. The element and the inverse combine to give the identity element.

$$AA^{-1} = A^{-1}A = E$$

Addition or multiplication or a symmetry operation can be the combination process of the elements of a group. The set of numbers between $-\infty$ and $+\infty$ form a group by the multiplication process. **Note that zero is not included as an element of the group.**

Types of Groups.

1. Abelian and non-Abelian Groups. A group is said to be Abelian if all the elements commute and non-Abelian if all the symmetry elements do not commute with one another. Water molecule belongs to an Abelian group and NH_3 to a non-Abelian group.

2. Cyclic Groups. A group is said to be cyclic if all of its elements can be generated from one symmetry element. Thus $A, A^2, A^3, \ldots, A^n$ form the elements of a cyclic group; here $A^n = E$ is the identity element. In general, the roots of the equation $x^n - 1 = 0$ form a cyclic group. Note that *all the cyclic groups are Abelian.*

3. Isomorphic Groups. If two groups have the same order and if the forms of their multiplication tables are the same, the groups are said to be **isomorphic**.

Order of a group. The total number of elements of a group is called the order (*h*) of the group.

Example. *Consider a water molecule. It has four symmetry elements, viz., E, $C_2(z)$, $\sigma_v(xz)$ and $\sigma_v'(yz)$ (Fig. 7).*

We can easily show that the product of any two symmetry elements is one of the four elements of the group $C_2(z)\ \sigma_v(xz) = \sigma_v'(yz)$ (Table 2).

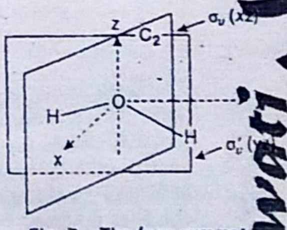

Fig. 7. The four symmetry elements of H_2O molecule.

Table 2. Group multiplication table of the symmetry operations of H_2O molecule.

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
E	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
$C_2(z)$	$C_2(z)$	E	$\sigma_v'(yz)$	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v'(yz)$	E	$C_2(z)$
$\sigma_v'(yz)$	$\sigma_v'(yz)$	$\sigma_v(xz)$	$C_2(z)$	E

SUB-GROUP.

A subset of element of a group forming a group of smaller order is referred to as a **sub-group**. If the addition of a symmetry element to an existing group produces a new group, this new group is called **super group** of the existing group. *The set of all the elements of a group is known as an* **improper or trivial** *subgroup.* The subgroup composed only of the identity element is also a trivial subgroup.

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A subgroup H of a group G is called a proper subgroup if H has a smaller number of elements than G. For instance, C_2 group ($= E, C_2$) is a proper subgroup of the point group $C_4(E, C_4, C_2, C_4^3)$. Proper subgroups of C_{3v} are C_3 and $3C_s$ groups. *The order of a subgroup must be a divisor of the order of the group.* A subgroup which contains the complete classes of the parent group is known as an invariant or **normal subgroup**. Accordingly, C_3 is normal subgroup of C_{3v} (and also D_3).

Relation Between a Group and its Subgroup.

Subgroups represent the consequence of a reduction in symmetry when a molecule of higher symmetry is distorted or substituted. Thus, the symmetry of an octahedral molecule AB_6 is reduced to D_{4h} if the two trans B groups are eliminated or changed or if the two trans (A-B) bond lengths changes equally. All the subgroups of a given group can be determined by systematically destroying the symmetry elements, that is, by descent in symmetry or by careful consideration of the different elements of a given group. For example, for the D_{4h} point group, the symmetry elements are $E, C_4, C_2, i, \sigma_v, \sigma_d, \sigma_h$ leading to (besides two improper subgroups D_{4h} and E), subgroups such as $D_4, C_{2v}, C_2, C_i, C_s$ etc.

Relation Between Orders of a Finite Group and its Subgroup.

Group containing finite number of elements is referred to as finite group whereas the infinite number of elements constitute infinite group ($h = \infty$). Consider finite group of order $h = 4$, that is $1, -1, i, -i$. The combining rule being algebraic multiplication $= i\sqrt{-1}$. The identity element is 1 and the inverse of 1, is -1, of i is $-i$ and of -1 is 1 etc. Note that the group $(1, -1)$ is a part of the larger group $1, -1, i, -i$. Thus $1, -1$, is said to be a subgroup of the group $1, -1, i, -i$. *The order of the group is an integral multiple of its subgroup.* However, $i, -i$ is not a group since there is no identity element and the ring closure does not hold.

MULTIPLICATION TABLE

Each group is characterized by a multiplication table. The *relationship between the elements of the group for the binary combinations* is reflected in the **group multiplication table**. Here the operation indicated by the elements in the top row is carried out first followed by the operation indicated by the appropriate element in the first column. The result of combination is given in the body of the table. Each element of the group occurs only once in each of the rows and columns. As an example, consider Table 3, for a group of order 4.

Table. 3. Multiplication table for the group $(1, i, -1, -i)$

	1	i	-1	$-i$
1	1	i	-1	$-i$
i	i	-1	$-i$	1
-1	-1	$-i$	1	i
$-i$	$-i$	1	i	$-i$

Group of order 1. The identity element E alone will constitute a group of order 1. One itself is a group of order 1.

Group of order 2. A group of order 2 should have two elements, namely, the identity element E and another element say A.

Group of order 3 is a cyclic group with elements $A, A^2, A^3 (= E)$ and in a group of order 4, elements $A, A^2, A^3, A^4 (= E)$ may be visualised.

CONJUGACY RELATION AND CLASSES

If A and X are the two elements of a group obeying the relation $X^{-1}AX = B$ where B is also in the same group, then B is called the **similarity transformation** of A by X and A and B are said to be conjugate to each other.

Class. *A set of elements in a group which are conjugate to one another is said to form class.* Let us perform the similarity transformation of the C_2 operation of H_2O molecule with all the other operations.

$$E^{-1}C_2E = C_2 \; ; \quad \sigma_v^{-1}C_2\sigma_v = C_2$$

$$(\sigma_v')^{-1}C_2\sigma_v' = C_2 \; ; \quad (C_2)^{-1}C_2C_2 = C_2$$

C_2 belongs to a separate class since the similarity transformation of C_2 with all the operations generates C_2. A symmetry operation which commutes with all the symmetry operations is in a separate class. Thus E, σ_h and i belong to separate class. In an Abelian group, every symmetry operation belongs to a separate class.

Note that : *The order of a class of group must be an integral factor of the order of the group.* The similarity transformation method is too elaborate to find the classes of symmetry operations in molecules with high symmetry.

Alternative Method to find the Classes of Symmetry Operations in a Group. *A symmetry operation which commutes with all the symmetry operations is in a separate class. A rotation operation and its inverse belong to the same class if there are n vertical planes or n perpendicular C_2 axes.*

- An operation about the improper axis and its inverse belong to the same class if there are n vertical planes or n perpendicular C_2 axes.
- Two rotations about different axes (or two reflections about different planes) belong to the same class if there is a third operation which interchanges points on the two planes.

Square planar AB_4 type molecule can be considered as an example to verify these rules. This molecule has 16 symmetry operations. $E, \sigma_h, i, C_4^1, C_2^1, C_4^3, S_4^1 S_4^3, 4\sigma_v$ and $4C_2^1$. However, E, σ_h, i, C_2^1 belong to separate classes. C_4^1 and C_4^3 (also S_4^1 and S_4^3) belong to the same class since there are four vertical planes. Two C_2^1 operations about the C_2 axes correspond to one class. Two C_2^1 operations about the C_2^1 axes belong to another class since there is a reflection operation. Two reflection operations in two σ_v planes (and in two σ_v' planes) belong to one class.

POINT GROUPS

All the symmetry operations in a molecule can be combined to form a molecular group. This group is called the *point group* since all the symmetry elements of the molecule intersect at a common point which remains fixed under all the symmetry operations. Crystals have

Table 4. Point groups and symmetry elements.

Point group	Symmetry elements	Point group	Symmetry elements
C_1	E	C_{2h}	E, C_2, σ_h, i
C_2	E, C_2	D_{2h}	$E, 3C_2, 3\sigma, i$
C_3	E, C_3	D_{3h}	$E, 2C_3, 3C_2$ ($\perp$ to C_3), $3\sigma_v, \sigma_h, 2S_3$
C_s	E, σ_v	D_{4h}	$E, C_4, 4C_2$ ($\perp$ to C_4), $2\sigma_v, 2\sigma_d, \sigma_h, C_2, S_4$ (coincident with C_4), i
C_{2v}	$E, C_2, 2\sigma_v$	D_{6h}	$E, 2C_6, 6C_2$ ($\perp$ to C_6), $3\sigma_v, 3\sigma_d, \sigma_h, C_2, 2C_3, 2S_6, 2S_3, i$
C_{3v}	$E, C_3, 3\sigma_v$	T_d	$E, 4C_3, 3C_2, 3S_4$ (coincident with C_2) $6\sigma_d$
$C_{\infty v}$	E, C_∞, σ_v	O_h	$E, 3C_4, 4C_3, 3S_4$ and $3C_2$ (both coincident with the C_4 axes), $6C_2, 4S_6, 3\sigma_h, 6\sigma_d$

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very high symmetry. In fact, they have *translational symmetry* which is not found in gases [...] molecules. The molecular point groups are represented by the Schoenflies symbols whereas the point groups for crystals are denoted by ***Hermann-Mauguin symbols.***

SCHOENFLIES SYMBOLS

A group of symmetry operations in which a point is left invariant under each operation is called a point group. Each molecular point group is identified by a symbol known as **Schoenflies notation** that consists of a capital letter and a subscript. These are :

C : Simple rotation axis. **D** : *n*-fold rotation axis perpendicular to principal axis. **S** : Rotation-reflection axis. **T, O, I** : Symmetry based on tetrahedron, octahedron and icosahedron respectively. The subscript indicates the order *n* of the principal axis and whether plane of symmetry occurs. **s** : Only plane of symmetry. **i** : Only centre of symmetry.

n : Only *n*-fold rotation axis.

nv : Vertical symmetry plane σ_v that contains principal rotation axis.

nh : Horizontal symmetry plane σ_h perpendicular to principal rotation axis.

nd : Dihedral symmetry plane σ_d perpendicular to principal rotation axis.

Table 5. Molecular point groups and Schoenflies symbols.

Type	Schoenflies symbol	Generating set	Order of group	Examples	Comments
Low symmetry point groups	C_1	E	1	CHFBrI	No symmetry
	C_s	σ	2	ONCl, NH_2F	
	C_i	i	2	BrClHC – CHClBr	$C_i = S_2$
Axial point groups	C_n	C_n	n	H_2O_2, N_2H_4	
	C_{nv}	C_n, σ_v	$2n$	NO_2, H_2O, ClF_3, NH_3, BrF_5	$C_{1v} = C_s$
	C_{nh}	C_n, σ_h	$2n$	$B(OH)_3$, $[Ni(CN)_4]^{2-}$	$C_{1h} = C_s$
	S_{2h}	S_{2n}	$2n$	$[Co(NO_2)_6]^{3-}$	$S_1 = C_s$
Dihedral point groups	D_n	C_n, C_2	$2n$	Gauche form of C_2H_6	$D_1 = C_2$
	D_{nh}	C_n, C_2, σ_h	$4n$	C_2H_4, BF_3, NO_3^- CO_3^{2-}	$D_{1h} = C_{2v}$
	D_{nd}	C_n, C_2, σ_d	$4n$	$H_2C = C = CH_2$, TaF_8^{3-}	$D_{1d} = C_2h$
Higher symmetry groups (i) Cubic	T	C_3, C_2	12	CH_4, SiF_4	Angle between C_3 and C_2 is 54·74°
	T_d	C_3, S_4	24	P_4, ClO_4^-	
	T_h	C_3, C_2, i	24	SO_4^{2-}	
	O	C_4, C_3	24	$Cr(CO)_6$, TiF_8^{3-}	Angle between C_3 and C_4 is 54·74°
	O_h	C_4, C_3, i	48	$Co(NH_3)_6^{3+}$, SF_6	
(ii) Icosahedral	I	C_5, C_3	60	$B_{12}H_{12}^{2-}$	Angle between C_3 and C_5 is 37·38°
	I_h	C_5, C_3, i	120		
Infinite point groups. Linear molecules.	C_∞	C_∞	∞	HCl, HCN	
	$C_{\infty v}$	C_∞, σ_v	∞	CO_2, C_2H_2	
	$D_{\infty h}$	$C_\infty, C_2 \cdot \sigma_h$	∞	H_2	
Spherical groups	K	$C(\phi), C'(\phi)$	∞		
	K_h	$C(\phi), C'(\phi), i$	∞		

Exercise. *List the symmetry elements and locate them diagrammatically for the following molecules :*

(a) CH_4, *(b)* $[PtCl_4]^{2-}$, *(c)* H_2, *(d) HF, (e) HCN and (f)* C_2H_2.

Solution : (a) CH_4 **(Tetrahedral).** It belongs to the T_d point group. The symmetry elements are E, $4C_3$, $3C_2$, $3S_4$ and $6\sigma_d$ (Fig. 8).

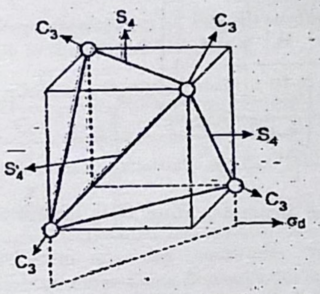

Fig. 8. Symmetry elements of the T_d point group.

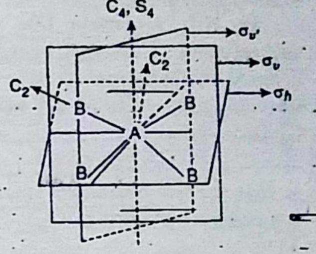

Fig. 9. Symmetry elements of the D_{4h} point group.

(b) $[PtCl_4]^{2-}$ **(Square planar).** This molecule has the general formula AB_4 and belongs to the D_{4h} point group. The symmetry elements are $E, C_4, S_4, 4C_2, 4\sigma_v, \sigma_h$ and i (Fig. 9).

(c) H_2 **[linear with a centre of symmetry, (i)].** H_2 belongs to the $D_{\infty h}$ point group. It has the symmetry elements E, $2C_\infty$, $\infty\sigma_v$, σ_h, i, $2S_\infty$ and ∞C_2 (Fig.10).

(d) HF [linear without centre of symmetry, (i)]. It belongs to the $C_{\infty v}$ point group and has the symmetry elements : E, C_∞ and $\infty\sigma_v$ (Fig. 11).

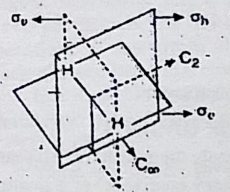

Fig. 10. Symmetry elements of the $D_{\infty h}$ point group in H_2.

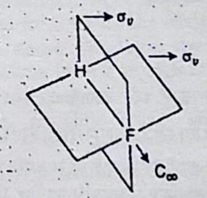

Fig. 11. Symmetry elements of the $C_{\infty v}$ point group in HF.

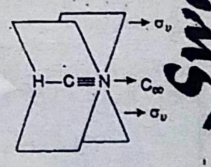

Fig. 12. Symmetry elements of the $C_{\infty v}$ point group in HCN.

(e) HC ≡ N [linear without a centre of symmetry (i)]. It belongs to $C_{\infty v}$ point group and possesses the symmetry elements : E, C_∞ and $\infty\sigma_v$ (Fig. 12).

(f) HC ≡ CH [linear with centre of symmetry, (i)]. It belongs to the $D_{\infty h}$ point group and has the symmetry elements : E, $2C_\infty$, $\infty\sigma_v$, σ_h, i, $2S_\infty$, and ∞C_2 (Fig. 13).

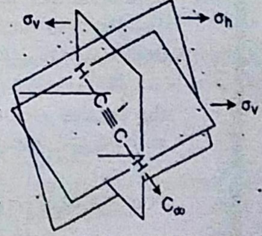

Fig. 13. Symmetry elements of the $D_{\infty h}$ point group in C_2H_2.

Exercise. *Illustrate diagrammatically that* H_2O *molecule is Abelian whereas* NH_3 *molecule is non-Abelian.*

Solution. A molecule is said to be Abelian if all the symmetry elements commute with one another and non-Abelian if they do not commute with one another. In

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H_2O molecule (Fig. 14), the application of C_2^1 followed by σ_v gives the same configuration as the application of σ_v followed by C_2^1. Hence, C_2^1 and σ_v commute, *i.e.*, $\sigma_v C_2^1 = C_2^1 \sigma_v$.

Thus, H_2O molecule belongs to an Abelian point group (C_{2v}).

In NH_3 molecule (Fig. 15) the application of C_3^1 followed by σ_v^1 gives a different configuration of NH_3 molecule than the application of σ_v^1 followed by C_3^1, *i.e.*,

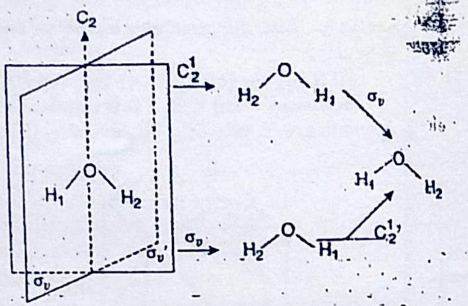

Fig. 14. Illustration of an Abelian group.

$$\sigma_v^1 C_3^1 \neq C_3^1 \sigma_v^1$$

so that the two symmetry operations do not commute. Thus, NH_3 molecule belongs to a non-Abelian point group (C_{3v}).

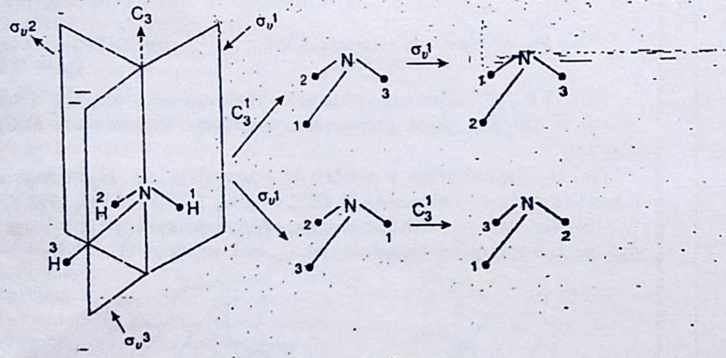

Fig. 15. Illustration of a non-Abelian group.

MATRIX REPRESENTATION OF GROUPS

A matrix is a rectangular array of numbers or symbols for numbers. The set of matrices corresponding to the symmetry operations (or the symmetry elements) of a group is called its **representation.** Symmetry operations such as rotations, reflections etc. are coordinate transformations which modify the mathematical statement of the atomic positions rather than the positions themselves. Combination of group elements involve matrix multiplication. Such sets of matrices are said to form a representation of the point group.

Each atom in a molecule can be specified by three coordinates x_i, y_i, and z_i which defines the position vector from the origin to the particular atom i. From these coordinates the position and orientation of each atom in space can be exactly defined. The vector can be represented as $\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$.

If a molecule is subjected to symmetry operation, the coordinates x_i, y_i, z_i will be transformed to new values x'_i, y'_i, z'_i. This transformation of coordinates can always be written as a set of linear equations of the form

$$x'_i = a_{11} x_i + a_{12} y_i + a_{13} z_i$$
$$y'_i = a_{21} x_i + a_{22} y_i + a_{23} z_i$$
$$z'_i = a_{31} x_i + a_{32} y_i + a_{33} z_i$$

or

$$\begin{pmatrix} x'_i \\ y'_i \\ z'_i \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

in matrix form. The coefficients a_{ij}'s form a transformation matrix. If all symmetry operations are represented by transformation matrix, then point groups can be shown in terms of these matrices. For example, identity operation, E, leaves x, y, z axes unchanged and hence correspond to transformation matrix as

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

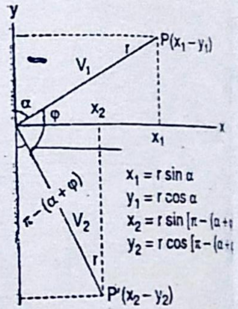

Fig. 16. Transformation by a symmetry axis C(α). The operation of rotation is C(α) at z-axis.

Now, consider the rotation about an axis, C_{n}, as illustrated in **Fig. 16.** In a set of x, y, z axes, a unit vector V_1 of length r is rotated at an angle, φ and changed to a new vector V_2.

$x_1 = r \sin \alpha$; $x_2 = r \sin[\pi - \{\alpha + \varphi\}]$; or $x_2 = r \sin(\alpha + \varphi)$

$y_1 = r \cos \alpha$; $-y_2 = r \cos[\pi - (\alpha + \varphi)]$ or $y_2 = r \cos(\alpha + \varphi)$

Hence, $x_1 = r \sin \alpha$; $x_2 = r \sin(\alpha + \varphi)$ or $x_2 = r(\sin \alpha \cos \varphi + \cos \alpha \sin \varphi)$

$y_1 = r \cos \alpha$; $y_2 = r \cos(\alpha + \varphi)$ or $y_2 = r(\cos \alpha \cos \varphi - \sin \alpha \sin \varphi)$

So,

$$x_2 = x_1 \cos \varphi + y_1 \sin \varphi$$
$$y_2 = y_1 \cos \varphi - y_1 \sin \varphi$$

Hence rotation by an angle, φ gives

$$x_1 \to x_1 \cos \varphi + y_1 \sin \varphi$$
$$y_1 \to -y_1 \sin \varphi + y_1 \cos \varphi$$

and z coordinate remains unchanged. This rotation operation can be represented by matrix as follows :

$$\begin{pmatrix} \cos \varphi & \sin \varphi & 0 \\ -\sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Thus when rotation is at an angle 180° or φ = 180° the rotation matrix for C_2 will be

$$\begin{pmatrix} \cos \pi & \sin \pi & 0 \\ -\sin \pi & \cos \pi & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ or } \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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When $\varphi = 120°$ or $2\pi/3$, the matrix will be of the form

$$\begin{pmatrix} \cos\frac{2\pi}{3} & \sin\frac{2\pi}{3} & 0 \\ -\sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ or } \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Now consider reflection in a mirror plane σ (Fig. 17). The vectors are directed along x, y, z axes. Hence,

$$x_1 = r\cos 2\beta;\ x_2 = r\cos\left(\frac{\pi}{2} - 2\beta\right) \text{ or } -r\sin 2\beta$$

$$y_1 = r\sin 2\beta;\ -y_2 = r\sin\left(\frac{\pi}{2} - 2\beta\right) \text{ or } r\cos 2\beta$$

and z remains unchanged. Thus transformation matrix under reflection through σ plane is

$$\begin{pmatrix} \cos 2\beta & \sin 2\beta & 0 \\ \sin 2\beta & -\cos 2\beta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

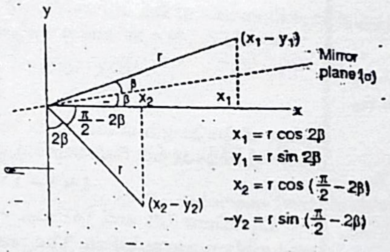

Fig. 17. Transformation by a mirror plane σ. The z-axis lies in the mirror plane.

The set of matrices shown below forms a group. Apparently one can obtain a set of 3 × 3 matrices which forms a representation of any point group. The symbol Γ is used to represent the point group.

Matrix Representation of Symmetry Operations E, C_2, i, σ_h of the Point Group C_{2h}.

$$\text{Point group, } \Gamma = \overset{E}{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}} \overset{C_2}{\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}} \overset{\sigma_h}{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}} \overset{i}{\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}}$$

Matrix Representation of Symmetry Operations in C_{2v} Group.

$$\Gamma = \overset{E}{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 1 & 1 \end{pmatrix}} \overset{C_2}{\begin{pmatrix} \cos\pi & \sin\pi & 0 \\ -\sin\pi & \cos\pi & 0 \\ 0 & 0 & 1 \end{pmatrix}} \text{ or } \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \overset{\sigma_v}{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}} \overset{i}{\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}}$$

$$\text{Also } \sigma_{yz} = \begin{pmatrix} \cos 2\pi & \sin 2\pi & 0 \\ \sin 2\pi & -\cos 2\pi & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{ or } \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},\quad \sigma_{yz} = \begin{pmatrix} \cos\pi & \sin\pi & 0 \\ \sin\pi & -\cos\pi & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ or } \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$\beta = 180°$ $\qquad\qquad$ $\beta = 90°$

Matrix Representation of Symmetry Operations in C_{3v} Group.

Consider NH_3, $\beta = 0$ for σ_1; ~~$\beta = -60°$~~ for σ_2 and $\beta = 60°$ for σ_3; $\phi = 120°$ for C_3^1 and 240° for C_3^2

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix};\ C_3^1 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix};\ C_3^2 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\sigma_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix};\ \sigma_2 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix};\ \sigma_3 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Representation of x, y, z coordinates under different symmetry operation for water molecule is illustrated in Table 6.

Table 6. Representation of x, y, z in C_{2v} point group in H_2O molecule.

C_{2v}	E	C_{2v}	σ_{xz}	σ_{yz}
x	1	−1	1	−1
y	1	−1	−1	1
z	1	1	1	1

To sum up, the molecular point group thus consists of certain orthogonal transformations ~~in three~~ dimensional space. The representation of a group is a set of matrices which expresses mathematically the operations of the group on the basis set.

REDUCIBLE REPRESENTATION OF GROUPS

Representation of a group consists of a set of matrices each of which corresponds to a symmetry element in a group and these matrices combine in the same way as the symmetry elements do. But these are certainly not the unique set. The aim is to find out the most fundamental set of matrices from which other representations can be derived. Thus it is possible to simplify a matrix representation by performing the same similarity transformation on each of the matrices so that they are all reduced to the same block diagonalized form. *The original representation is then said to be reducible.* In the reduction of representation, the block diagonal form for all the matrices corresponding to the symmetry operations of the group should be same. The lower dimensional matrices formed from the block diagonalized matrices themselves form a representation of the group.

Let A, B, C be the matrices which form the representation of a group and X be the similarity transformation matrix of this group such that $X^{-1}AX = A'$, $X^{-1}BX = B'$, $X^{-1}CX = C'$.

Then if X is the proper transformation matrix, we have

$$X^{-1}AX = A' = \begin{bmatrix} a'_1 & 0 & 0 & 0 \\ 0 & a'_2 & 0 & 0 \\ 0 & 0 & a'_3 & 0 \\ 0 & 0 & 0 & a'_4 \end{bmatrix} \text{ or } X^{-1}BX = B' = \begin{bmatrix} b'_1 & 0 & 0 & 0 \\ 0 & b'_2 & 0 & 0 \\ 0 & 0 & b'_3 & 0 \\ 0 & 0 & 0 & b'_4 \end{bmatrix} \text{ etc.}$$

The new matrix A' (or B') is now blocked out along the diagonal into smaller matrices a'_1, a'_2, a'_3, a'_4 (or b'_1, b'_2, b'_3, b'_4) etc. with the off diagonal elements equal to zero. Thus a given set of matrices form a reducible representation.

IRREDUCIBLE REPRESENTATION OF GROUPS

If it is not possible to find a similarity transformation to perform the reduction of all the matrices *viz.* $A, B, C, \ldots$ to block diagonalized form, the representation is called an irreducible representation (IRs).

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Exercise. *Illustrate reducible and irreducible representations considering C_{3v} point group.*

Solution. For C_{3v} point group (as described earliar for NH_3), write all matrices in a general form

$$(R) = \begin{pmatrix} a_{11} & a_{12} & 0 \\ a_{21} & a_{22} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

or symbolically as

$$(R) = \left[\begin{array}{c|c} R' & 0 \\ \hline 0 & R'' \end{array}\right]$$

where

$$(R') = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \text{ and } R'' = (1)$$

It means that (R) matrix is a direct sum of (R') and (R'') and separately give a representation of C_{3v} point group. The point group is usually denoted by Γ (gamma) and the direct sum is written as

$$\Gamma = \Gamma_3 + \Gamma_1$$

where Γ_3 is the representation by matrix (R'), a two dimensional matrix and Γ_1 by (R''). Thus representation is reduced to a sum of two dimensional matrix Γ_3 and one dimensional matrix Γ_1. It can be noticed that Γ_3 cannot be reduced further. Thus, both Γ_3 and Γ_1 are irreducible representations.

The number of irreducible representations (IRs) is equal to the number of classes in the group. In C_{3v} **point group** there are three classes of elements namely, E, $2C_3$ and $3\sigma_v$. Therefore, there are three IRs of C_{3v} point group. **Note that in C_{2v} point group,** there are four classes of elements, E, C_2, σ_{xz}, σ_{yz}, thus it will have four IRs.

GREAT ORTHOGONALITY THEOREM

The relationship between the elements of unitary matrices used to form group representations is given by Great Orthogonality theorem (GOT). As the name indicates, the theorem shows orthogonal relationships that exist between the matrix elements of the different representations of a group. The theorem is valid for all non-equivalent irreducible representations of any group.

Mathematical statement of GOT is

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij}\,\delta_{mn}\,\delta_{m'n'} \quad \ldots(1)$$

where h = order of the group.

l_i and l_j represent the dimensions of two IRs (i and j) of the group.

R = various symmetry operations of the group.

m and n represents mth row and nth column of the matrix and

* represent the complex conjugate.

δ is **Kronecker delta** which means $\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$

Each element is normalized and orthogonal to the other element in the matrix. The character of the ith representation of operation R, is just the sum of the diagonal elements of the matrix representing R (or trace of the matrix). The equation (1) can be put in three simpler equations.

1. If $i \neq j$, $\delta_{ij} = 0$ and $m = m'$ and $n = n'$, then

$$\sum_R \Gamma_i(R)_{mn}\,\Gamma_j(R)_{mn} = 0 \quad \text{or} \quad \sum_R \chi_i(R)\,\chi_j(R) = 0 \quad \ldots(2)$$

Elements corresponding to matrices of different irreducible representations are orthogonal.

For example, selecting reducible representations and E from Table 6 as C_{2v} point group (in water molecule) we have from equation (2).

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

2. If $m \neq m'$ and $n \neq n'$, $\delta_{mm'} = 0$ and $\delta_{nn'} = 0$, then

$$\sum_R \Gamma_i(R)_{mm'}\,\Gamma_j(R)_{nn'} = 0 \quad \ldots(3)$$

Elements of the different sets of the matrices of the same IR's are orthogonal.

3. If $i = j$, $m = m'$ and $n = n'$, $\delta_{ij} = 1$, $\delta_{mn} = 1$, then

$$\sum_R \Gamma_i(R)_{mn}\,\Gamma_j(R)^2_{mn} = \frac{h}{l}$$

square of the length of any such vector is h/l, h is the order which is 4 in the C_{2v} point group (Table 6) and l is one dimensional length. For example, again choosing both R's as C_{2v} we get

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

Equations (2) and (4) can be used to decompose any reducible representation into irreducible representation. The reducible representation can be written as linear combination of irreducible representations.

$$\Gamma = n_1\Gamma_1 + n_2\Gamma_2 + n_3\Gamma_3$$

Importance of Great Orthogonality Theorem (GOT).

Following rules can be derived from GOT for irreducible representations of group.

1. *Number of IR's in a group is equal to the number of classes of operation in the group.*
2. *Sum of the squares of the dimensions of the IR's is equal to the order of the group.*

$$\sum_i l_i^2 = l_1^2 + l_2^2 + l_3^2 + \ldots = h$$

where the summation is taken overall the representations Γ_i. Since the dimension of an IR is equal to the character of its identity operation E, so the sum of the squares of the characters of E of IR's of group is equal to the order of group.

$$\sum_i [\chi_i(E)]^2 = h$$

3. *The sum of the squares of the characters of an IR is equal to the order of the group. Thus each row is normalized to h, the order of the group.*

$$\sum_i [\chi_i(R)]^2 = h$$

4. *The characters of the IR's of the same group are orthogonal to each other. The columns of the IR's in the character table form orthogonal vectors.*

$$\sum_i [\chi_i(R)\chi_j(R)] = 0$$

5. *The characters of the elements of the same class (conjugate elements) of an reducible representation are same.*

Derivation for Reducible Representation.

In general any reducible representation Γ can be written as linear combination of irreducible representations as

$$\Gamma = n_1\Gamma_1 + n_2\Gamma_2 + n_3\Gamma_3 + \ldots \quad ...(10)$$

where Γ_1, Γ_2... are IR's and n's are the number of times each IR occurs. From C_{2v} point group in Table 6 ($\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$) we note that

$$\chi(R) = \Sigma\, n_i\, \chi_i(R)$$

$\chi(R)$ is the character of reducible representation which corresponds to Rth operation. Multiply it by $\chi_j(R)$ and summing over R, we have

$$\sum_R \chi_j(R)\,\chi(R) = \sum_R \Sigma\, n_i\, \chi_j(R)\,\chi_i(R)$$

except for $i = j$, all terms on RHS are zero. Thus,

$$\sum_R \chi_j(R)\,\chi(R) = n_j\,h \text{ or } n_j = \frac{1}{h}\sum_R \chi_j(R)\,\chi(R) \quad\text{and}\quad n_j = \Sigma\, a_k\,\chi_j(R)\,\chi(R) \quad ...(11)$$

when a_R = no. of elements in the class. This corresponds to the reduction formula (or the magic formula).

CONSTRUCTION OF CHARACTER TABLE FROM GOT RULES

Character table contains all the basic information that the group theory can provide.

1. Construction of Character Table for C_{3v} Point Group.

Classes of operations in C_{3v} group are three, that is, $E, 2C_3, 3\sigma_v$.

(a) Since there are three classes of operations, there should be three IR's, *viz.*

$$\Gamma_1, \Gamma_2, \Gamma_3$$

(b) The order of the group is 6 (1 + 2 + 3), therefore, the sum of the squares of the dimensions (character of the identity operations) should be equal to 6. Since dimension has to be an integer, $l_1 = 1, l_2 = 1$ and $l_3 = 2$ ($1^2 + 1^2 + 2^2 = 6$) so there should be two 1-dimensional and one 2-dimensional representations. The irreducible representations of identity operations E, are $\Gamma_1 = 1, \Gamma_2 = 1$ and $\Gamma_3 = 2$.

(c) For any point group, there should be one IR which is symmetrical to all the operations. The character corresponding to all the operations is +1. Thus, IR, Γ_1 is written as

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1

The sum of the squares of the characters of the operations should be 6.

$$1^2 \times 1 + 1^2 \times 2 + 1^2 \times 3 = 6$$

since there is $1E$, $2C_3$ and $3\sigma_v$ operations.

(d) For other IR's we know that the character of IR's are orthogonal to each other. The character of E for Γ_2 is 1. Hence, the character of the C_3 (χ_{C_3}) and the character of σ_v (χ_{σ_v}) should be such that

$$1 \times 1 \times \chi_E + 2 \times 1 \times \chi_{C_3} + 3 \times 1 \times \chi_{\sigma_v} = 0$$

When $\chi_{C_3} = 1$, then $\chi_{\sigma_v} = -1$. Thus, Γ_2 is represented as

	E	$2C_3$	$3\sigma_v$
Γ_2	1	1	−1

The character of Γ_3 should be orthogonal to Γ_1 and Γ_2. The character of E in Γ_3 is 2. Let the character of C_3 be χ'_{C_3} and that of σ_v, $\chi'\sigma_v$ is Γ_3; then by considering the orthogonality of Γ_1 and Γ_3, we get

$$1 \times 1 \times 2 + 2 \times 1 \times \chi'_{C_3} + 3 \times 1 \times \chi'_{\sigma_v} = 0 \quad ...(12)$$

By considering the orthogonality of Γ_2 and Γ_3.

$$1 \times 1 \times 2 + 2 \times 1 \times \chi'_{C_3} + 3 \times 1(-1) \times \chi'_{\sigma_v} = 0 \quad ...(13)$$

Substracting equation (13) from (12), we have

$$6\,\chi'_{\sigma_v} = 0, \text{ hence } \chi'_{\sigma_v} = 0$$

Hence substituting for $\chi_{\sigma_v} = 0$, in equation (12) we obtain

$$1 \times 1 \times 2 + 2 \times 1 \times \chi'_{C_3} + 3 \times 1 \times 0 = 0$$

$$\chi'_{C_3} = -1$$

	E	$2C_3$	$3\sigma_v$
Hence the characters of Γ_3 are	2	−1	0

Table 7. Character table for C_{3v} point group.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	−1
Γ_3	2	−1	0

Construction of Character Table for C_{2v} Point Group.

The symmetry operations are, $E, C_2, \sigma_{xz}, \sigma_{yz}$ that is, total 4 operations.

(a) So 4 IR's are possible : $\Gamma_1, \Gamma_2, \Gamma_3$ and Γ_4.

(b) Sum of the squares of the dimensions of the IR's should be 4 (order) hence each IR should be one dimensional $1^2 + 1^2 + 1^2 + 1^2 = 4$.

(c) The dimension of the representation is equal to the character E. The irreducible representation of E must be equal to 1 for all.

(d) Sum of the squares of the characters of IR's and orthogonal to Γ_1. The characters must include two +1 and two − 1.

3. Construction of character table for D_5 point group. The symmetry elements for D_5 point group are categorised into four classes *viz.* $E, 2C_5, 2C_5^2, 5C_2$. Hence, there are four irreducible representations, two of which are singly degenerate and the other two are doubly degenerate. The order of the group is 10. Initially the character table can be written as shown in Table 8.

Table 8. Derivation of character table for D_5 group.

D_5	E	$2C_5$	$2C_5^2$	$5C_2$
Γ_1	1	1	1	1
Γ_2	1	1	1	−1
Γ_3	2	a	b	c
Γ_4	2	d	e	f

Apply the following equation

$$\sum_{p=1}^{k} g_p\,\chi_i(R_p)\,\chi_j(R_p) = h\,\delta_{ij}$$

[Where g_p is the number of elements in a symmetry class p, h is the order of the point group and R_p is a symmetry operation in the pth class], to get

(i) $2 + 2a + 2b + 5c = 0$ (ii) $2 + 2a + 2b - 5c = 0$

which gives $10c = 0$ or $c = 0$. Similarly,

(iii) $2 + 2d + 2e + 5f = 0$ (iv) $2 + 2d + 2e - 5f = 0$

leading to $10f = 0$ or $f = 0$.

Equations (i) and (ii) on addition give $4 + 4a + 4b = 0$ or $a + b = -1$. Using equation (8) we obtain $4 + 2a^2 + 2b^2 = 10$.

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That is, $2a^2 + 2b^2 = 10 - 4 = 6$ or $a^2 + b^2 = 3$.

Since $(a + b) = -1$. $(a + b)^2 = 1$, that is, $a^2 + b^2 + 2ab = 1$.

Since $a^2 + b^3 = 3$, we get $3 + 2ab = 1$, that is, $ab = -1$.

Again $(a - b)^2 = (a + b)^2 - 4ab$

$= 1 + 4 = 5$ giving $a - b = \sqrt{5}$

Since $a + b = -1$, taking $a - b = +\sqrt{5}$, we get,

$$a = \frac{-1+\sqrt{5}}{2} \quad \text{and} \quad b = \frac{-1-\sqrt{5}}{2}$$

Since $\cos 72 = \sin 18 = \frac{-1+\sqrt{5}}{4}$ and $\cos 144 = -\cos 36 = \frac{-1-\sqrt{5}}{2}$

We have $a = 2\cos 72$ or $2\cos\theta$ and

$b = 2\cos 144$ or $2\cos 2\theta$, where $\theta = 72°$.

Similarly, it can be shown that $d = 2\cos 2\theta$ and $e = 2\cos\theta$.

The character table for the D_5 group can be completed by substituting the values for $a, b \ldots f$ and represented in Table 9.

Isomorphic groups have the same character table *(also the same order and same forms of their multiplication tables)* and thus simplifies the construction of character tables. Following point groups are isomorphic. $C_{nv} \sim D_n$, $C_n \sim S_n$ (n even), $C_{nh} \sim C_{2n}$ (n odd), $D_{2nd} \sim D_{nd}$, $D_{nh} \sim D_{nd}$ (n odd), $O \sim T_d$. Hence, the point groups C_{3v} and D_3 have the same character table, although their symmetry operations are different.

Table 9. Character table for D_5 point group.

D_5	E	$2C_5$	$2C_5^2$	$5C_2$
Γ_1	1	1	1	1
Γ_2	1	1	1	-1
Γ_3	2	$2\cos\theta$	$2\cos 2\theta$	0
Γ_4	2	$2\cos 2\theta$	$2\cos\theta$	0

CHARACTER OF IRREDUCIBLE REPRESENTATION

The irreducible representations follow a pattern of symmetry behaviour, so these are referred to as **symmetry species**. However, in the application of group theory to molecular spectra, irreducible representations are not used directly but their characters are used. Also the labelling of IR's as Γ_i is not very informative. The symbols formulated by **R.S. Mulliken** are usually employed to distinguish the IR's of the point group.

Table 10. Standard format of a character table.

Schoenflies symbol of group	Symbol for each class in group and number of elements in the class	Symmetry properties	
R.S. Mulliken symbol for each IR	Character of IR's of each class	Translations, Rotations	Product function of coordinates

NOTATIONS FOR IRREDUCIBLE REPRESENTATIONS

Mulliken's symbols denote the dimension of an IR as follows : **A or B** are labelled for **one dimensional IR's** according to whether the character of a proper or improper rotation by $2\pi/n$ about the symmetry axis of highest order n is +1 or −1 respectively.

- **A** is labelled for symmetric w.r.t. principal C_n axis or S_n axis for some D_{nd} and S_n groups when n is even.
  A is also used for symmetric w.r.t. all three C_2 axes for D_2 group and for C_1, C_s, C_i where no C_n axis exists.

- **B** is used for antisymmetric w.r.t. principal C_n axis or S_n axis for D_{nd} and S_n point groups when n is even.
- **E** is labelled for two dimensional IR (not to be confused with identity E) and for doubly degenerate representations.
- **T or F** are used for 3D IR's and for triply degenerate representations.
- Symmetry with respect to rotation about subsidiary axes or plane is designated by a subscript 1 and 2.
  A_1, B_1, E_1, T_1 are used for symmetrical with respect to subsidiary axes or σ_v plane (no change of sign).
  A_2, B_2, E_2, T_2 are used for unsymmetrical with respect to subsidiary axes or σ_v plane (change of sign).
- Symmetry with respect to horizontal plane or molecular plane is denoted by prime (′) or (″),
  A', B', E', T' are used for character +1 for σ_h plane.
  A'', B'', E'', T'' are used for character −1 for σ_h plane.
- The two **infinite groups** $C_{\infty v}$ and $D_{\infty h}$ have their own notations. Greek letters $\Sigma, \Pi, \Delta, \Phi, \ldots$ corresponding to $l = 0, 1, 2, 3, \ldots$ where l is the component of orbital angular momentum about the molecular axis are used. The equivalent symbols in Mulliken's notation are $A_1, E_1, E_2, E_3 \ldots$ respectively.
- For IR's Σ^+, Σ^- indicate the symmetry behaviour with respect to a plane which contains the molecular axis.
- The IR's of $D_{\infty h}$ are distinguished by adding subscript g (gerade) or u (ungerade) as usual to specify the symmetry with respect to inversion centre.
- If there is no centre of symmetry, g or u are not used.

Exercise. *Indicate Mulliken's notations for C_{3v} point group considering. Table 7.*

Solution. Γ_1 : One dimensional ($\chi_E = 1$), symmetrical to C_3 axis (principal axis) and the vertical plane, hence it is A_1

Γ_2 : One dimensional ($\chi_E = 1$), symmetrical to C_3 axis (principal axis) unsymmetrical with respect to σ_v vertical plane ($\chi_{\sigma_v} = -1$). Hence it is A_2.

Γ_3 : Two-dimensional ($\chi_E = 2$), hence it is E.

Exercise. *State Mulliken's symbols for C_{2v} point group using Table 6.*

Solution.

Γ_1 : 1-dimensional ($\chi_E = 1$), symmetrical to principal axis C_2 and to σ_{xz} plane, it is A_1.

Γ_2 : 1-dimensional ($\chi_E = 1$) symmetrical to principal axis C_2 and unsymmetrical to σ_{yz} plane ($\chi_{\sigma_v} = -1$), thus it is A_2.

Γ_3 : 1-dimensional, ($\chi_E = 1$), unsymmetrical to C_2 ($\chi_{C_2} = -1$), but symmetrical to σ_{xz} plane ($\chi_{xz} = 1$). So it is B_1.

Γ_4 : 1-dimensional ($\chi_E = 1$), unsymmetrical to C_2 and also to σ_{xz} plane ($\chi_{\sigma_{xz}}$ =

Therefore it is B_2.

CHARACTER TABLES AND THEIR USE

The trace, that is the *sum of the diagonal elements of a matrix which is a part of the representation of a point group is referred to as the character* (χ) *in group theory*. For one dimensional representations, the character (+1 or −1) is same as the matrix itself. The character of a symmetry operation is unchanged by a similarity transformation. Symmetry operations belonging to the same symmetry class have the same character. Character tables of molecular point groups are extremely important for their applications in solving chemical problems related to molecular spectroscopy. Character tables find their extensive use in (i) Symmetry properties of orbitals. (ii) Huckel molecular orbital theory. (iii) Electronic transitions. (iv) Infrared and Raman active vibrations. (v) Structure elucidation of molecules.

Character tables for some of the important point groups:

C_{2v} group	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		—
A_1	1	1	1	1	T_z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
A_2	1	1	−1	−1	R_z	α_{xy}
B_1	1	−1	1	−1	T_x, R_y	α_{xz}
B_2	1	−1	−1	1	T_y, R_x	α_{yz}

C_{5v} group	E	$2C_5$	$2C_5^2$	$5\sigma_v$	$\sigma = 72°$	—
A_1	1	1	1	1	T_z	$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A_2	1	1	1	−1	R_z	—
E_1	2	2 cos α	2 cos 2α	0	$(T_x, T_y), (R_x, R_y)$	$(\alpha_{yz}, \alpha_{zx})$
E_2	2	2 cos 2α	2 cos α	0	—	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$

C_{2h} group	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
B_g	1	−1	1	−1	R_x, R_y	$\alpha_{xy}, \alpha_{yz}, \alpha_{xz}$
A_u	1	1	−1	−1	T_z	
B_u	1	−1	−1	1	T_x, T_y	-

$D_{2h} = V_h$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	α_{xy}
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	α_{zx}
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	α_{yz}
A_u	1	1	1	1	−1	−1	−1	−1		-
B_{1u}	1	1	−1	−1	−1	−1	1	1	T_z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	T_y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	T_x	—

Character tables for the cubic group.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$
$T_1 \equiv F_1$	3	0	−1	1	−1	(R_x, R_y, R_z)	
$T_2 \equiv F_2$	3	0	−1	−1	1	(T_x, T_y, T_z)	$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$

O_h	E	$8C_3$	$3C_2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	-	$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1		
E_g	2	−1	2	0	0	2	−1	2	0	0		$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$
$T_{1g} \equiv F_{1g}$	3	0	−1	1	−1	3	0	−1	1	−1	(R_x, R_y, R_z)	
$T_{2g} \equiv F_{2g}$	3	0	−1	−1	1	3	0	−1	−1	1		$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1		
E_u	2	−1	2	0	0	−2	1	−2	0	0	–	
$T_{1u} \equiv F_{1u}$	3	0	−1	1	−1	−3	0	1	−1	1	(T_x, T_y, T_z)	
$T_{2u} \equiv F_{2u}$	3	0	−1	−1	1	−3	0	1	1	−1		

APPLICATIONS OF GROUP THEORY

- Group theory is an extremely useful tool to predict the probability of transitions in atomic and molecular spectroscopy.
- It helps in the classification of the normal vibrations according to the irreducible representations of the point group of molecules.
- It aids in qualitatively finding out the infrared and Raman spectral activity of the fundamental as well as the overtone and combinations bands.
- Group theory can be applied in the construction of hybrid orbitals and symmetry adapted linear combinations of atomic orbitals in MOT. Group theory helps in determining optical activity and polarity of molecules, classification of elementary particles into fermions and bosons and simplifying the secular equation which is a special feature of the quantum mechanical calculations in both VBT and MOT. It thus saves computational labour and cost of calculations on digital computer.

SHORT ANSWER QUESTIONS

1. *List the fundamental symmetry operations.*
   Ans. (i) Identity operation (ii) Rotation operation (iii) Reflection operation (iv) Centre of inversion operation (v) Rotation-reflection operation.
2. *How many times Γ_i occurs in point group Γ for C_{2v} point group?*
   Ans. Transformation vectors in C_{2v} point group are :

$$E : \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, C_2 : \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \sigma_{xz} : \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \sigma_{yz} : \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\chi_i(R) : \chi_E = 2, \chi_{C_2} = -2, \chi_{\sigma_{xz}} = 0, \chi_{\sigma_{yz}} = 0$$

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Using reduction equation (11) $h = 4$. $a_R = h$ of elements in class = 1 each.

$$n_j = \frac{1}{h} \Sigma a_R \chi_j(R) \chi(R)$$

$$n_1(\Gamma_1) = \frac{1}{4}[1\times 2 + 1\times -2 + 1\times 0 + 1\times 0] = 0$$

$$n_2(\Gamma_2) = \frac{1}{4}[1\times 2 + 1\times -2 + (-1)\times 0 + (-1)\times 0] = 0$$

$$n_3(\Gamma_3) = \frac{1}{4}[1\times 2 + (-1)\times(-2) + 1\times 0 + (-1)\times 0] = 1$$

$$n_4(\Gamma_4) = \frac{1}{4}[1\times 2 + (-1)\times(-2) + (-1)\times 0 + 1\times 0] = 1$$

Hence $\Gamma = \Gamma_3 + \Gamma_4$

3. *Whether 1, 0, −1 form a group, the rule of combination being (a) addition (b) multiplication.*
Ans. The elements do not form a group. (a) $1 + 1 = 2$, which is not a member of the group and (b) there is no inverse for 0.

4. *Why a set of numbers cannot form a group by the process of division?*
Ans. Because the associative law of combination is not obeyed. For example $A/(B/C)$ is not equal to $(A/B)/C$.

5. *Prove that each element of a group appears only once in each row and column of a group multiplication table.*
Ans. If any two entries in the same row (or column) say OP and OR are equal, it would follow $P = R$.

6. *Whether the point groups C_{2v} and D_2 are isomorphic?*
Ans. Since the order and structure of the multiplication table for the groups C_{2v} and D_2 are same, they are isomorphic.

7. *Mention the subgroups of (a) S_4 and (b) D_{2d}.*
Ans. (a) E, S_4, C_2 (b) $E, D_{2d}, D_2, S_4, C_{2v}, C_2, C_s$.

8. *Give the operation equivalent of (a) $\sigma_v(1)C_3\sigma_v(1)^{-1}$ (b) $(C_3^2)^{-1}\sigma_v(1)C_3$ (c) C_2S_3 of the point group D_{3h}.*
Ans. (a) C_3^2 (b) $\sigma_v(1)$ since $(C_3^2)^{-1} = C_3$ (c) $\sigma_v(3)$

9. *State the generators of point groups (a) S_3 (b) C_{4v} and (c) D_{3h}.*
Ans. (a) S_3 (b) C_4, σ_v (c) $C_3, C_2 \perp C_3, \sigma_h$

10. *Which group is obtained by adding or deleting the symmetry operations indicated below? (a) D_{4h} minus S_4 (b) D_3 plus i (c) C_3 plus S_6 (d) C_3 plus i (e) C_{50} plus i (f) D_{4d} minus S_8 (g) C_4 plus i (h) C_{3h} minus S_6^5*
Ans. (a) D_4 (b) D_{3d} (c) S_6 (d) S_6 (e) D_{5d}
(f) D_4 (g) C_4 (h) C_3.

11. *Find the irreducible representations present in the following reducible representations :*

T	E	$4C_3$	$4C_3^2$	$3C_2^2$
T	9	0	0	1

Ans. $A + E + 2F$.

12. *List the Schoenflies notations for the point groups of (a) Staggered and eclipsed form of ferrocene (b) Be(acac)$_2$ (c) Trans-NiCl$_2$. 2 pyridine (d) Mo($S_2C_2H_2$)$_3$ dithiolene complex.*
Ans. (a) D_{5d}, D_{5h} (b) D_{2d} (c) D_{2h} (d) D_{3h}.

13. *Put trans-dichloroethylene in an appropriate coordinate system and find the symmetry species to which each of the rotations R_x, R_y, R_z and each of the translations T_x, T_y, T_z belong?*
Ans. Taking C = C bond as Y axis and Z axis perpendicular to the molecular plane, T_x, T_y, T_z transform as B_u, B_u, A_u and R_x, R_y, R_z transform as B_g, B_g, A_g respectively.

14. *Determine the direct product of the following for the point group D_{3h} (a) $A'_2 \times A'_2$ (b) $E' \times E''$ (c) $E' \times E' \times E''$.*
Ans. (a) A'_1 (b) $A''_1 + A''_2 + E''$ (c) $A''_1 + A''_2 + 3E''$.

15. *List the important symmetry elements present in the following molecules and indicate the point group to which each molecule belongs. (a) S_4N_4 (b) Cyclopropane (c) Boat and chair form of cyclohexane.*
Ans. (a) $C_2, 2C_2 \perp C_2, \sigma_d$; D_{2d} (b) $C_3, 3C_2, \sigma_h$; D_{3h}
(c) Boat form : C_2, σ_v, C_{2v}, chair form $C_3, 3C_2 \perp C_3, \sigma_d$; D_3d.

16. *For an octahedral molecule XY_6, certain Y atoms are replaced by different Z atoms in (a) XY_5Z (b) XY_4Z_2 (c) XY_3Z_3. State the point group to which the resulting molecule belongs?*
Ans. (a) C_{4v} (b) Trans D_{4h}, Cis C_{2v} (c) fac C_{3v}, mer C_{2v}.

17. *Assign the symmetry group and rotation group to biphenyl (a) with phenyl rings coplanar (b) with rings in perpendicular planes (c) with rings in planes making 45°.*
Ans. (a) D_{2h} (b) D_{2d}, (c) D_2. Rotation group is D_2.

18. *Find the dimensions of IR's for the group with order 48 and class 10.*
Ans. 4, 2 and 4 one-, two- and three- dimensional representations respectively.

19. Derive the symmetry species for the vibrational states of H_2O for (111) and (012).
Ans. (111) : $A_1 \times A_1 \times B_2 = B_2$
(012) : $A_1 \times B_2 \times B_2 = A_1$.

20. How a study of IR and Raman spectra could be used to differentiate between cis and trans planar structures for N_2F_2?
Ans. For *cis* isomer, the vibrations $(3A_1 + A_2 + 2B_1)$ are all Raman and IR active except A_2 which is IR inactive. For the *trans* isomer $(3A_g + A_u + 2B_u)$, the *g* and *u* modes are Raman and IR active.

MULTIPLE CHOICE QUESTIONS.

1. Two-fold axes of rotation are absent in
(a) HCl (b) HCN (c) Both (a) and (b) (d) HF

2. Both vertical mirror planes ($3\sigma_v$) and horizontal plane of symmetry exist in
(a) BF_3 (b) NH_3 (c) H_2O (d) $B(OH)_3$

3. The group of 24 operations is designated by the point group O. The rotation symmetry operations of an octahedron are
(a) E (b) $8C_3, 6C_4$ (c) $3C_2, 6C_2$ (d) All

4. Cubic point groups are
(a) O, Oh (b) T, T_d, T_h (c) I, I_h (d) All

5. The staggered form of dibenzene chromium belongs to group
(a) D_{5d} (b) D_{6d} (c) D_{4d} (d) D_{3d}

6. The order of the groups C_{40}, D_{40} and S_{40} are respectively
(a) 40, 80, 40 (b) 40, 40, 40 (c) 80, 40, 40 (d) 40, 40, 80

7. Which of the following molecules are optically active?
(a) $Co(en)_3^{3+}$ (b) CHF BrCl (c) $(C_6H_5)_2$ (d) All
[**Hint.** A molecule with a S_n axis is optically inactive].

8. Which of the following molecule has no dipole moment?
(a) CO_2 (b) C_6H_6 (c) Both (a) and (b) (d) NH_3

9. For which of the following groups are the C_n and C_n^{n-1} operations in the same class?
(a) C_{nh} (b) C_{nv} and D_n (c) C_n (d) D_{nh}

10. The irreducible representations contained in the following reducible representations

C_3	E	C_3	C_3^2
Γ	8	2	2

are
(a) $4A + 2E$ (b) $2A + 4E$ (c) $6A + 6E$ (d) $2A + 2E$

11. Schoenflies notations for the point groups of B_2Cl_4, NO_2^+ and 1, 3-dichloroallene are respectively
(a) $D_{\alpha h}, D_{2d}, C_2$ (b) $D_{2d}, D_{\alpha h}, C_2$ (c) $C_2, D_{2d}, D_{\alpha h}$ (d) $D_{\alpha h}, C_2, D_{2d}$

12. The character table for S_6 can be constructed as a product of groups
(a) $C_3 \times C_2$ (b) $C_2 \times C_2$ (c) $C_3 \times C_i$ (d) $C_i \times C_i$

13. The rotation group in 1, 3, 5-trinitrobenzene with all NO_2 groups coplanar is
(a) D_3 (b) D_2 (c) C_3 (d) C_2

14. The dimensions of irreducible representations for the group with order 32 and class 11 are
(a) 4 and 2 one dimensional representation
(b) 4 and 7, the 1-*D* and 2-*D* representations respectively
(c) 2 and 2, the 1*D* representation
(d) 3 and 4 with 2*D* representation

15. The irreducible representations to which the translational and rotational vector components transform in C_{3h} are
(a) $A_1 + E$ (b) $A'' + E', A' + E''$ (c) $A_2 + E, A' + E'$ (d) $A_2 + E''$

16. The order of improper axis in $SiCl_4$, $Ni(CO)_4$ and allene are
(a) 3, 4, 4 (b) 4, 4, 4 (c) 2, 3, 4 (d) 4, 3, 2

17. H_3BO_3 belongs to point group
(a) C_n (b) C_{2h} (c) C_{3h} (d) D_4

18. Axial point groups are
(a) C_n, C_{nv}, C_{nh}, S_n (b) D_n, D_{nh}, D_{nd} (c) O, Oh (d) T, T_d

19. Mulliken's notations for infinite groups like $C_{\alpha v}$ and $D_{\alpha h}$ are
(a) $\Sigma, \pi, \Delta, \phi$... (b) A_1, E_1, E_2, E_3... (c) E, σ_v (d) C_u, g_u

20. The simplest 1*D* representation obtained by representing each of the symmetry operation by +1 corresponds to trivial homomorphism. It is known as
(a) Totally symmetric representation (b) Irreducible representation
(c) Isomorphic representation (d) All

ANSWERS

1. (c)	2. (a)	3. (d)	4. (d)	5. (b)	6. (a)	7. (d)	8. (c)	9. (b)	10. (a)
11. (b)	12. (c)	13. (a)	14. (b)	15. (b)	16. (b)	17. (c)	18. (a)	19. (b)	20. (a)

□