DR. S. VALARSELVAN, Ph.D
ASST. PROFESSOR OF
CHEMISTRY

II-M.Sc CHEMISTRY

SUBJECT CODE: 18PCH8

TITLE OF THE PAPER: PHYSICAL CHEMISTRY – II

UNIT – III

Fundamentals of Group Theory

Molecular symmetry elements and symmetry operations, point groups- low symmetry, higher symmetry and special symmetry point groups–Group-definition and properties of a group,group multiplication table for C_2V and C_3V point groups-- matrix representation of symmetry operations and transformation matrices —– representation of a group-reducible and irreducible representations – Great orthogonality theorem –characters – construction of a character tables– C_2V, C_3V, C_2h.

SYMMETRY AND GROUP THEORY

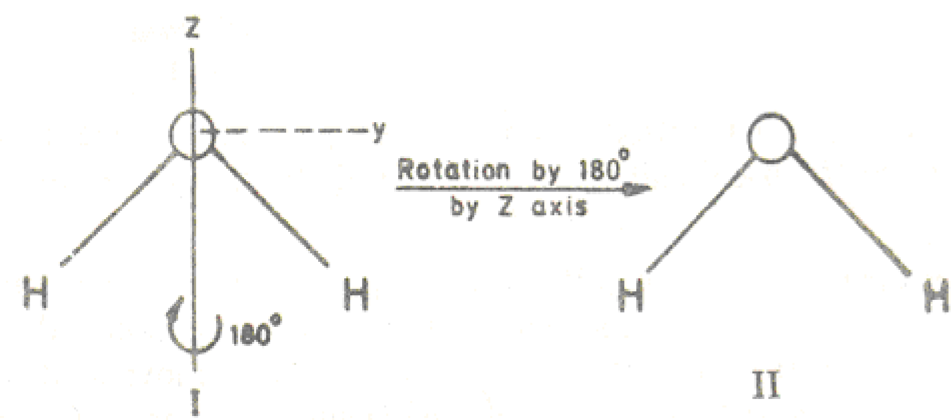
Group Theory is a mathematical method by which aspects of a molecules symmetry can be determined. It is found in geometrical figures such as a cube, a sphere, an equilateral triangle, a rectangle, a square, a regular pentagon, a regular hexagon etc. The symmetry of a molecule reveals information about its properties (i.e., structure, spectra, polarity, chirality, etc…)

Symmetry Operations/Elements

A molecule or object is said to possess a particular operation if that operation when applied leaves the molecule unchanged.

Each operation is performed relative to a point, line, or plane - called a symmetry element.

For example consider water molecule. The two hydrogen atoms of H_2O are equivalent.



H_2O molecule after rotation by 180^o with respect to z - axis has a configuration(II) indistinguishable from the original configuration (I). I and II are not identical. The hydrogen atom on the left hand side of configuration I is on the right hand side in II. As a result of this operation an atom in the body of the molecule has taken up the position of an equivalent atom in the molecule, i.e. two equivalent atoms have exchanged their positions. Thus I and II match perfectly well. If we rotate by 90^o the new configuration does not match with the original one. Thus rotation by 90^o is not a symmetry operation for H_2O.

The various symmetry operations that can be performed on an object or molecule may be listed in Table - 1.

Table : 1

SYMMETRY OPERATION	SYMBOL	SYMMETRY ELEMENTS
1.Identify	E	Does not arise.
2.Rotation	C_n	Axis of symmetry(a line).
3.Refection	σ	Plane of reflection(a plane).
4.Improper rotation	S_n	Rotation (C_n) about an axis and reflection with respect to the plane perpendicular to the rotational axis.
5.Inversion	i	Centre of symmetry.

1. IDENTITY:

Identity is the operation of not doing anything. When we do not do anything we leave the system unchanged and identical to the original system in all respects .It is denoted by the symbol E.

2. Rotation about an axis (C_n)

If Θ is the smallest angle by which we rotate the obiect with respect to an axis and get an indistinguishable configuration the rotation is referred to as a symmetry operation C_n. Symbol C stands for rotation which means making a circular rotation about an axis. We have to do n rotations sucessively to get a full circle and hence the subscript n, where $n = 2\pi/\Theta$ and is called order of the symmetry axis. If there are C_n axis of different orders in a molecule, the axis with the highest order is referred to as the principal axis. For example, in boron trichloride molecule an axis of symmetry is located perpendicular to the plane containing all the atoms. This is known as the C_3 axis of symmetry. Boron trichloride molecule has three C_2 axes of symmetry in addition to the C_3 axis (Fig 1). The C_3 axis in this molecule is known as the principal axis

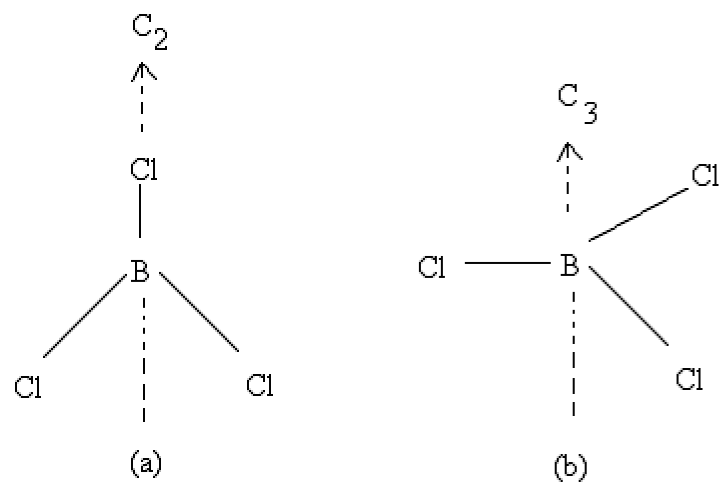


Fig 1 (a) The C_2 axis of symmetry in BCl_3 molecule
(b) The C_3 prinicpal axis in BCl_3 molecule

As a second example we shall take a regular hexagon eg. benzene. The axis perpendicular to the plane (z - axis) is a C_{6Z} axes. There are other rotational axes also (Fig 2). Performing C_{6Z} twice , thrice, etc are also symmetry operations. They are

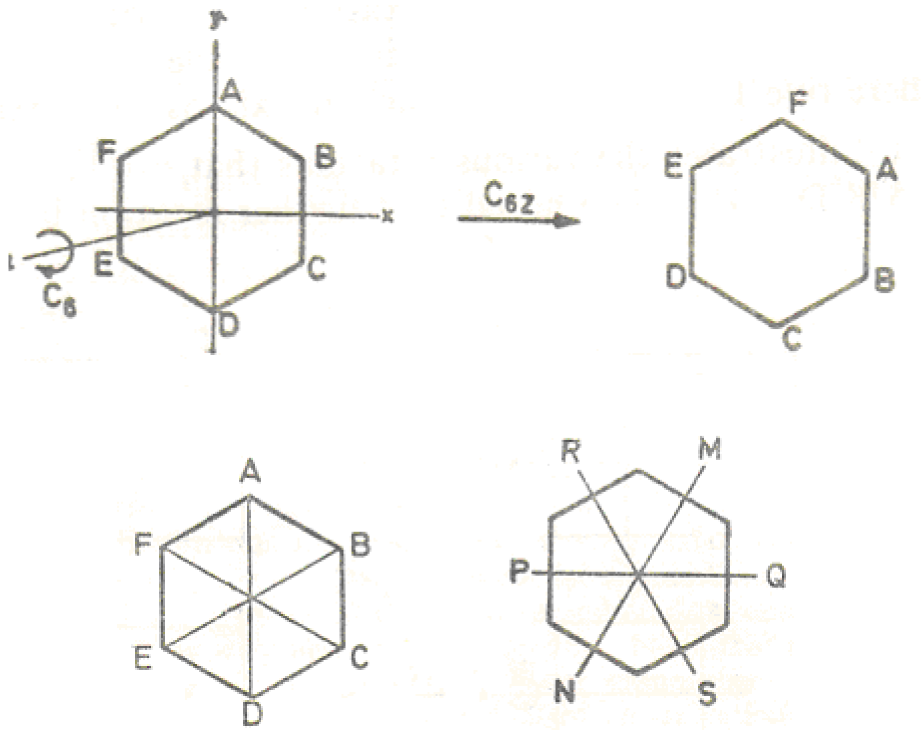


Fig 2 Rotational axes of a hexagon.

designated as C^2_{6Z}, C^3_{6Z} etc. Besides these, there are other axes which lie in the plane of benzene. They are AD, BE. CF and PQ, MN and RS. These are C_2 axes. Note that the highest order axis is the C_6 axis .

For a linear molecule like ABC or AB rotation around its inter nuclear axis by any angle is a symmetry operation . The minimum angle being infinitesimally small, this would be C_α operation.

We can perform rotations several times. If we perform C_n operation m times successively we call it a C_n^m operation.

It is obvious that

$$C^2_{2z} = E; \quad C^n_n = E \text{ for any n}$$

$$C^2_6 = C_3$$

Thus successive application of the same symmetry operation leads to new symmetry operations

If rotation by $360^0/n$ in a clockwise fashion is a symmetry operation C_n, rotation by the same angle in anticlockwise direction is labeled as C_n^{-1}. Using C_n and C_n^{-1} successively is equivalent to identity, as C_n^{-1} restores the molecule to the original position after C_n has been performed.

That is $C_n^{-1}\ C_n = E$

3. Reflection (σ)

A plane which bisects a molecule into two halves so that one is exactly the mirror image of the other is a reflection plane.

The angular water molecule has a reflection plane passing through the oxygen atom and another one containing all the atom (Fig 3). The plane containing all the atoms is called as molecular plane.

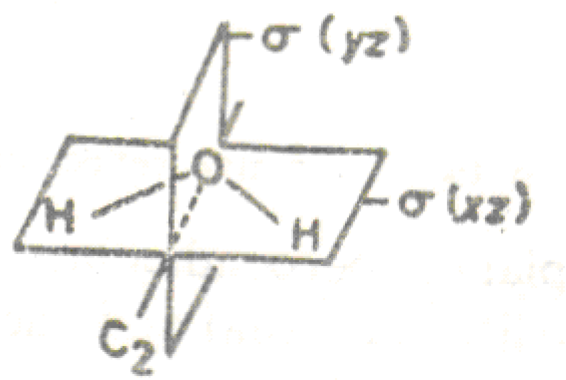


Fig 3 Reflection planes of H_2O

The Square planar complex ion $[PtCl_4]^{2-}$ contains a molecular plane and four more reflection planes. Fig4.

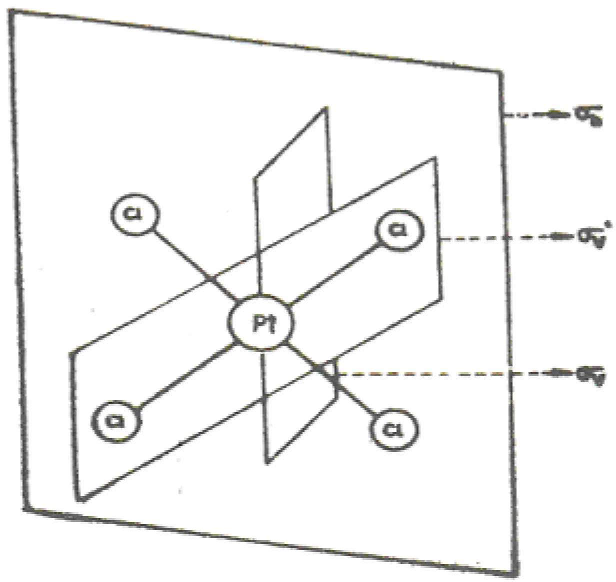


Fig .4 The reflection planes in $[PtCl_4]^{2-}$ ion

The reflection planes can be classified into three types based on their relation with the principal axis. A plane is referred to as horizontal plane (σ_h) if it is perpendicular to the principal axis. A reflection plane which contains the principal axis is called as vertical plane(σ_v). A vertical plane which bisects two perpendicular C_2 axes is called a dihedral plane(σ_d).

Doing σ twice successively, $\sigma . \sigma = \sigma^2$ is equivalent to doing nothing. In the case of water, doing a σ twice leads to a configuration identical in all respects with the original (Fig 5) Obviously this is true of all molecules and hence we have the general relationship $\sigma^2 = E$.

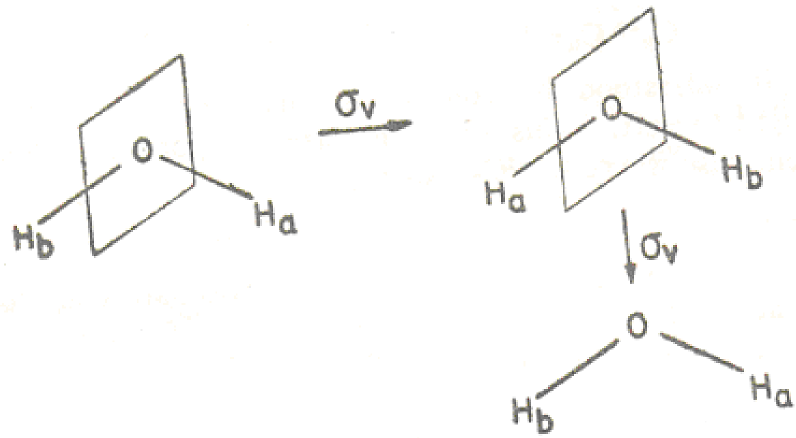


Fig 5 Effect of two successive reflections on water

4. Improper rotation(S_n)

It is a process of rotation (C_n) followed by reflection in a plane perpendicular to the axis of rotation (σ). Fig 6 shows the S_6 axis in staggered form of ethane.

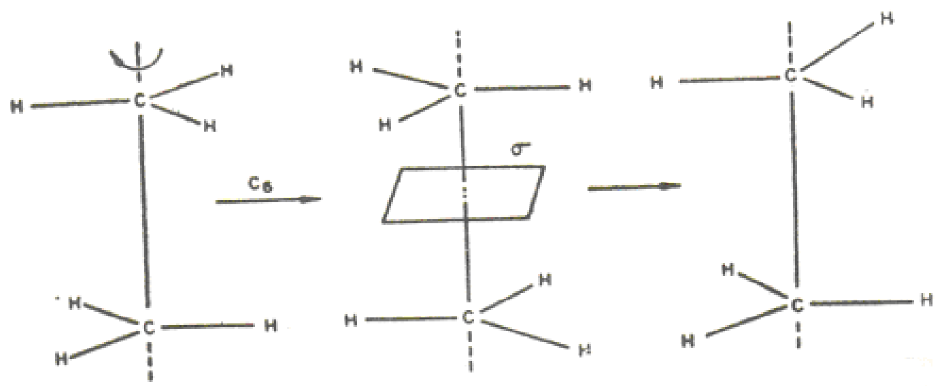


Fig. 6 The S_6 axis in staggered form of ethane

Note that in Fig 6, C_6 is not a symmetry operation but $\sigma C_6 = S_6$ is a symmetry operation.

Also $\sigma C_n = C_n\sigma$ since these two operations commute. It is easily seen $S_6{}^2 = C_3$

$S_6{}^2 = (\sigma C_6).(\sigma C_6)$. Since σ and C_6 commute.

We have $S_6{}^2 = C_6\,\sigma\,\sigma\,C_6 = C_6\,E\,C_6 = C_6{}^2 = C_3$ $[\sigma^2 = E]$

Similarly $S_6{}^4 = C_3{}^2$

5. Inversion (i)

In molecule like that in Fig (7), if we join any atom to the centre of the molecule and extend the line on the other side by the same distance we meet a similar atom. Molecules where atoms are geometrically arranged in this manner are said to possess a centre of symmetry or inversion centre. Inversion is a symmetry operation for such molecules.

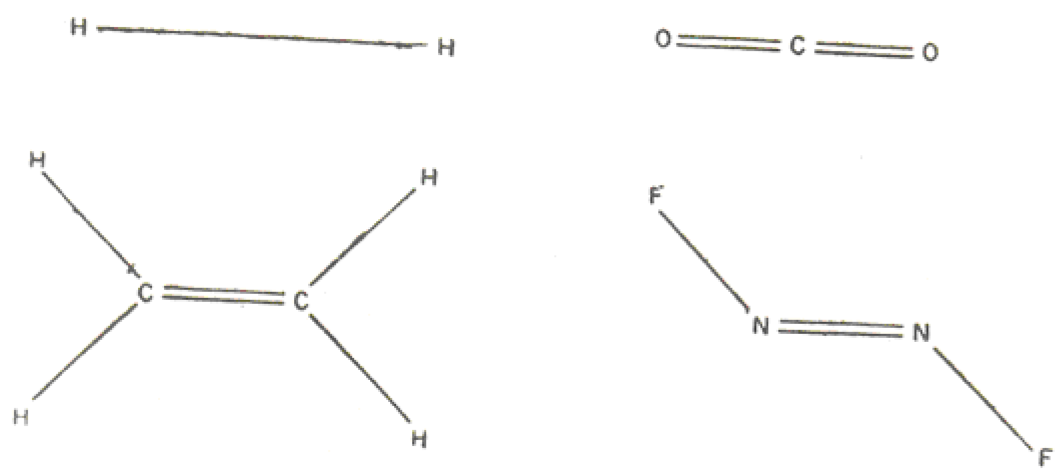


Fig 7 Diagram showing molecules with centre of symmetry

All homonuclear diatomic molecules possess the centre of symmetry.

GROUP

A group is a collection of elements which are interrelated according to certain rules. The symmetry operations of a molecule form a group.

Rules of the group :-

In order for any set of elements to form mathematical group the following rules must be satisfied.

1. The product of any two elements in the group and the square of each element must be an element in the group.

2. One element in the group must commute with all others and leave them unchanged.

3. The associative law of multiplication should be valid.

4. Every element must have a reciprocal, which is also an element of the group.

Rule 1:

If A and B are the elements of the group and if AB=C, C must be a member of the group. Usually AB ≠ BA and so C ≠ D. However there may be some special elements A and B such that AB=BA. Then A and B are said to 'commute' with each other or the multiplication of A and B is commutative. Such a group where any two elements commute is called an 'abelian' group. H_2O belongs to an abelian group.

Rule 2:

Each group must necessarily have an element which commutes with every other element of the group and leaves it unchanged.

Let A and B be the elements of the group. Let X be the element satisfying rule 2.

i.e. XA = AX = A and also XB = BX = B

$BA = BX^2A$; $BX^2 = B = BE$, where we have set

$X^2 = E$(identity)

It is clear $BE^n = B$, n being any integer. This kind of element E which does not effect any change when multiplied with any element, is a unique element and is called an identity operation E.

Rule 3:

Associative law of multiplication must be valid. This means ABCD is the same as (AB) (CD), (A). (BCD) or (ABC) (D). ABC is the same as A(BC) or (AB) C.

Rule 4:

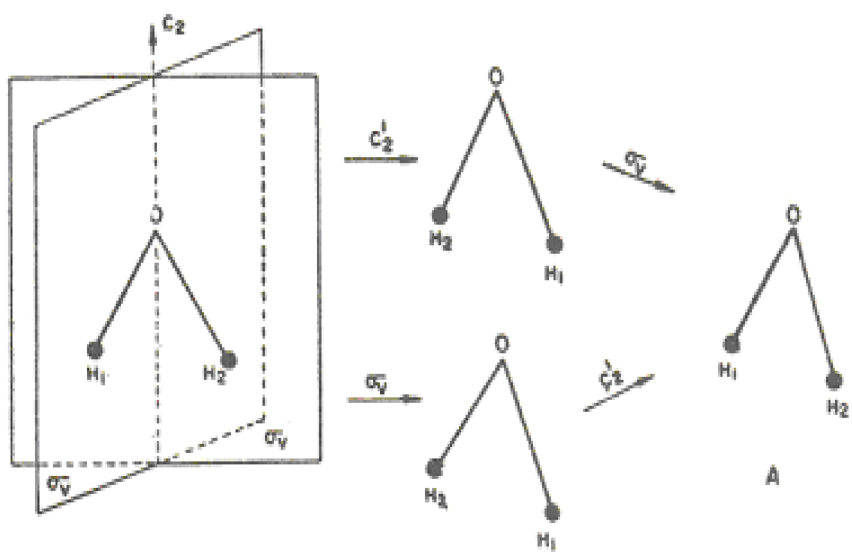
Inverse of an element A is denoted by A^{-1} (this does not mean 1/A). It is simply an element of the group such that $A^{-1}A = E$. In the case of symmetry groups, A^{-1} is that element which undoes or annuls the effect of A. For H_2O we have, for example, $C_2C_2 = E$. Therefore $C_2^{-1} = C_2$ i.e. C_2 is its own inverse. This is true of all other elements for H_2O. But this is not general. Therefore C_6^{-1} is not C_6.

Abelian Group.

A group is said to be abelian if for all pairs of elements of the group, the binary combination is commutative. That is AB=BA; BC=CB and so on.

Example:

The elements of C_{2v} point group E, C_{2v}, σ_v, and σ_v' form an abelian group as all the elements of this group commute with each other. Fig 3.7 illustrates the idea that the symmetry operation of water molecule obey the commutative law. C_2^1 operation followed by σ_v operation leads to the configuration A. σ_v operation followed by C_2^1 leads to the same configuration as shown in Fig 8.



(9)

Fig 8 diagram illustrating the idea that the symmetry operation of water molecule obey the commutative law of a group.

Non Abelian Group.

A group is said to be non abelian if the commutative law does not hold for the binary combination of the elements of the group , i.e, AB $\neq$ BA.

Example:

The elements of C_{3v} point group E, C_3^1, C_3^2, σ_v^1, σ_v^2 and σ_v^3 do not constitute an abelian group. Since the elements do not follow commutative law. C_3^1 operation followed by σ_v^1 operation leads to the configuration A. σ_v^1 operation followed by C_3^1 opreration leads to the configuration B. Fig 9

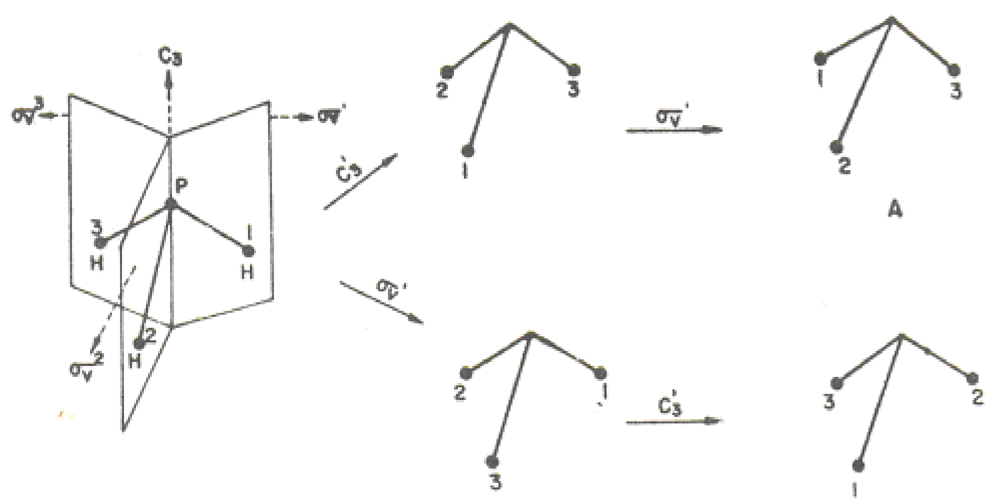


Fig.9 Diagram illustrating the idea that the symmetry operations of Phosphine molecule do not obey the commutative law of the group.

Sub Groups:

Any subset of a collection of elements which forms a group is called a sub group. The elements of a sub group should obey the following conditions:

1. The elements should satisfy all the rules of the group.
2. If h is the order of the group and g is the order of the sub group, then h/g is a natural number.

There are four sub groups in water molecule.

1. E
2. E and , C_2^1
3. E and σ_v
4. E and σ_v'

Cyclic Group

A group is said to be cyclic if all the elements of a group can be generated from one element. A, A^2, A^3….. A^h form the element of of a cyclic group with A^h as the identity element . h refers to the total number of elements and is called the order of the group

Trans 1,2 - dichlorocyclopropane and hydrogen peroxide are examples of molecules which possess symmetry operations corresponding to a cyclic group of order two. C_2^1 and C_2^2 are the two symmetry operations present in them. Every cyclic group is Abelian but the converse is not true. The symmetry operations of trans-1,2 dichlorocyclopropane form an Abelian cyclic group, whereas the operations in water molecule form an Abelian group only.

SIMILARITY TRANSFORMATION AND CLASSES

Let A and X be the elements of a group and let us define B such that

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

B is called the similarity transform of A by X,or A is said to be subjected to similarity transformation with respect to X. If A and B are related by a similarity transformation they are called “conjugate” elements. Take the NH_3 molecule , for instance. Fig 10.

z - axis is the C_3 axis.

There are three reflection planes. These are usually designated as follows

1. Plane formed by z - axis and NH_a bond: σ’
2. Plane formed by z- axis and NH_b bond: σ”
3. Plane formed by z- axis and NH_c bond: σ”’

Let us perform a reflection (σ’’’) with respect to the plane formed by NH_c and z-axis. Let us perform σ again. $\sigma'''^{2} = E$

Now let as find the similarity transform of C_3 w.r.t σ”’, i.e., $(\sigma''')^{-1} C_3 \sigma''' = ?$

It is seen from Fig 10 that $(\sigma''')^{-1} C_3 (\sigma''') = C_3^2$

Remember $(\sigma''') = (\sigma''')^{-1}$. Thus C_3 and C_3^2 are conjugate elements.

The following rules about conjugated elements are notable;

1. Every element is conjugate of itself because every element is the similarity transform of itself w.r.t. identity (E).

$E = E^{-1}$ and $A = E^{-1} AE$

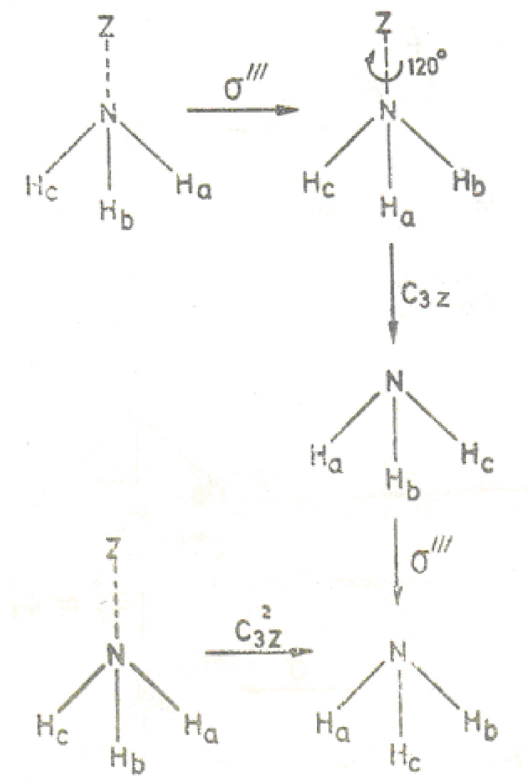


Fig 10 Similarity transformation on NH_3

2. If A is the conjugate of B then B is the conjugate of A. This means that if A is the similarity transform of B by X,B is the similarity transform of A by X^{-1}. We have

$A = X^{-1} BX;$

But, $(X^{-1})^{-1}A X^{-1} = XA X^{-1} = X (X^{-1} BX) X^{-1}$

$= (XX^{-1}) B(XX^{-1}) = B$ (associative law)

3. If A is the conjugate of B and B is the conjugate of C, then A,B and C are mutually conjugate.

CLASS

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

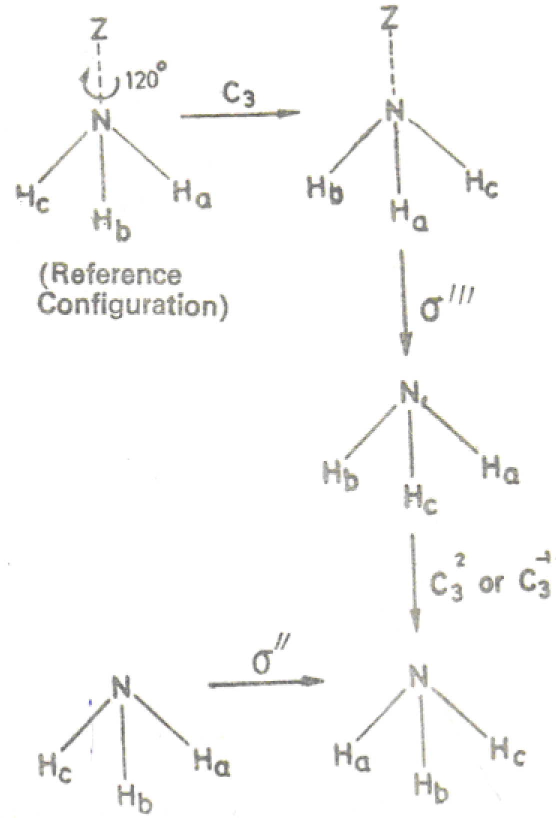


Fig 11 Illustration of equivalence of reflectons in NH_3

Let us consider NH_3 . Set up the coordinate system in such a manner that ZNH_a is in the yz plane. Fig 11 σ' is then σ_{yz}. Without disturbing the NH_3 molecule rotate the coordinate system by 120° w.r.t. z axis ., i.e., subject the coordinate system to C_3. Now yz plane is ZNH_b. σ_{yz} is σ''. σ' and σ'' are equivalent. σ' becomes same as that of σ'' if we change the coordinate system by a symmetry operation (C_3) of the point group. σ' and σ'' are therefore in the same class.

Example

The three reflections of NH_3 constitute a class.

It is not difficult to show that $C_3^2 . C_3 = E$

Hence $C_3^2 = (C_3)^{-1}$

Let us perform the similarity transformation of σ' by C_3 in NH_3

C_3^{-1} σ’ C_3 . = C_3^2 σ’ C_3 =σ’’

Thus σ’ and σ’’ are conjugate. Similarly we can show that σ’, σ’’ and σ’’’ are mutually conjugate.

Therefore σ’, σ’’, and σ’’’ form a class.

Order of a group can be shown to be an integral multiple of the number of elements in a class of the group.

GROUP MULTIPLICATION TABLE

Every group is characterized by a multiplication table. The relationship between the elements of the binary combinations is reflected in the multiplication table.

Consider water molecule. It has four symmetry elements, viz, E, $C_{2(z)}$, $\sigma_{v(xz)}$ and $\sigma_{v(yz)}$ Fig 12

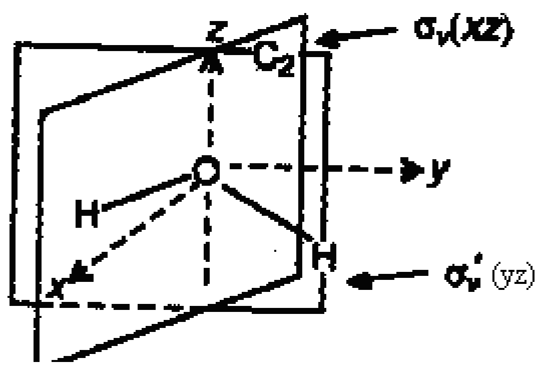


Fig 12 The Four symmetry elements of H_2O

We can easily show that the product of any two symmetry elements is one of the four elements of the group Thus for instance $C_{2(z)}$, $\sigma_{v(xz)} = \sigma'_{v(yz)}$. Proceeding this way the symmetry operations of H_2O can be listed in a group multiplication table. (Table3.)

	E	C_{2z}	$\sigma_{v(xz)}$	$\sigma'_{v(yz)}$
E	E	C_{2z}	$\sigma_{v(xz)}$	$\sigma'_{v(yz)}$
C_{2z}	C_{2z}	E	$\sigma'_{v(yz)}$	$\sigma_{v(xz)}$
$\sigma_{v(xz)}$	$\sigma_{v(xz)}$	$\sigma'_{v(yz)}$	E	C_{2z}
$\sigma'_{v(yz)}$	$\sigma'_{v(yz)}$	$\sigma_{v(xz)}$	C_{2z}	E

Table 3. Group multiplication table of the symmetry operations of H_2O molecule.

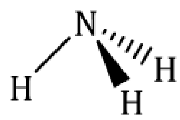
Important characteristics of a group multiplication Table.

1. It consists of h rows and h columns where h is the order of the group.
2. Each column and row is labeled with group element
3. The entry in the table under a given column and along a given row is the product of the elements which head that column and that row.
4. At the intersection of the column labeled by X and the row labeled by Y we found the element which is the product XY
5. The following rearrangement theorem holds good for every group multiplication table,

"Each row and each column in the table lists each of the group elements once and only once. No two rows may be identical nor any two columns be identical. Thus each row and each column is a rearranged list of the group elements".

. **Group multiplication table of the symmetry operations of NH_3 molecule.**

Consider all of the symmetry operations in NH_3



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

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

Similarity transformation and Classes in ammonia

To determine the classes of symmetry operations for this point group. Let's start with the similarity transforms for the vertical mirror planes:

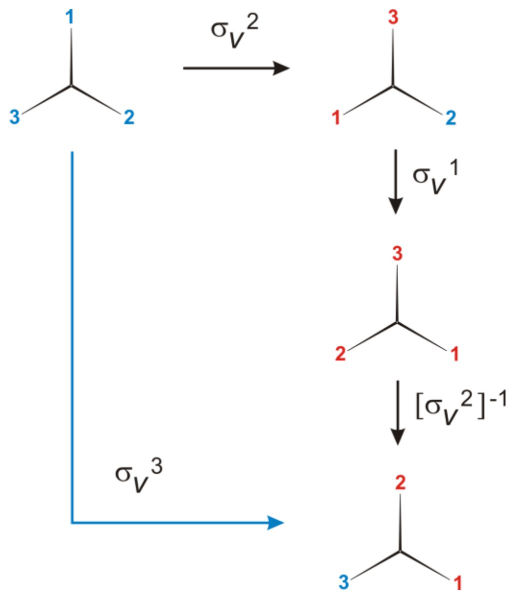
$$\sigma_v^1\ \sigma_v^1\ [\sigma_v^1]^{-1} = \sigma_v^1$$

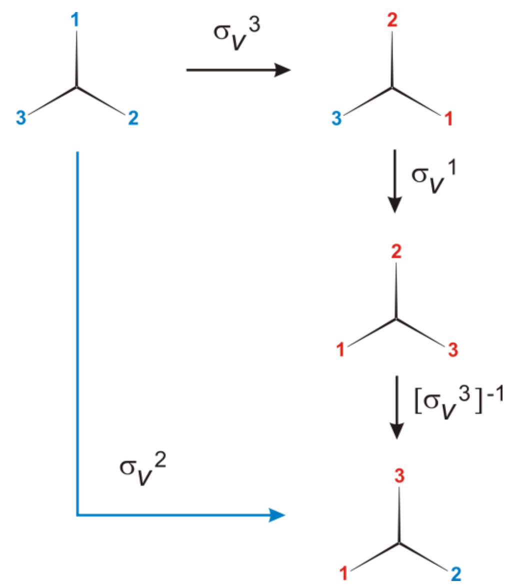
$$\sigma_v^2\ \sigma_v^1\ [\sigma_v^2]^{-1} = \sigma_v^3$$

$$\sigma_v^3\ \sigma_v^1\ [\sigma_v^3]^{-1} = \sigma_v^2$$

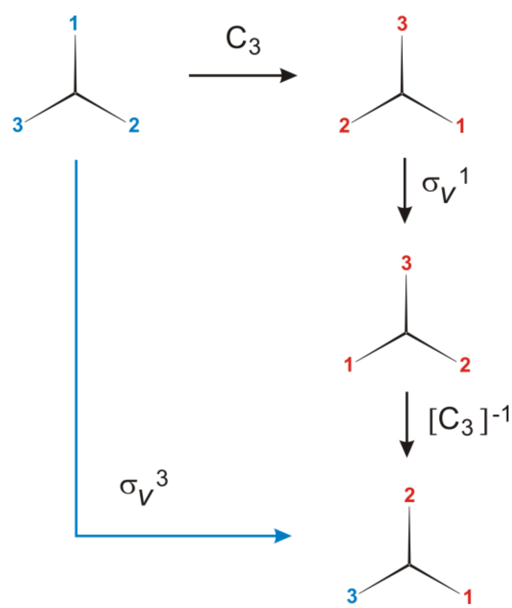
It can be shown as given, how the similarity transformation takes place

$\sigma_v^{2}\,\sigma_v^{1}\,[\sigma_v^{2}]^{-1} = \sigma_v^{3}$ $\sigma_v^{3}\,\sigma_v^{1}\,[\sigma_v^{3}]^{-1} = \sigma_v^{2}$





$$C_3\,\sigma_v^{1}\,[C_3]^{-1} = \sigma_v^{3}$$



If we continue these similarity transforms we find that the various symmetry operations for C_{3v} break down into the following classes:

E

C_3, C_3^2

σ_v^1, σ_v^2, σ_v^3

If we examine the character tables the symmetry operations are listed and grouped together in these very same classes:

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

Matrix Representations of Symmetry Operations

We will now use matrices to represent symmetry operations. Consider how an {x,y,z} vector is transformed in space. Any symmetry operation about a symmetry element in a molecule involves the transformation of a set of coordinates x, y and z of an atom into a set of new coordinates x', y' and z'. The two sets of coordinates of the atom can be related by a set of equations. This set of equations may also be formulated in matrix notation. Thus each symmetry operation can be represented by a specific matrix. A knowledge of the matrices of the various operations in a molecule will be useful to solve structural problems in chemistry. For example, the symmetry of vibrational modes in molecules can be analysed using the matrices for the different operations.

Identity

E

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

Reflection

σ_{xy}

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

σ_{xz}

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

Inversion

i

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

Rotation

C_n about the z axis

The transformation matrix for a clockwise rotation by ϕ is:

$$\begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z \end{bmatrix}$$

Improper Rotations (S_n)

Because an improper rotation may be expressed as σ_{xy} C_n we can write the following since matrices also follow the associative law.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

$$\begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

The sum of the diagonal elements of a square matrix is called the trace or character of the matrix. The characters of the various matrices corresponding to the symmetry operations are listed in Table

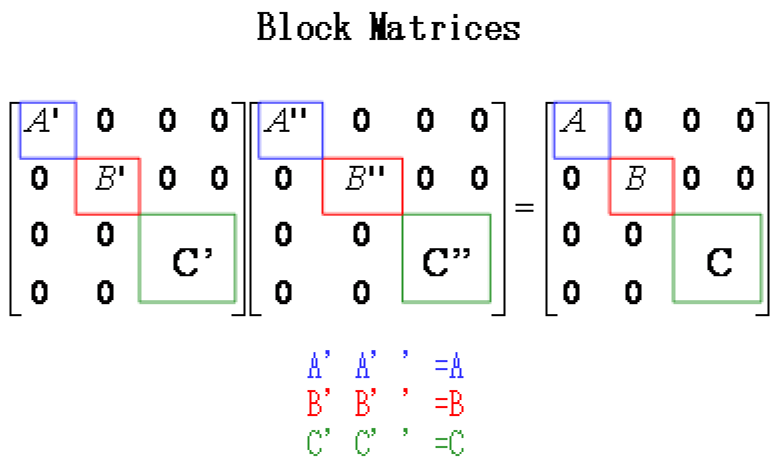
Symmetry Operation	**Character of Matrix**
Identity	3
Rotation	2 cos ϕ + 1
Inversion	-3
Improper rotation	2 cos ϕ -1
Reflection	1

ϕ refers to the angle of rotation about the axis.

REDUCIBLE AND IRREDUCIBLE REPRESENTATIONS

- Matrix representations of symmetry operations can often be reduced into *block matrices*. Similarity transformations may help to reduce representations further. The goal is to find the *irreducible representation*, the only representation that can not be reduced further.
- The same ”type” of operations (rotations, reflections etc) belong to the same *class*. Formally *R* and *R'* belong to the same class if there is a symmetry operation *S* such that $R' = S^{-1}RS$. Symmetry operations of the same class will always have the same character.
- If a matrix representing a symmetry operation is transformed into block diagonal form then each little block is also a representation of the operation since they obey the same multiplication laws.
- When a matrix can not be reduced further we have reached the *irreducible representation*. The number of reducible representations of symmetry operations is infinite but there is a small finite number of irreducible representations.

- The number of irreducible representations is always equal to the number of classes of the symmetry point group.



GROUP REPRESENTATION AND CHARACTER TABLE

The set of four matrices that describe all of the possible symmetry operations in the C_{2v} point group that can act on a point with coordinates *x*, *y*, *z* is called the total representation of the C_{2v} group.

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

Note that each of these matrices is block diagonalized, i.e., the total matrix can be broken up into blocks of smaller matrices that have no off-diagonal elements between blocks. These block diagonalized matrices can be broken down, or reduced into simpler one-dimensional representations of the 3-dimensional matrix. If we consider symmetry operations on a point that only has an *x* coordinate (e.g., *x*, 0, 0), then only the first row of our total representation is required:

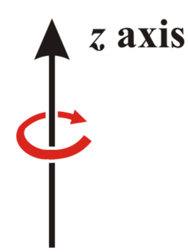
If we consider symmetry operations on a point that only has an *x* coordinate (e.g., *x*, 0, 0), then only the first row of our total representation is required:

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ_1	1	-1	1	-1	*x*

We can do a similar breakdown of the y and z coordinates to setup a table:

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ_1	1	-1	1	-1	*x*
Γ_2	1	-1	-1	1	*y*
Γ_3	1	1	1	1	*z*

These three 1-dimensional representations are as simple as we can get and are called irreducible representations. There is one additional irreducible representation in the C_{2v} point group. Consider a rotation R_z :The identity operation and the C_2 rotation operations leave the direction of the rotation R_z unchanged. The mirror planes, however, reverse the direction of the rotation (clockwise to counter-clockwise), so the irreducible representation can be written as:



C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ_4	1	1	-1	-1	R_z

4 Classes of symmetry operations = 4 Irreducible representations!!

Each irreducible representation of a group has a label called a symmetry species, generally noted Γ. When the type of irreducible representation is determined it is assigned a *Mulliken symbol*:

One-dimensional irreducible representations are called *A* or *B*.

Two-dimensional irreducible representations are called *E*.

Three-dimensional irreducible representations are called *T (F)*.

The basis for an irreducible representation is said to *span* the irreducible representation.

The difference between *A* and *B* is that the character for a rotation C_n is always 1 for *A* and -1 for *B*.

The subscripts 1, 2, 3 etc. are arbitrary labels.

Subscripts *g* and *u* stands for gerade and ungerade, meaning symmetric or antisymmetric with respect to inversion.

Superscripts ' and '' denotes symmetry or antisymmetry with respect to reflection through a horizontal mirror plane.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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

CHARACTER TABLE FOR AMMONIA

Now lets consider a case where we have a 2-dimensional irreducible representation.

Consider the matrices for C_{3v}

$$\underset{E}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}} \quad \underset{C_3}{\begin{bmatrix} \cos 120^{o} & -\sin 120^{o} & 0 \\ \sin 120^{o} & \cos 120^{o} & 0 \\ 0 & 0 & 1 \end{bmatrix}} \quad \underset{\sigma_v}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}$$

In this case the matrices block diagonalize to give two reduced matrices. One that is 1-dimensional for the *z* coordinate, and the other that is 2-dimensional relating the *x* and *y* coordinates. Multidimensional matrices are represented by their characters (trace), which is the sum of the diagonal elements. Since cos(120º) = □0.50, we can write out the irreducible representations for the 1- (*z*) and 2-dimensional "degenerate" *x* and *y* representations:

C_{3v}	E	$2C_3$	$3\sigma_v$	
Γ_1	1	1	1	*z*
Γ_2	2	-1	0	*x,y*

As with the C_{2v} example, we have another irreducible representation (3 symmetry classes = 3 irreducible representations) based on the R_z rotation axis. This generates the full group representation table:

C_{3v}	E	$2C_3$	$3\sigma_v$	
Γ_1	1	1	1	*z*
Γ_2	2	-1	0	*x,y*
Γ_3	1	1	-1	R_z

C_{3v}	E	$2C_3$	$3\sigma_v$			
A_1	1	1	1	z	$x^2 + y^2, z^2$	$z^3, x(x^2 - 3y^2)$
A_2	1	1	−1	R_z		$y(3x^2 - y^2)$
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$	$(xz^2, yz^2), [xyz, z(x^2 - y^2)]$
$\Gamma_{x,y,z}$	3	0	1			

CHARACTER TABLES (SOME OTHER EXAMPLES)

C_2 (2)	E	C_2		
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	–1	x, y, R_x, R_y	yz, xz

C_3 (3)	E	C_3	C_3^2		$\varepsilon = \exp(2\pi i/3)$
A	1	1	1	z, R_z	$x^2 + y^2, z^2$
E	$\left\{\begin{matrix}1 \\ 1\end{matrix}\right.$	$\begin{matrix}\varepsilon \\ \varepsilon^*\end{matrix}$	$\left.\begin{matrix}\varepsilon^* \\ \varepsilon\end{matrix}\right\}$	$(x, y)(R_x, R_y)$	$(x^2 - y^2, 2xy)(yz, xz)$

C_{2h} (2/m)	E	C_2	I	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	–1	1	–1	R_x, R_y	xz, yz
A_u	1	1	–1	–1	z	
B_u	1	–1	–1	1	x, y	

D_{2h} (mmm)	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		x^2, y^2, z^2
B_{1g}	1	1	–1	–1	1	1	–1	–1	R_z	xy
B_{2g}	1	–1	1	–1	1	–1	1	–1	R_y	xz
B_{3g}	1	–1	–1	1	1	–1	–1	1	R_x	yz
A_u	1	1	1	1	–1	–1	–1	–1		
B_{1u}	1	1	–1	–1	–1	–1	1	1	z	
B_{2u}	1	–1	1	–1	–1	1	–1	1	y	
B_{3u}	1	–1	–1	1	–1	1	1	–1	x	

GREAT ORTHOGONALITY THEOREM

This theorem is concerned with the elements of matrices constituting the irreducible representations of a point group. Let us consider two irreducible representations i and j of a point group. Let l_i and l_j be the dimensions of these representations. h is the order (total number of symmetry operatons) of the point group. R denotes a particular symmetry operation in the group. $(\Gamma_i (R))_{mn}$ is an element in the mth row and nth 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 $(\Gamma_j(R))^*_{m'n'}$. the elements $(\Gamma_i(R))_{mn}$ and $(\Gamma_j(R))^*_{m'n'}$ are related to h, l_i and l_j by the orthogonality theorem as follows:

$$\sum\left[\Gamma_i(R)_{mn}\right]\left[\Gamma_j(R)_{m'n'}\right]^* = \frac{h}{\sqrt{l_i l_j}}\delta_{ij}\delta_{mm'}\delta_{nn'}$$

$\Gamma_i (R)_{mn}$	The element in the m^{th} row and n^{th} column of the matrix corresponding to the operation R in the i^{th} irreducible representation Γ_i.
$\Gamma_i (R)_{mn}^*$	complex conjugate used when imaginary or complex #'s are present (otherwise ignored)
h	the order of the group
l_i	the dimension of the i^{th} representation (A = 1, B = 1, E = 2, T = 3)
δ	delta functions, = 1 when $i = j$, $m = m'$, or $n = n'$; = 0 otherwise

The different irreducible representations may be thought of as a series of orthonormal vectors in *h*-space, where *h* is the order of the group.

Because of the presence of the delta functions, the equation = 0 unless *i* = *j*, *m* = *m'*, or *n* = *n'*. Therefore, there is only one case that will play a direct role in our chemical applications:

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}] = 0 \quad \textbf{if I} \neq \textbf{j}$$

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}] = 0 \quad \textbf{if m} \neq \textbf{m' n} \neq \textbf{n'}$$

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_i(R)_{mn}] = \frac{h}{l_i}$$

Five "Rules" about Irreducible Representations:

1) The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order, *h*, of a group.

$$\sum l_i^2 = h$$

For example, consider the D_{3h} point group:

h = 12 (order of group)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

$$l(A_1')^2 + l(A_2')^2 + l(E')^2 + l(A_1'')^2 + l(A_2'')^2 + l(E'')^2$$

$$(1)^2 + (1)^2 + (2)^2 + (1)^2 + (1)^2 + (2)^2 = 12$$

2) **The sum of the squares of the characters in any irreducible representation is also equal to the order of the group *h*.**

$$\sum_{R} g\left[\chi_i(R)\right]^2 = h$$

***g* = No. of symmetry operations *R* in a class**

For example, for the E' representation in D_{3h}:

$$(2)^2 + 2(-1)^2 + 3(0)^2 + (2)^2 + 2(-1)^2 + 3(0)^2 = 12$$

3) **The vectors whose components are the characters of two different irreducible representations are orthogonal.**

$$\sum_{R} g\,\chi_i(R)\,\chi_j(R) = 0$$

For example, multiply out the A_2' and E' representations in D_{3h}:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0

1(1)(2) + 2(1)(-1) + 3(-1)(0) + 1(1)(2) + 2(1)(-1) + 3(-1)(0)

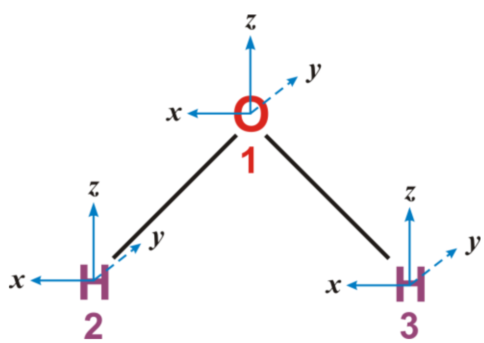
2 + (-2) + 0 + 2 + (-2) + 0 = 0

4) **In a given representation the characters of all matrices belonging to operations in the same class are identical.**

5) **The number of irreducible representations in a group is equal to the number of classes in the group.**

Applications : Molecular vibrations (IR spectroscopy)

Molecular vibrations are the result of the superposition of a number of relatively simple vibratory motions known as normal vibrations or normal modes of vibrations. There are 3N – 6 fundamental modes of normal vibrations for a non-linear molecule (3N – 5 for a linear molecule). We will find that each of these normal modes has a certain symmetry and can be classified by an irreducible representation from the molecular point group. Consider a water molecule with a Cartesian coordinate system on each atom (the *z* axis is in the plane and the primary rotation axis, the *x* axis is also in plane):



The full matrix transformation of the vector coordinates by a C_2 rotation is as follows:

	O1			**H2**			**H3**		
C_2	x_1	y_1	z_1	x_2	y_2	z_2	x_3	y_3	z_3
x_1	**-1**	**0**	**0**						
y_1	**0**	**-1**	**0**		**0**			**0**	
z_1	**0**	**0**	**1**						
x_2							**-1**	**0**	**0**
y_2		**0**			**0**		**0**	**-1**	**0**
z_2							**0**	**0**	**1**
x_3				**-1**	**0**	**0**			
y_3		**0**		**0**	**-1**	**0**		**0**	
z_3				**0**	**0**	**1**			

The character of this matrix is the sum of the diagonal elements, which = -1

Note that if an atom is moved by the symmetry operation it does NOT contribute to the character of the matrix because it then appears as an off-diagonal term.

The σ_v(xz) mirror plane operation does not move any atoms, so all count. It keeps the *x* and *z* axes the same (+1 characters for each), while flipping the *y* axis (□1 character). So each atom contributes: 1 + 1 + (□1) = 1 to the trace, for a total trace value (3 atoms) of 3.

The σ_v(yz) mirror plane operation, on the other hand, moves H2 and H3 (reflects them), so these will not contribute to the trace for this operation. For the O atom, it keeps the *y* and *z* axes the same (+1 characters for each), while flipping the *x* axis (□1 character). So the O contributes: 1 + 1 + (□1) = 1 to the trace.

The total representation for all the C_{2v} symmetry operations acting on the 3 atoms (9 *xyz* coordinates) of water is:

C_{2v}	E	C_2	σ_v(xz)	σ_v(yz)
Γ_T	9	−1	3	1

The # of times that one of the irreducible representations occurs in a reducible representation (our total representation for the water molecule) is given by the formula:

$$a_i = \frac{1}{h}\sum_{R} g\,\chi_T(R)\,\chi_i(R)$$

Where:

	a_i	the no. of times the irreducible representation *i* occurs in the total representation T
	h	the order of the group
	R	the symmetry operations
	g	the number of symmetry operations in a class

$\chi(R)$ the character associated with the symmetry operation R

The character table of water with total representation is given as

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1
Γ_T	9	−1	3	1

$$A_1 = \frac{1}{4}[(9)(1) + (-1)(1) + (3)(1) + (1)(1)] = (\frac{1}{4})(12) = 3$$

$$A_2 = \frac{1}{4}[(9)(1) + (-1)(1) + (3)(-1) + (1)(-1)] = (\frac{1}{4})(4) = 1$$

$$B_1 = \frac{1}{4}[(9)(1) + (-1)(-1) + (3)(1) + (1)(-1)] = (\frac{1}{4})(12) = 3$$

$$B_2 = \frac{1}{4}[(9)(1) + (-1)(-1) + (3)(-1) + (1)(1)] = (\frac{1}{4})(8) = 2$$

We find, therefore, that our total representation breaks down into 9 1-D irreducible representations: $3A_1$, A_2, $3B_1$, and $2B_2$.

These 9 irreducible representations represent the 3N degrees of freedom for H_2O. To find which represent our 3 normal mode vibrations we need to subtract out the 3 translational (x, y, z) and 3 rotational (R_x, R_y, R_z) modes.

By looking at the character table we can pick out the irreducible representations that correspond to these:

$x = B_1$ $R_x = B_2$

$y = B_2$ $\quad\quad$ $R_y = B_1$

$z = A_1$ $\quad\quad$ $R_z = A_2$

Subtracting these six irreducible reps (A_1, A_2, $2B_1$, and $2B_2$) from the 9 that we projected from the total representation ($3A_1$, A_2, $3B_1$, and $2B_2$) leaves us with the 3 normal vibrational modes for H_2O:

$$2A_1 \text{ and } B_1$$

Infrared selection rules

Consider our total vibrational wavefunction Ψ_v, which is equal to the product of the k normal mode wavefunctions, $\phi(n_i)$:

$$\Psi_v = \phi(n_1)\,\phi(n_2)\,\phi(n_3)\,\phi(n_4)\,.\,.\,.\,\phi(n_k)$$

If we denote the ground state wavefunction by Ψ_v° and the excited state by Ψ_v^{j} (indicating a transition to the j^{th} normal mode), the for a fundamental transition to occur by absorption of IR dipole radiation it is necessary that one or more of the following integrals be non-zero:

$$\int \psi_v^{\circ}\, x\, \psi_v^{j}\, d\tau \neq 0$$

$$\int \psi_v^{\circ}\, y\, \psi_v^{j}\, d\tau \neq 0$$

$$\int \psi_v^{\circ}\, z\, \psi_v^{j}\, d\tau \neq 0$$

x, *y* and *z* in the integrals refer to the orientation of the oscillating electric vector of the radiation field relative to a Cartesian coordinate system fixed on the molecule.

In order for one (or more) of these integrals to be non-zero, the normal mode vibrational wavefunction, Ψ_v^j, must belong to the same representation as *x*, *y*, or *z*.

Therefore:

A fundamental will be infrared active if the normal mode that is being excited belongs to the same representation as any one (or several) of the Cartesian coordinates.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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

For Raman scattering it is necessary that at least one integral of the type below be non-zero:

$$\int \psi_v^{\circ} \, \boldsymbol{P} \, \psi_v^{j} \, d\tau \neq 0$$

P represents the polarizability tensor of the molecule and is equal to one of the quadratic (square) or binary functions of the Cartesian coordinates:

$$P = x^2, y^2, z^2, \text{xy, xz, yz}$$

and combinations of (e.g., x^2-y^2)

A fundamental will be Raman active if the normal mode that is being excited belongs to the same representation as any one (or several) of the components of the polarizability tensor of the molecule.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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

In general, for any molecule that has an inversion center of symmetry (*i*), there will NOT be any fundamental normal modes in common between IR and Raman spectra.

H_2O has fairly low C_{2v} symmetry (no inversion center) so there is extensive overlap of the IR and Raman active modes:

	IR	Raman
$2A_1$	z	x^2, y^2, z^2
B_1	x	Xz

IR spectra of water