Molecular Symmetry and Group Theory

Rijoy Kodiyan Jacob

July 9, 2020

विद्यास्मद परदेवता

Symmetry and Symmetry Elements

Symmetry

An object is said to possess symmetry if it can take up two or more spatial orientation that are indistinguishable from each other, i,e, if it can take up two or more equivalent orientations.

Symmetry and Symmetry Elements

Symmetry

An object is said to possess symmetry if it can take up two or more spatial orientation that are indistinguishable from each other, i,e, if it can take up two or more equivalent orientations.

A symmetry operation is an action which when performed on an object yields a new orientation of it; i.e. indistinguishable from the original, though not necessarily identical with it.

Symmetry and Symmetry Elements

Symmetry

An object is said to possess symmetry if it can take up two or more spatial orientation that are indistinguishable from each other, i,e, if it can take up two or more equivalent orientations.

A symmetry operation is an action which when performed on an object yields a new orientation of it; i.e. indistinguishable from the original, though not necessarily identical with it.

In other words, a symmetry operation is the movement of an object that brings into an equivalent configuration.

Symmetry and Symmetry Elements

Symmetry

An object is said to possess symmetry if it can take up two or more spatial orientation that are indistinguishable from each other, i,e, if it can take up two or more equivalent orientations.

A symmetry operation is an action which when performed on an object yields a new orientation of it; i.e. indistinguishable from the original, though not necessarily identical with it.

In other words, a symmetry operation is the movement of an object that brings into an equivalent configuration.

Every symmetry operation is considered to be associated with a symmetry element with respect to which that operation is carried out.

Every symmetry operation is considered to be associated with a symmetry element with respect to which that operation is carried out.

A symmetry element (element of symmetry) is a geometrical entity such as a line, a plane, or a point with respect to which a symmetry operation may be performed.

Important Symmetry Elements

- The identity operation - identity element ‘E’.

Important Symmetry Elements

- The identity operation - identity element 'E'.
- The proper rotation operation - Proper rotation axis 'C_n.

Important Symmetry Elements

- The identity operation - identity element 'E'.
- The proper rotation operation - Proper rotation axis 'C_n.
- The reflection operation - Plane of symmetry or Mirror plane 'σ'.

Important Symmetry Elements

- The identity operation - identity element ‘E’.
- The proper rotation operation - Proper rotation axis ‘C_n.
- The reflection operation - Plane of symmetry or Mirror plane ‘σ’.
- The improper rotation operation - Improper rotation axis ‘S_n’.

Important Symmetry Elements

- The identity operation - identity element ‘E’.
- The proper rotation operation - Proper rotation axis ‘C_n.
- The reflection operation - Plane of symmetry or Mirror plane ‘σ’.
- The improper rotation operation - Improper rotation axis ‘S_n’.
- The inversion operation - Centre of symmetry ‘i’ or Inversion Centre.

1. Identity Element

- The identity operation is the one in which the molecule remains in its original state.

1. Identity Element

- The identity operation is the one in which the molecule remains in its original state.
- It is effectively ‘do nothing’ or ‘leave the system alone’ or ‘leave the system unchanged’ operation.

1. Identity Element

- The identity operation is the one in which the molecule remains in its original state.
- It is effectively 'do nothing' or 'leave the system alone' or 'leave the system unchanged' operation.
- It is denoted by the symbol 'E'.
- All molecules possess this symmetry element.

2. Axis of Symmetry, C_n

An axis of symmetry or proper rotation axis is a line about which rotation through a certain angle brings a molecule or object into an orientation that is indistinguishable from and super imposable on the original.

2. Axis of Symmetry, C_n

An axis of symmetry or proper rotation axis is a line about which rotation through a certain angle brings a molecule or object into an orientation that is indistinguishable from and super imposable on the original.

In other words it is a line about which molecule or object may be rotated so that it presents exactly the same appearance more than once in the course of complete revolution.

2. Axis of Symmetry, C_n

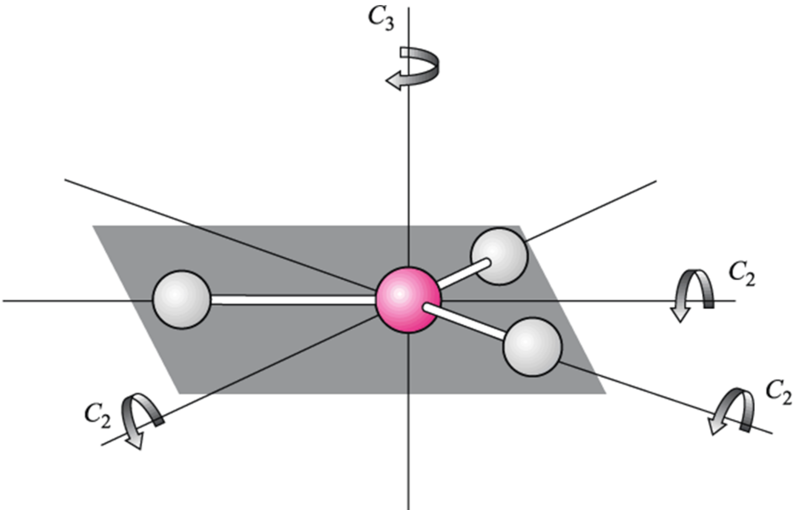
An axis of symmetry or proper rotation axis is a line about which rotation through a certain angle brings a molecule or object into an orientation that is indistinguishable from and super imposable on the original.

In other words it is a line about which molecule or object may be rotated so that it presents exactly the same appearance more than once in the course of complete revolution.

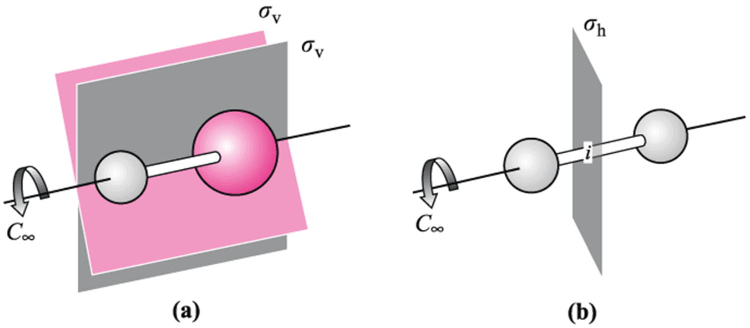
An axis of symmetry is given the general symbol C_n and is called a n-fold rotation axis where 'n' is referred as the order of the rotation. It means that a rotation of a molecule in the anti clockwise direction about the axis through an angle of (360/n) degrees produces an equivalent configuration.

BF_3 molecule has one C_3 axis (principal axis), and three C_2 axis

BF_3 molecule has one C_3 axis (principal axis), and three C_2 axis



$C\infty$ Axis



3. Plane of Symmetry, 'σ'

It is a plane which bisects the molecule into two halves which are mirror images of each other.

3. Plane of Symmetry, ‘σ’

It is a plane which bisects the molecule into two halves which are mirror images of each other.

There are three types mirror planes in a molecule.

- Vertical plane of symmetry or vertical plane ‘σ_v’.

3. Plane of Symmetry, ‘σ’

It is a plane which bisects the molecule into two halves which are mirror images of each other.

There are three types mirror planes in a molecule.

- Vertical plane of symmetry or vertical plane ‘σ_v’.
- Horizontal plane of symmetry or horizontal mirror plane ‘σ_h’.

3. Plane of Symmetry, 'σ'

It is a plane which bisects the molecule into two halves which are mirror images of each other.

There are three types mirror planes in a molecule.

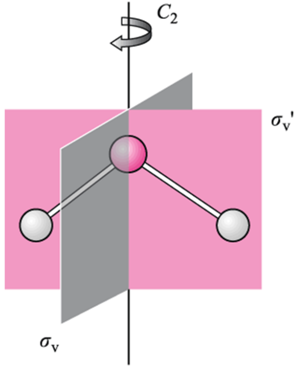
- Vertical plane of symmetry or vertical plane 'σ_v'.
- Horizontal plane of symmetry or horizontal mirror plane 'σ_h'.
- Dihedral plane of symmetry or dihedral mirror plane 'σ_d'.

Vertical plane of symmetry, 'σ_v'.

A symmetry plane contains the principal axis of rotation of the molecule is called a vertical plane of symmetry, 'σ_v'.

Vertical plane of symmetry, 'σ_v'.

A symmetry plane contains the principal axis of rotation of the molecule is called a vertical plane of symmetry, 'σ_v'.

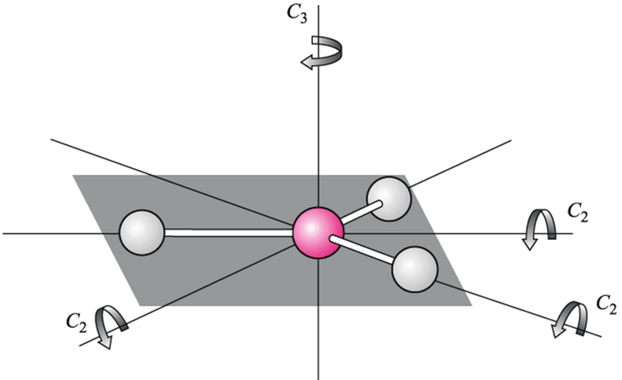


Horizontal plane of symmetry, 'σ_h'.

A symmetry plane perpendicular to the principal axis of rotation of the molecule is called a horizontal plane of symmetry, 'σ_h'.

Horizontal plane of symmetry, 'σ_h'.

A symmetry plane perpendicular to the principal axis of rotation of the molecule is called a horizontal plane of symmetry, 'σ_h'.

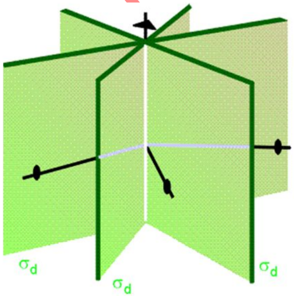


Dihedral plane of symmetry, 'σ_d'.

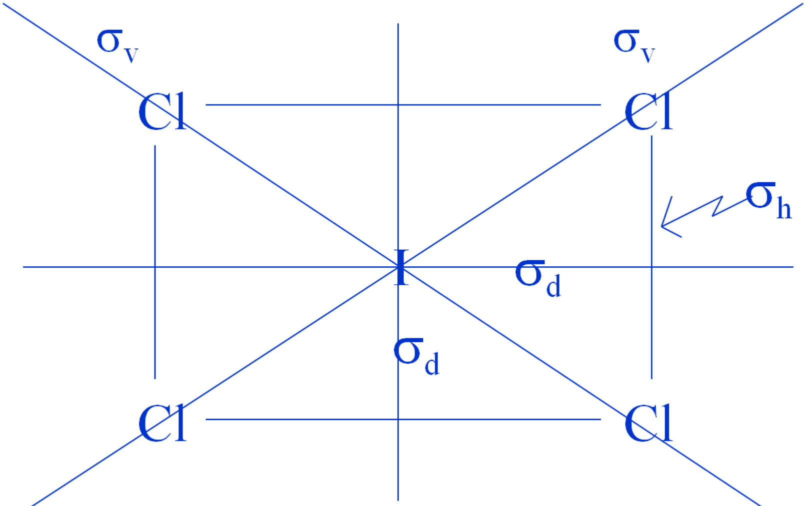
A symmetry plane contains the principal axis of rotation of the molecule and at the same time bisects the angle between two similar C_2 axis adjacent to the principal axis in the molecule is called a dihedral plane of symmetry or dihedral mirror plane 'σ_d'.

Dihedral plane of symmetry, 'σ_d'.

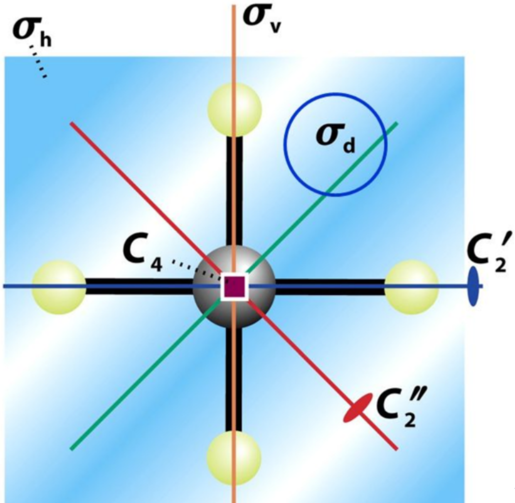
A symmetry plane contains the principal axis of rotation of the molecule and at the same time bisects the angle between two similar C_2 axis adjacent to the principal axis in the molecule is called a dihedral plane of symmetry or dihedral mirror plane 'σ_d'.



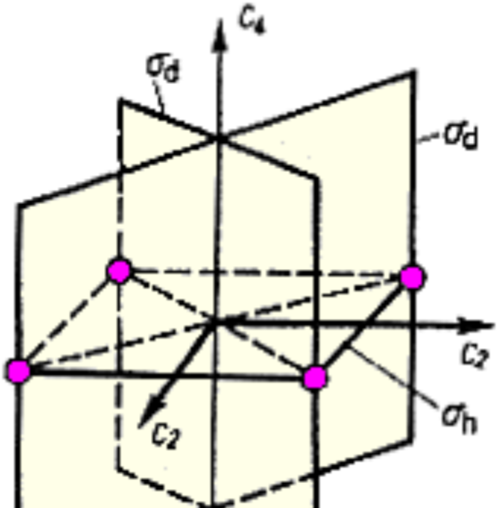
Possible Mirror Planes



Possible Mirror Planes



Possible axes and Mirror Planes



Centre of Symmetry ‘i’

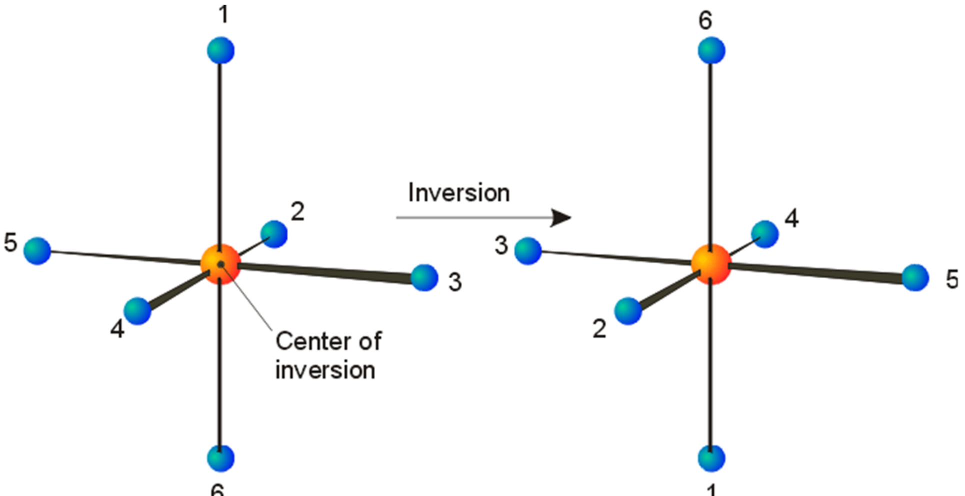
Centre of symmetry is a point from which lines are drawn on either side, will meet at identical positions in a molecule.

Centre of Symmetry 'i'

Centre of symmetry is a point from which lines are drawn on either side, will meet at identical positions in a molecule.

It is a point with respect to which a molecule is inverted, will give a configuration indistinguishable from the original or super imposable on the original.

Centre of Symmetry

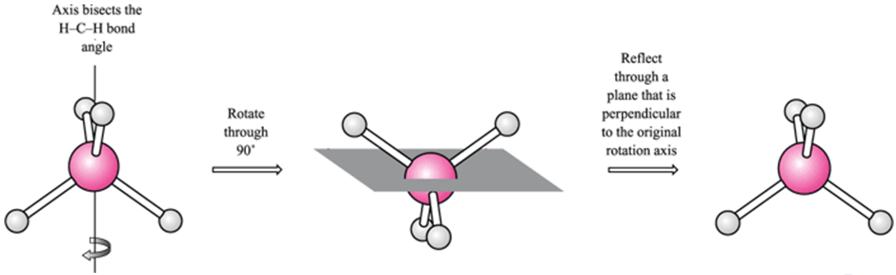


5. Improper Axis of Rotation, 'S_n'

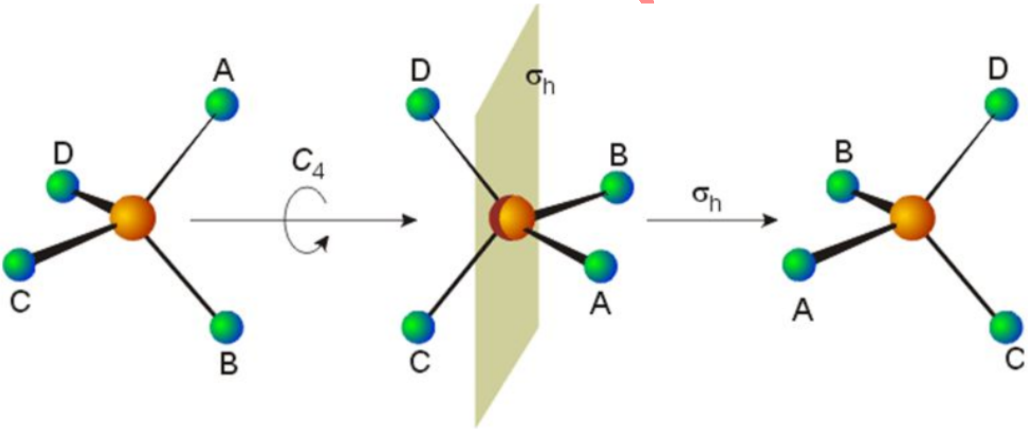
If rotation of the molecule through a certain angle,followed by reflection in a plane perpendicular to the axis yields an equivalent configuration, the axis is called improper axis of rotation or rotation reflection axis, S_n.

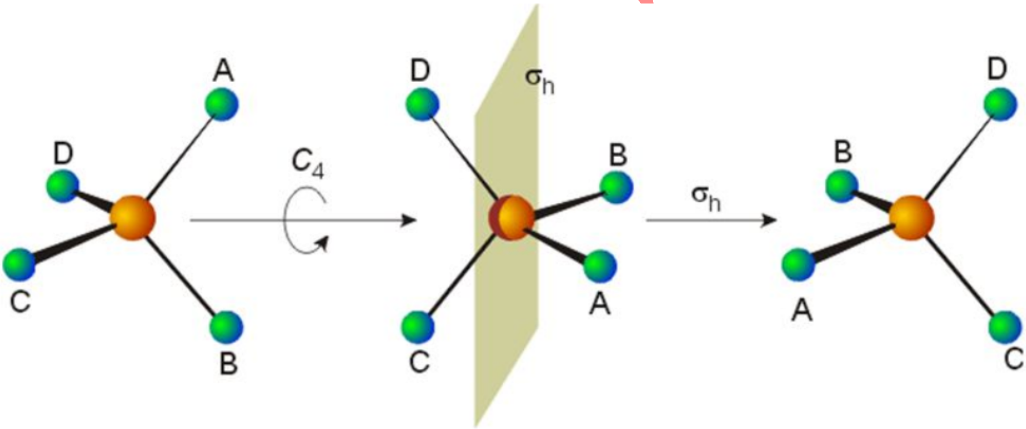
5. Improper Axis of Rotation, ‘S_n’

If rotation of the molecule through a certain angle,followed by reflection in a plane perpendicular to the axis yields an equivalent configuration, the axis is called improper axis of rotation or rotation reflection axis, S_n.

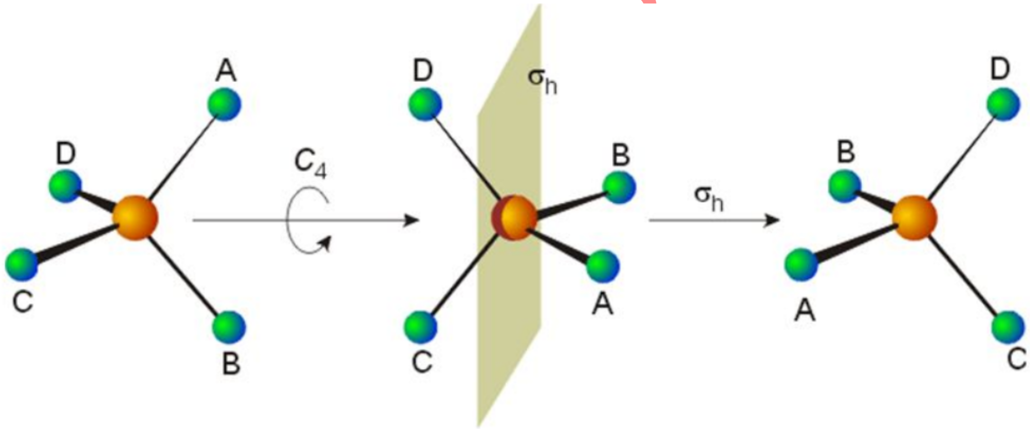


Various Symmetry Elements





Rotation through C_n axis followed by reflection in a perpendicular plane is known as S_n axis.



Rotation through C_n axis followed by reflection in a perpendicular plane is known as S_n axis.

Multiplication or Combination of Symmetry Operations

Performing a series of symmetry operations in succession on a molecule is represented algebraically as a multiplication.

Multiplication or Combination of Symmetry Operations

Performing a series of symmetry operations in succession on a molecule is represented algebraically as a multiplication.

Example

If we perform symmetry operation 'A' on a molecule followed by another operation 'B', then it is said to be a multiplication and is represented by 'BA'.

Example

The effect of the multiplication is the same what would be obtained from a single operation 'C' on a molecule.

Example

The effect of the multiplication is the same what would be obtained from a single operation 'C' on a molecule.

$$BA = C$$

Example

The effect of the multiplication is the same what would be obtained from a single operation 'C' on a molecule.

$$BA = C$$

In such a case C is said to be the product of A and B.

By convention representation of multiplication should be done right to left order.

By convention representation of multiplication should be done right to left order.

Example

BA means 'apply A first, then B'

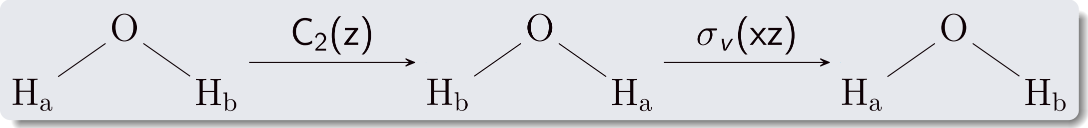
By convention representation of multiplication should be done right to left order.

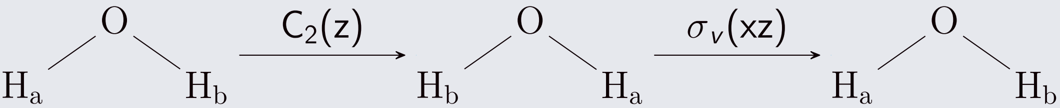
Example

BA means 'apply A first, then B'

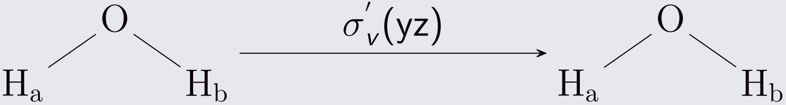
If the order of two symmetry operations, say And B are performed on a molecule is immaterial such that BA = AB, then it is said that the multiplication is commutative and that the operations A and B commute.

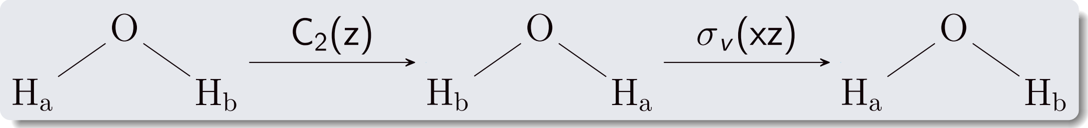
Multiplication of Symmetry Operations



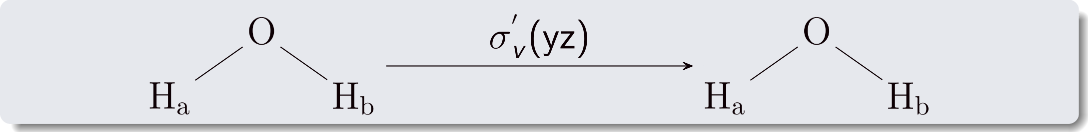


This is same as the following operation





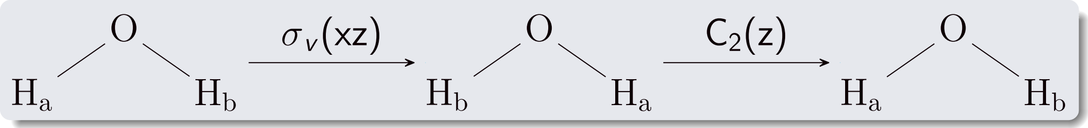
This is same as the following operation



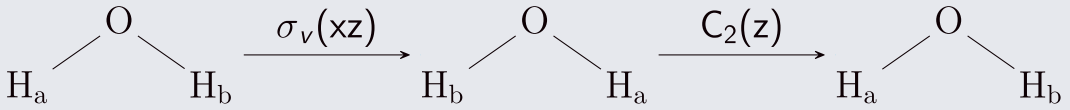
Therefore

$$\sigma_v(xz).C_2(z) = \sigma_v^{'}(yz)$$

On the contrary if we apply $\sigma_v(xz)$ operation first and followed by $c_2(z)$ operation

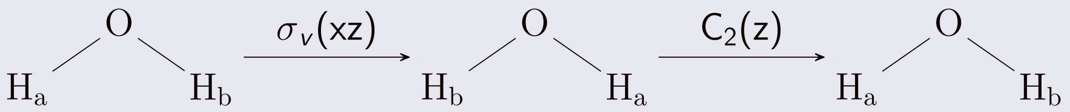


On the contrary if we apply $\sigma_v(xz)$ operation first and followed by $c_2(z)$ operation

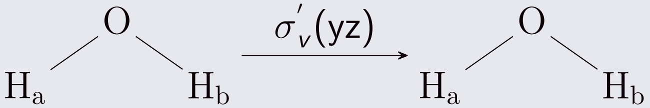


This will give the same result as that of the above operation

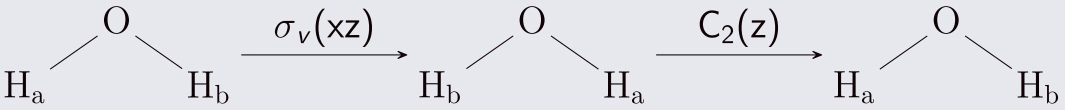
On the contrary if we apply $\sigma_v(xz)$ operation first and followed by $c_2(z)$ operation



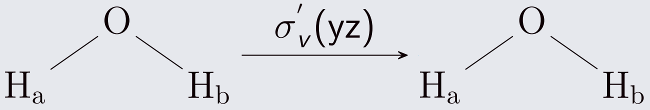
This will give the same result as that of the above operation



On the contrary if we apply $\sigma_v(xz)$ operation first and followed by $c_2(z)$ operation

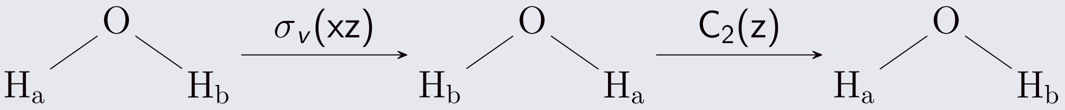


This will give the same result as that of the above operation

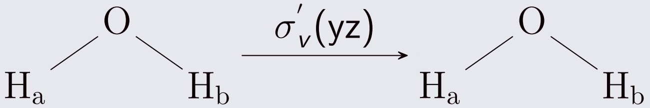


$$C_2(z).\sigma_v(xz) = \sigma_v'(yz)$$

On the contrary if we apply $\sigma_v(xz)$ operation first and followed by $c_2(z)$ operation



This will give the same result as that of the above operation

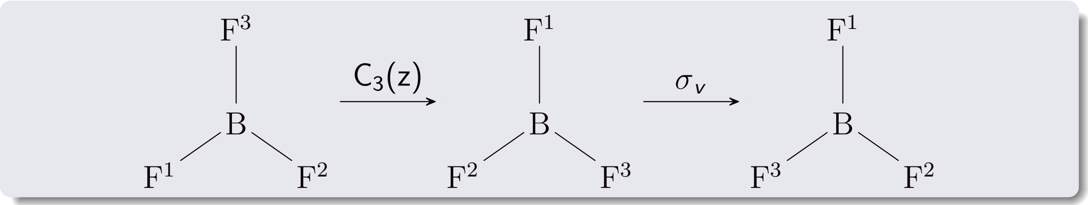


$$C_2(z).\sigma_v(xz) = \sigma'_v(yz)$$

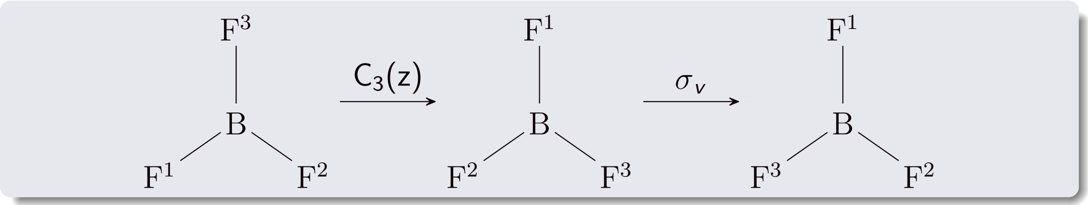
This means that the above multiplication is commutative. i.e.

If the product of two symmetry operations A and B depends upon the order in which the two operations are preferred so that BA$\neq$ AB, then it is said that the multiplication is non commutative. and the two operators A and B do not commute.

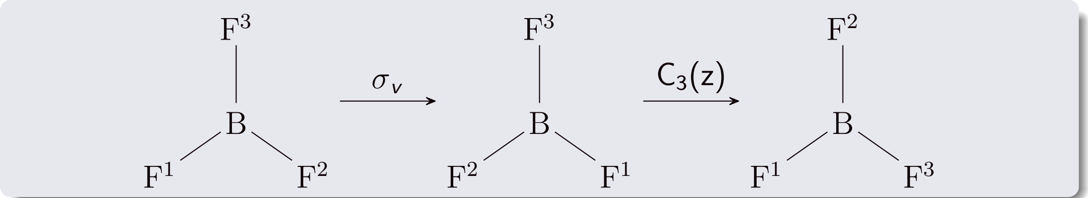
Non Commutative Operation



Non Commutative Operation



This is not the same as



i.e. $C_3(z).\sigma_v \neq \sigma_v.C_3(z)$

i.e. $C_3(z).\sigma_v \neq \sigma_v.C_3(z)$

In the case of BF_3 the operators $C_3(z)$ and σ_v do not commute.

Inverse Operations

For any symmetry operation that can be performed on a molecule, there will be another symmetry operation which will completely undo what the first operation does to the molecule; the second operation is then said to be the inverse of the first operation.

Inverse Operations

For any symmetry operation that can be performed on a molecule, there will be another symmetry operation which will completely undo what the first operation does to the molecule; the second operation is then said to be the inverse of the first operation.

For any operation A, there exists another operation X such that

Inverse Operations

For any symmetry operation that can be performed on a molecule, there will be another symmetry operation which will completely undo what the first operation does to the molecule; the second operation is then said to be the inverse of the first operation.

For any operation A, there exists another operation X such that

$$XA = E = AX$$

In this case X is said to be the inverse of A and vice versa.

Inverse Operations

For any symmetry operation that can be performed on a molecule, there will be another symmetry operation which will completely undo what the first operation does to the molecule; the second operation is then said to be the inverse of the first operation.

For any operation A, there exists another operation X such that

$$XA = E = AX$$

In this case X is said to be the inverse of A and vice versa.

$$\text{i.e. } X = A^{-1}$$
$$A^{-1}A = AA^{-1} = E$$

An operator and its inverse is always commute.

We also know that

We also know that

$$C_2^2 = E$$
$$\sigma^2 = E$$
$$i^2 = E$$

We also know that

$$C_2^2 = E$$
$$\sigma^2 = E$$
$$i^2 = E$$

$$C_2^{-1} = C_2$$
$$\sigma^{-1} = \sigma$$
$$i^{-1} = i$$

We also know that

$$C_2^2 = E$$
$$\sigma^2 = E$$
$$i^2 = E$$

$$C_2^{-1} = C_2$$
$$\sigma^{-1} = \sigma$$
$$i^{-1} = i$$

In the above cases the operation is also its inverse.

Inverse Operations for Proper Rotations

Now consider a rotation of 120^0 about C_3 axis in the counter clock wise direction. Its effect is undone by a further rotation through $240^0(C_3^2)$ i.e C_3^2 is the inverse of C_3^{-1}

Inverse Operations for Proper Rotations

Now consider a rotation of 120^0 about C_3 axis in the counter clock wise direction. Its effect is undone by a further rotation through $240^0(C_3^2)$ i.e C_3^2 is the inverse of C_3^{-1}

$$C_3^{-1} = C_3^2$$

Inverse Operations for Proper Rotations

Now consider a rotation of 120^0 about C_3 axis in the counter clock wise direction. Its effect is undone by a further rotation through $240^0(C_3^2)$ i.e C_3^2 is the inverse of C_3^{-1}

$$C_3^{-1} = C_3^2$$

In general, for rotations other than C_2, the relationship is

$$
\begin{aligned}
C_n^{n-1}.C_n^1 &= E \\
C_n^{-1} &= C_n^{n-1} \\
\text{In general, the inverse of } C_n^m &= C_n^{n-m}
\end{aligned}
$$

In general, for rotations other than C_2, the relationship is

$$\begin{aligned} C_n^{n-1}.C_n^1 &= E \\ C_n^{-1} &= C_n^{n-1} \\ \text{In general, the inverse of } C_n^m &= C_n^{n-m} \end{aligned}$$

Inverse Operations for Improper Rotations

Inverse Operations for Improper Rotations

For the rotation reflection operation S_n,

$$
\begin{aligned}
S_n^n &= E && \text{when 'n' is even.} \\
S_n^{n-1}.S_n^1 &= E && \text{when 'n' is even.} \\
S_n^{-1} &= S_n^{n-1} && \text{when 'n' is even.}
\end{aligned}
$$

Inverse Operations for Improper Rotations

For the rotation reflection operation S_n,

$$S_n^n = E \quad \text{when 'n' is even.}$$
$$S_n^{n-1}.S_n^1 = E \quad \text{when 'n' is even.}$$
$$S_n^{-1} = S_n^{n-1} \quad \text{when 'n' is even.}$$

S_n^{n-1} = is the inverse of S_n when 'n' is even.

Inverse Operations for Improper Rotations

For the rotation reflection operation S_n,

$$S_n^n = E \quad \text{when 'n' is even.}$$
$$S_n^{n-1}.S_n^1 = E \quad \text{when 'n' is even.}$$
$$S_n^{-1} = S_n^{n-1} \quad \text{when 'n' is even.}$$

S_n^{n-1} = is the inverse of S_n when 'n' is even.

$$S_n^{2n} = E \quad \text{when 'n' is odd.}$$
$$S_n^{2n-1}.S_n^1 = E \quad \text{when 'n' is odd.}$$
$$S_n^{-1} = S_n^{2n-1} \quad \text{when 'n' is odd.}$$

Inverse Operations for Improper Rotations

For the rotation reflection operation S_n,

$$S_n^n = E \quad \text{when 'n' is even.}$$
$$S_n^{n-1}.S_n^1 = E \quad \text{when 'n' is even.}$$
$$S_n^{-1} = S_n^{n-1} \quad \text{when 'n' is even.}$$

S_n^{n-1} = is the inverse of S_n when 'n' is even.

$$S_n^{2n} = E \quad \text{when 'n' is odd.}$$
$$S_n^{2n-1}.S_n^1 = E \quad \text{when 'n' is odd.}$$
$$S_n^{-1} = S_n^{2n-1} \quad \text{when 'n' is odd.}$$

S_n^{2n-1} = is the inverse of S_n when 'n' is odd.

Mathematical Groups

Mathematical Groups

Group

A group is a collection of mathematical objects known as elements or members which are related to each other according to certain rules. They are:

Mathematical Groups

Group

A group is a collection of mathematical objects known as elements or members which are related to each other according to certain rules. They are:

- Closure rule.

Mathematical Groups

Group

A group is a collection of mathematical objects known as elements or members which are related to each other according to certain rules. They are:

- Closure rule.
- Identity rule.

Mathematical Groups

Group

A group is a collection of mathematical objects known as elements or members which are related to each other according to certain rules. They are:

- Closure rule.
- Identity rule.
- Associative rule.

Mathematical Groups

Group

A group is a collection of mathematical objects known as elements or members which are related to each other according to certain rules. They are:

- Closure rule.
- Identity rule.
- Associative rule.
- Inverse rule.

Mathematical Groups

Group

A group is a collection of mathematical objects known as elements or members which are related to each other according to certain rules. They are:

- Closure rule.
- Identity rule.
- Associative rule.
- Inverse rule.

Mathematical Groups

Group

A group is a collection of mathematical objects known as elements or members which are related to each other according to certain rules. They are:

- Closure rule.
- Identity rule.
- Associative rule.
- Inverse rule.

The elements of a group are numbers, matrices, vectors, or symmetry operations.

Point Groups

Point Groups

In group theory related to symmetry, we consider the elements of group as symmetry operations.

Point Groups

In group theory related to symmetry, we consider the elements of group as symmetry operations.

A given set of symmetry operations will characterise a given set of molecules.

Point Groups

In group theory related to symmetry, we consider the elements of group as symmetry operations.

A given set of symmetry operations will characterise a given set of molecules.

The symmetry operations that can be applied to a given molecule in its equilibrium configuration form a mathematical group.

A very important feature of molecular symmetry is that all symmetry elements in a molecule will intersect at a common point, namely the centre of gravity.

A very important feature of molecular symmetry is that all symmetry elements in a molecule will intersect at a common point, namely the centre of gravity.

Hence these symmetry operations are termed elements of point symmetry or point group symmetry.

A very important feature of molecular symmetry is that all symmetry elements in a molecule will intersect at a common point, namely the centre of gravity.

Hence these symmetry operations are termed elements of point symmetry or point group symmetry.

Point Group

A point group is defined as a set of all the symmetry operation, the action of which leaves at least of the molecule unmoved or invariant.

A very important feature of molecular symmetry is that all symmetry elements in a molecule will intersect at a common point, namely the centre of gravity.

Hence these symmetry operations are termed elements of point symmetry or point group symmetry.

Point Group

A point group is defined as a set of all the symmetry operation, the action of which leaves at least of the molecule unmoved or invariant.

Conditions for a Point Group

If a set of symmetry operations is to form a point group, the following rules must be satisfied.

Conditions for a Point Group

If a set of symmetry operations is to form a point group, the following rules must be satisfied.

Closure rule

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

Conditions for a Point Group

If a set of symmetry operations is to form a point group, the following rules must be satisfied.

Closure rule

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

Example

Let A and B two elements of a group and let $AB = C$, $A^2 = F$ and $B^2 = G$, then C, F and G would be the elements of the same group. If $BA = D$, that also form another element of the group. i.e. the elements need not be commutative.

Identity Rule

In each group, there should be an identity element which commutes with all others and leaves them unchanged.

Identity Rule

In each group, there should be an identity element which commutes with all others and leaves them unchanged.

Example

The identity element is represented as E and defined by the expression:

Identity Rule

In each group, there should be an identity element which commutes with all others and leaves them unchanged.

Example

The identity element is represented as E and defined by the expression:

$$AE = EA = A$$

Identity Rule

In each group, there should be an identity element which commutes with all others and leaves them unchanged.

Example

The identity element is represented as E and defined by the expression:

$$AE = EA = A$$

Where A is any other element of the group.

Associative Rule

The associative law of multiplication must hold

Associative Rule

The associative law of multiplication must hold

Example

If A, B and C are any three elements of the group, then

Associative Rule

The associative law of multiplication must hold

Example

If A, B and C are any three elements of the group, then

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

Associative Rule

The associative law of multiplication must hold

Example

If A, B and C are any three elements of the group, then

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

In other words, if $BC = Y$ and $AB = Z$, then

Associative Rule

The associative law of multiplication must hold

Example

If A, B and C are any three elements of the group, then

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

In other words, if $BC = Y$ and $AB = Z$, then

$$AY = ZC$$

Point Groups

Inverse Rule

Each element of the group has an inverse or reciprocal that is also an element of the group.

Inverse Rule

Each element of the group has an inverse or reciprocal that is also an element of the group.

Example

For any element A, there occurs another element X in the group such that

Inverse Rule

Each element of the group has an inverse or reciprocal that is also an element of the group.

Example

For any element A, there occurs another element X in the group such that

$$XA = AX = E$$

Inverse Rule

Each element of the group has an inverse or reciprocal that is also an element of the group.

Example

For any element A, there occurs another element X in the group such that

$$XA = AX = E$$

where $X = A^{-1}$, is called the inverse of A. Similarly A is the inverse of X too.

Inverse Rule

Each element of the group has an inverse or reciprocal that is also an element of the group.

Example

For any element A, there occurs another element X in the group such that

$$XA = AX = E$$

where $X = A^{-1}$, is called the inverse of A. Similarly A is the inverse of X too.

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

The complete set of symmetry operations the can be performed on a molecule a point group will satisfy the four criteria for a mathematical group. E.g Consider water molecule such that it is in yz plane and its c_2 axis coincides with the z axis.

The complete set of symmetry operations the can be performed on a molecule a point group will satisfy the four criteria for a mathematical group. E.g Consider water molecule such that it is in yz plane and its c_2 axis coincides with the z axis.

The molecule has the symmetry elements E, $C_2(z)$, $\sigma_v(xz)$ and $\sigma'_v(yz)$

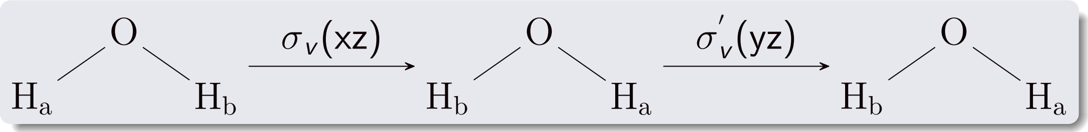
The complete set of symmetry operations the can be performed on a molecule a point group will satisfy the four criteria for a mathematical group. E.g Consider water molecule such that it is in yz plane and its c_2 axis coincides with the z axis.

The molecule has the symmetry elements E, $C_2(z)$, $\sigma_v(xz)$ and $\sigma'_v(yz)$
The set of four symmetry operations $\{E, C_2(z), \sigma_v(xz), \sigma'_v(yz)\}$ is said to form a point group and it can be easily shown that the set satisfies all the four conditions required for a point group.

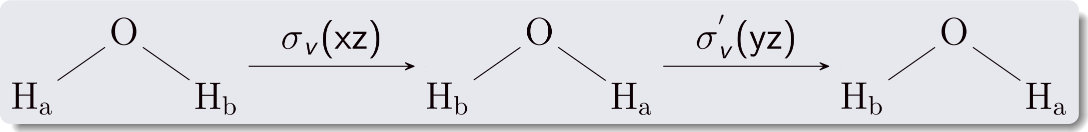
The complete set of symmetry operations the can be performed on a molecule a point group will satisfy the four criteria for a mathematical group. E.g Consider water molecule such that it is in yz plane and its c_2 axis coincides with the z axis.

The molecule has the symmetry elements E, $C_2(z)$, $\sigma_v(xz)$ and $\sigma_v^{'}(yz)$
The set of four symmetry operations $\{E, C_2(z), \sigma_v(xz), \sigma_v^{'}(yz)\}$ is said to form a point group and it can be easily shown that the set satisfies all the four conditions required for a point group.

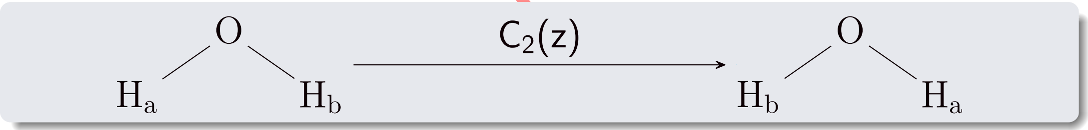
Adherence to the Closure Rule



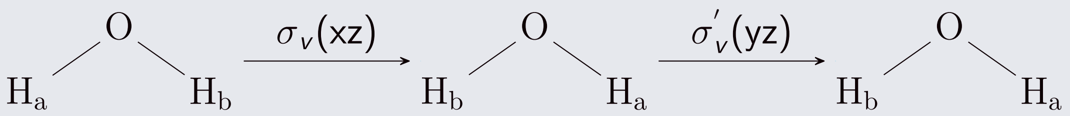
Adherence to the Closure Rule



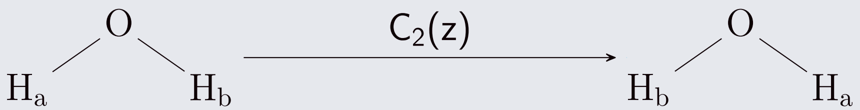
This is same as the operation $C_2(z)$



Adherence to the Closure Rule

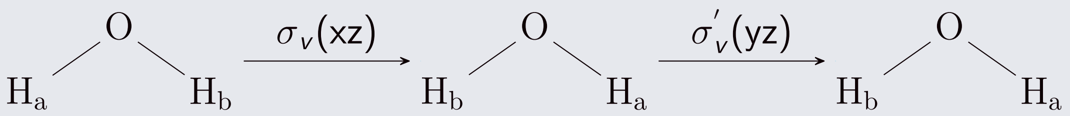


This is same as the operation $C_2(z)$

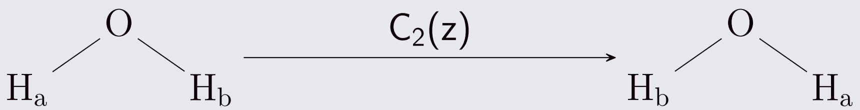


$$\sigma'_v(yz).\sigma_v(xz) = C_2(z)$$

Adherence to the Closure Rule



This is same as the operation $C_2(z)$

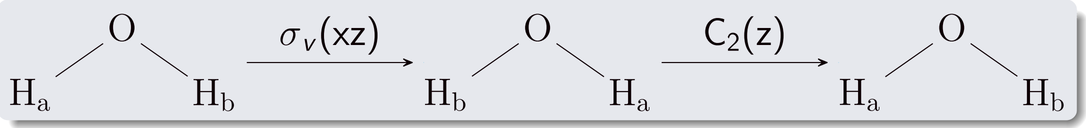


$$\sigma'_v(yz).\sigma_v(xz) = C_2(z)$$

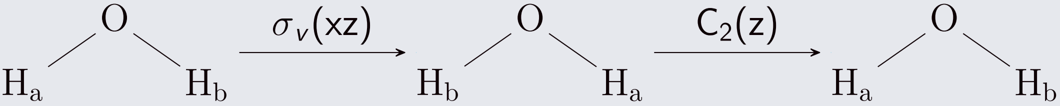
The product $C_2(z)$ is also an element of the group.

Consider another multiplication,

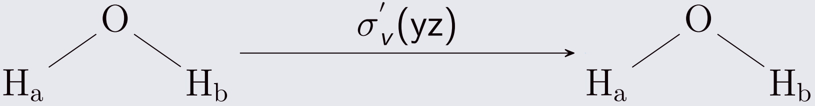
Consider another multiplication,



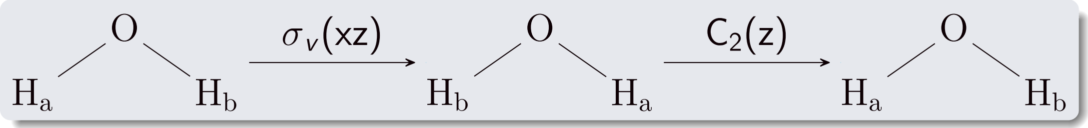
Consider another multiplication,



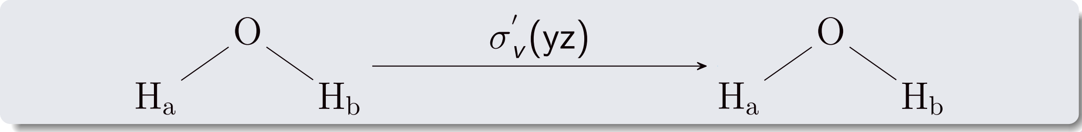
This equivalent to another single operation.



Consider another multiplication,



This equivalent to another single operation.



$$\sigma_v(xz).C_2(z) = \sigma_v'(yz)$$

$$\sigma_v(xz).C_2(z) = \sigma_v^{'}(yz)$$

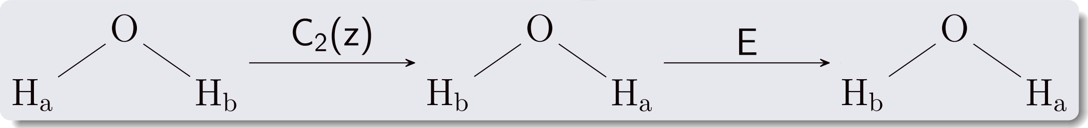
The product $\sigma_v^{'}(yz)$ is also a member of the group. It can be shown that any other binary multiplication will also yield a product which is a member of the group.

Adherence to Identity Rule

The group has an identity operation as one element which commutes with all others and leaves them unchanged.

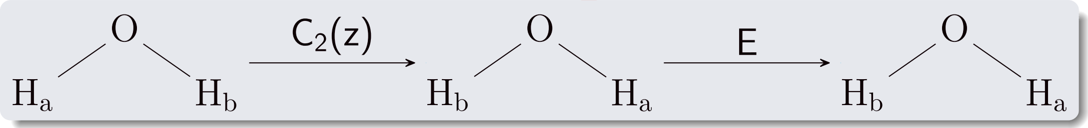
Adherence to Identity Rule

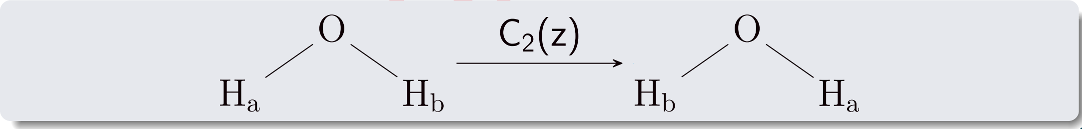
The group has an identity operation as one element which commutes with all others and leaves them unchanged.



Adherence to Identity Rule

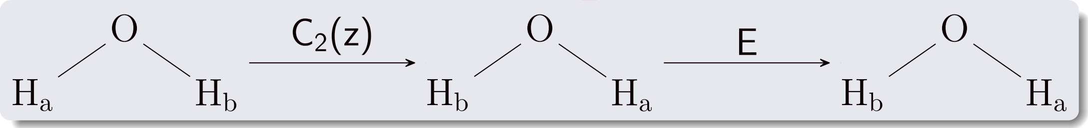
The group has an identity operation as one element which commutes with all others and leaves them unchanged.

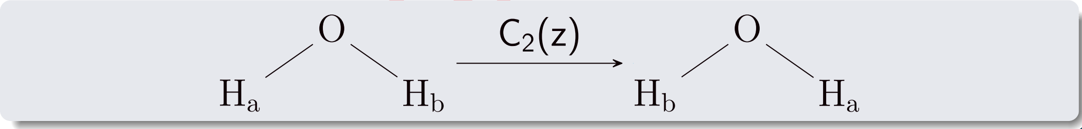


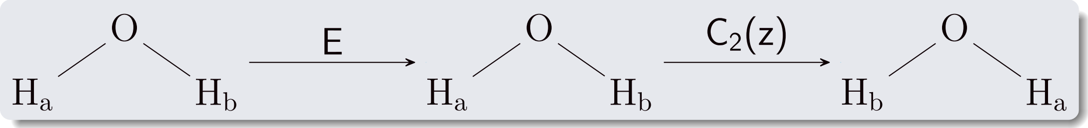


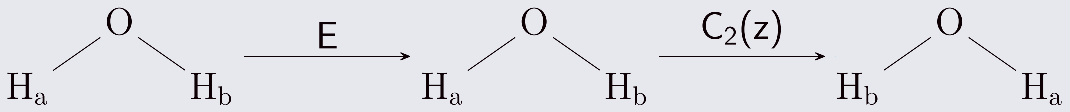
Adherence to Identity Rule

The group has an identity operation as one element which commutes with all others and leaves them unchanged.





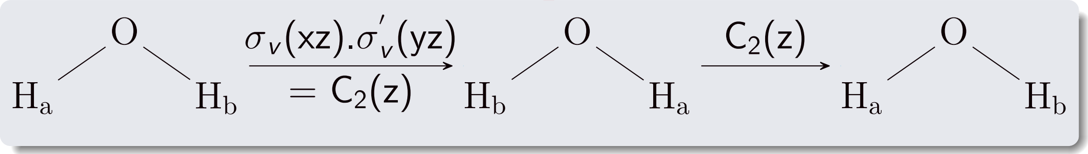

O
H a
H b
E
O
H a
H b
C 2 (z)
O
H b
H a



i.e. $C_2(z).E = E.C_2(z) = C_2(z)$

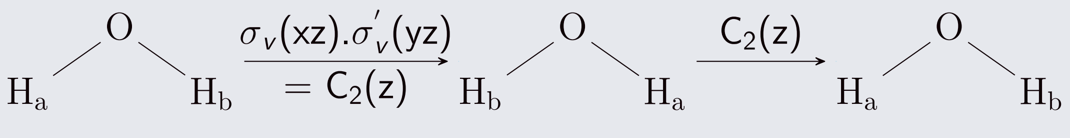
Associative Rule

The multiplication A(BC) i.e $C_2(z).[\sigma_v(xz).\sigma_v^{'}(yz)]$ is shown below

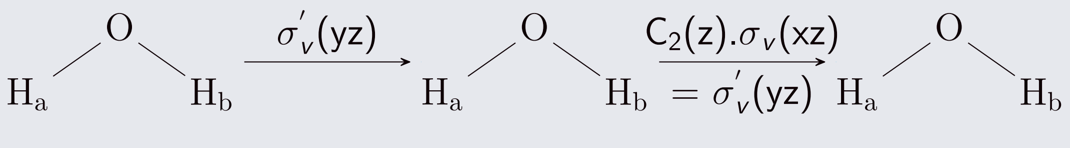


Associative Rule

The multiplication A(BC) i.e $C_2(z).[\sigma_v(xz).\sigma_v^{'}(yz)]$ is shown below

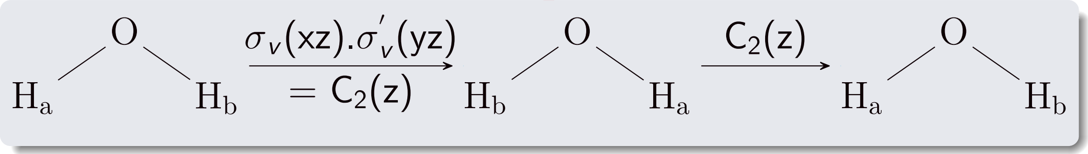


The multiplication (AB)C i.e $[C_2(z).\sigma_v(xz)].\sigma_v^{'}(yz)$ is shown as

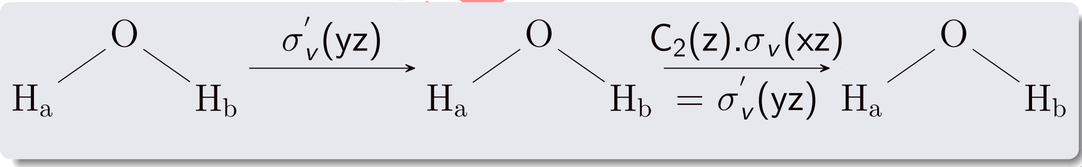


Associative Rule

The multiplication A(BC) i.e $C_2(z).[\sigma_v(xz).\sigma_v'(yz)]$ is shown below



The multiplication (AB)C i.e $[C_2(z).\sigma_v(xz)].\sigma_v'(yz)$ is shown as



It is seen that the final configuration is the same.

$$\text{i.e.} \quad C_2(z).[\sigma_v(xz).\sigma'_v(yz)] = [C_2(z).\sigma_v(xz)].\sigma'_v(yz)$$

The example shows that multiplication is associative.

Adherence to Inverse Rule

With respect to the set of symmetry operations under consideration, we can see that each operation in the set is the inverse of itself.

Adherence to Inverse Rule

With respect to the set of symmetry operations under consideration, we can see that each operation in the set is the inverse of itself.

Example

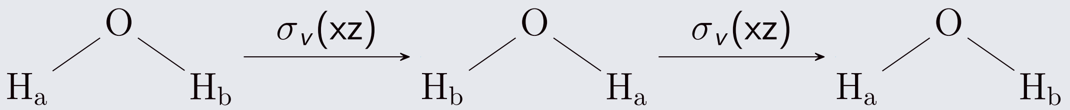
$$\text{i.e. } \sigma_v(xz).\sigma_v(xz) = E$$

Adherence to Inverse Rule

With respect to the set of symmetry operations under consideration, we can see that each operation in the set is the inverse of itself.

Example

$$\text{i.e. } \sigma_v(xz).\sigma_v(xz) = E$$



The fourth condition, namely the inverse rule is thus satisfied.

Finite and Infinite Groups

In a finite group, there are only a limited number of elements. Thus the group $\{E, A_1, A_2, A_3, ..., A_n\}$ represents a finite group.

Finite and Infinite Groups

In a finite group, there are only a limited number of elements. Thus the group {E, A_1, A_2, A_3,...., A_n} represents a finite group.

In an infinite group, there will be an unlimited number of elements. A group like {E, A_1, A_2, A_3,...., A_∞} represents a infinite group.

Finite and Infinite Groups

In a finite group, there are only a limited number of elements. Thus the group {E, A_1, A_2, A_3,...., A_n} represents a finite group.

In an infinite group, there will be an unlimited number of elements. A group like {E, A_1, A_2, A_3,...., A_∞} represents a infinite group.

Example

A group like C_∞ and D_∞ associated linear molecules, would be an infinite group.

Finite and Infinite Groups

In a finite group, there are only a limited number of elements. Thus the group {E, A_1, A_2, A_3,...., A_n} represents a finite group.

In an infinite group, there will be an unlimited number of elements. A group like {E, A_1, A_2, A_3,...., A_∞} represents a infinite group.

Example

A group like C_∞ and D_∞ associated linear molecules, would be an infinite group.

The number of elements in a finite group is called its order (h). The point group C_{2v} to which water molecule belongs containing elements

$$\{E,\ C_2(z),\ \sigma_v(xz),\ \sigma_v'(yz)\}$$

has an order 4.

The number of elements in a finite group is called its order (h).
The point group C_{2v} to which water molecule belongs containing elements

$$\{E,\ C_2(z),\ \sigma_v(xz),\ \sigma_v^{'}(yz)\}$$

has an order 4.
The point group C_{3v} to which NH_3 belongs containing elements.

$$\{E,\ C_3,\ C_3^2,\ \sigma_v,\ \sigma_v^{'},\ \sigma_v^{''}\}$$

The number of elements in a finite group is called its order (h).
The point group C_{2v} to which water molecule belongs containing elements

$$\{E,\ C_2(z),\ \sigma_v(xz),\ \sigma_v^{'}(yz)\}$$

has an order 4.
The point group C_{3v} to which NH_3 belongs containing elements.

$$\{E,\ C_3,\ C_3^2,\ \sigma_v,\ \sigma_v^{'},\ \sigma_v^{''}\}$$

has an order 6.

Abelian Groups and Non-abelian Groups

Abelian Groups

A group in which the elements commute with each other is called an Abelian groups(or commutative groups).

Abelian Groups and Non-abelian Groups

Abelian Groups

A group in which the elements commute with each other is called an Abelian groups(or commutative groups).

Example

The group C_{2v} to which H_2O belongs is an Abelian group. The multiplication is commutative for any pair of its elements, E, $C_2(z)$, $\sigma_v(xz)$,and $\sigma_v^{'}(yz)$

Abelian and Non-abelian Groups - Contd...

Non-abelian Group

A group for which multiplication is not commutative for some pairs of the elements is called Non-abelian group.

Abelian and Non-abelian Groups - Contd...

Non-abelian Group

A group for which multiplication is not commutative for some pairs of the elements is called Non-abelian group.

Example

The point group C_{3v} to which NH_3 belongs containing elements, E, C_3, C_3^2, σ_v, $\sigma_v^{'}$, and $\sigma_v^{''}$ is a non-abelian group even though some elements commute with each other, some will not.

Point Groups - The Schoenflies Notation

The Schoenflies symbol representing a point group denotes sufficient symmetry elements in molecules conforming to that group and the associated operations can be identified from the symbol.

Point Groups - The Schoenflies Notation

The Schoenflies symbol representing a point group denotes sufficient symmetry elements in molecules conforming to that group and the associated operations can be identified from the symbol.

Based on the degree of symmetry they possess, molecules may broadly be categorised into three classes.

1. Molecules of low symmetry.

Point Groups - The Schoenflies Notation

The Schoenflies symbol representing a point group denotes sufficient symmetry elements in molecules conforming to that group and the associated operations can be identified from the symbol.

Based on the degree of symmetry they possess, molecules may broadly be categorised into three classes.

1. Molecules of low symmetry.
2. Molecules of high symmetry.

Point Groups - The Schoenflies Notation

The Schoenflies symbol representing a point group denotes sufficient symmetry elements in molecules conforming to that group and the associated operations can be identified from the symbol.

Based on the degree of symmetry they possess, molecules may broadly be categorised into three classes.

1. Molecules of low symmetry.
2. Molecules of high symmetry.
3. Molecules of special symmetry.

1.Molecules of Low Symmetry(MLS)

The MLS class contains molecules which possess only a mirror plane 'σ' or an inversion centre 'i' as their characteristic symmetry element or no symmetry element at all other than 'E'.

1.Molecules of Low Symmetry(MLS)

The MLS class contains molecules which possess only a mirror plane 'σ' or an inversion centre 'i' as their characteristic symmetry element or no symmetry element at all other than 'E'.

Group C_1

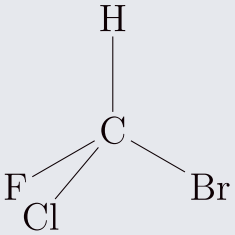
Molecules having no symmetry elements at all other than E are said to belong the group C_1

1.Molecules of Low Symmetry(MLS)

The MLS class contains molecules which possess only a mirror plane 'σ' or an inversion centre 'i' as their characteristic symmetry element or no symmetry element at all other than 'E'.

Group C_1

Molecules having no symmetry elements at all other than E are said to belong the group C_1



MLS Contd...

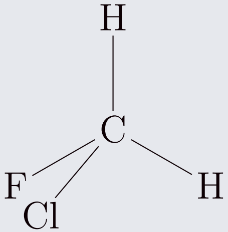
Group C_s

Molecules which have merely a plane of symmetry 'σ' in addition to E are included in the group C_s

MLS Contd...

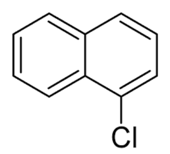
Group C_s

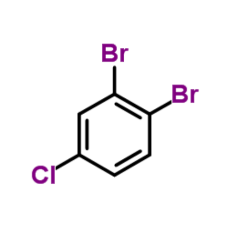
Molecules which have merely a plane of symmetry 'σ' in addition to E are included in the group C_s



Other Examples for C_s

Other Examples are α-chloro naphthalene and 4-chloro-1,2-dibromobenzene





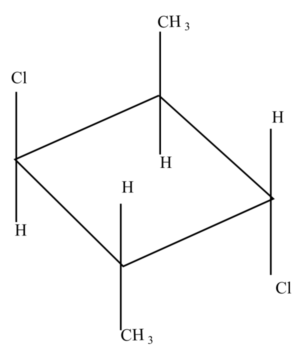
Group C_i

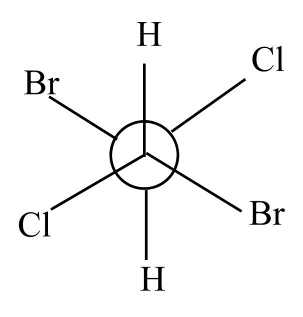
Molecules which possess just an inversion centre 'i' as their symmetry element in addition to E are said to belong to the group C_i. e,g Trans-1,3-dichlorotrans-2,4-dimethylcyclobutane and Trans-1,2-dibromotrans-1,2-dichloroethane.

Group C_i

Molecules which possess just an inversion centre 'i' as their symmetry element in addition to E are said to belong to the group C_i. e,g Trans-1,3-dichlorotrans-2,4-dimethylcyclobutane and Trans-1,2-dibromotrans-1,2-dichloroethane.

Examples for C_i





Molecules of High Symmetry(MHS)

The MHS class contains molecules characterised by the presence of a C_n axis along with other symmetry elements.

Molecules of High Symmetry(MHS)

The MHS class contains molecules characterised by the presence of a C_n axis along with other symmetry elements.

Group C_n

Those molecules for which the only symmetry element other than E us a proper rotation axis C_n are said to belong to the group C_n.

Molecules of High Symmetry(MHS)

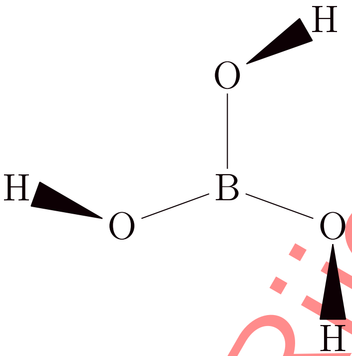
The MHS class contains molecules characterised by the presence of a C_n axis along with other symmetry elements.

Group C_n

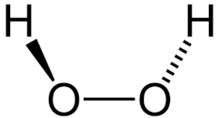
Those molecules for which the only symmetry element other than E us a proper rotation axis C_n are said to belong to the group C_n.

E.g. H_2O_2 belong to C_2 and H_3BO_3 belong to C_3

Examples for C_3 and C_2

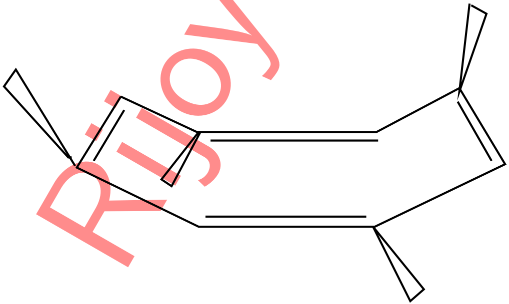


H_3BO_3



Group S_n

In case if a molecule possess S_n axis, it would always be associated with a $C_{n/2}$ axis, collinear with S_n axis. If no other symmetry element is present except possibly 'i', the molecule is said to belong the point group called S_n. E.g.1,3,5,7-tetrafluoracyclooctatetraene.



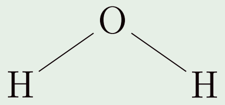
Group C_{nv}

Molecules which have a c_n axis as well as 'n' number of σ_v s without any other characteristic elements are said to belong to the point group C_{nv}

Group C_{nv}

Molecules which have a c_n axis as well as 'n' number of σ_v s without any other characteristic elements are said to belong to the point group C_{nv}

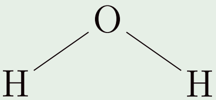
C_{2v}

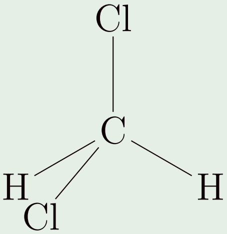


Group C_{nv}

Molecules which have a c_n axis as well as 'n' number of σ_v s without any other characteristic elements are said to belong to the point group C_{nv}

C_{2v}



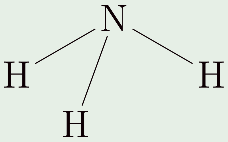


Group C_{nv} Contd...

C_{3v}

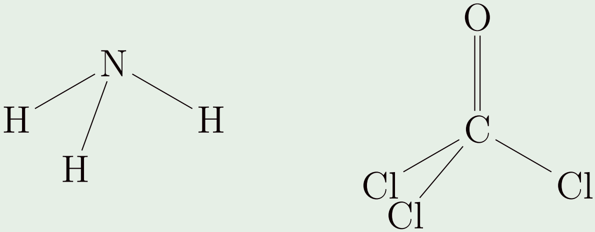
Group C_{nv} Contd...

C_{3v}



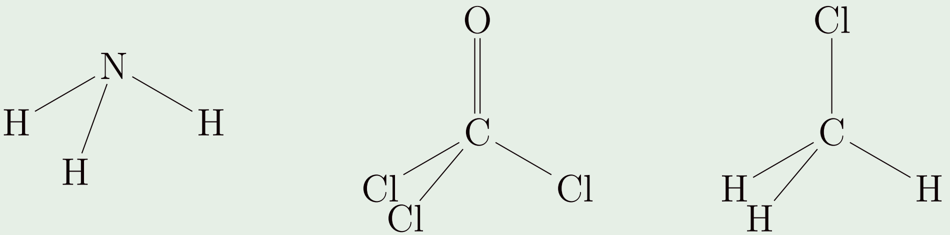
Group C_{nv} Contd...

C_{3v}



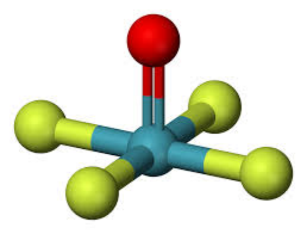
Group C_{nv} Contd...

C_{3v}



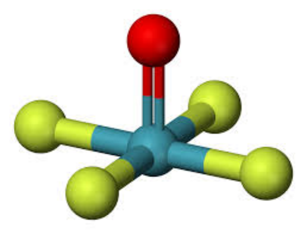
C_{nv} Contd...

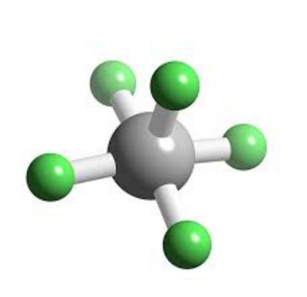
C_{4v} $XeOF_4$ and SbF_5



C_{nv} Contd...

C_{4v} $XeOF_4$ and SbF_5





Group C_{nh}

Molecules which have a C_n axis and a σ_h but no 'n' number of σ_v s are said to belong to the point group C_{nh}.(An $S_n$axis would obviously be present) e.g. Trans-1,2-dichloroethene and planar hydroboric acid.

Group C_{nh}

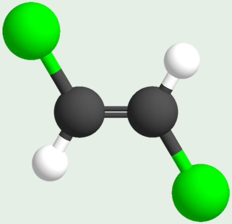
Molecules which have a C_n axis and a σ_h but no 'n' number of σ_v s are said to belong to the point group C_{nh}.(An $S_n$axis would obviously be present) e.g. Trans-1,2-dichloroethene and planar hydroboric acid.

C_{nh}

Group C_{nh}

Molecules which have a C_n axis and a σ_h but no 'n' number of σ_v s are said to belong to the point group C_{nh}.(An $S_n$axis would obviously be present) e.g. Trans-1,2-dichloroethene and planar hydroboric acid.

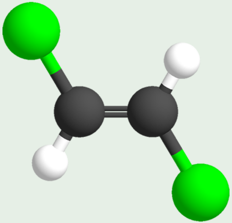
C_{nh}

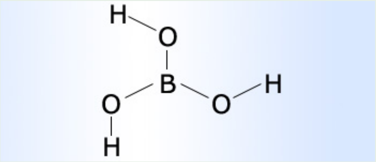


Group C_{nh}

Molecules which have a C_n axis and a σ_h but no 'n' number of σ_v s are said to belong to the point group C_{nh}.(An $S_n$axis would obviously be present) e.g. Trans-1,2-dichloroethene and planar hydroboric acid.

C_{nh}





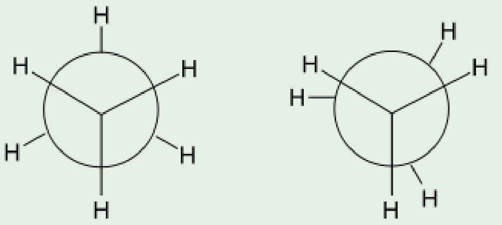
Group D_n

Molecules having a C_n axis and 'n' number of equally spaced C_2 axes perpendicular to principal axes as the only symmetry elements belong to the point group D_n.

Group D_n

Molecules having a C_n axis and 'n' number of equally spaced C_2 axes perpendicular to principal axes as the only symmetry elements belong to the point group D_n.

D_3 e.g. Skew conformer of ethane



Group D_{nh}

Molecules conforming to the group D_{nh} will contain a c_n axis, n equally spaced c_2 axis perpendicular to c_n axis abd a σ_h. They would automatically have 'n' number of σ_v s also.

Group D_{nh}

Molecules conforming to the group D_{nh} will contain a c_n axis, n equally spaced c_2 axis perpendicular to c_n axis abd a σ_h. They would automatically have 'n' number of σ_v s also.

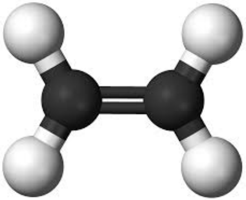


Figure: Ethylene (D_{2h})

Group D_{nh}

Molecules conforming to the group D_{nh} will contain a c_n axis, n equally spaced c_2 axis perpendicular to c_n axis abd a σ_h. They would automatically have 'n' number of σ_v s also.

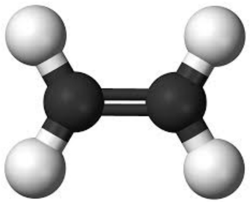


Figure: Ethylene (D_{2h})

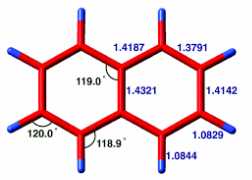
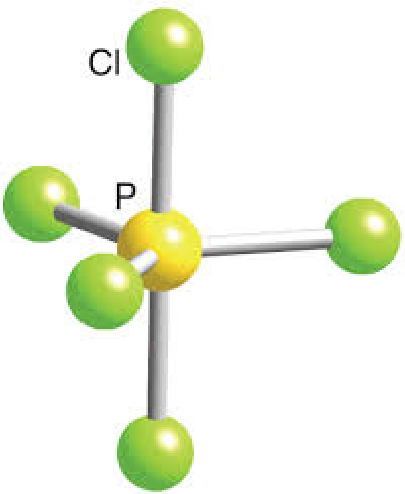


Figure: Naphthalene (D_{2h})

Other Examples of Group D_{3h}



D_{nh} - Contd...

When 'n' is even and $\geq$ 4, (n/2)σ_v s and (n/2)σ_d s will be present. Further, combinations of c_n and σ_h generate operations of S_n axis.

D_{nh} - Contd...

When 'n' is even and $\geq$ 4, (n/2)σ_v s and (n/2)σ_d s will be present. Further, combinations of c_n and σ_h generate operations of S_n axis. Other Examples are:

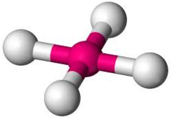


Figure: Tetra-chloroplatinate ion (D_{4h})

D_{nh} - Contd...

When 'n' is even and $\geq$ 4, $(n/2)\sigma_v$ s and $(n/2)\sigma_d$ s will be present. Further, combinations of c_n and σ_h generate operations of S_n axis. Other Examples are:

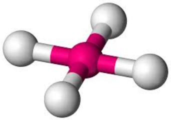


Figure: Tetra-chloroplatinate ion (D_{4h})

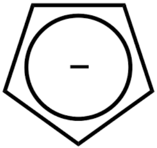


Figure: Cyclopentadienyl Anion (D_{5h})

D_{nh} - Contd...

When 'n' is even and $\geq$ 4, $(n/2)\sigma_v$ s and $(n/2)\sigma_d$ s will be present. Further, combinations of c_n and σ_h generate operations of S_n axis. Other Examples are:

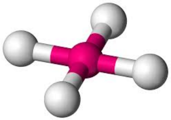


Figure: Tetra-chloroplatinate ion (D_{4h})

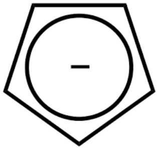


Figure: Cyclopentadienyl Anion (D_{5h})

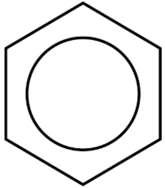


Figure: Benzene (D_{6h})

Group D_{nd}

For molecules conforming to group D_{nd}, the symmetry elements present would be a C_n axis, 'n' equally spaced c_2 axes perpendicular to C_n and 'n' σ_ds. The combination also requires the presence of a S_{2n} axis collinear with the c_n axis. Some examples are shown below:

Group D_{nd}

For molecules conforming to group D_{nd}, the symmetry elements present would be a C_n axis, 'n' equally spaced c_2 axes perpendicular to C_n and 'n' σ_ds. The combination also requires the presence of a S_{2n} axis collinear with the c_n axis. Some examples are shown below:

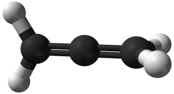


Figure: Allene (D_2d)

Group D_{nd}

For molecules conforming to group D_{nd}, the symmetry elements present would be a C_n axis, 'n' equally spaced c_2 axes perpendicular to C_n and 'n' σ_ds. The combination also requires the presence of a S_{2n} axis collinear with the c_n axis. Some examples are shown below:

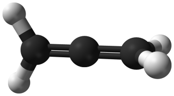


Figure: Allene (D_2d)

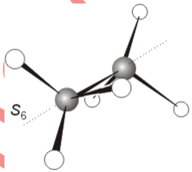


Figure: Stag. C_2H_6 (D_3d)

Group D_{nd}

For molecules conforming to group D_{nd}, the symmetry elements present would be a C_n axis, 'n' equally spaced c_2 axes perpendicular to C_n and 'n' σ_ds. The combination also requires the presence of a S_{2n} axis collinear with the c_n axis. Some examples are shown below:

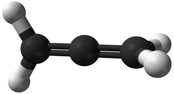


Figure: Allene (D_2d)

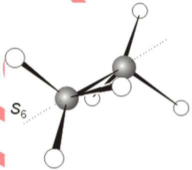


Figure: Stag. C_2H_6 (D_3d)

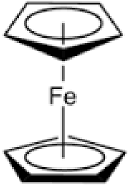


Figure: Staggered Ferrocene(D_5d)

Molecules of Special Symmetry

This MSS class includes mainly two categories of molecules.

Molecules of Special Symmetry

This MSS class includes mainly two categories of molecules.

1. Linear Molecules and

Molecules of Special Symmetry

This MSS class includes mainly two categories of molecules.

1. Linear Molecules and
2. Molecules containing multiple higher order axes.

Molecules of Special Symmetry

This MSS class includes mainly two categories of molecules.

1. Linear Molecules and
2. Molecules containing multiple higher order axes.

1. Linear molecules

Group $D_{\infty h}$:- Consider a a linear molecules like H_2, N_2, CO_2 etc. which consists of two equivalent halves. It will have a C_∞ axis. an infinite number of σ_vs, a σ_h axis perpendicular to the molecular axis(c_∞ axis), an infinite number of C_2 axis which are perpendicular bisectors of the C_∞ axis and an 'i'. The set of symmetry operations constitutes a point group of order ∞ and is named $D_{\infty h}$

Example for $D_{\infty h}$

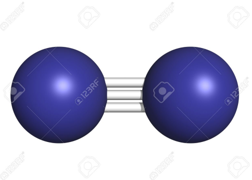


Figure: Nitrogen

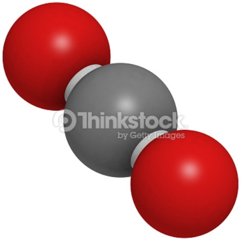
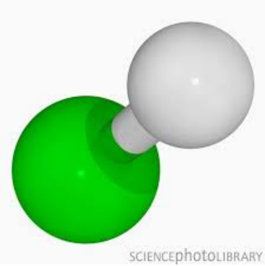
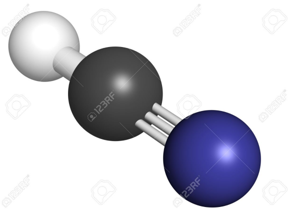


Figure: Carbon Dioxide

Linear Molecules - Contd...

Group $C_{\infty v}$:- Consider a molecule like HCl or HCN. Such a molecule has a C_{∞} axis and an infinite number of σ_v s, but neither a C_2 axis or 'i'. The associated symmetry operations constitute a point group $C_{\infty v}$





Molecules Containing Multiple Higher Order Axis

There are several molecules which contain more than one higher order C_n axis (n¿2). These have geometries which are regular polyhedra having faces perpendicular to the higher order axis.

A total of seven point groups are possible on the basis of these regular geometries. They are

- The three tetrahedral point groups T, T_d, T_h.
- The two octahedral point groups, O, O_h and
- Two icosahedral point groups, I, I_h.

MSS Examples

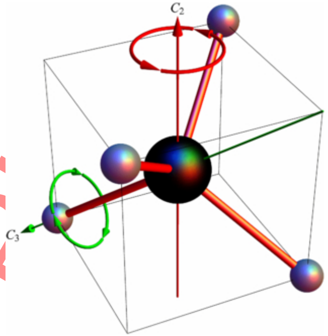
Group T_d

The molecules belonging to this class contain 4 C_3 axis, three S_4 axes which are also C_2 axes, and six σ_d. E.g. CCl_4, CH_4, etc.

MSS Examples

Group T_d

The molecules belonging to this class contain 4 C_3 axis, three S_4 axes which are also C_2 axes, and six σ_d. E.g. CCl_4, CH_4, etc.



Group O_h

They contain the following symmetry elements.

Group O_h

They contain the following symmetry elements.

1. Three C_4 axes(each passing through opposite apices), which are also S_4 axes.

Group O_h

They contain the following symmetry elements.

1. Three C_4 axes(each passing through opposite apices), which are also S_4 axes.
2. Four C_3 axes(each passing through the centres of a pair of opposite triangular faces), which are also S_6 axes.

Group O_h

They contain the following symmetry elements.

1. Three C_4 axes(each passing through opposite apices), which are also S_4 axes.
2. Four C_3 axes(each passing through the centres of a pair of opposite triangular faces), which are also S_6 axes.
3. Six C_2 axes(which bisects opposite edges).

Group O_h

They contain the following symmetry elements.

1. Three C_4 axes(each passing through opposite apices), which are also S_4 axes.
2. Four C_3 axes(each passing through the centres of a pair of opposite triangular faces), which are also S_6 axes.
3. Six C_2 axes(which bisects opposite edges).
4. Three σ_hs (which pass through four of the six apices).

Group O_h

They contain the following symmetry elements.

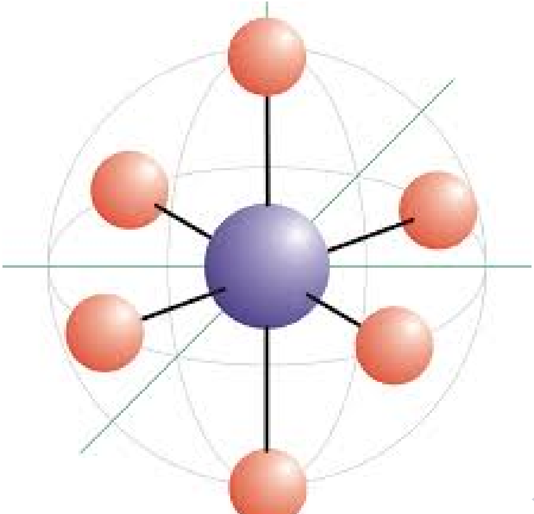
1. Three C_4 axes(each passing through opposite apices), which are also S_4 axes.
2. Four C_3 axes(each passing through the centres of a pair of opposite triangular faces), which are also S_6 axes.
3. Six C_2 axes(which bisects opposite edges).
4. Three σ_hs (which pass through four of the six apices).
5. Six σ_ds (which pass through two apices and bisect opposite edges) and

Group O_h

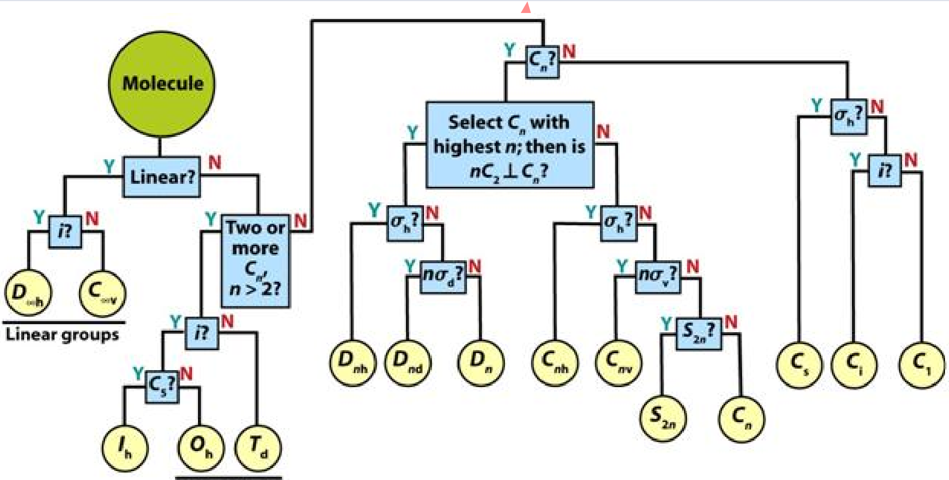
They contain the following symmetry elements.

1. Three C_4 axes(each passing through opposite apices), which are also S_4 axes.
2. Four C_3 axes(each passing through the centres of a pair of opposite triangular faces), which are also S_6 axes.
3. Six C_2 axes(which bisects opposite edges).
4. Three σ_hs (which pass through four of the six apices).
5. Six σ_ds (which pass through two apices and bisect opposite edges) and
6. an 'i'.

Example for Group O_h



Flow chart for Point Group Determination



1. Determine whether the molecule belongs to one of the special groups.

1. Determine whether the molecule belongs to one of the special groups.
    1. If the molecule is linear, see whether 'i' present or not. If 'i' present the point group is $D_{\infty h}$ and if not $C_{\infty h}$.

1. Determine whether the molecule belongs to one of the special groups.
   1. If the molecule is linear, see whether 'i' present or not. If 'i' present the point group is $D_{\infty h}$ and if not $C_{\infty h}$.
   2. If the molecule is not linear, see whether the molecule belongs to special point group such as T_d, O_h.

1. Determine whether the molecule belongs to one of the special groups.
   1. If the molecule is linear, see whether 'i' present or not. If 'i' present the point group is $D_{\infty h}$ and if not $C_{\infty h}$.
   2. If the molecule is not linear, see whether the molecule belongs to special point group such as T_d, O_h.

2 If the molecule does not belong to one of the special point groups such as $D_{\infty h}$, $C_{\infty h}$, T_d, O_h,etc. look for rotation axes, mirror planes, and centre of inversion.

2. If the molecule does not belong to one of the special point groups such as $D_{\infty h}$, $C_{\infty h}$, T_d, O_h,etc. look for rotation axes, mirror planes, and centre of inversion.
   1. If no symmetry axis of any kind is present, but a plane of symmetry (σ) exists, the point group is C_s.

2. If the molecule does not belong to one of the special point groups such as $D_{\infty h}$, $C_{\infty h}$, T_d, O_h,etc. look for rotation axes, mirror planes, and centre of inversion.
   1. If no symmetry axis of any kind is present, but a plane of symmetry (σ) exists, the point group is C_s.
   2. If no symmetry axis present, but a centre of symmetry 'i' present, the point group is C_i.

2. If the molecule does not belong to one of the special point groups such as $D_{\infty h}$, $C_{\infty h}$, T_d, O_h,etc. look for rotation axes, mirror planes, and centre of inversion.
   1. If no symmetry axis of any kind is present, but a plane of symmetry (σ) exists, the point group is C_s.
   2. If no symmetry axis present, but a centre of symmetry 'i' present, the point group is C_i.
   3. If the molecule does not contain a symmetry element of any kind except identity, the point group is C_1.

2. If the molecule does not belong to one of the special point groups such as $D_{\infty h}$, $C_{\infty h}$, T_d, O_h,etc. look for rotation axes, mirror planes, and centre of inversion.
   1. If no symmetry axis of any kind is present, but a plane of symmetry (σ) exists, the point group is C_s.
   2. If no symmetry axis present, but a centre of symmetry 'i' present, the point group is C_i.
   3. If the molecule does not contain a symmetry element of any kind except identity, the point group is C_1.

3 If an improper rotation axis S_n of even order is present, which automatically requires the presence of a $C_{n/2}$ axis collinear with it, but does not contain any other proper rotation axis or a mirror plane, the point group is S_n.

3. If an improper rotation axis S_n of even order is present, which automatically requires the presence of a $C_{n/2}$ axis collinear with it, but does not contain any other proper rotation axis or a mirror plane, the point group is S_n.
4. If a proper rotation axis is found to be present, look for other proper axis. If such axes are present, locate the principal axis C_n, and see whether there exists a set of n equally spaced c_2 axis perpendicular to the c_n axis. If such c_2 axis exist the molecule belong to one of the point groups D_{nh}, D_{nd} and D_n,which is determined by the presence of absence of symmetry planes as specified below