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TABLE OF CONTENTS

1. Learning Outcomes

After studying this module, you shall be able to

- Know/state the characteristics of a group
- Verify the characteristics of the group through common examples
- Know the total symmetry operations generated by a symmetry element.
- Total symmetry operations generated by all elements of the molecule.
- It is the symmetry operations that constitute the group and not the symmetry elements.
- See the effects of symmetry operations on H_2O molecule and equilateral triangle. Define sub group
- Find sub groups in main groups
- Examples of main groups and sub groups in it
- Know what is similarity transformation
- Characteristics of conjugate elements
- How to find a class in a group?
- Sub groups in H_2O and PH_3 molecular point groups
- Some simple rules for finding a class in a group

2. Introduction

In order to utilize the molecular symmetry of molecules for solving problems connected with molecular structure, bonding and spectroscopy, it is necessary to link these symmetry properties through group theory (a branch of mathematics) to various properties of the molecules. Molecular symmetry and group theory together can help in

- Simplification of quantum mechanical equations
- Explaining hybridization theory
- Chemical reaction theory
- Finding Wave function
- Spectroscopy
- John-Teller Theorem
- Catalysis theory
- Theoretical prediction of molecular geometry
- Dipole moment
- Optical activity
- Ligand field theory
- Many other chemical applications

Cataloging the molecules symmetry wise is vital and very important. Symmetry of the molecule reveals many properties. A-B-A and A-A-B molecules are very different and this can be easily asserted with the help of symmetry of the molecules and group theory. The important aspects of the symmetry of H_2O and CF_2Cl_2 are the same. But they are quite different molecular species. This is not clear without the help of

Group Theory. Therefore, one should have some basic knowledge of mathematical group theory in order to deal with the subject of molecular symmetry. Group theory began as a branch of pure mathematics dealing with pure numbers only. Group theory is the mathematics of symmetry. Historical development of group theory has three basic roots and these are (i) theory of algebraic equations (ii) number theory and (iii) geometry theory. Discussion of all these routes is not a part of this module.

In order to prove that there is no general algebraic solution for the roots of quintic equations or any general polynomial equation of degree greater than four, group theory was developed independently through the efforts of Abel and Galois in the beginning of ninth century. In this module basics of group theory, as relevant to discussion molecular symmetry of molecules, will be discussed.
A number of books confuse the students by saying that symmetry elements of the molecule constitute a group which is not so. It is the symmetry operations that constitute a group in true sense. After ascertaining the symmetry of the molecule in terms of types of symmetry elements present in the molecule it is necessary to know whether the symmetry operations generated by these elements constitute a group or not. In this module various examples will be taken to explain the fact that **symmetry operations constitute a group.**
The number of elements in the group represents its order. It is a whole number only. Now we will see whether it is possible that smaller number of elements in the group constitute a group of lower order that satisfies al the four properties of a group. Can we divide further the group into smaller order groups? Smaller order groups in the main group are termed as sub groups.

3. Definition of group

According to the formal definition of a group, a group is a set /collection of elements, which are combined with certain operation *, such that:

1. The group contains an **identity**
2. The group contains **inverses**
3. The operation is **associative**
4. The group is **closed** under the operation or

In mathematical sense a group may be defined as, "collection/set of elements/numbers having certain properties in common i.e. these elements are bound by certain conditions, known as group properties/postulates". The elements do not need to have some physical significance. My emphasis will be mainly on ''**symmetry operations as the collection of elements of the group**".

3.1 Basic properties of a group:

There are four basic properties/conditions/postulates/characteristics of a group .The elements belonging to the group should follow/adhere to these conditions in a true sense. Let us state these conditions and explain these by taking suitable examples. Let the elements of the group be [A, B, C, D, E----X-]. The four conditions are:

(I) In the collection (i.e. group) there must an element such when it combines/multiplies with each and every other elements of the group, it leaves them unchanged. This element is the identity element symbolized as 'E' and this property can be expressed as:
AE=A, BE=B, CE=C, DE=D and so on. Further this type of combination with E is commutative (order of combination/product is immaterial) i.e. when order of combination is reversed the results, EA=A, EB=B, EC=C, ED=D are also true. Here mode of combination may be multiplication, addition, subtraction in mathematical sense or in symmetry sense one symmetry operation followed by another symmetry operation. There is only one identity element for every group.

(II) Each and every element in the group must have an inverse, say (X) , which is also the member of the group i.e. AX = XA = E . Here, X is the inverse of A and A is the inverse of X i.e. AX =XA=E
or $A=X^{-1}$, $A^{-1}=X$ ie $AA^{-1}= E$.
Inverses are unique. It is to be noted that there exists only one identity for every single element in the group but each element in the group has a different inverse.

(III) Although the combination of two elements may or may not be commutative, but it must be associative. In group { A,B,C,D----X---} following relations are valid A(BC)=(AB)C=ABC. Provided the order of combination is not changed. This associative property can be extended to any number of elements of the group. This associative result of elements must be an element of the group.

(IV) Closure: Results of combination (multiplication, addition, subtraction) of two or more elements or square of the element (the element is combined with itself) must be equivalent to an element of the group, which is also the member of the group. The group is closed under the given combination.
In group [A, B, C, D---X-] these type of combinations and their results may be AB=C, AC=D, BC= another element of the group only. It is not necessary that combination AB= combination BA i.e. combination may be commutative or non-commutative. Order of combination matters in a group .This order of combination is very significant. This is true in case of symmetry product of symmetry operations.

3.2 Examples of group and verification of the characteristics

Example 1
Show that a group [0] and mode of combination as addition constitutes a group.
Group contains a single element 0 in it. Property number [I] that there should be an element in the group such that when it combines with each and every element of the group leaves it unchanged. Since group contains only 0 as the element, such element will be 0 itself as 0+0=0.
Element 0 is unchanged. Property [II] each element in the group must have its unique inverse. Here inverse of 0 is 0 itself, as $0+0^{-1}=0$.Other properties are easy to verify as there is a single element in the group.

Example 2
Show that the integers [------ -3,-2,-1, 0,+1,+2,+3-----] under the mode of combination as addition and zero as the **identity** element constitutes a group of infinite order.

Here, the identity element is 0.You add 0 to any element of the group and it will remain unchanged.
3+0=3,5+0=5 ,-6+0=-6 and so on. Addition of 0 to the right or left to the number does not matter, i.e. 4+0=4 or 0+4+4.So property [I] is satisfied. According to property [II] each element in the group has its

unique inverse. Let inverse of integer n is n^{-1}.Since the mode of combination is addition in this example the inverse of +n will -n as (n)+(-n)=0(identity). Element when combined with its inverse gives identity. For example -3+3=0, (+4)+(-4)=0 and so on. According to property [III], you can combine any number of elements, the net result will be an element of the group. Order of combination of elements should not be changed. In this example changing of order does not matter. But when we deal with symmetry elements of the group it matters a lot. For example (-3)+(-2) +(-1) =[-3+(-2)]+(-1) = (-3) + [(-2) +(-1)]= -6 Since this group is of infinite order, property (III) is easily satisfied. Let us take property (IV). Identity is zero. A combination of two or more elements or square of the element (addition of number to itself) must give a number that belongs to group.

-2+(-1)=-3, and -3 belongs to group (because it is of infinite order)

-2+- 2 = -4 (square of the element),-4 belongs to group

-2 +-3 +3 = -2 (more elements combined).-2 belongs to group

Thus property (IV) is satisfied.

This group under the mode of combination as multiplication does not constitute a group as the identity element 0 when combined (here multiplied) with other elements, changes them i.e. 4x0=0, thus 4 changes to 0.

The set of natural numbers 0, 1, 2, 3,----- under addition is not a group as there is no inverse of the elements except that of zero .

Example 3

Show that the group [-1,1] under the mode of multiplication constitutes a group.

First let us find the identity element in the group. There are three possibilities -1 is the inverse,+1 is the inverse or there is no inverse. Let us take the following products:

1x1=1, -1x1=-1, -1x-1=1, number 1 does not change 1or -1 when these are combined (here multiplication) with 1.-1 is not the identity as it change the element when it is combined with other element. Now we need to find the inverse of the element of the group and it should be such that 1x1-1=1, -1x-1-1=1.

Here, 1x1=1 so 1 is the inverse of 1and -1x-1=1 so the inverse of -1 is -1 itself as these products give identity 1 as the element. Since in the group there are only two elements you combine in any way you will get the same result and net result will be an element of the group.

1x1=1, -1x-1=1, -1x1=-1(element is combined with itself or square of the element) or 1x-1=-1 etc.

The group [-1, 1] under the mode of addition does not constitute a group. As 1+-1=0 and 0 is not the element of the group and so on you can verify other properties.

Example 4

Show that the group [1,-1, i, -i] under mode of combination as **multiplication** and 1 as the identity element constitutes a group.

Let us prove four properties of the group.

Property (I) AE=A etc. 1x1=1, 1x-1=-1, i x1=i,–i x1=-I, i.e. number are not changed. So 1 is the identity here

Property (II) Let us find the inverses, $(-1)^{-1} = -1, (-i)^{-1} = i, (i)^{-1} = -i, (1)^{-1} = 1$.
It can be checked that when element and its inverse is combined identity 1 is obtained
$(-1)x(-1)=1$, $(-i)x(i)=-i^2=1$, $(i)x(-i)=-i^2=1$, $(1)x(1)=1$
Property (III) Law of associative multiplication (AB)C=A(BC)-----
$(1)x(-1)x(i) = \{1x-1\}x(i) = 1x\{-1x\ i\} = -i$.
Property (IV) AB=C----etc
1x-1=-1 ,-1x-1=1, 1x1=1 , i x i=-1 , i x-i=1, i x1=i, i x-1=-i , 1x i x-i=1 etc.

You combine any number of elements you will get the element of the group.

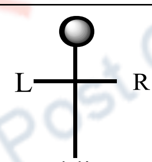
Example 5

Show that all powers of [------2^{-2}, 2^{-1}, 2^0, 2^1, 2^2, -----] form an infinite group with mode of combination as multiplication.
Let us first find the identity by taking the following products: $2^{-2}x2^0=2^{-2}$, $2^{-1}x2^0=2^{-1}$ the element is not changed. So 2^0 is the identity here. Inverse of an element 2^n is 2^{-n} as $2^n x\ 2^{-n}=2^0$(identity). Further you combine any number of element in any way here you will get the element of the group only.

$2^{-2}x2^{-1}x\ 2^0=2^{-3}$, $2\text{-}^1\ x2^2=2^1$ and so on .Law of closure can also be verified in similar manner.

Example 6

Let us explain the group properties by taking an example of face movements of a soldier in exercise drill.

L stands for Left Turn command **R stands for Right Turn command** **A stands for About Turn command** **E means no command or stand at ease**	

These four face movements L,R,A,E of soldier constitute a group with E (stand at ease) as identity and mode of **combination** is one face **movement on command** followed by the other face movement on command i.e. these four face movements on command constitute a group [L,R,A,E].Let us now verify the four properties of this group. According to property (I) there must be an element into the group which on combination with other element does not change the element. This is E here ie no command is given to the soldier AE=A , means E movement followed A (about turn)movement i.e. soldier follows the face movements in the order as; **stand at ease followed by about turn by 180^o**. This combined movement is equivalent to A. Also EA=A .Similarly, LE=EL=L and RE=ER=R etc. Here order of face movement matters.
According to property (IV) the product or combination of any two or more elements or square of an element must be an element of the group.

$\overleftarrow{LR}=E$ $\overleftarrow{AR}=L$ $\overleftarrow{AA}=E$ $\overleftarrow{LAR}=A$

Direction of arrow indicates the order of face movement to be carried i.e. move from right to left and must be followed in all cases. Results of some face movements are shown in Figure 1.

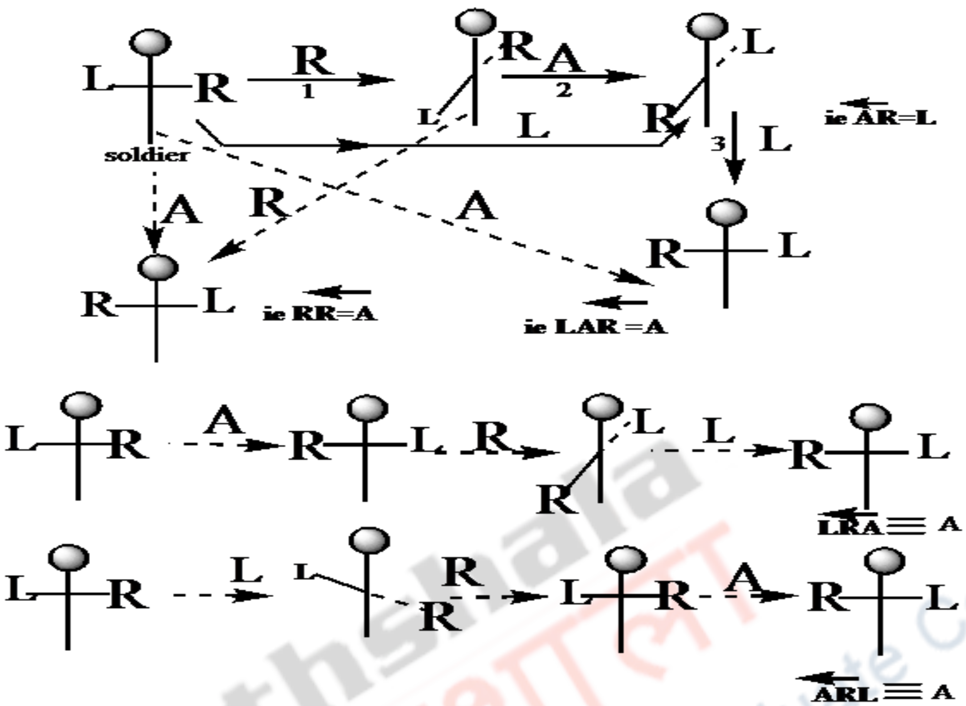


Figure 1

You can verify all other group properties of this group.

3.3 Theorem of Reciprocals

In a group **the reciprocal of the product of two or more than two elements is equal to the product of the reciprocals of elements taken in reverse order.**

Let the group be [A, B, C, D, E, ----------X]. Then according to the theorem reciprocals

$$(ABCD\text{----------})^{-1} = (D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

Let us prove this . If A, B, C, D,---- are the elements of the group then the product (ABCD) must be an element of the group (property IV of the group) and (ABCD) product is equivalent another element X of the group such that

$$(ABCD)=X$$

Right multiply both sides with $(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$

$$(ABCD)(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

Taking help of law of associative multiplication we can work out the left hand side of this relation as;

$$(ABC)(D)(D^{-1})(C^{-1}B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

$$(ABC)(DD^{-1})(C^{-1}B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

$$\mathbf{(ABC)(E)(C^{-1}B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})}$$

Element and its reciprocal when combined gives identity E and identity E when combined with element leaves it unchanged

$$\mathbf{(ABC)(E)(C^{-1}B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})}$$

$$\mathbf{(ABC)(C^{-1}B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})}$$

$$\mathbf{(AB)(CC^{-1})(B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})}$$

$$\mathbf{(AB)(E)(B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})}$$

$$\mathbf{(AB)(B^{-1}A^{-1}\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})}$$

$$\mathbf{(A)(B\,B^{-1})(A^{-1})\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})}$$

$$(A)(E)(A^{-1})\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

$$(A)(A^{-1})\text{--------}) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

$$(E) = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

$$E = X(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

Since X combined with $(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$ gives identity E, therefore, X and $(D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$ are inverse to each other or

$$X^{-1} = (D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

And X=ABCD-----as defined earlier. Putting the value of X one gets

$$(ABCD\text{----})^{-1} = (D^{-1}C^{-1}B^{-1}A^{-1}\text{--------})$$

Hence the theorem is proved.

4. Some common types of groups

During the discussion of group theory and its applications in chemistry you will come across some more common types of group. Some basic knowledge of these is must.

4.1 Abelian group

In our previous discussion on group properties the order of combination of elements was stressed. In case of integers and addition as the mode of combination the order of combination does not matter but in symmetry operations as group elements it matters a lot. An abelian group is that group in which all elements when combine in either way give the same result. In a group [A, B, C, D----] all combination products

AB=BA, AC=CA, BC=CB-------- are true i.e. the elements commute with each other.

The integers [------ -3, -2, -1, 0, +1, +2, +3-----] under the mode of combination as addition and zero as the identity element constitutes an abelian group of infinite order.

4.2 Cyclic group

In this group the elements are generated by taking the power of one group element. Let the element be X that generates all other group elements. Then the group elements are X^1, X^2, X^3, X^4---------X^n =E. There are n elements in the group and thus the order of the group is n. Cyclic group is always an abelian group as powers are additive and their order of combination does not matter.
$X^1+X^2=X^2+X^1=X^3$

4.3 Finite and infinite groups

The group which has infinite number of elements in it is called infinite group. All positive and negative integers with zero as the identity and addition as the mode of combination constitute an infinite order group ie [------4, 3, 2, 1 0,-1,-1,-3,-4-------] with addition as mode is a n infinite group
In finite group the number of elements is finite. The group (1,-1, i,-i) is a finite group of order **four**.

5. Total symmetry elements and total operations generated

Let us take the example of water molecule and find total symmetry elements in it and total symmetry operations generated by these symmetry elements. Figure 2 shows the various symmetry elements in structure of water molecule.

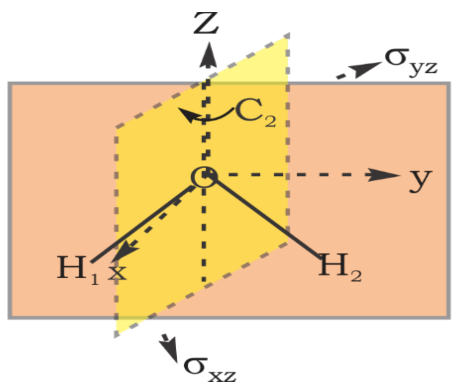


Figure 2: Various symmetry elements in H_2O molecule

There are four symmetry elements σ_{xz} , σ_{yz} ,C_2 and E in H_2O molecule. Total symmetry elements are four. Let us find the symmetry operations generated by each of these.

(i) E generates only one operation and it is **E.**

(ii) σ_{xz} generates σ_{xz}^1 and σ_{xz}^2 =E symmetry operations and these are $\boldsymbol{\sigma_{xz}}$ **and E** only.

(iii) σ_{yz} generates σ_{yz}^1 and σ_{yz}^2 =E symmetry operations and these are $\boldsymbol{\sigma_{yz}}$ **and E** only.

(iv) C_2 generates C_2^1 andC_2^2=E symmetry operations and these are **C_2 and E only.**

Thus total symmetry operations generated here: σ_{xz}, σ_{yz} , C_2 and E in H_2O i.e. only four symmetry operations are generated by four symmetry elements. In case of H_2O molecule number of symmetry elements and symmetry operations are same. It is not same always.

These four symmetry operations constitute a group ie [σ_{xz}, σ_{yz} , C_2 , E] is a group of order four. **Number of elements in a group is its order**. Now let us verify the four group properties.

(I) Here E is the identity, EE=E, $EC_2=C_2E = C_2$; $E\sigma_{xz}= \sigma_{xz}E = \sigma_{xz}$; $E\sigma_{yz} = \sigma_{yz}E = \sigma_{yz}$,thus group element remains unchanged. Figure 3 shows all these results.

Symmetry operations are always carried out from right to left.

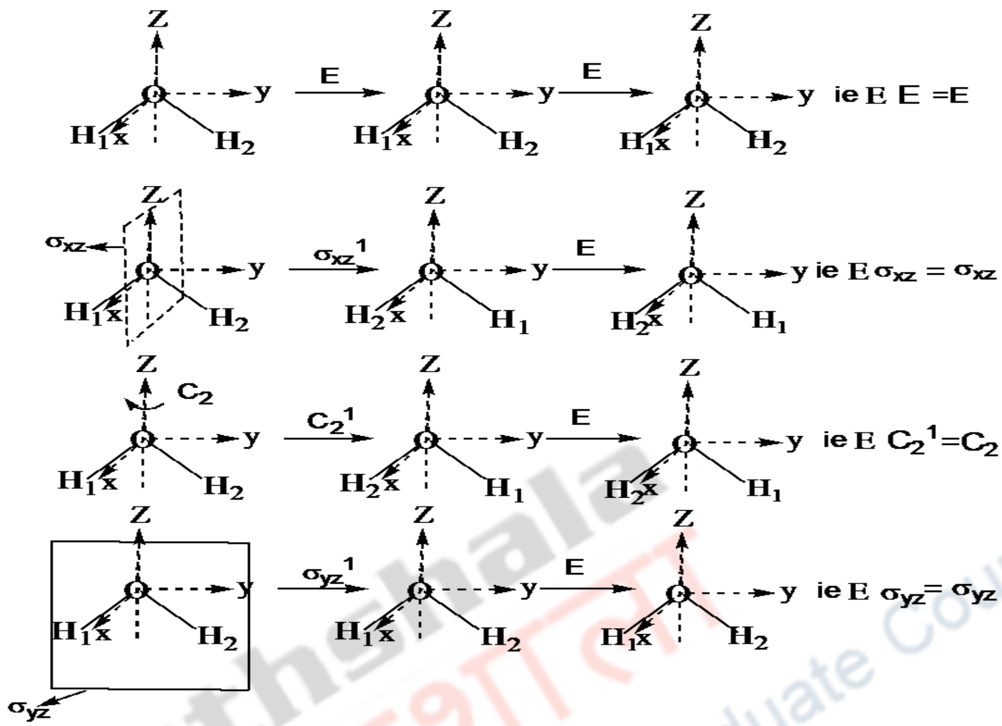


Figure 3: Combination of E with C_2 ,σ_{xz} , σ_{yz}

(II) Every element has its reciprocal (i.e. inverse)
Here $(\sigma_{xz})^{-1}$ is (σ_{xz}) ; $(\sigma_{yz})^{-1} = \sigma_{yz}$ and $(C_2)^{-1}$ is C_2^1. Symmetry operation and its reciprocal when combined give identity i.e.

$$\sigma_{xz}\,(\sigma_{xz})^{-1} = E \;\; ; \sigma_{yz}\,(\sigma_{yz})^{-1} = E; \;\; C_2^1(\,C_2^1)^{-1} = E$$

In Figure 4 we notice that the symmetry product $C_2.C_2 = E$, it means $C_2$is its own inverse i.e. $(C_2)^{-1} = C_2$. Similarly $\sigma_{xz} = E$, therefore, σ_{xz} is the inverse of itself and similarly inverse of σ_{yz} is σ_{yz}.. Thus in the group each element has a unique inverse. Here each and every group element (symmetry operation) is the inverse of itself.

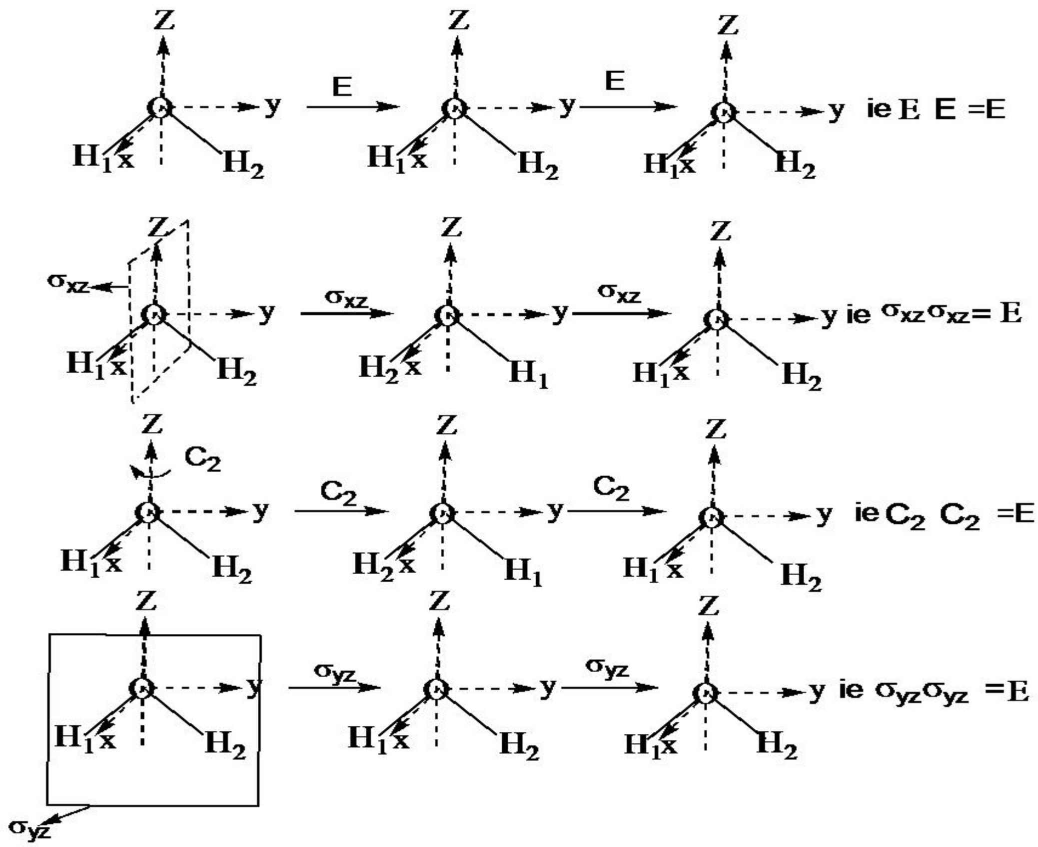


Figure 4: Combination of C_2 with C_2, σ_{xz} with σ_{xz}, σ_{yz} with σ_{yz}

(III) Law of associative multiplication (order of multiplication should not be changed).
$(C_2^1\ \sigma_{xz})\ \sigma_{yz} = C_2^1(\sigma_{xz}\ \sigma_{yz})$. These products are shown in the Figure 5.

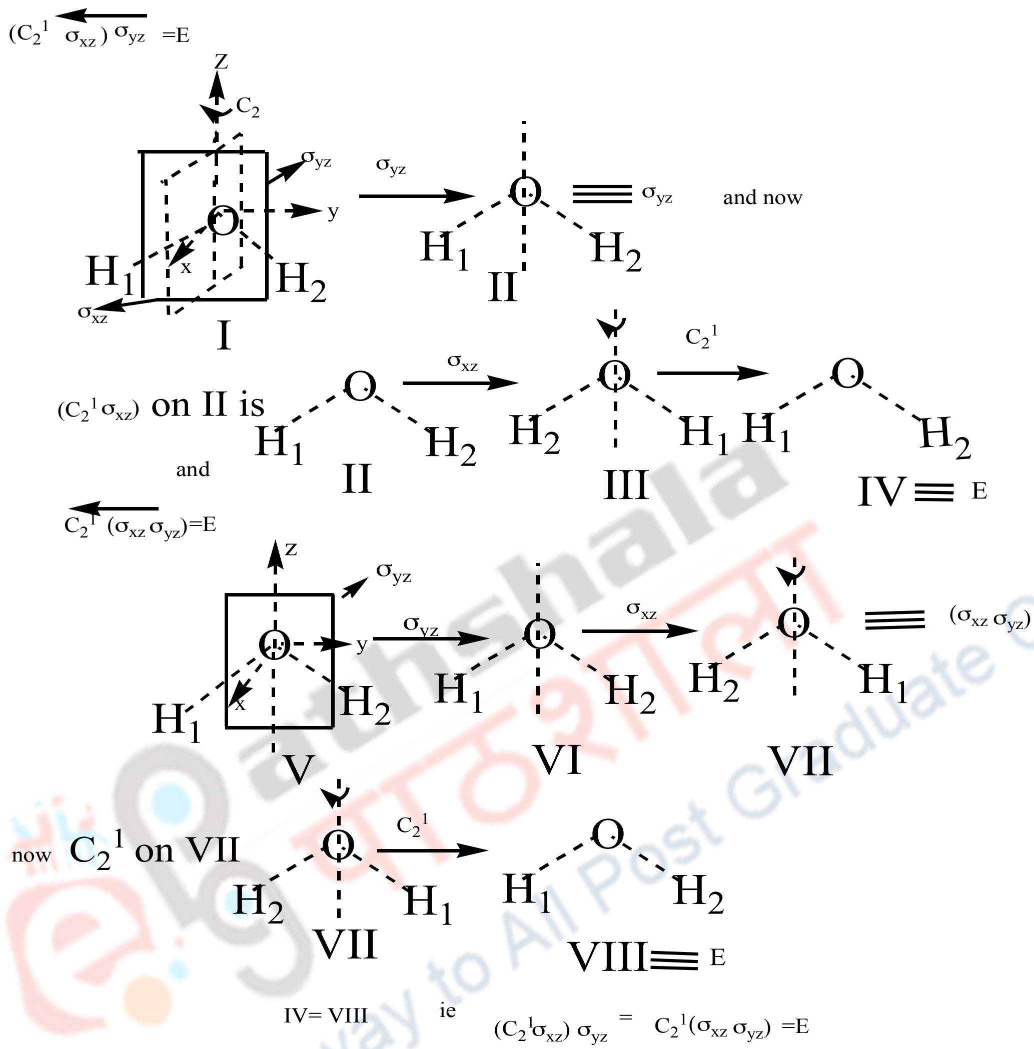
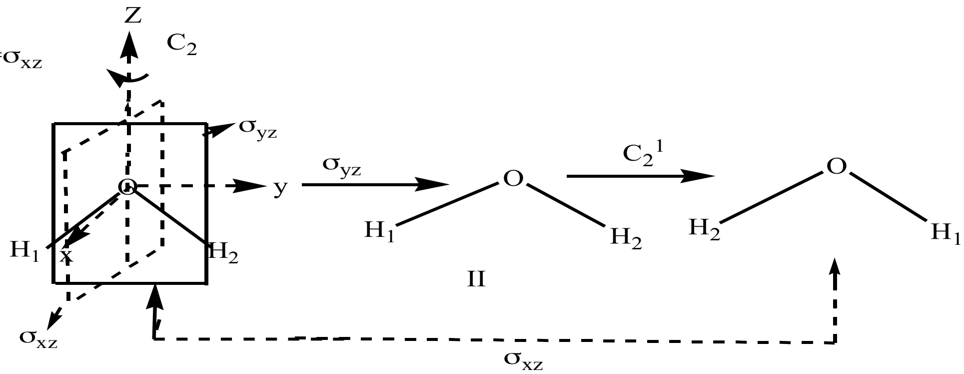


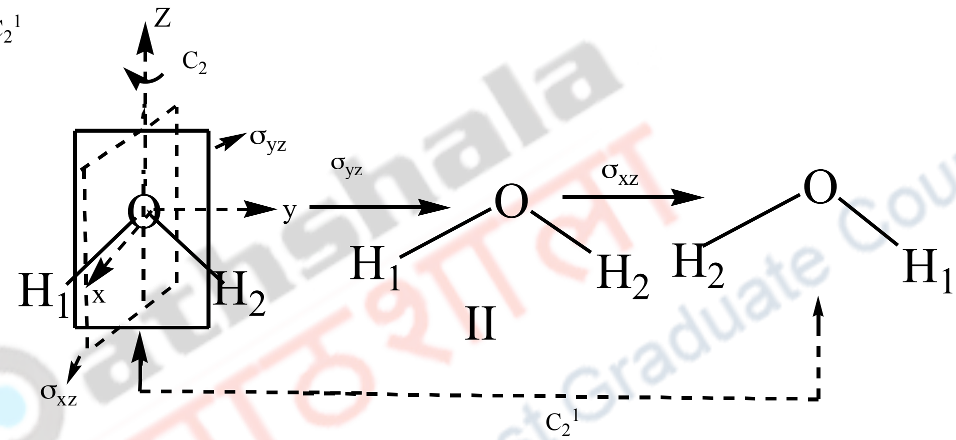
Figure 5: Associative products (C_2 σ_{xz}) σ_{yz} = $C_2^1(\sigma_{xz}\,\sigma_{yz})$ for H_2O molecule

(IV) Product of two or more elements or square of the element must be an element of the group. The combinations of various symmetry operations are shown in figure 6

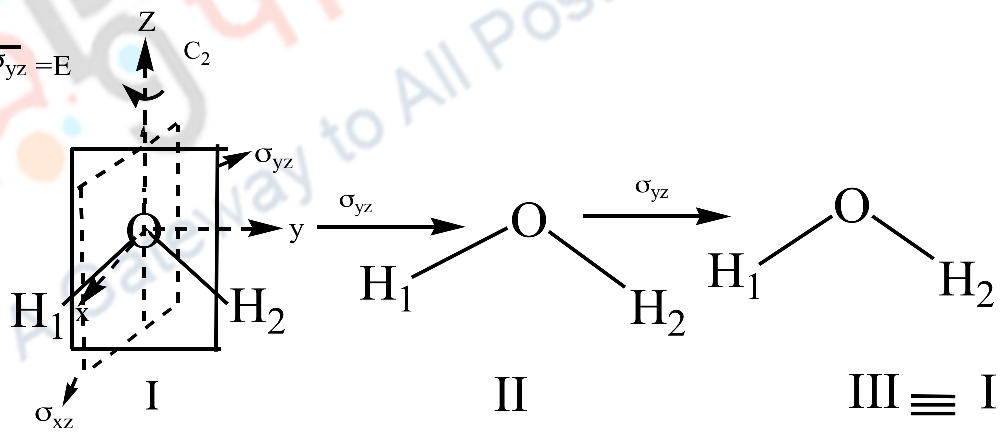
(ii) $C_2^1\sigma_{yz}=\sigma_{xz}$



(i) $\sigma_{xz}\sigma_{yz}=C_2^1$



(iii) $\sigma_{yz}\sigma_{yz}=E$



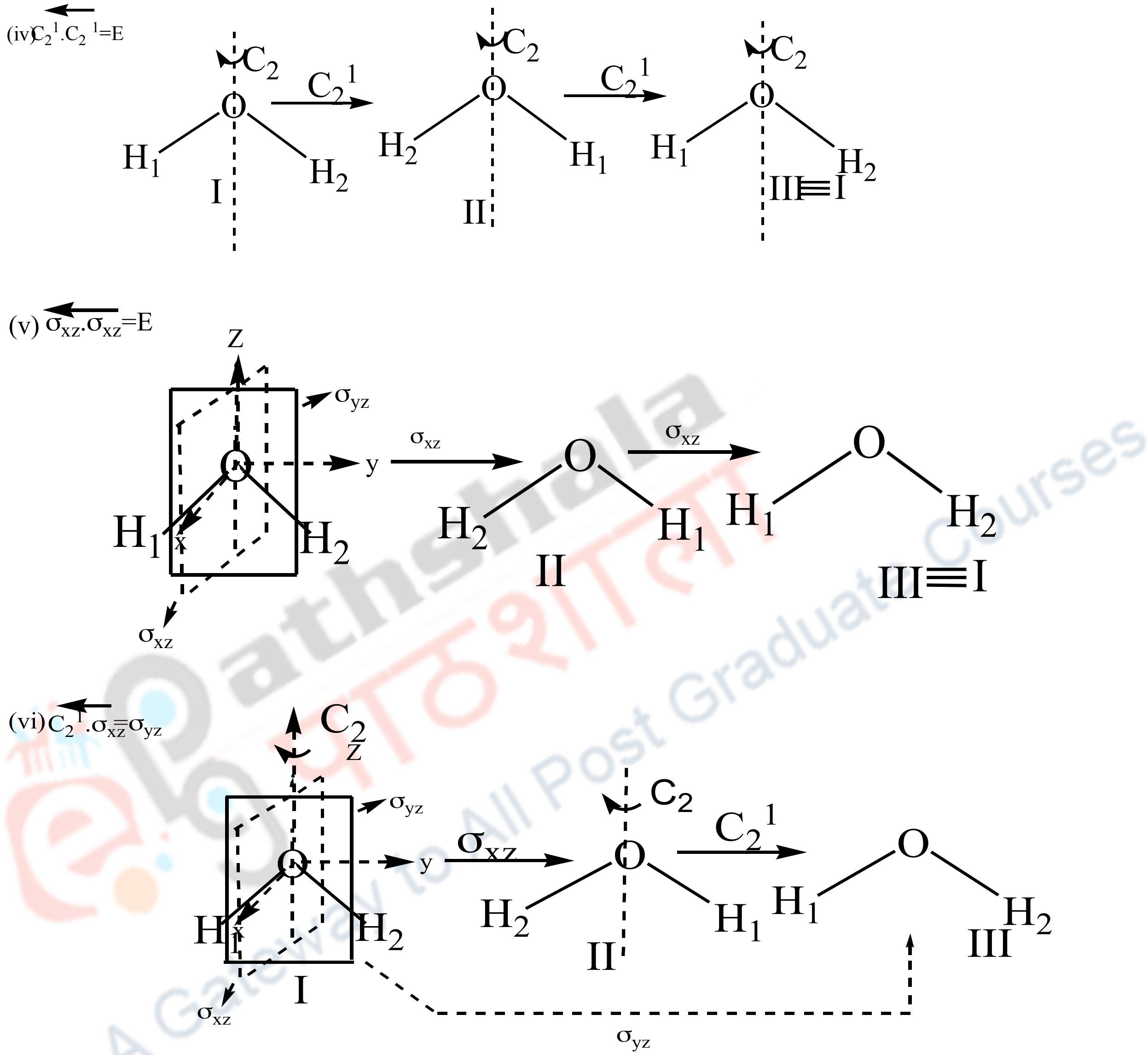


Figure 6: Effect of Combination of Symmetry Operations on H_2O Molecule

Thus all the four properties of a group [σ_{xz} , σ_{yz} ,C_2 , E] have been verified. Let us take another example of C_3 axis in an equilateral triangle and see that operations generated by C_3 axis constitute a group.C_3 axis generates the following symmetry operations: C_3^1,C_3^2, C_3^3 =E i.e. in all three symmetry operations are generated. Various symmetry products are shown in Figure 7.

Similarly other symmetry products can be worked out and all the four properties of the group can be verified. Let us now find the following products or inverses.

$C_3^1.C_3^2=?$; $(C_3^1)^{-1}=?$
$C_3^2.C_3^2=?$ $C_3^1.C_3^1=?$; $(C_3^1)[(C_3^2)(C_3^3)] = [(C_3^1)(C_3^2)](C_3^3)$

Inverse of $C_3^1)^{-1}=C_3^2$ so now show that $C_3^1.C_3^2=E$.

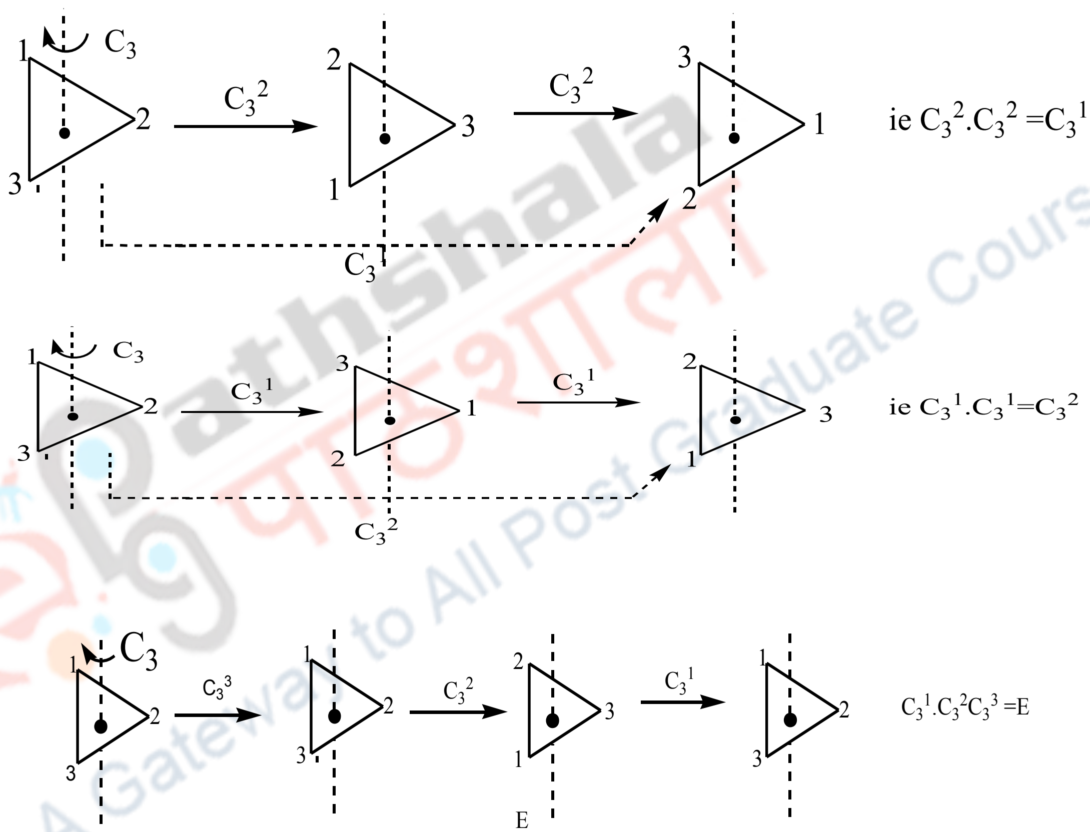


Figure 7: Various symmetry products of Total symmetry elements present in the given molecule symmetry operations C_3^1, C_3^2, C_3^3

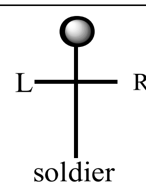
6. Definition of a subgroup

It is defined as a part of the main group which satisfies all the properties of the group ie within the main group of order' h' there may be smaller groups of lower order then 'h'.

(i) Sub group always contains identity element E.
(ii) E itself constitutes a group of order **one** and it is trival.
(iii)The sub group of order **two** also contains identity element E .
(iv) Groups of order two can be E,A ; E,B ; E,C etc in the main group A,B,C,E.
(v) Sub groups always follow the group conditions of the main group.
(vi) Order of the sub group is an integral factor of the order of the main group.
(vii)If the order of sub group is' g' then h/g is an integer and not in fraction.
(viii)If the order of the main group is six, then sub groups can have orders 1,2,3 only(6/6=1,6/2=3,6/3=2) only and 6/4 or 6/5 are fractions.

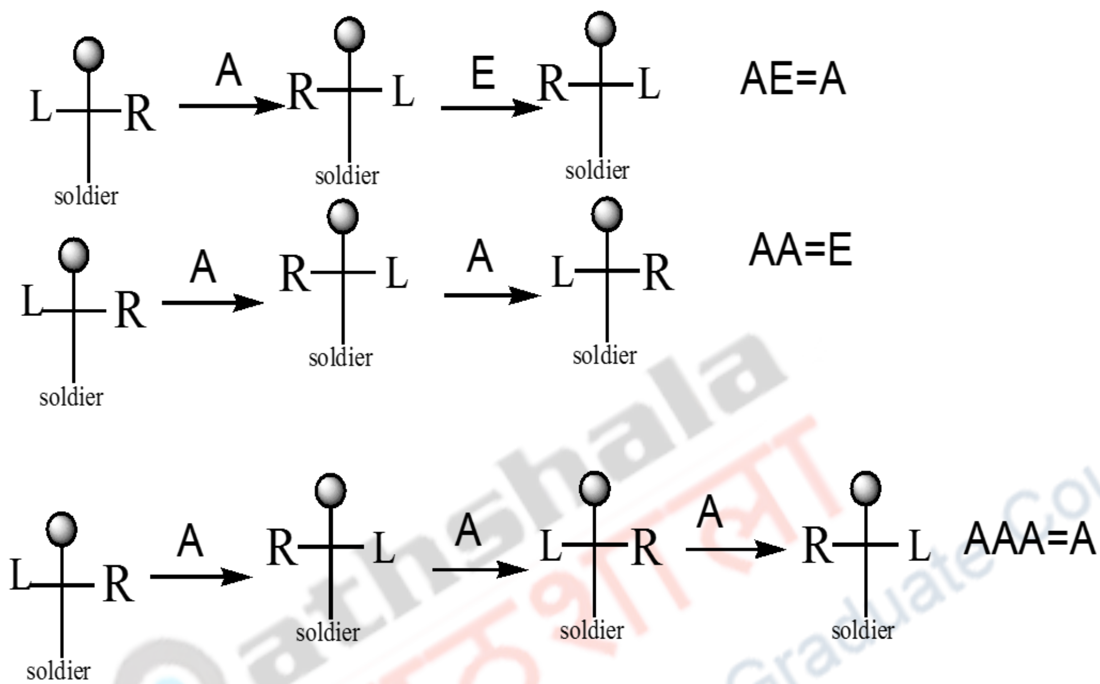
Let us now try to find some sub groups in main group by taking suitable examples. [1,-1,I,-I] is a group of order four under the mode of combination as multiplication. Since the order of the group is four, the sub groups order can be 4/2=2,4/4=1. There will be no sub group of order 4/3=1.33. Since identity always constitutes a sub group order one. Here, identity is 1. So a sub group of order one is [1] .It satisfies all four group properties. The other sub groups of order two in it can be [1,-1], [I,-I], [-1,i] [1,I], [1,-I], [-1,-I] . In these groups of order two, only group [1-1] satisfies all four group properties under the mode of multiplication and 1 as the identity. Here we write some products of this sub group as: 1x1=1, 1x-1=-1, -1x-1=1. Multiplication with 1 does not change the number. Number multiplied with itself also gives the element belonging to the sub group. Thus [1,-1] constitutes a sub group of order two and there are only two sub groups [1] of order 1and [1,-1] of order two in the main group [1,-1,I,-i] of order four.

Let us take another example of face movements of a soldier during exercise. Here L stands for left turn, R stands for right turn , A stands for about turn and E stands for stand at ease or do nothing or stand still. Thus main group is [L, R, A, E].

L stands for Left Turn command **R stands for Right Turn command** **A stands for About Turn command** **E means no command or stand at ease**	

Let us find sub groups in the main group [L, R, A, E] . Here E is trival group of order **one** and non trival sub groups of order of two can be[E,A], [E,L], [E,R] ,[L,R],[A,L],[A,R] (because 4/2= 2 is integer) and so on. Out of [E,A], [E,L], [E,R] sub groups only [E,A]sub group satisfies all the group condition and this is the only subgroup of order two of the main group (L,R,A,E).

EA=AE=A, AA=E, AAA=A, $(A)^{-1}$=A and E^{-1} is E and so on. See Figure 1 for these products.



The remaining groups of order of order two [E,L], [E,R],[L,R],[A,L],[A,R] etc do not constitute groups

To verify that the [E,L] and [E,R] etc do not constitute sub groups is left an exercise for the reader.All sub groups of order g (h/g=integer) need not be sub groups in true sense and that may not follow the conditions of the group.

Symmetry operations σ_{xz} , σ_{yz} ,C_2 and E in H_2O molecules constitute a group. This has been verified in section -5 symmetry operations as group elements. Let us now try to find the sub group in the group [σ_{xz} , σ_{yz} ,C_2 ,E]. E is always a sub group of order one. The other sub groups of order two may be [E,C_2] , [E, σ_{yz}] , [E, σ_{xz}] ,[σ_{xz} , σ_{yz}], [C_2, σ_{yz}], [C_2, σ_{xz}] and so on. Here [E,C_2] ,[E, σ_{yz}] **and** [E, σ_{xz}] **are the sub groups of order two and** [σ_{xz} , σ_{yz}], [C_2, σ_{yz}]and [C_2, σ_{xz}] are not the sub groups of order two. Let us see some of the products by taking example of water molecule. Results are given in Figure 8 and Figure 9.

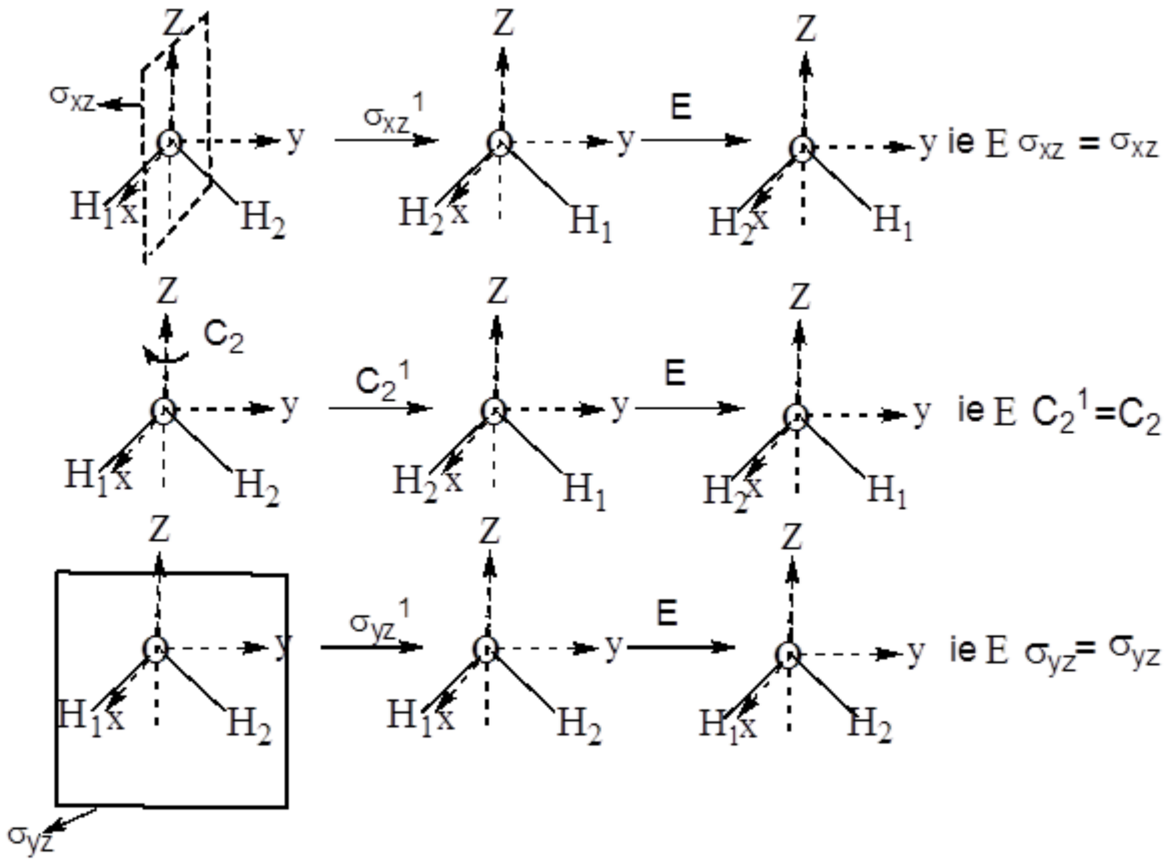


Fig. 8 Combination of E with C_2, σ_{xz} and σ_{yz}

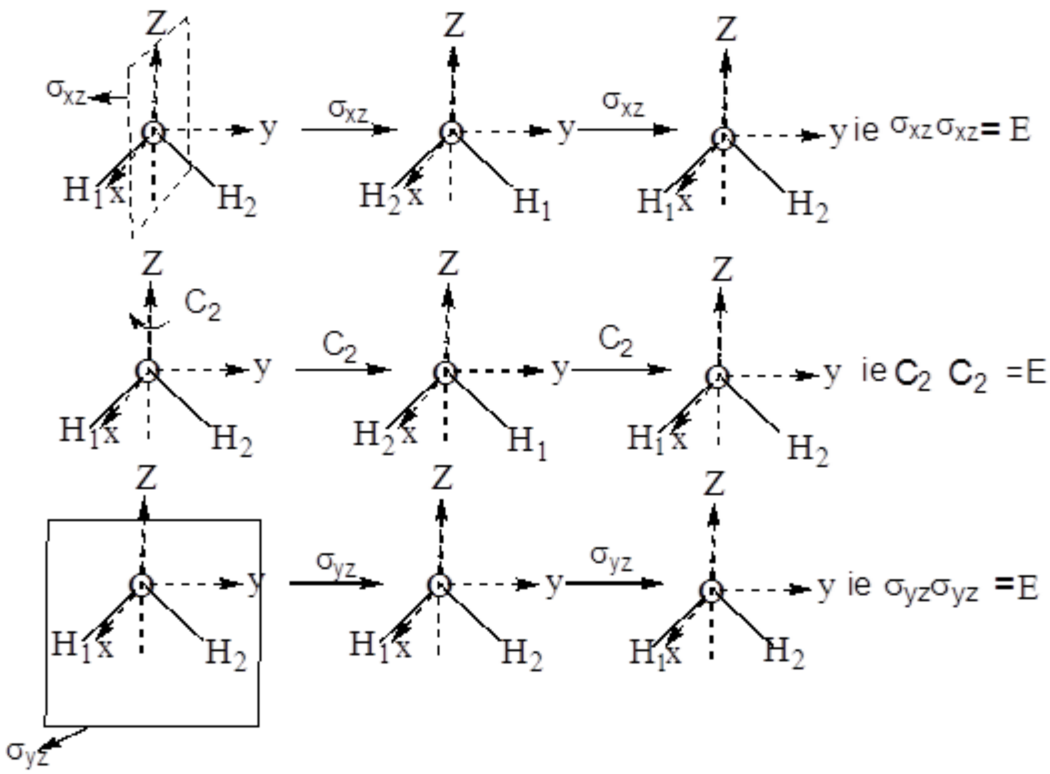


Fig. 9 Combination of C_2 with C_2, σ_{xz}, with σ_{xz} and σ_{yz} and σ_{yz}

These results clearly show that E, [E,C_2] , [E, σ_{yz}] **and** [E, σ_{xz}] **are sub groups of the main group** [σ_{xz} , σ_{yz} ,C_2 ,E].

7. Definition of a Class

This is another way of subdividing a group into smaller collection of elements. It is defined as the collection of all conjugate elements of the group. It has different bases for the division of the group. All conjugate elements are related by similarity transformation. **The order of a class is the integral factor of the order of the main group.**

7.1 Similarity Transformation

If A and X are the element of the group then $X^{-1}AX$ operation will be equal to some element of the group say it is B (or it may be same). This transformation is written as:

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

We can express the result by saying that **B is the similarity transformation of A by X or we can say that A and B are conjugate elements of the group.**

7.2 Characteristics of conjugate elements

Conjugate elements have some characteristic properties and these are given as:

(i) Every element is conjugating with itself. It means if we take element A, then it must be possible to find one element, X, in the group such that

(ii) If A is conjugate to B, then B is conjugate to A ie
$A=X^{-1}BX$ then there must be another element in the group say Y such that $B=Y^{-1}AY$ holds good.

(iii) If A is conjugate with B and C separately, then B and C are conjugate with each other or if A is conjugate to B and B is conjugate to C, then A will be conjugate with C also.

$A=X^{-1}BX$ (A is conjugate with B)
$A=Z^{-1}CZ$ (A is conjugate with C)
Then $B=Y^{-1}CY$ (B is conjugate with C)

7.3 To find a class in group

Let us take finite group [A, B, C, D, E, and F] of order six with E as the identity element in this group. We have to find the classes in this group. We take the similarity transformation of each and every element by all the elements of the group including the element itself. Let us first write down all the similarity transformations for E by all the element including E itself and these are:
$E^{-1}EE=E$(element it self) ; $A^{-1}EA=E$; $B^{-1}EB=E$; $C^{-1}EC=E$; $D^{-1}ED=E$; $F^{-1}EF=E$ ie E transforms into itself by all these transformations. Therefore, E constitutes a separate class itself and number of elements in this class equals to one ie **order is one.**
Now take element A and perform similar transformations on it and say the results are

$A^{-1}AE = A$ $D^{-1}AD = B$(say)
$B^{-1}AB = C$ (say) $F^{-1}AF = C$ (say)
$C^{-1}AC = B$ (say) $A^{-1}AA = A$

In all these transformations A is transformed into A ,B ,C only. Thus A, B, C constitute a class of order three.
Now find similarity transformation for D and the results say are

$E^{-1}DE = D$ $C^{-1}DC = F$
$A^{-1}DA = F$ $D^{-1}DD = D$
$E^{-1}DB = F$ $F^{-1}DF = D$

Here D transforms into D and F only. Therefore, D and F constitute a separate class of order two.
Now take the similarity transformations of F

$E^{-1}FE = F$ $C^{-1}FC = D$
$A^{-1}FA = D$ $D^{-1}FD = F$
$E^{-1}FB = D$ $F^{-1}FF = F$

F transforms to D or F only so no new class is obtained. Thus the [A, B, C, D, E, and F] group can be divided into three classes as: (i) E of order one (ii) A,B,C in a class of order three and (iii) D, F in class of order two.
Let us find similarity transformations for PH_3 molecule. In Figure 10 top view of PH_3 together with various symmetry elements is shown.

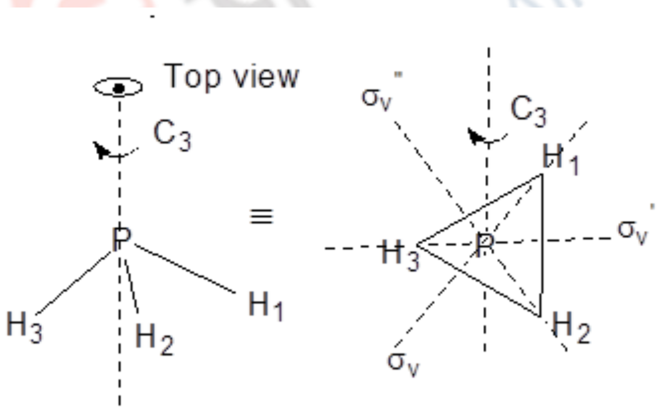


Fig. 10 Top view of PH_3 molecule

Total symmetry operations for the molecule PH_3 are C_3^1, C_3^2, $C_3^3 = E$, σ_v, σ_v' and σ_v'' and these constitute a group . Let us see whether σ_v, σ_v' and σ_v'' symmetry operations (σ generates only one operation) belong to a class. For this let us find the following transformations:

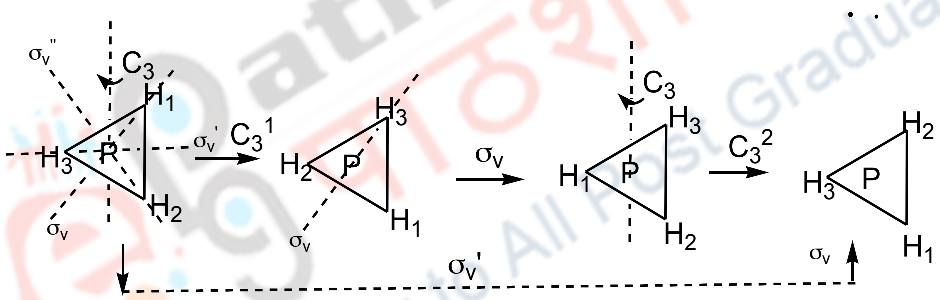
(i) $E\,\sigma_v\,E = \sigma_v$ (ii) $C_3^2\,\sigma_v C_3^1 = \sigma_v'$ (iii) $C_3^1\sigma_v C_3^2 = \sigma_v''$ (iv) $(\sigma_v')^{-1}\,\sigma_v\,\sigma_v' = \sigma_v''$(v) $(\sigma_v)^{-1}\,\sigma_v\,\sigma_v = \sigma_v$

(vi) $(\sigma_v'')^{-1}\,\sigma_v\,\sigma_v'' = \sigma_v'$

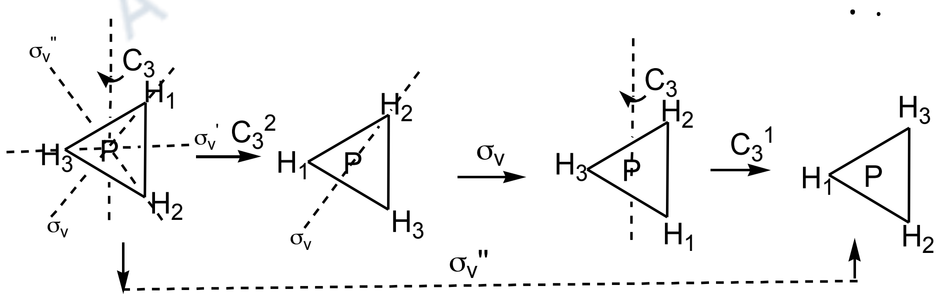
During rotations/reflections the already defined symmetry elements and their frame work do not shift with molecular rotations/reflection ie **reference frame remains intact**. The results of similarity transformations are shown in figure.11. C_3^2 and C_3^1 are inverse of each other so also each σ is the inverse of itself.

(i) $E\,\sigma_v\,E = \sigma_v$

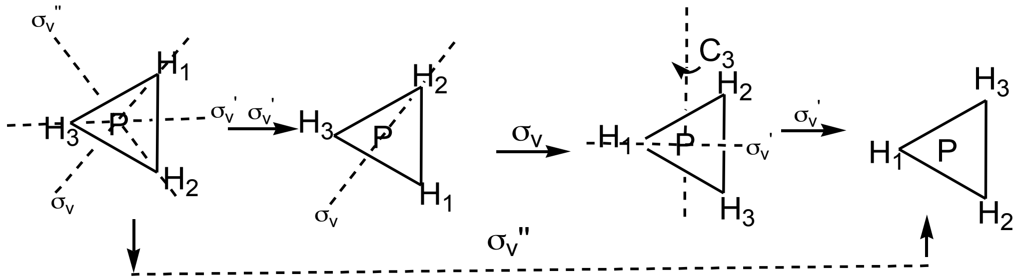
(ii) $C_3^2\sigma_v C_3^1 = \sigma_v'$



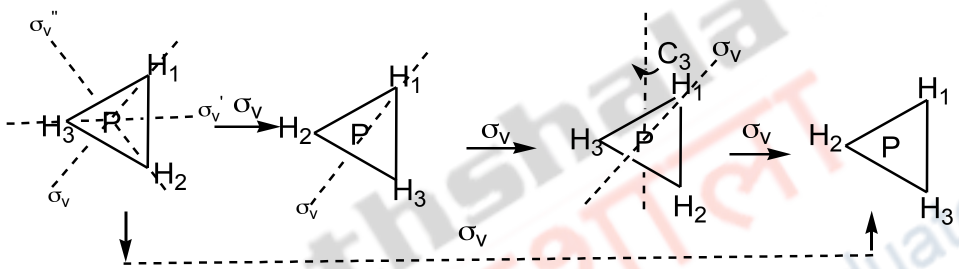
(iii) $C_3^1\sigma_v C_3^2 = \sigma_v''$



(iv) $(\sigma_v')^{-1}\,\sigma_v\,\sigma_v' = \sigma_v''$



(v) $(\sigma_v)^{-1}\ \sigma_v\ \sigma_v = \sigma_v$



(vi) $(\sigma_v'')^{-1}\sigma_v\ \sigma_v'' = \sigma_v'$

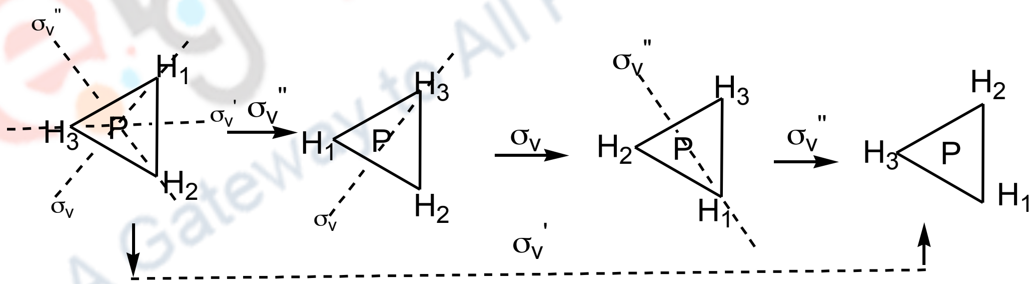


Figure 11: Effect of successive symmetry operations in PH_3 molecule

Thus all the similarity transformations on σ_v by E, C_3^1, C_3^2, σ_v, σ_v', σ_v'' give results as σ_v, σ_v', σ_v'' only. Similarly by carrying out similarity transformation on σ_v', σ_v'' by E, C_3^1, C_3^2, σ_v, σ_v', σ_v'' give the results as σ_v, σ_v', σ_v'' only. Thus out of six operations of PH_3 $3\sigma^{'}_{s}$ (σ_v, σ_v', σ_v'') constitute a separate class. Similarly it can be shown with the help of a diagram that C_3^1 and C_3^2 constitute a separate class.

Thus in a group $[C_3^1, C_3^2, ,\sigma_v, ,\sigma_v' \ \sigma_v'']$ there are three classes (i) E of order one (ii) $\sigma_v, \sigma_v', \sigma_v''$ of order three and (iii) C_3^1, C_3^2 of order two. To find classes in this way is very cumbersome and takes lot of time.

For example in case of equilateral triangle there are 12 symmetry operations which constitute a group. To find classes in this group one has to carry out $X^{-1}AX$ types of similarity transformations 144 times. The procedure can be simplified if certain rules, which are normal, be followed in practice and these are:

4.4 Some simple rules for finding classes

(i) The symmetry operations, E, i and σ_h each are in separate class themselves.

(ii) Same (rule ii) is true for S_n^k and S_n^{-k} improper axes of rotation as it is true for C_n^k and C_n^{-k} axes.

(iii) Two reflections σ and σ' will belong to a same class if there is another symmetry operation into the group which moves all the points on σ' into corresponding points on σ.

(iv) σ_v and σ_d will belong to different classes.

The simplest way of arranging the symmetry operations into classes is to arrange them into sets of equivalent symmetry operations which have equivalent effects on the molecule. You will learn about equivalent symmetry operations in another module.

8. Summary

- Importance of group theory and its historical development mentioned in very brief
- Definition of group is given and explained
- Group postulates are stated and explained
- Group postulates are verified by taking several common examples
- Example of face movements of soldier has been explained in detail with the help of diagram
- Theorem of reciprocals stated and dually verified
- Definitions of some more common types of groups abelian group, cyclic group, finite and infinite groups have been introduced Total symmetry elements present in the given molecule.
- Total symmetry operations generated by all the symmetry elements.
- All symmetry operations so generated constitute a group.
- Symmetry operations generated by C_3 axis of an equilateral triangle also constitute a group.
- It is the symmetry operations that constitute a group and not the symmetry elements.