NANI

GROUP THEORY 1 COPY

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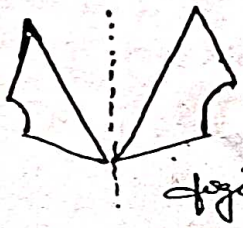
Introduction:

Everything & every object in nature has geometry and natures loves symmetry. Objects are made up of molecules. The most important properties of a molecule are its geometry and its electronic structure. These two properties are related to each other. All chemical and physical properties of a molecule can be inferred from these two properties. Symmetry is a physical property of the molecules and is quite intimately related to the geometry of the molecule. Symmetry is an essential theme for defining the molecular structure.

The word 'symmetry' means that a certain part & portion of an object looks exactly like another part.

figure(a)



figure(b)

In the figure(a) the upper part is just like the lower part and in figure(b) the left part is similar to right side part. i.e. one part & the object is in harmony with the other part. Therefore, the word symmetry implies a structure in which the parts are in harmony with each other, as well as to the whole structure ie. the structure & an object & molecule is proportional and well balanced. In a scientific sense, an object is said to be possessing symmetry, if the object can take up more than one equivalent (indistinguishable) orientations (three dimensional space arrangements)

The symmetry relationships in the molecular structure provide the basis for a mathematical theory, called group theory. The group theory of mathematics involves algebra. A molecule is a geometrical entity and group theory dealing with such molecules is also called as the g^r algebra of geometry.

Group theory of molecules is a predictive science: It is useful in number of ways. for example:

(i) it is useful; to give the symmetry & symmetries of electronic orbitals, nuclear vibrations etc.
(ii) to predict whether the vibrations are IR & Raman active.
(iii) to correlate the orbitals of a reactant with the orbitals of a product in a thermal & photochemical reaction (woodward-Hoffmann orbital symmetry conservation rule) and thus predicts the stereochemical course of the reactions.

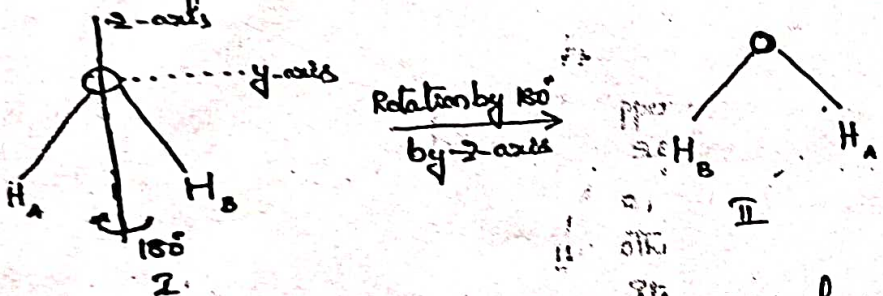
'Group' means a set of entities & elements related to each other by certain rules.

Symmetry elements and Symmetry operations:

Symmetry arises when the molecule possesses identical atoms in certain parts of it. These identical atoms are initially equivalent. In H_2O molecule the two hydrogen atoms are identical. Geometrical operations such as reflection, rotation, inversion etc can be carried out over a molecule and these operations do not alter the bond lengths & angles. All the operations that are being performed on the molecule cannot be called as symmetric operations.

Symmetry operation is the geometrical operation such as reflection, rotation, inversion etc. which leads to a configuration indistinguishable from the original configuration. It is necessary to know that the two configurations (before and after operation) are not exactly identical, but they look alike in all respects so that one is not able to say whether any change has been affected or not.

The above fact can be explained by taking water molecule as example



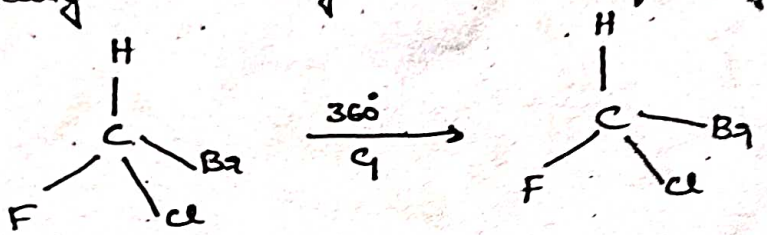
H_2O after rotation by 180° with respect to z-axis has a configuration (II) indistinguishable from the original configuration (I). I & II are certainly not identical. As a result of operation, two equivalent atoms have exchanged their positions. If the molecule is rotated by 90°, the new configuration does not match with the original one. Thus rotation by 90° is not a symmetry operation for H_2O.

The symmetry operations in turn generate the corresponding symmetry elements. Therefore an operation generates an element and these are related to each other. In other words one does not exist in the absence of the other.

A symmetry element is geometrical entity i.e. a point, a line or a plane on the molecule. The three geometrical entities a point, a line and a plane will give rise to five types of symmetry elements.

1. Identity Element (E):

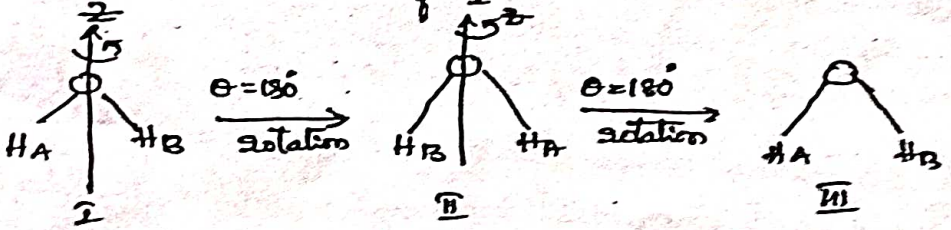
This element is obtained by an operation called 'identity element operation'. Identity operation can be visualised in two ways. Either (i) doing nothing on the molecule or (ii) rotating the molecule by 360°. Consider the following molecule



Every molecule has this element of symmetry. This is denoted by a special symbol E.

2. Rotational axis of Symmetry (C_n):

Consider the case of H_2O molecule.



Initially H_2O molecule is in configuration I, lying flat on the plane of the paper (YZ plane). Consider an axis (Z axis) passing through oxygen and bisecting the HOH angle and by means of the axis if the molecule is rotated through 180° then the configuration II results. Configuration II is equivalent to configuration I but not identical. If the molecule in configuration II is further rotated through Z-axis by 180° then it results in configuration III. Configuration III is identical to configuration I. Hence H_2O molecule can be rotated only once by 180° and the rotation through Z axis by another 180° results in original configuration. The symmetry operation i.e. rotation can be carried out on the molecule until a configuration identical with the original one is reached. The rotational axis C_n may be defined as follows.

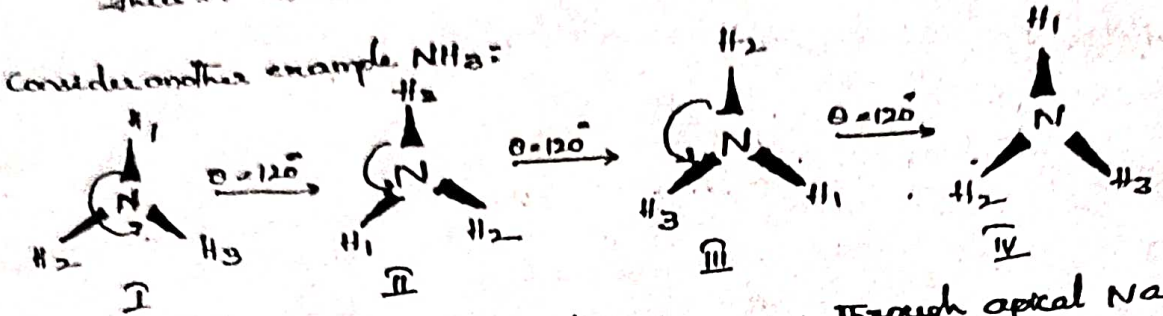
$$n = \frac{360^\circ}{\theta}$$

Where θ is the smallest angle by which one can rotate the object with respect to an axis and get an indistinguishable configuration.

n is the number of times the molecule can be rotated for another identical configuration and is called the order of the symmetry axis.

Then the C_n axis in H_2O molecule is C_2, since $n = 360/180 = 2$.

Consider another example NH_3:



The rotational axis considered in NH_3 passes through apical N atom and emerging through the centroid of the basal triangle of H atoms [$\because NH_3$ molecule is a trigonal pyramidal molecule]. Configuration IV is identical with I. Configurations II and III are equivalent to configuration I and the rotational axis in NH_3 molecule is C_3 [$\because n = \frac{360}{120} = 3$].

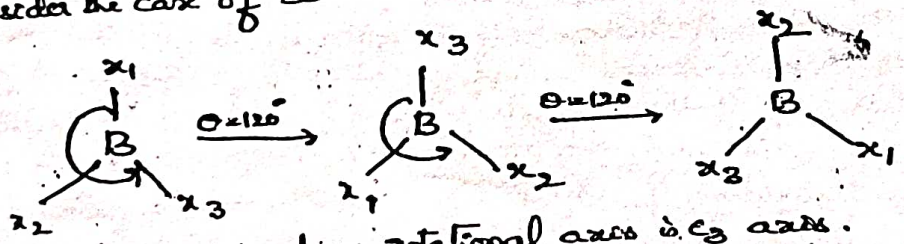
The above two examples contain only one type of C_n axis.

In certain molecules two types of rotational axes are possible.

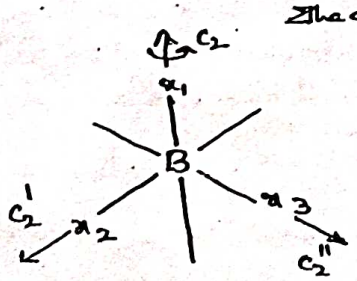
(i) Principal rotational axis, C_n (n = highest). This is also called highest fold rotational axis.

(ii) Simple or secondary rotational axes. These secondary axes may be often C_2 axes and the number of such axes present is always equal to n, the order of principal axis, C_n.

Consider the case of BX_3 trihalides.



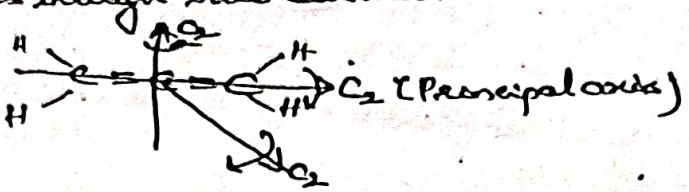
The above rotational axis is C_3 axis.



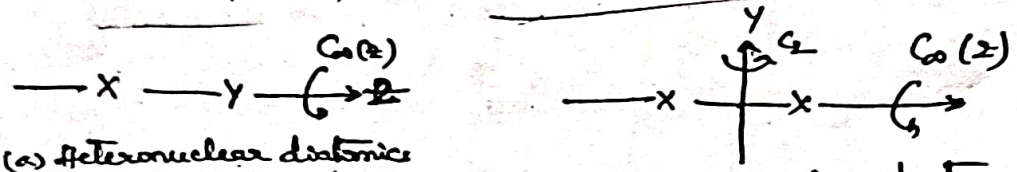
All the three axes are C_2 axis and these are perpendicular to C_3 axes (Principal axis). The three C_2 axes are called secondary or simple axes.

In certain molecules, all the rotational axes are of the same order. In such situation, the axis passing through the largest number of atoms must be taken as the z-axis. If one does not find such an axis, z is the one passing through a large number of bonds.

For example in allenes, three C_2 axes are possible, but the principal axis is one which passes through three carbons.



In linear molecule, the rotational axis is C_∞ axis

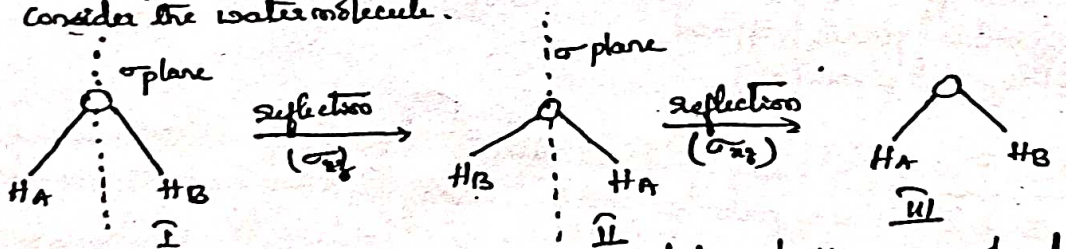


For heteronuclear molecules only C_∞ axis present. In case of Homonuclear linear molecules in addition to C_∞ axis, ∞C_2 & C_∞ are also possible.

Plane of Symmetry (σ):

This symmetry element is obtained by the reflection operation. A plane which bisects a molecule into two halves so that one is exactly the mirror image of the other is a reflection plane. For a planar molecule its own plane is a reflection plane.

Consider the water molecule.



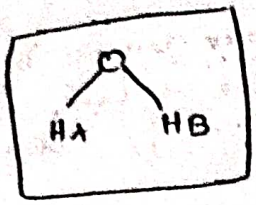
The plane considered above in fact bisects the H_2O molecule into two halves so that one half of the molecule is reflected into the other.

σ^1 (once reflection) $\longrightarrow$ II

σ^2 (twice reflection) $\longrightarrow$ III = I

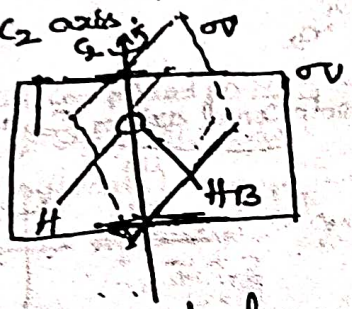
σ^3 (thrice reflection) $\longrightarrow$ II

σ^n (n = odd) $\longrightarrow$ II & (n = even) $\longrightarrow$ III = I



σ_{yz} plane.

In addition to the above plane, H_2O molecule has another reflection plane which is nothing but the molecular plane. One half of each atom is reflected into the other half in this plane and results in the same or identical reflected configuration. The above two planes considered for water molecule intersect along a line and the two of which forms a C_2 axis.



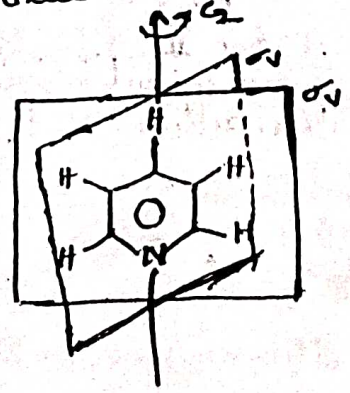
The planes which intersect along a line are generally called as simply vertical planes.

Classification of planes of symmetry:

As the regularity in the structure of the molecule increases, more no of planes are possible. The various planes can be classified into three types

(i) Vertical planes (σ_v)
(ii) Dihedral planes (σ_d) and
(iii) Horizontal planes (σ_h)

(i) Vertical Planes (σ_v): The two planes discussed in case of H_2O molecule are vertical planes. These two planes include C_2 axis. Therefore, a vertical plane contains the principal axis.

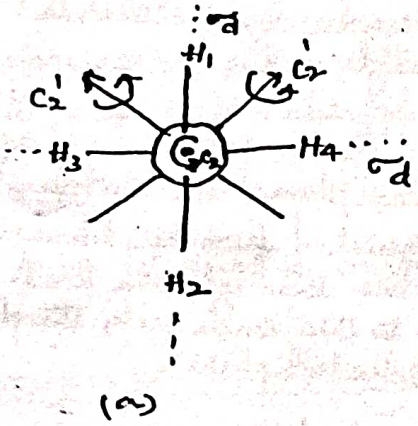


Even pyridine molecule contains two vertical planes, one vertical plane is the molecular plane and the second vertical plane bisects the molecule into exactly two halves.

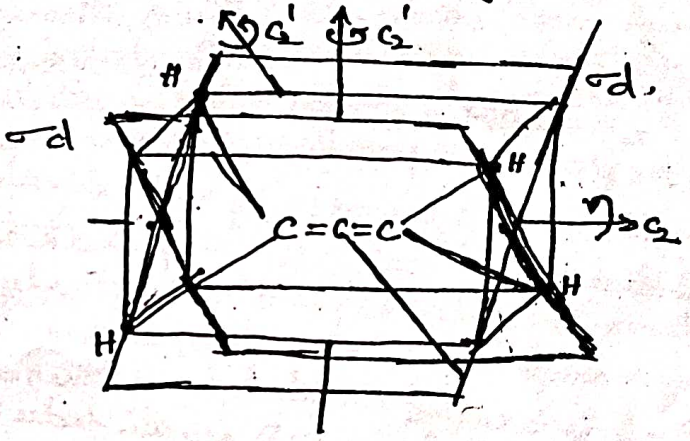
In case of NH_3 molecule, there are three planes which include the principal axis i.e. the three planes are vertical planes in NH_3 molecule. In NH_3 molecule there is no molecular plane. Each vertical plane includes nitrogen and one hydrogen and bisects the angle between two other hydrogens and nitrogen (HNH angle).

(iii) Dihedral plane (σ_d):

This is a special plane and is different from the vertical plane. Allene, methane and ethane (staggered) are the best examples of molecules that contain only this type of planes. A dihedral plane is one which bisects the angle subtended between two similar consecutive C_2 axes. A dihedral plane can also be defined as the plane which bisects the dihedral angle between σ_v planes.



(a)

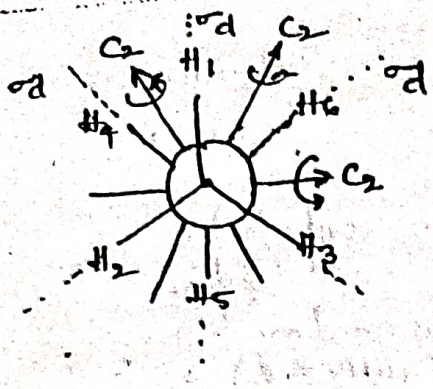


(b)

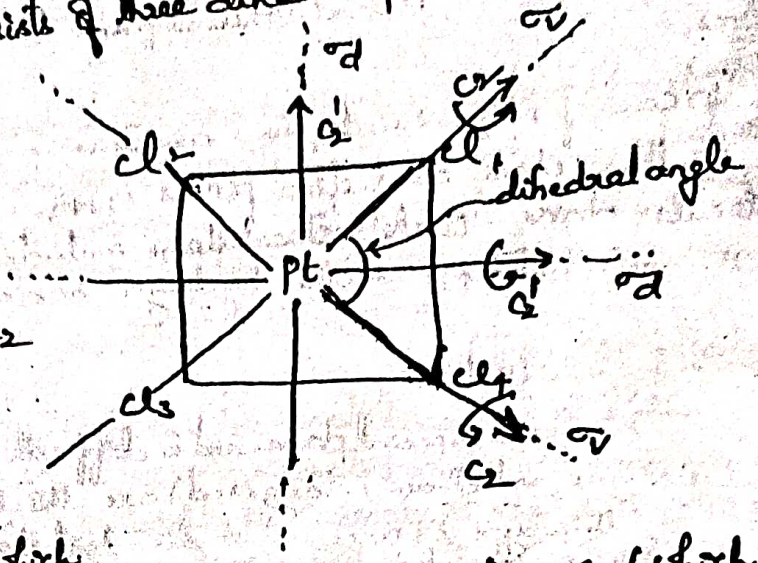
(a) Newman projection of allene molecule with end on C=C=C skeletal view. Each σ_d is coplanar with $C=C=CH_2$.

(b) Allene molecule inscribed in a rectangular box. σ_d planes cut through a pair of opposite edges.

The two C_2' axes are consecutive and similar C_2 axes and the angle between them is a dihedral angle. The two σ_d planes bisect the angle between two consecutive and similar C_2 axes.



The adjacent fogeree is staggered ethane which consists of three dihedral planes.



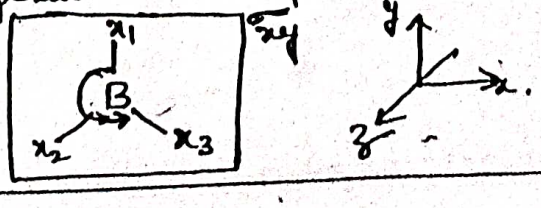
The principal axis of $[PtCl_4]^{-2}$ molecule is C_4 axis. In addition to C_4 axis the molecule contains $4C_2 + C_4$ axis. Out of the four C_2 axes, two C_2' axes are of one type (which pass through Pt and opposite edges) and the other two axes of other type C_2 (which pass through two chlorides and platinum). Through all these C_2 axes four planes are possible, which bisect the molecule into two equal halves. The angle subtended between two C_2 axes of two C_2' axes could be the dihedral angle. As a consequence, any of the planes that pass through either a pair of opposite vertices & a pair of opposite sides of square, may be the dihedral plane. All the four planes are not dihedral planes. Out of the four planes two are vertical planes and two are dihedral planes. The vertical planes can be clearly distinguished from the dihedral planes by a simple rule. The rule is; a plane that passes through the least number of atoms is called dihedral plane. Then according to this simple rule, the plane passing through a pair of opposite sides is the dihedral plane.

Similarly benzene molecule has $3\sigma_v$ and $3\sigma_d$ planes.

(iii) Horizontal plane (σ_h):

A plane perpendicular to the principal axis (C_n) is called a horizontal plane. BX_3 is a trigonal planar molecule containing a $C_3(z)$ axis. The $C_3(z)$ axis is perpendicular to the plane of the molecule. The molecular plane σ_{xy} is nothing but the σ_h plane for the molecule.

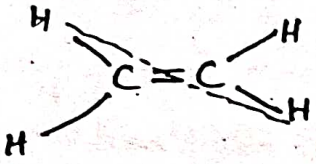
Similarly, the square planar molecule $PtCl_4^{-2}$ also has a horizontal plane (σ_h) perpendicular to the C_4 axis.

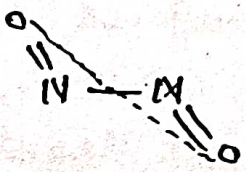


(4) Inversion centre or Centre of Symmetry (i):

This element is generated when all the atoms are inverted through the centre of the molecule. Inversion operation requires that all the atoms or groups lying outside the centre of gravity of the molecule must always occur in pairs and must be diagonally placed with each other.

Inversion centre can be defined as imaginary point in the centre of the molecule through which the reflection of each atom can be carried out, to result in the coincidence with an equivalent atom.





Centre of symmetry is an imaginary point in the molecule, if any atom is connected with the centre of symmetry and extended equally on the other side, it meets another equivalent atom.

$[Ni(CN)_4]^{-2}$ and $[Co(NH_3)_6]^{+3}$ have centre of symmetries.

-A tetrahedral molecule like CH_4 has no centre of symmetry.

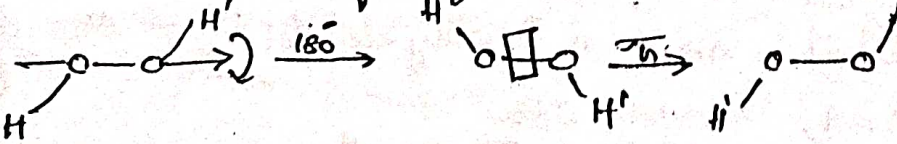
(5) Improper rotational axis (S_n):

This symmetry element is generated when two symmetry operations rotation and reflection are applied one after the other. If rotation of the molecule is carried out through $C_n(z)$ axis then reflection should be considered in a plane perpendicular to the z-axis.

$\therefore S_n(z) = C_n(z) \cdot \sigma_{xy}$

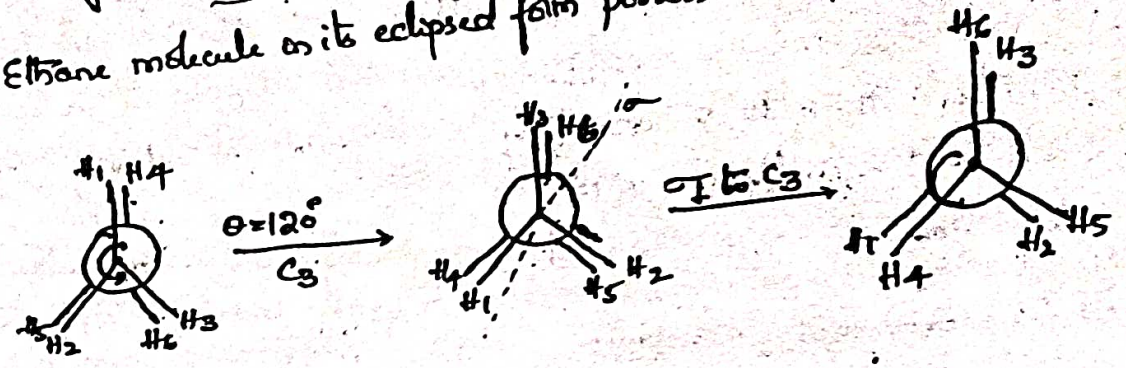
-For example, BH_3 molecule has C_3 axis which is perpendicular to its molecular plane (σ_h). This combination produces S_3 axis.

The transform of H_2O_2 molecule has S_2 axis.



only one improper rotation operation S_2^1 is possible.

Ethane molecule in its eclipsed form possess an improper rotational axis.



Group:

When all the symmetry elements of a molecule are placed in a set it becomes necessary to check whether the set of elements obey all the rules of a group.

A set of elements which obey all the four rules i.e closure, Associative, identity and inverse is called as a group.

(1) closure property: The product of any two elements and the square of any element must be the element of the same set

For example: If A and B are two elements of a set then AB=C, where if C is also an element of the same set, the set elements are said to obey the closure property.

(2) Associative property: All the symmetry elements must obey the associative law of multiplication

If A, B and C are the elements of a set, then

(AB)C = A(BC) is said to be the associative rule.

(3) There must be an element in the set which commutes with every other element and leaves it unchanged.

Such an element is known as Identity element.

Eg: AE = EA = A, BE = EB = B etc

Where A, B, E are the elements of the same set.

4. Inverse rule:

Each element has a reciprocal, which is also an element of the same set.

A reciprocal of element is one which when multiplied by the element will give identity as the product.

$$AR = RA = E$$

Where R is the inverse of A and E is the identity.

If the set of elements obey all these four rules then the set of symmetry elements can be called as a group.

In addition to the above four rules, if the set of elements in a group obey commutative property then the group of elements can be called as an Abelian group.

Commutative property: If A and B are the elements of group and if $AB = BA$ then A is commutative with B and B commutes with A.

For H_2O molecule, the symmetry elements are $E, C_2, \sigma_{vxz}, \sigma_{vyz}$

The set of all the four symmetry elements $\{E, C_2, \sigma_{vxz}, \sigma_{vyz}\}$ obey all the four rules of a group. Hence the set of four symmetry elements of H_2O is a group.

4) closure property:

For example: $C_2' \cdot \sigma_{vxz} = \sigma_{vyz}$; $\sigma_{vxz}\ \sigma_{vyz} = C_2'$

$C_2' \cdot \sigma_{vyz} = \sigma_{vxz}$; $C_2' \cdot C_2' = E$.

Similarly the set of elements obey associative property, E is the identity element in the set and every element has inverse in the same set. In addition to the above four rules, the group elements also commute with each other

$\sigma_{vxz} \cdot C_2' = \sigma_{yz}$

$C_2' \cdot \sigma_{xz} = \sigma_{yz}$.

Non abelian group: A group of elements which do not commute with each other is called as non-abelian group.

The group of symmetry elements of BF_3 molecule, $E, 2C_3, 3C_2, 2S_3, 3\sigma_v, \sigma_h$ is an example for non-abelian group.

After listing out all of all the possible symmetry elements of a molecule it becomes necessary to name the group and there should be a notation for the group elements of a molecule.

Two methods are in use, inorder to develop a nomenclature for the group of elements. one is Schoenflies nomenclature which is popularly used for molecular point groups. The second method is Hermann-Mauguin symbolism This method is used for naming the crystals and space groups.

Point group: A group of symmetry elements that leave a point unchanged, used in classifying a molecule is known as point group.

Rotation, reflection and inverse symmetry operations carried out in molecules do not alter the energy of the molecule. In all the simple symmetry operations the centre (centre of gravity) of the molecule is not altered as none of the operations involves a total translation movement of the molecule. The geometrical entities corresponding to these operations will pass through that centre of gravity point. What ever may be the operation carried over the molecule, one point remains unchanged. Hence these groups are classified as point groups.

Space group: A group of symmetry elements applying to a molecule lattice is known as space group.

operations such as 'screw rotations' and 'glid plane' reflections will be carried out in crystal structures. Screw rotation involves a rotation with respect to an axis and then translation in the direction of the same axis. Glide plane reflection is a reflection in a plane followed by a translation along a line in that plane. Now even a single point remains unchanged. There are particular to crystals and the group of such symmetry elements is called as space group.

Order of a group (h): The number of symmetry elements in a group is known as order of the group.

Notation of point groups:

There will be a descriptive symbol for every point group which signifies the presence of some defining combination of symmetry elements. There are two types of symbolisms in this regard.

(1) Schoenflies Notation:

(i) The alphabetical symbol is used to refer the axis of highest symmetry in the molecule.

C – stands for highest-fold proper axis

S – stands for highest-fold improper axis.

D – stands for highest-fold proper axis in combination with ne2 axes perpendicular to it.

T, O and I are used to represent the highly symmetric tetrahedral, octahedral (cube) and icosahedral groups.

(ii) The numerical subscript followed by any of the symbols indicate the order of the highest-order rotational axis.

(iii) Sometimes the numerical subscript along with an alphabetical subscript is used to notate the point group. The alphabetical subscript indicates the presence of certain type of planes of symmetry. Thus,

V is used for the presence of vertical planes (σ_v)
d is used for the presence of dihedral planes (σ_d) and
h is used for a plane perpendicular to the principal axis.

(iv) The subscript i alone is used when the molecule contains only i element along with identity (C_i)

(v) The subscript s alone is used when molecules contain only a plane of symmetry (σ), the point group is C_s.

(vi) The linear molecules are given the symbols $C_{\infty v}$ and $D_{\infty h}$.

Group generating elements:

In order to determine the point group of a molecule, it is necessary to have knowledge of the generators of the symmetry operations. In the entire list of symmetry elements, a small number of elements called a 'subset' will be very important to define the point group. The elements contained in this subset are called the 'group generating elements' of 'group generators'. This subset may contain one or more elements.

Point Group	Group Generating elements
	E.
C_1	σ
C_s	i
C_i	C_n'
C_n	C_n', σ_v
C_{nv}	C_n', σ_h
C_{nh}	$C_n', nC_2 \perp C_n$
D_n	$C_n', nC_2 \perp C_n, \sigma_d$
D_{nd}	$C_n', nC_2 \perp C_n, \sigma_h$
D_{nh}	S_n'
S_n (n=even)	C_∞, σ_v
$C_{\infty v}$	$C_\infty, \infty C_2 \perp C_\infty, \sigma_h$
$D_{\infty h}$	

Systematic classification of point groups:

In order to systematically assign the point group of a molecule, one should be in a position to know all the possible symmetry elements of the molecules. All the molecules can be broadly classified into three categories

(i) Molecules of low symmetry [MLS]
(ii) Molecules of high symmetry [MHS]
(iii) Molecules of special symmetry [MSS]

(i) Molecules of low symmetry [MLS]:

These are the molecules which do not contain C_n axis. Lack of C_n makes the molecule to be lack of many other symmetry elements.

(a) A molecule which has no rotational axis but has a plane of symmetry such molecule belongs to C_s point group.

(b) If the molecule has inversion centre (i) then molecule belongs to the symmetry point group C_i.

(c) If a molecule has none of the symmetry elements except E then the molecule belong to the point group C_1.

(ii) Molecules of high symmetry:

Those molecules which contain C_n and/or S_n axes are called as Molecules of high symmetry, where $n \geq 2$. This category is further divided into three types.

(a) S_n point group molecules:

This type of molecules are possible when n = even and S_n axes alone exists.

(b) C type point groups:

These molecules contain C_n (n = even or odd) axis with or without other elements.

C_n point groups ⟶ C_n axis alone.
C_{nv} point groups ⟶ C_n and n σ_v planes.
C_{nh} point groups ⟶ C_n and σ_h perpendicular to C_n.

(c) D type point groups:
These molecules contain C_n axes, $n\,C_2$ (perpendicular) to C_n with & without other elements.

D_n point groups: C_n and $nC_2 \perp C_n$ and no other symmetry elements.

D_{nd} point groups: C_n and nC_2's $\perp C_n$ and $n\sigma_d$ planes.

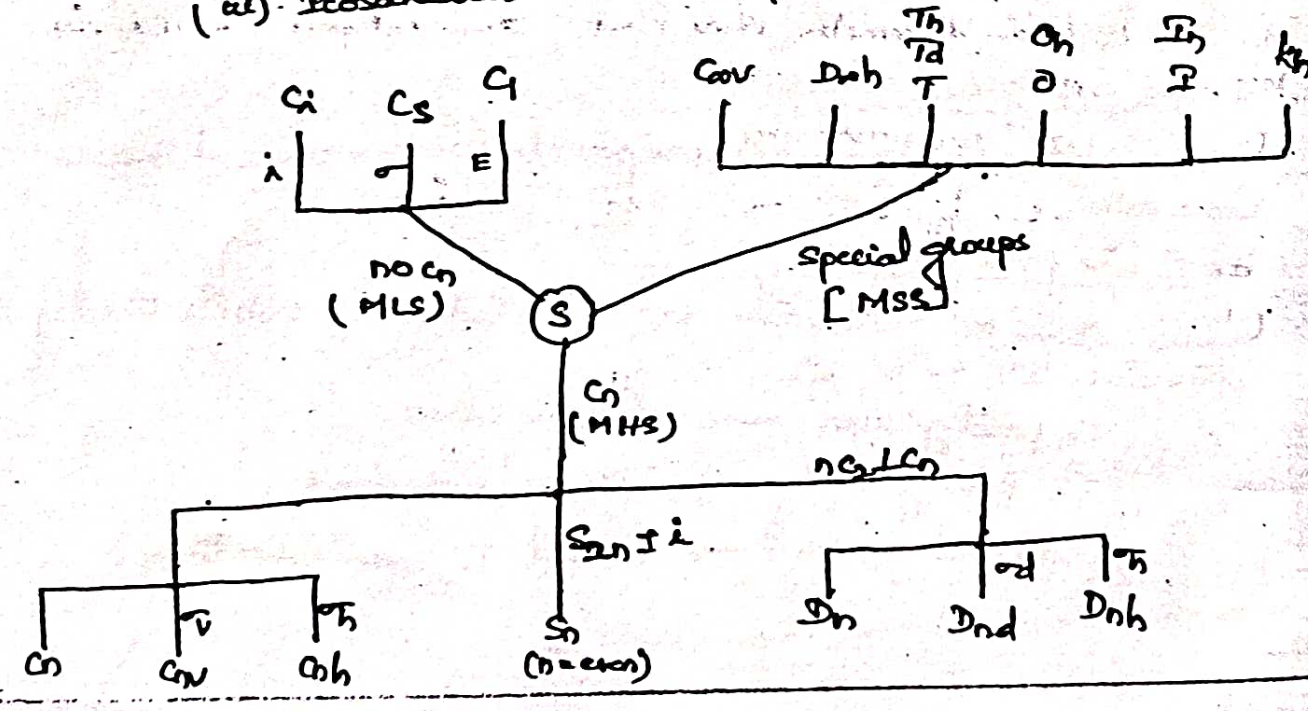
D_{nh} point groups: C_n and nC_2's $\perp C_n$ with σ_h plane.

(iii) Molecules of special symmetry [MSS]
This category is further divided into two types

(a) Molecules with infinite point groups: If the molecule is a linear molecule then it contains C_∞ axis. If the molecule has centre of symmetry (i) then the molecule will belong to the point group $D_{\infty h}$. If the molecules lacks centre of symmetry then the point group of the molecule will be $C_{\infty v}$.

(b) Molecules which contain multiple higher-fold C_n axes ($n \geq 3$):
This type of multiple higher fold axis is possible in tetrahedral, octahedral, Dodecahedral and Icosahedral molecules.

(i) Tetrahedral – multiple C_3 axis (T_d, T_h, T)
(ii) octahedral and Cubic – multiple C_4 axis (O_h, O)
(iii) Icosahedral – multiple C_5 axis (I_h, I)



Group Multiplication Table:

All the algebraic properties of group can be represented in the form of a table called 'Group Multiplication Table' [GMT]. These GMT's are nothing but 'Latin squares', in which an element occurs once, and only once in any row of column.

GMT is constructed by taking the possible symmetry elements for a molecule both in a row and a column. If E, A and B are the elements of a group then all the three elements are written in a row as well as in a column starting with E. E must always be the first element in both the row and column since it is a trivial element. The Latin square is constructed by taking product of these elements. The order of multiplication must be either a row-into-column or a column-into-row.

Consider the order of column-into-row to construct the table.

	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

	E	A	B
E			
A			
B			

Group multiplication table for C_{2v} point group:

H_2O molecule belongs to C_{2v} point group because the symmetry elements are E, $C_2(z)$, σ_{xz}, σ_{yz}.

C_{2v}	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

From the group multiplication table it is clear that C_{2v} point group is an abelian group.

Group Multiplication table for C_{3v}

C_{3v}	E	C_3^1	C_3^2	σ_v	σ_v^1	σ_v^{11}
E	E	C_3^1	C_3^2	σ_v	σ_v^1	σ_v^{11}
C_3^1	C_3^1	C_3^2	E	σ_v^{11}	σ_v	σ_v^1
C_3^2	C_3^2	E	C_3^1	σ_v^1	σ_v^{11}	σ_v
σ_v	σ_v	σ_v^1	σ_v^{11}	E	C_3^1	C_3^2
σ_v^1	σ_v^1	σ_v^{11}	σ_v	C_3^2	E	C_3^1
σ_v^{11}	σ_v^{11}	σ_v	σ_v^1	C_3^1	C_3^2	E

The C_{3v} point group is not an abelian group.

Very few point groups are abelian groups.

C_n, C_{nh}, C_{2v}, D_2, D_{2h} and S_n (n = even) are abelian groups.

All other groups are non-abelian groups.

In all abelian point groups each element is in a class by itself i.e. the number of classes is equal to the number of elements.

In non-abelian group, the number of classes is always less than the order of the group.

Sub group:

A group consists of several elements compiled together. A few elements from the group can obey all the conditions of a group, such a small group within a larger group can be called as subgroup. These sub groups are of two types.

(i) Trivial subgroup: A subgroup which contain only one element E and the order of the subgroup is one.

(ii) Non Trivial subgroup: These subgroups contain some other elements, in addition to E and the order of these groups begins with two.

If the order of the subgroup is g, and that of a full group, h. Then

$\frac{h}{g} = k$ where k is an integer. The order of subgroup (g) is always an integral divisor of the order of the full group (h).

Taking C_{3v} point group as an example.

$C_{3v} \longrightarrow E, C_3', C_3'', \sigma_v, \sigma_v', \sigma_v''$

The subgroups of this group can be written as

$C_1 \longrightarrow E \quad [g=1]$

$C_3 \longrightarrow E, C_3', C_3'' \quad [g=3]$

$C_s \longrightarrow E, \sigma_v \quad [g=2]$

$C_s' \longrightarrow E, \sigma_v' \quad [g=2]$

$C_s'' \longrightarrow E, \sigma_v'' \quad [g=2]$

There are five subgroups in C_{3v} group.

Classes:

A set of elements which are conjugate to one another is called a class of the group.

In order to rearrange elements into classes it is necessary to know a new operation called 'similarity transformation'.

If A and B are elements of a group and X is another element of the same group such that

$$X^{-1}AX = B.$$

X^{-1} inverse is the inverse of X. The product element B is called the similarity transform of A by X. When this relation is satisfied for A and B, then we can call A and B as conjugate elements.

The following are the important properties of the conjugate elements.

(i) Every element is conjugate with itself (self conjugation). For a particular element A, there exists always another element X in the group such that

$$X^{-1}AX = A.$$

(ii) If A is conjugate with B, then B is conjugate with A (mutual conjugation). The following relations explains the property.

$$X^{-1}AX = B.$$

B is similarity transformation of A by X. There must be some other element Y in the same group such that

$$Y^{-1}BY = A.$$

Where A is the similarity transform of B by Y. Then A and B are mutually conjugate.

(iii) If A is conjugate with B and C, then B and C are conjugate with each other. Associative Conjugation.

i.e. $X^{-1}AX = B$ and $Y^{-1}AY = C$ then

$$P^{-1}BP = C \text{ and } Q^{-1}CQ = B.$$

Consider the C_{3v} point group as an example.

$C_{3v} \rightarrow E, C_3^1, C_3^2, \sigma_v, \sigma_v^1, \sigma_v^{11}$

In order to know how many classes are there in the C_{3v} point group we have to work out similarity transformations with their elements.

σ_v, σ_v' and σ_v'' are three plane inverses and C_3' and C_3^2 are the inverse of each other.

E

$E\,E\,E = E$
$C_3^2\,E\,C_3' = E$
$C_3'\,E\,C_3^2 = E$
$\sigma_v\,E\,\sigma_v = E$
$\sigma_v'\,E\,\sigma_v' = E$
$\sigma_v''\,E\,\sigma_v'' = E$.

E is conjugate to itself and E is class of itself.

The similarity transforms of C_3' and C_3^2 can be worked out as below.

C_3'

$E\,C_3'\,E = C_3'$
$C_3^2\,C_3'\,C_3' = C_3'$
$C_3'\,C_3'\,C_3^2 = C_3'$
$\sigma_v\,C_3'\,\sigma_v = C_3^2$
$\sigma_v'\,C_3'\,\sigma_v' = C_3^2$
$\sigma_v''\,C_3'\,\sigma_v'' = C_3^2$

C_3^2

$E\,C_3^2\,E = C_3^2$
$C_3^2\,C_3^2\,C_3' = C_3^2$
$C_3'\,C_3^2\,C_3^2 = C_3^2$
$\sigma_v\,C_3^2\,\sigma_v = C_3'$
$\sigma_v'\,C_3^2\,\sigma_v' = C_3'$
$\sigma_v''\,C_3^2\,\sigma_v'' = C_3'$

From the above exercises it is clear that C_3' and C_3^2 are conjugate to each other, hence they can be in one class.

σ_v

$E\,\sigma_v\,E = \sigma_v$
$C_3^2\,\sigma_v\,C_3' = \sigma_v''$
$C_3'\,\sigma_v\,C_3^2 = \sigma_v'$
$\sigma_v\,\sigma_v\,\sigma_v = \sigma_v$
$\sigma_v'\,\sigma_v\,\sigma_v' = \sigma_v''$
$\sigma_v''\,\sigma_v\,\sigma_v'' = \sigma_v'$

σ_v'

$E\,\sigma_v'\,E = \sigma_v'$
$C_3^2\,\sigma_v'\,C_3' = \sigma_v$
$C_3'\,\sigma_v'\,C_3^2 = \sigma_v''$
$\sigma_v'\,\sigma_v'\,\sigma_v = \sigma_v''$
$\sigma_v'\,\sigma_v'\,\sigma_v' = \sigma_v'$
$\sigma_v''\,\sigma_v'\,\sigma_v'' = \sigma_v$

σ_v''

$E\,\sigma_v''\,E = \sigma_v''$
$C_3^2\,\sigma_v''\,C_3^2 = \sigma_v'$
$C_3'\,\sigma_v''\,C_3^2 = \sigma_v$
$\sigma_v\,\sigma_v''\,\sigma_v = \sigma_v'$
$\sigma_v'\,\sigma_v''\,\sigma_v' = \sigma_v$
$\sigma_v''\,\sigma_v'\,\sigma_v'' = \sigma_v''$

From the above transformations it is clear that σ_v and σ_v' and σ_v'' are conjugate to each other. Hence they belong to one class.

Therefore in C_{3v} point group there are three classes E, $2C_3$, $3\sigma_v$

Matrix representation of symmetry operations and point groups:

The various symmetry operations of molecules are better understood by means of diagrams. This procedure is no doubt useful, but if the configurations are not most carefully examined one may be led to certain doubtful conclusion. The safest and most accurate method is to find out the effect of each operation on the co-ordinates and express the change in the form of a matrix. This matrix referred to as the transformation matrix. and this matrix expresses quantitatively the net effect of each operation.

Matrix notations for all the symmetry elements can be worked out as follows.

(i) E-matrix.

Consider the transformation of a general point defined by x_1, y_1, z_1 co-ordinates

$$[x_1, y_1, z_1] \xrightarrow[\text{operation}]{\text{Identity}} [x_2, y_2, z_2]$$

Initial (Before operation) — Final (After operation)

In case of identity operation the final co-ordinates are equal to initial co-ordinates.

i.e. $x_2 = x_1$, $y_2 = y_1$ and $z_2 = z_1$

The above conditions can be written as

$$x_2 = 1 \cdot x_1 + 0 \cdot y_1 + 0 z_1$$

$$y_2 = 0 \cdot x_1 + 1 \cdot y_1 + 0 z_1$$

$$z_2 = 0 \cdot x_1 + 0 \cdot y_1 + 1 \cdot z_1$$

The above three equations can be represented in the form of matrix equation.

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

The matrix of coefficients is a unit matrix. Hence E matrix has the form $E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

(ii) i matrix.

$[x_1, y_1, z_1]$ i inversion $[x_2, y_2, z_2]$

The changes associated with inversion can be represented as

$$x_2 = -x_1, \quad y_2 = -y_1, \quad z_2 = -z_1$$

on expanding the above, we get.

$$x_2 = -1 \cdot x_1 + 0 \cdot y_1 + 0 \cdot z_1$$
$$y_2 = 0 \cdot x_1 + (-1) \cdot y_1 + 0 \cdot z_1$$
$$z_2 = 0 \cdot x_1 + 0 \cdot y_1 + (-1) \cdot z_1$$

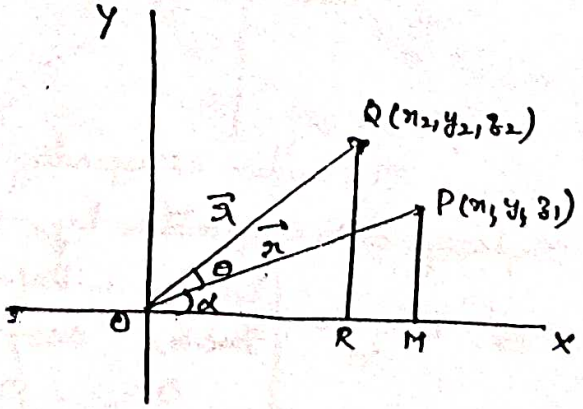
The above equations can be represented in the form of a matrix

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

∴ The i matrix form is $\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

(iii) Rotations:

Let us consider the rotation of a vector $\vec{x}$ by θ. This rotation is done with respect to the z-axis and hence the z coordinates of the points do not change. The point $P(x_1, y_1, z_1)$ moves to $Q(x_2, y_2, z_2)$ and $z_1 = z_2$. The rotation is in anticlockwise direction.



From the figure

$OM = x_1 = r\cos\alpha$

$PM = y_1 = r\sin\alpha$

$OR = x_2 = r\cos(\theta+\alpha) = r\cdot\cos(\theta+\alpha)$

$QR = y_2 = r\sin(\theta+\alpha) = r\sin(\theta+\alpha)$

$\therefore x_2 = r\cos\theta\cos\alpha - r\sin\theta\sin\alpha$

$\Rightarrow x_2 = x_1\cos\theta - y_1\sin\theta$

$y_2 = r\cos\alpha\sin\theta + r\sin\alpha\cos\theta$

$\Rightarrow y_2 = x_1\sin\theta + y_1\cos\theta$

$z_2 = z_1$

We can express the relationship between (x_2, y_2, z_2) and (x_1, y_1, z_1) as

$x_2 = x_1\cos\theta - y_1\sin\theta + 0z_1$

$y_2 = x_1\sin\theta + y_1\cos\theta + 0\cdot z_1$

$z_2 = 0\cdot x_1 + 0\cdot y_1 + 1\cdot z_1$

The above equations in matrix form can be represented as follows

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$

The matrix representation for $C_n(z)$ axis is $\begin{bmatrix} \cos\theta & -\sin\theta & \\ \sin\theta & \cos\theta & \\ 0 & 0 & \end{bmatrix}$

The matrix corresponding to clockwise rotation is obtained by simply replacing θ in $C_n(z)$ matrix by $-\theta$.

ex. $C_n(z) = \begin{bmatrix} \cos(-\theta) & -\sin(-\theta) & 0 \\ \sin(-\theta) & \cos(-\theta) & 0 \\ 0 & 0 & 1 \end{bmatrix} \Rightarrow C_n(z) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$\because \sin(-\theta) = -\sin\theta$ and $\cos(-\theta) = \cos\theta$.

If the rotational axis is y & x then the corresponding matrices are

$$C_{n(x)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix} \text{ & } C_{n(y)} = \begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}$$

$C_{2(z)}$ axis is obtained by rotation through 180°.

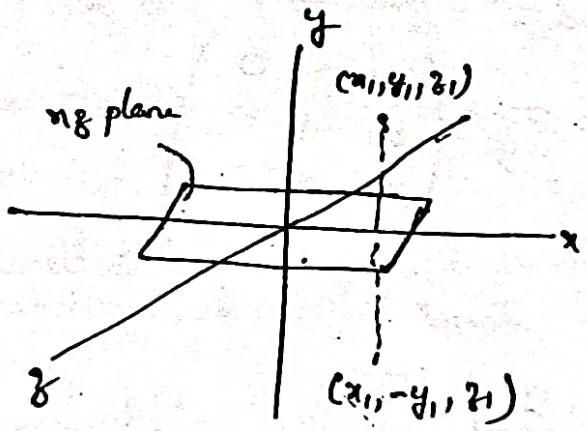
$$C_n = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \Rightarrow C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\theta = 120°$

$$C_3' = \begin{bmatrix} -1/2 & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(iv) Reflection:

Let us reflect a vector $\vec{x}$ w.r.t to xz plane. The original coordinates (x_1, y_1, z_1) transform to (x_2, y_2, z_2). Only the y-coordinate changes.



$\therefore x_2 = 1 \cdot x_1 + 0 y_1 + 0 z_1$

$y_2 = 0 x_1 - 1 y_1 + 0 \cdot z_1$

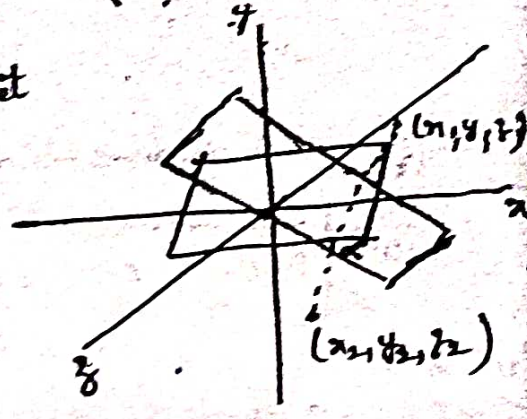
$z_2 = 0 \cdot x_1 + 0 \cdot y_1 + 1 \cdot z_1$

$$\text{or } \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}$$

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

Similarly $\sigma_{xy} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$, $\sigma_{yz} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

Let us consider the reflection with respect to a plane inclined to xz plane with α angle. Such an inclined plane can be represented by the matrix.



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

In C_{3v} molecule there are three σ_v (i.e. σ_v, σ_v' and σ_v'')

If σ_v is considered as xz plane then σ_v' is inclined at an angle $\alpha = 60°$ and σ_v'' is inclined at an angle $\alpha = 120°$

$$\therefore \sigma_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma_v' = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \sigma_v'' = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(v) S_n rotation:

If the rotational axis, C_n is taken as z-axis, then by definition

$$S_n(z) = C_n(z) \cdot \sigma_{xy}$$

$C_n(z)$ and σ_{xy} are perpendicular to each other

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

Similarly $S_n(x)$ and $S_n(y)$ can be represented as follows.

$$S_n(x) = C_n(x) \cdot \sigma_{yz}$$

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

$$S_n(y) = C_n(y) \cdot \sigma_{xy}$$

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

Matrix representation of point groups

A set of symmetry elements constitute a point group if the four rules are satisfied. The matrices representing each of these elements also should satisfy these rules.

Consider H_2O molecule, which belongs to C_{2v} point group

$C_{2v} \longrightarrow E, C_2, \sigma_{xz}, \sigma_{yz}$

$$E \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2 \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{xz} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{yz} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

This is the matrix representation of C_{3v} group. All these four matrices collectively form a set called 'representation'.

$C_{3v} \rightarrow E, C_3^1, C_3^2, \sigma_v, \sigma_v^I, \sigma_v^{II}$

$$E \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^1 \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^2 \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \sigma_v^I \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v^{II} \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Character of a matrix:

It is a number represented by the Greek symbol χ (chi). The sum of the diagonal elements of a square matrix is known as character.

$$[A] = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

$$\chi(A) = a_{11} + a_{22} + a_{33}.$$

Character of a representation:

A representation is nothing but a set of matrices corresponding to all the symmetry elements of the group. Then the character of a representation is the set of characters of all matrices. The representation may be RR or IR.

If a group is represented by $E, A, B, C \ldots$ matrices, then a row of their characters $\chi(E), \chi(A), \chi(B), \chi(C) \ldots$ is called the character of a representation.

Reducible and Irreducible representations:

Symmetry operations i.e. rotation, reflection and inversion, can be expressed in form of matrices. These matrices obey the group multiplication table. Therefore, a symmetry group can be represented by a set of matrices. Such a set of quantities or numbers or matrices obeying the group multiplication table of a point group is called a representation of the group.

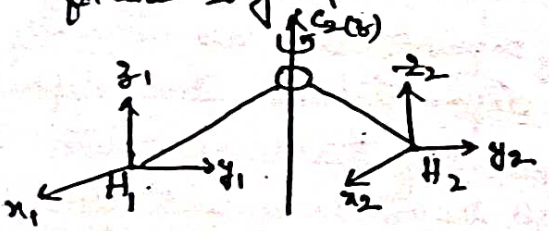
It is possible to make use of atomic orbitals & vectors for all molecules of C_{2v} group and generate an infinite number of representations, i.e. A given point can be represented by unlimited number of different matrices. Let us consider few examples.

(i) In a C_{2v} point group, the cartesian system (x, y, z) can be used to obtain a full representation for this group.

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_2(z) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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

(ii) In a second method, it is possible to develop a six dimensional representation for the C_{2v} group.



By rotation through C_2 axis the change in co-ordinates can be represented as follows.

$$\begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{bmatrix} \xrightarrow{C_2(z)} \begin{bmatrix} -x_2 \\ -y_2 \\ -z_2 \\ -x_1 \\ -y_1 \\ z_1 \end{bmatrix}$$

The above transformation can be represented in form of a matrix.

$C_2(z)$

$$\left[\begin{array}{ccc|ccc} 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ \hline -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{array}\right]$$

Similarly the other matrices can be worked out as

E

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right]$$

σ_{xz}

$$\left[\begin{array}{ccc|ccc} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ \hline 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{array}\right]$$

σ_{yz}

$$\left[\begin{array}{ccc|ccc} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right]$$

All these matrices are of 6×6 dimension. If coordinates are assumed for all the three atoms in H_2O molecule then a 9×9 dimensional representation would be obtained. This how we can say that how infinite representations are possible for a molecule.

All these indefinite number of representations are actually appropriate combinations of some definite representations. These definite representations are basic and will not contain any other representation. They are called irreducible representations. All the other representations obtained by combining these basic IRs are called Reducible representations. Reducible representations are linear combinations of irreducible representations.

Reducible representations are the matrices of high dimension. The dimension of which can be reduced by diagonalisation and block factoring.

The diagonalisation of a matrix can be achieved by making use of similarity transformation. It is possible to find out a 'similarity transformation matrix' which would transform all the matrices of a group representation into 'diagonalised matrices' with identical blocks of sub matrices along the diagonals of all the matrices. Let $A, B, C \ldots E$ be the matrix representation of a group and P be the similarity transformation matrix, so that

$$P^{-1}EP = E'$$
$$P^{-1}AP = A'$$
$$P^{-1}BP = B'$$
$$P^{-1}CP = C'$$
$$\ldots\ldots$$
$$\ldots\ldots$$

As $A, B, C \ldots E$ represent the symmetry group, the new set of diagonalised matrices, $A', B', C' \ldots E'$ also represent the full group. The diagonalised matrices can be represented as.

$$[E] = \begin{bmatrix} E_1' & & \\ & E_2' & \\ & & E_3' \\ & & & \ddots \end{bmatrix} \qquad [A'] = \begin{bmatrix} A_1' & & \\ & A_2' & \\ & & A_3' \\ & & & \ddots \end{bmatrix}$$

$$[B'] = \begin{bmatrix} B_1' & & \\ & B_2' & \\ & & B_3' \\ & & & \ddots \end{bmatrix} \qquad [C'] = \begin{bmatrix} C_1' & & \\ & C_2' & \\ & & C_3' \\ & & & \ddots \end{bmatrix}$$

The matrices $A', B', C' \ldots E'$ are identically block-factored along the diagonal.

If $[A'][B'] = [C']$ then

$$[A_1'][B_1'] = [C_1']$$
$$[A_2'][B_2'] = [C_2']$$
$$\cdots\cdots\cdots$$
$$\cdots\cdots\cdots$$

The sub matrices $A_1', B_1' C_1' \ldots E_1'$ will have identical dimensions and so also be $A_2', B_2', C_2' \ldots E_2'$. A full representation of the group can now be written as follows.

$E_1', A_1', B_1', C_1' \ldots$
$E_2', A_2', B_2', C_2' \ldots$
$E_3', A_3', B_3', C_3' \ldots$
$\cdots\cdots\cdots$
$\cdots\cdots\cdots$

Each of the above row of sub-matrices is a representation by itself. If it is not possible further to reduce any of these rows of matrices by any similarity transformation matrix, then each of these rows is said to be an irreducible representation. An IR can be one, two, three, four & five dimensional and this dimensionality corresponds to the dimensionality of the sub matrices it comprises of.

$E, A, B, C \ldots$ & its diagonalised matrices $E', A', B', C' \ldots$ are called Reducible representation (RR). There is no limit to the dimensionality of these RRs.

Great Orthogonality Theorem and Properties of Irreducible Representations:

The mathematical statement of the theorem is as follows

$$\sum_R [T_i(R)_{mn}][T_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$$

This theorem is concerned with the elements of the matrices which constitute the irreducible representations of a group. The i and j are two irreducible representations of a point group, l_i and l_j are dimensions of the irreducible representations, h is order of the group. R denotes a particular symmetry operation in the group. $T_i(R)_{mn}$ is an element in the m^{th} row and n^{th} column of a matrix in the i th irreducible representation. The complex conjugate of the element in the m'^{th} row and n'^{th} column of a matrix in the j th irreducible representation is denoted by $[T_j(R)_{m'n'}]^*$. The δ_{ij}, $\delta_{mm'}$ and $\delta_{nn'}$ denote the Kronecker delta symbols. The kronecker delta symbol δ_{ij} has the meaning $\delta_{ij}=0$ for $i \neq j$ and $\delta_{ij}=1$ for $i=j$. The mathetical statement implies that each element in a matrix is normalised and is orthogonal to other elements in the same matrix and elements of corresponding matrices of different irreducible representations.

The above theorem covers three cases.

case(i) If $i \neq j$ the $\sum_R [T_i(R)_{mn}][T_j(R)_{m'n'}] = 0$.

i.e. Elements of corresponding matrices of different irreducible representations are orthogonal.

case(ii) If $m \neq m'$ and/or $n \neq n'$ then $\sum_R [T_i(R)_{mn}][T_j(R)_{m'n'}] = 0$.

i.e. elements of different sets of matrices of the same irreducible representations are orthogonal.

case(iii) If $i=j$, $m=m'$ and $n=n'$ then $\sum_R [T_i(R)_{mn}][T_j(R)_{mn}] = \frac{h}{l_i}$

i.e. $\delta_{ij} = \delta_{mm'} = \delta_{nn'} = 1$.

By making use of above three cases, five important conclusions of five corollaries can be derived. These conclusion give five properties about irreducible representations of a group and their characters. A knowledge of the properties of irreducible representations is essential to construct the character table of a point group.

1. The number of irreducible representations in a group is equal to the number of classes in the group.

2. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group.

$$\sum_{i=1}^{k} l_i^2 = h.$$

$$\text{i.e. } l_1^2 + l_2^2 + l_3^2 + l_4^2 + \ldots = h.$$

3. The sum of the squares of the characters of identity operation in the irreducible representations is equal to the order of the group.

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

Since the dimension of an irreducible representation is equal to the character of its identity operation $\chi(E)$.

4. The characters of symmetry operations in two different irreducible represent. satisfy the relation.

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

When i is not equal to j the above equation becomes.

$$\sum_{p=1}^{k} g_p \chi_i(R_p) \chi_j(R_p) = 0.$$

When $i = j$ then equation (1) becomes.

$$\sum_{p=1}^{k} g_p [\chi_i(R_p)]^2 = h$$

g_p in these equations refers to the number of symmetry operations in p^{th} class. R_p is the symmetry operation in the p^{th} class. $\chi_i(R_p)$ and $\chi_j(R_p)$ are the characters of the matrix for the operation R_p in the representations i and j.

5. The characters of all matrices belonging to the operations in the same class are identical.

Construction of character tables:

With the knowledge of classes, characters and representations it is possible to generate a very useful and ultimate tool called 'character table'. These character table contain tremendous amount of information pertaining to the point group it corresponds to. Let us consider the problem of constructing the character table for a given point group. This table contain the characters under each class for each of the irreducible representations.

For example consider C_{2v} point group:

Character table for C_{2v} Point group:

$C_{2v} \rightarrow E, C_2(z), \sigma_{xz}, \sigma_{yz}$

(i) Number of Irreducible representations (IRs) in a group:

As there are four classes of operations, there will be four IRs in C_{2v} character table according to the first corollary of orthogonality theorem.

Let the IRs be $\Gamma_1, \Gamma_2, \Gamma_3$ and Γ_4

(ii) Dimensionality of IRs

Let the dimension of $\Gamma_1, \Gamma_2, \Gamma_3$ and Γ_4 be l_1, l_2, l_3 and l_4 respectively.

Then according to the second property of IRs

$$l_1^2 + l_2^2 + l_3^2 + l_4^2 = 4$$

By trial and error method, we can determine the dimensions of the IRs

Let $l_1 = l_2 = l_3 = l_4 = 1$.

Thus all the IRs of C_{2v} group are one dimensional.

(iii) Character set of each IR:

As All the IRs of C_{2v} point group are one dimensional. The character under E class of all these IRs is equal to the dimension of IRs

$$\chi_i(E) = l_i \text{ if } \sum_k \chi_i^2(E) = h$$

is	E	C_2	σ_{xz}	σ_{yz}
Γ_1	1			
Γ_2	1			
Γ_3	1			
Γ_4	1			

(b) The sum of the squares of the characters of an irreducible representation is equal to the order of the group. So, for one of the irreducible representations [Γ_i] all the characters must be equal to 1.

i.e.	E	C_2	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1

(iv) Orthogonality of IR's:

According to this rule.

$$\sum_R g_p \chi_i(R_p)\chi_j(R_p) = 0. \quad \text{when } i \neq j$$

The sum of the products of the characters under two IRs, Γ_1 and Γ_2 is zero.

$$\Gamma_1\Gamma_2 : g(E)\chi_1(E)\chi_2(E) + g(C_2(z))\chi_1(C_2)\chi_2(C_2) + g(\sigma_{xz})\chi_1(\sigma_{xz})\chi_2(\sigma_{xz}) + g(\sigma_{yz})\chi_1(\sigma_{yz})\chi_2(\sigma_{yz}) = 0.$$

The order of any class i.e. $g(R)$ is one, the above condition is satisfied with two +1 and two −1 character for Γ_2 IR. $\chi_2(E) = +1$ always, therefore of the remaining three characters of Γ_2 i.e. $\chi_2(C_2(z))$, $\chi_2(\sigma_{xz})$, $\chi_2(\sigma_{yz})$ two should have a character of −1.

Let the characters for second IR Γ_2 be 1 1 −1 −1

i.e.	E	C_2	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1	1	−1	−1
Γ_3	1			
Γ_4	1			

Similarly by making use of orthogonality condition it is possible to determine the characters Γ_3 and Γ_4 IR's

i.e.	E	C_2	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1	1	−1	−1
Γ_3	1	−1	1	−1
Γ_4	1	−1	−1	1

The IV region of character table represents cartesian co-ordinates of rotation axis corresponding to the IR. To construct this region consider a vector along z-axis. The change in the vector during various symmetry operations of C_{2v} group are noted as follows.

vector	E	C_2	σ_{xz}	σ_{yz}	Symbol
z	1	1	1	1	A_1
y	1	-1	-1	1	B_2
x	1	-1	1	-1	B_1

During the symmetry, the z vector has character similar to A_1. Hence the z vector is placed against to A_1 IR in the character table. Similar operation on x and y show that they belong to IRs B_1 and B_2 respectively.

Similar assignment can be rotation axes R_x, R_y and R_z

The VI region of character table contains binary products and squares of the co-ordinates (vectors). The construction of this region can be done by squaring the characters of vectors and by direct product of characters of vectors.

For example characters of x^2 are

	E	C_2	σ_{xz}	σ_{yz}
	1×1	-1×-1	1×1	-1×-1
x^2 =	1	1	1	1

These characters are similar to that of IR A_1. Similarly y^2 and z^2 also belong to A_1 IR.

Direct product is obtained by multiplying the characters of the two vectors.

	E	C_2	σ_{xz}	σ_{yz}	Symbol
XY	1·1=1	1·-1=-1	1·-1=-1	-1·1=-1	A_2
XZ	1·1=1	1·-1=-1	1·1=1	-1·1=-1	B_1
YZ	1·1=1	1·-1=-1	1·-1=-1	1·1=1	B_2

Mulliken Symbolism rules for IRs

1. General: The one dimensional IRs are represented by A & B, whereas two, three, four and five dimensional IRs are given E, T, G and H labels respectively.

2. One dimensional representations

The rules for the symbolism of one dimensional IRs can be given as follows. When the representation is said to be symmetric, it means the character under the class of operations is +1, whereas unsymmetric means the character is −1. Thus,

$\chi(R) = +1$ symmetric
$\chi(R) = -1$ unsymmetric.

(i) Labels of one-dimensional IRs:

Those IRs which are symmetric with respect to the principal axis (C_n) are designated by A, and those which are unsymmetric by B etc.

$\chi(C_n) = +1$ for A.
$\chi(C_n) = -1$ for B.

(ii) Subscript rule:

Two types of subscripts are in use

(a) Numerical subscripts:

The representations which are symmetric with respect to second axis (C_2) are given the subscript 1, and for those which are unsymmetric are given the subscript 2.

$\chi(C_2) = +1$ for subscript 1.
$\chi(C_2) = -1$ for subscript 2.

In the absence of C_2 axis, the subscript rule must be checked against the presence of simple plane of symmetry (σ_v). Thus

$\chi(\sigma_v) = +1$ for subscript 1
$\chi(\sigma_v) = -1$ for subscript 2

(b) Alphabetical subscript:

The representations which are symmetric with respect i are given subscript g and for those which are unsymmetric are given u subscript.

$\chi(i) = +1$ for subscript g (gerade)

$\chi(i) = -1$ for subscript u (ungerade)

(iii) Superscipt rule:

The representations which are symmetric with respect to σ_h are given the superscript ' (single prime), and for those which are unsymmetric are given " (double prime)

$\chi(\sigma_h) = +1$ for single prime '

$\chi(\sigma_h) = -1$ for double prime "

Structure of character table:

The character table has the following format and structure.

I Point group	III ← classes →		
II ↑ IRs ↓	IV Array of character	V Linear and Rotational functions.	VI Binomial and other polynomial functions

The character table consists of six regions. The regions I, II III and IV are elaborately dealt.

Region-I: In this region the Schoenflies notation of the point group is enclosed.

Region-II: This area describes the nature and number of IRs required for a particular point group. Mulliken symbols for IRs are enclosed in this space.

Region-III : All the symmetry elements grouped into classes have been placed here.

Region IV : This part of the table contains the characters for the irreducible various symmetry operations. This region is very much useful for deducing the structural and spectral properties of molecules.

Region V : This area includes linear and rotational functions. These functions are useful in deducing the translational and rotational degrees of freedom. The p-orbitals are depicted along the three co-ordinate axes so that a symmetry operation has the same effect on the p-orbitals as it has on the co-ordinate axes.

Region VI : This part of character table lists square and binomial product of x, y & z coordinates. These functions represent both the polarizability parameters and d-atomic orbitals.

Application of group theory in IR and Raman Spectroscopy

IR spectroscopy:

The interaction of matter with IR radiations induce vibrations in the molecules. Vibrational motion is the displacement of atoms from their mean positions. The molecules will undergo transitions between vibrational levels. The vibrational levels are quantised and each level possess a specific amount of energy. Depending on the number of atoms in a molecule, a certain number of modes of vibrations are possible for a molecules.

Vibrational motion of a molecule is due to displacement of the constituent atoms in certain directions. For a molecule consisting of N atoms (each atom has three degrees of freedom along x, y and z axes) there can be a total of 3N fundamental movements of 3N degrees of above freedom. The 3N fundamental movements include translations, rotations and vibrations.

When all the atoms are simultaneous displaced in the direction of x it is referred to as translation motion along x. Similarly translations along y and z axes are also possible. A total of 3 translational degrees of freedom are possible.

In case of rotations, if a molecule is non-linear then three 3 rotational degrees of freedom are possible. If a molecule is linear ($I_1=0, I_2=I_3$) then only 2 rotational degrees of freedom are possible.

In total 6 & 5 translational and rotational degrees of freedom are possible for a molecule. Therefore the number of vibrational degrees of freedom of the number of modes of vibrations are 3N-6 for non-linear molecule and 3N-5 for linear molecules.

These (3N-6) & (3N-5) modes of vibrations include both stretching and bending modes. If N atom molecule is non cyclic then it contains (N-1) bonds and hence (N-1) stretching modes and the remaining are bending modes. All these modes of vibrations may not IR active. only those modes of vibrations which shows dipole moment change exists are going to be IR active.

For example; In H_2O molecule, which is a bent molecule, (3x3-6) modes of vibrations are possible i.e. 3 modes of vibrations. These three modes include two stretching and one bending.

It is possible to predict the possible modes of vibrations using $(3N-6)$ & $(3N-5)$ formula for simple molecules. It is not so easy in case bigger molecules. In such cases Group theory is helpful in solving this problem.

In order to prove how useful is group theory in predicting the no possible modes of vibrations, let us consider the simple case of H_2O molecule. The molecule belongs to C_{2v} point group. This group theoretical calculation involves the use of standard reduction formula.

Standard reduction formula is

$$n(\Gamma_i) = \frac{1}{h} \sum_R g(R)\, \chi_{IR}(R)\, \chi_{RR}(R)$$

$n(\Gamma_i)$ is the frequency of occurrence of ith Irreducible representation Γ_i

h is the order of the point group.

$g(R)$ is the order of the class under R operation

$\chi_{IR}(R)$ is the character of the Irreducible representation Γ_i in the class.

$\chi_{RR}(R)$ is the character of reducible representation in that class

This reduction formula is useful only to finite groups.

In H_2O molecule, all the three atoms have three degrees of freedom for each along x, y and z axis. The matrix representation is going to be of 9x9 dimension and the character of such representation can be obtained by finding out the total number of atoms that remain unshifted on performing the symmetry operation and the contribution to the total character by each of the unshifted atoms on performing the operation over the molecule.

To determine the number of unshifted atoms, the symmetry operations are performed over the molecule and the no of atoms remaining unchanged is noted.

	E	C_2	σ_{xz}	σ_{yz}
No of unshifted atoms	3	1	1	3
Contribution to total character by each atom (From matrix of corresponding element)	3	-1	1	1
Total character of χ_{red} of Γ_{cart}	9	-1	1	3

C_{2v} character table is

C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
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, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

With the help of C_{2v} character table and by applying standard reduction formula, the combination of irreducible representations can be determined as follows.

$$n(A_1) = \frac{1}{4}[1\cdot1\cdot9 + 1\cdot(-1)\cdot1 + 1\cdot1\cdot1 + 1\cdot3\cdot1] = 3 \quad \text{i.e. } 3A_1$$

$$n(A_2) = \frac{1}{4}[1\cdot1\cdot9 + 1\cdot(-1)\cdot1 + 1(1)(-1) + 1\cdot3\cdot(-1)] = 1 \quad \text{i.e. } 1A_2$$

$$n(B_1) = \frac{1}{4}[1\cdot1\cdot9 + 1(-1)(-1) + 1(1)(1) + 1\cdot3(-1)] = 2 \quad \text{i.e. } 2B_1$$

$$n(B_2) = \frac{1}{4}[1\cdot1\cdot9 + 1(-1)(1) + (1)(1)(-1) + 1\cdot3\cdot1] = 3 \quad \text{i.e. } 3B_2.$$

$\therefore \Gamma_{3N}$ or $\Gamma_{tot} = 3A_1 + A_2 + 2B_1 + 3B_2$

This includes translational, Rotational and vibrational motions.

$\therefore \Gamma_{vib} = \Gamma_{3N} - (\Gamma_{tran} + \Gamma_{Rot})$

Translations

$X \longrightarrow B_1$

$Y \longrightarrow B_2$

$Z \longrightarrow A_1$

$\Gamma_{tran} = A_1 + B_1 + B_2$.

Rotations

$R_x \longrightarrow B_2$

$R_y \longrightarrow B_1$

$R_z \longrightarrow A_2$.

$\Gamma_{rot} = A_2 + B_1 + B_2$

The above informations can be directly obtained from the character table by making use of $\vec{x}^2$ region in the character table.

$\Gamma_{tran+rot} = A_1 + A_2 + 2B_1 + 2B_2$.

$\therefore \Gamma_{vib} = \Gamma_{3N} - (\Gamma_{tran+rot})$

$= 2A_1 + B_2$

The above representation states that 3 modes of vibrations are possible to H_2O molecule.

In H_2O molecule, two stretching and one bending vibrations are possible. out of the two stretchings one is symmetric and the other is asymmetric stretching. the bending mode is also symmetric.

$\Gamma_{vib} = 2A_1 + B_2$.

Two vibrations belong to A_1 irreducible representation and one belongs to B_2 irreducible representation. the symmetrical stretching and symmetrical bending belong to two A_1 and asymmetrical stretching belongs to B_2 irreducible representation. Because all the characters under A_1 irreducible representation are symmetric.

Similar discussion can be extended to any type of molecules which possess finite point groups.

NH_3 molecule belongs to C_{3v} point group.

C_{3v}	E	$2C_3$	$3\sigma_v$
		1	2
No of unshifted atoms.	4	4	
	3	0	1
character per atom			
Total character of $\chi_{red}(R)$	12	0	2

Γ_{3N} can be determined by making use of standard reduction formula.

Raman Spectroscopy:

Raman spectroscopy was developed by Prof. C.V. Raman. When a radiation is passed through a solution, the scattered rays consists of wave lengths different from the incident radiation.

In a homonuclear diatomic molecule the stretching vibration causes no change in the dipole moment, but due to increase & decrease of bond polarizability changes during vibrations. Hence, symmetric stretching of homodiatomic molecules is Raman active. In heterodiatomic molecules the stretching vibration causes change to both in dipole moment and polarizability and hence the vibration is both IR and Raman active.

In case of polyatomic molecules the incident light wave can cause dipole moment change in three directions P_x, P_y and P_z. The relation between polarizabilities and dipole moments can be given by

$$P_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z$$

$$P_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z$$

$$P_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z$$

In normal Raman Scattering $\alpha_{xy} = \alpha_{yx}$, $\alpha_{yz} = \alpha_{zy}$ and $\alpha_{xz} = \alpha_{zx}$. The particular mode of vibration is Raman active, if it can cause change in at least one of the six components of polarizability α_{xx}, α_{yy}, α_{zz}, α_{xy} α_{yz} and α_{xz}.

The intensity of a Raman line as a result of the transfer of the molecule from lower vibrational level v'' to higher vibrational level v' can be given as follows.

$$I = \int \psi_{v''} \alpha \psi_{v'} \, d\tau$$

Six equations can be written by putting six different values of α. If one of the integrals is non-zero, the vibration is Raman active. Incase of H_2O molecule three modes of vibrations $2A_1 + B_2$ are possible. All these three modes of vibrations are Raman active.

These polarizability components correspond to the same irreducible representation as square of the component X, Y and Z of these binary products which can be observed in the VI region of character table.