M.Sc. Semester-II
Compulsory Paper-7 (CP-7)
Group Theory and Spectroscopy

I. Symmetry and Group Theory in Chemistry
Lecture 1 : Symmetry Elements and Symmetry Operation

Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi

Symmetry and Group Theory in Chemistry : 25 Hrs

Symmetry elements and symmetry operation, Group and Subgroup, Point group, Classification and representation of groups, The defining property of a group, Sub group and Class, Group multiplication table for C_{2V}, C_{2h} and C_{3V} point group, Generators and Cyclic groups. Similarity Transformation, Table of conjugates for C_{2V}, C_{2h} and C_{3V} point group, Schonflies symbols.

Matrix notation for symmetry operation, Representations of groups by matrices (representation for the Cn, Cnv, Cnh and Dnh groups to be worked out explicitly). Character of a representation, Mulliken symbols for irreducible representations, Direct product relationship, Applications of group theory to quantum mechanics-identifying non-zero matrix elements.

The great orthogonal theorem (without proof) and rules derived from this theorem. Derivation of the orthonormalization condition. Character table. Construction of character table: C_{2V} and C_{3V} (only). Reducible representations and their reduction. Total character and their calculation. Application of character table in determination of IR and Raman active vibrations: H_2O, BF_3 and N_2F_2

Coverage:

1. Symmetry elements
2. Symmetry operation

Lecture 1 : Symmetry Elements and Symmetry Operation

The term *symmetry* is derived from the Greek word “symmetria” which means “measured together”. An object is symmetric if one part (e.g. one side) of it is the same* as all of the other parts. You know intuitively if something is symmetric but we require a precise method to describe how an object or molecule is symmetric.

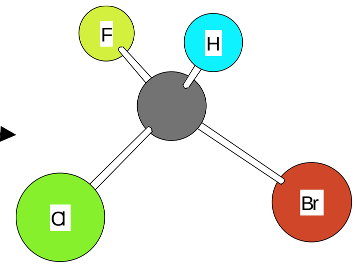
Group theory is a very powerful mathematical tool that allows us to rationalize and simplify many problems in Chemistry. A group consists of a set of symmetry elements (and associated symmetry operations) that completely describe the symmetry of an object.

We will use some aspects of group theory to help us understand the bonding and spectroscopic features of molecules.

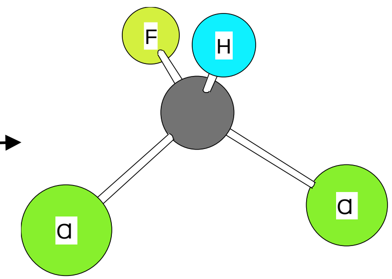
Lecture 1 : Symmetry Elements and Symmetry Operation

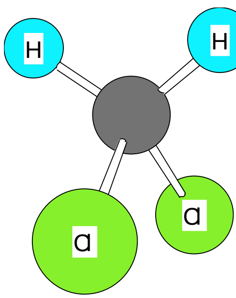
We need to be able to specify the symmetry of molecules clearly.

No symmetry – CHFClBr



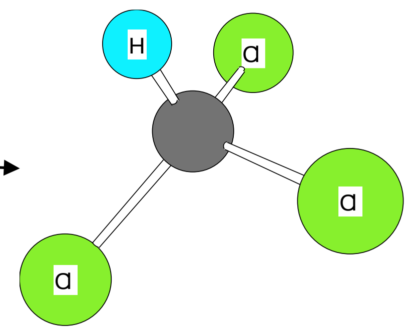
Some symmetry – $CHFCl_2$



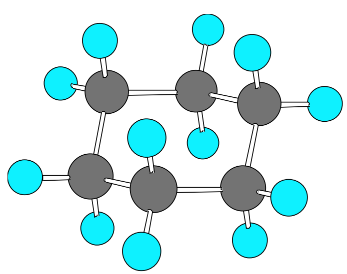


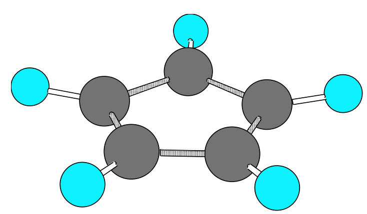
More symmetry – CH_2Cl_2

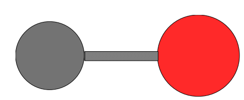
More symmetry ? – $CHCl_3$



What about ?







Point groups provide us with a way to indicate the symmetry unambiguously.

Lecture 1 : Symmetry Elements and Symmetry Operation

Point groups have symmetry about a single point at the center of mass of the system.

Symmetry elements are geometric entities about which a *symmetry operation* can be performed. In a point group, all symmetry elements must pass through the center of mass (the point). A symmetry operation is the action that produces an object identical to the initial object.

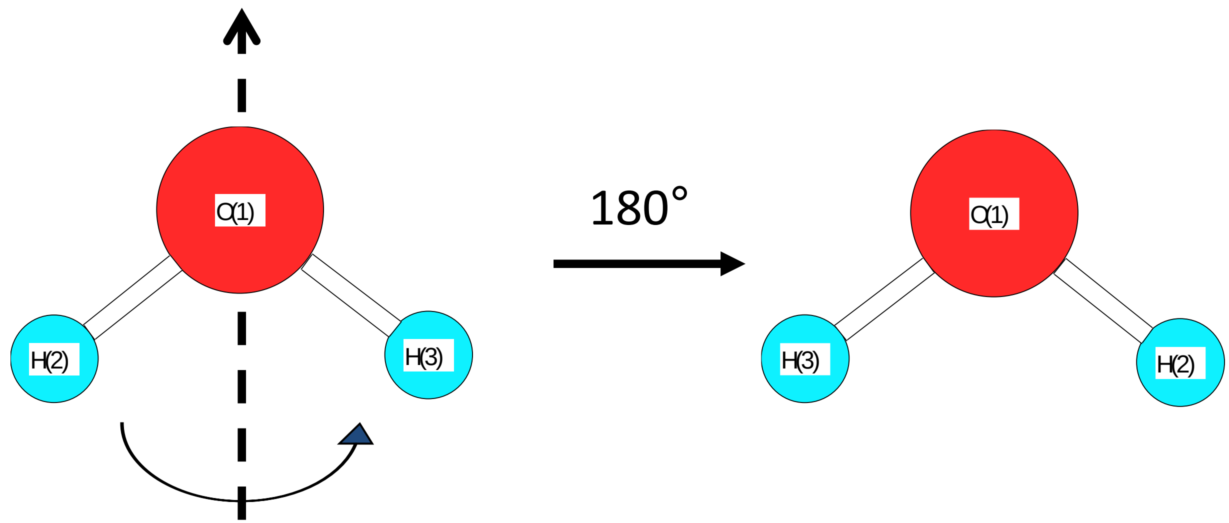
The symmetry elements and related operations that we will find in molecules are:

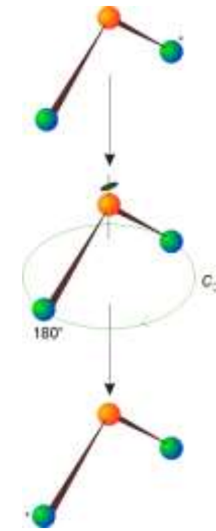
Element	Operation
Rotation axis, C_n	n-fold rotation
Improper rotation axis, S_n	n-fold improper rotation
Plane of symmetry, σ	Reflection
Center of symmetry, i	Inversion
Rotation through 360º	Identity, E

The Identity operation does nothing to the object – it is necessary for mathematical completeness, as we will see later.

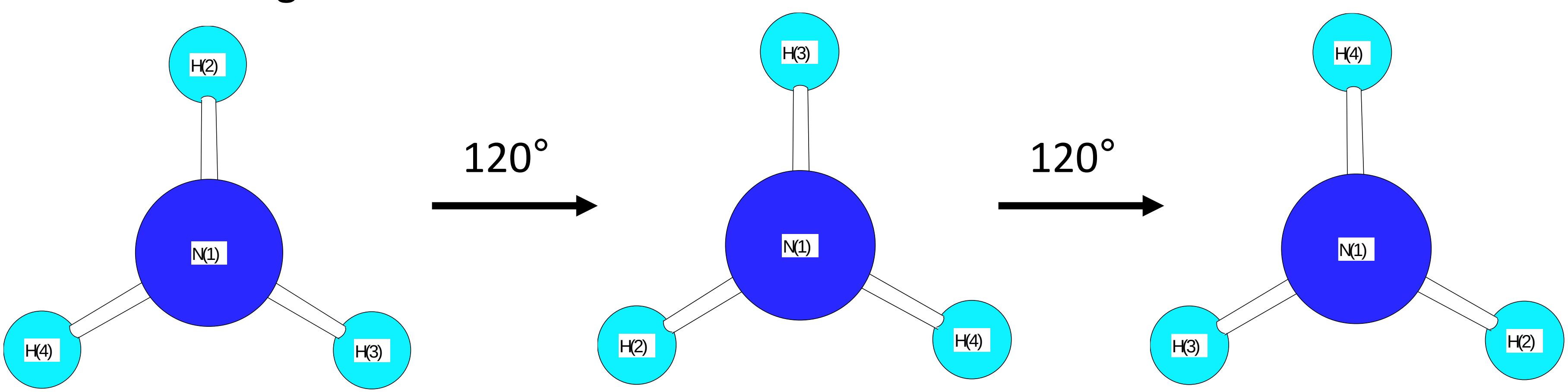
Lecture 1 : Symmetry Elements and Symmetry Operation

n-fold rotation - a rotation of 360°/n about the C_n axis ($n = 1$ to ∞)





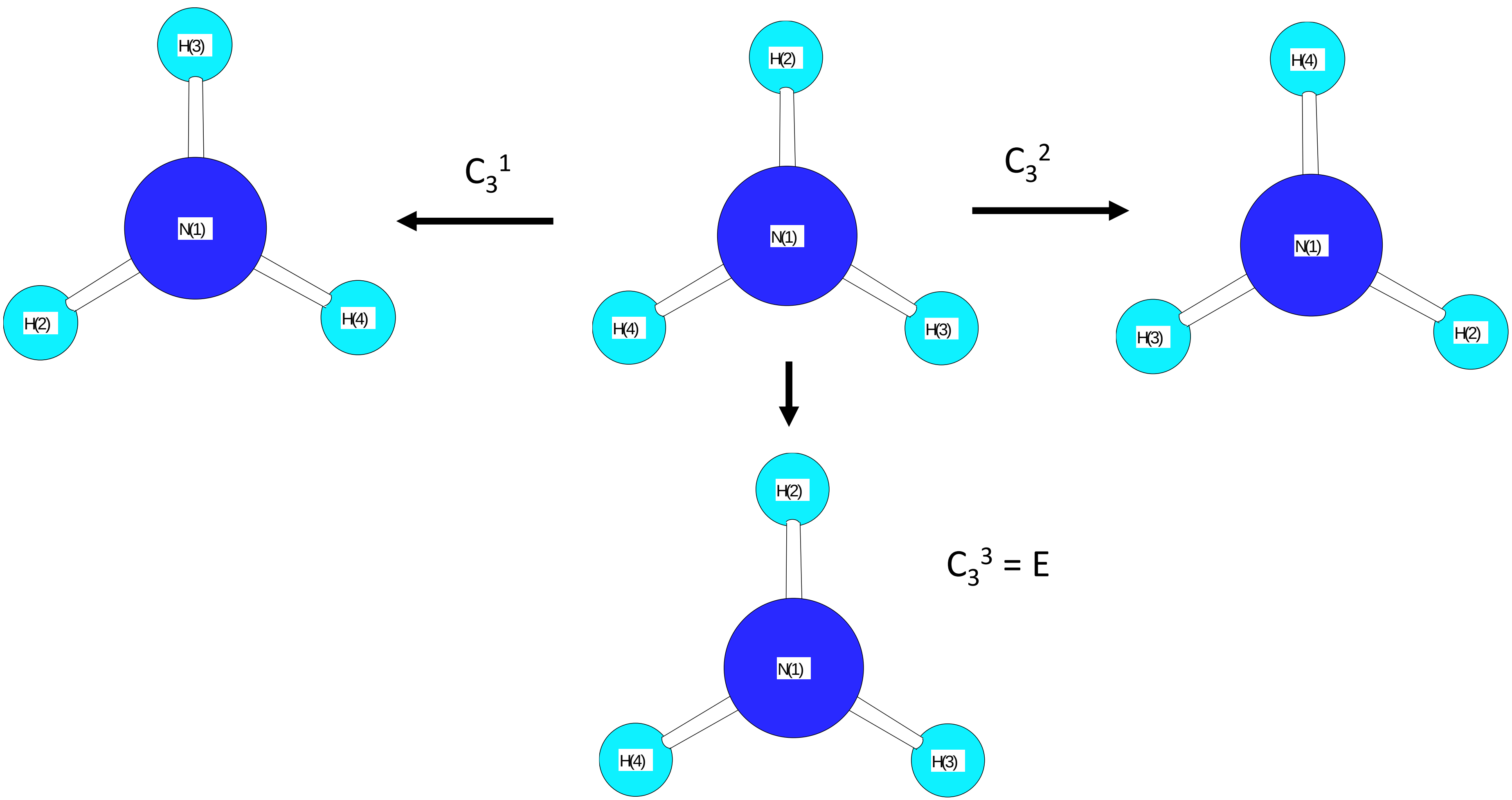
In water there is a C_2 axis so we can perform a 2-fold (180°) rotation to get the identical arrangement of atoms.



In ammonia there is a C_3 axis so we can perform 3-fold (120°) rotations to get identical arrangement of atoms.

Notes about rotation operations:

- Rotations are considered positive in the counter-clockwise direction.
- Each possible rotation operation is assigned using a superscript integer m of the form C_n^m.
- The rotation C_n^n is equivalent to the identity operation (nothing is moved).



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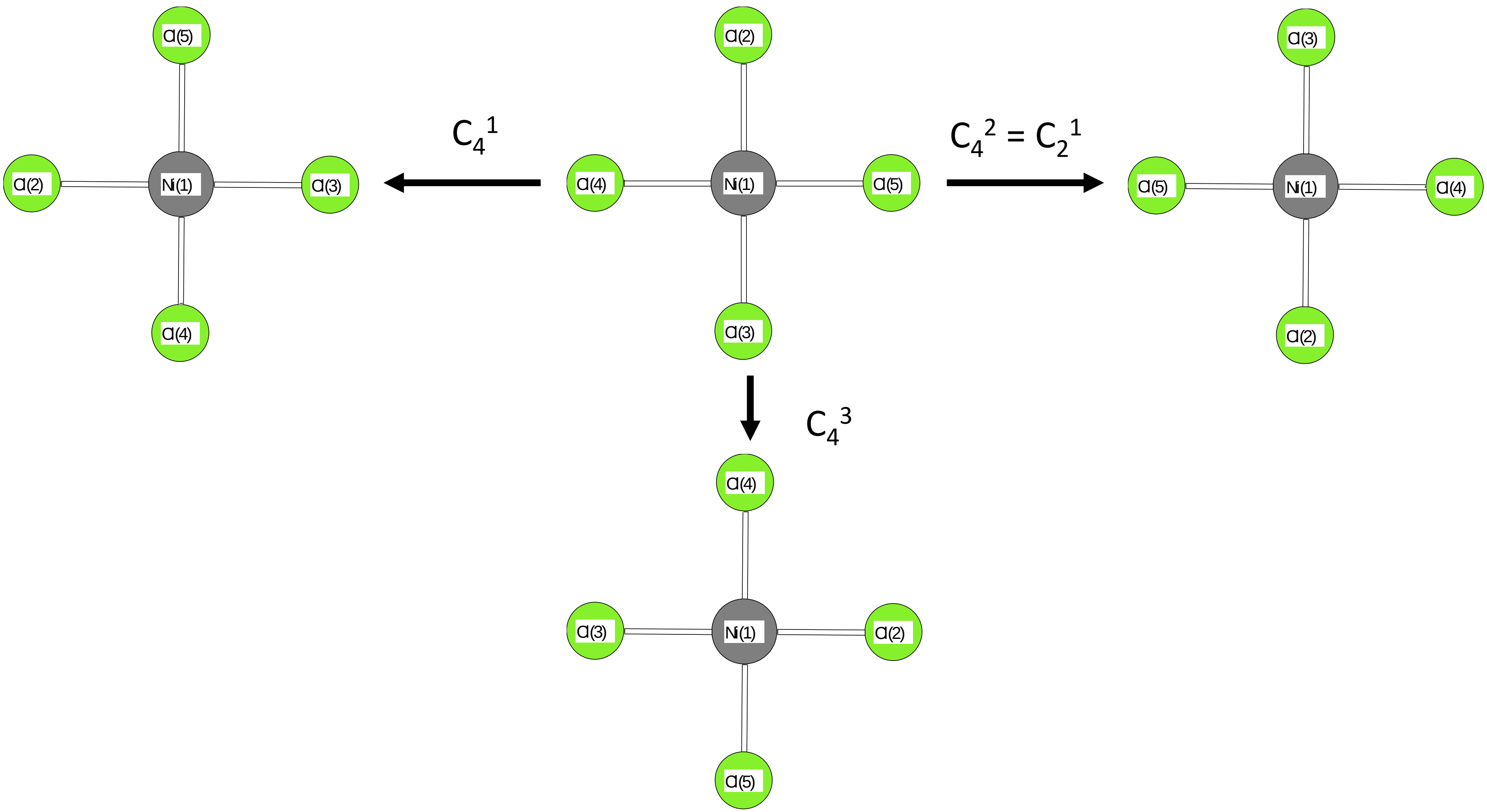
Notes about rotation operations, C_n^m:

- If n/m is an integer, then that rotation operation is equivalent to an n/m - fold rotation.

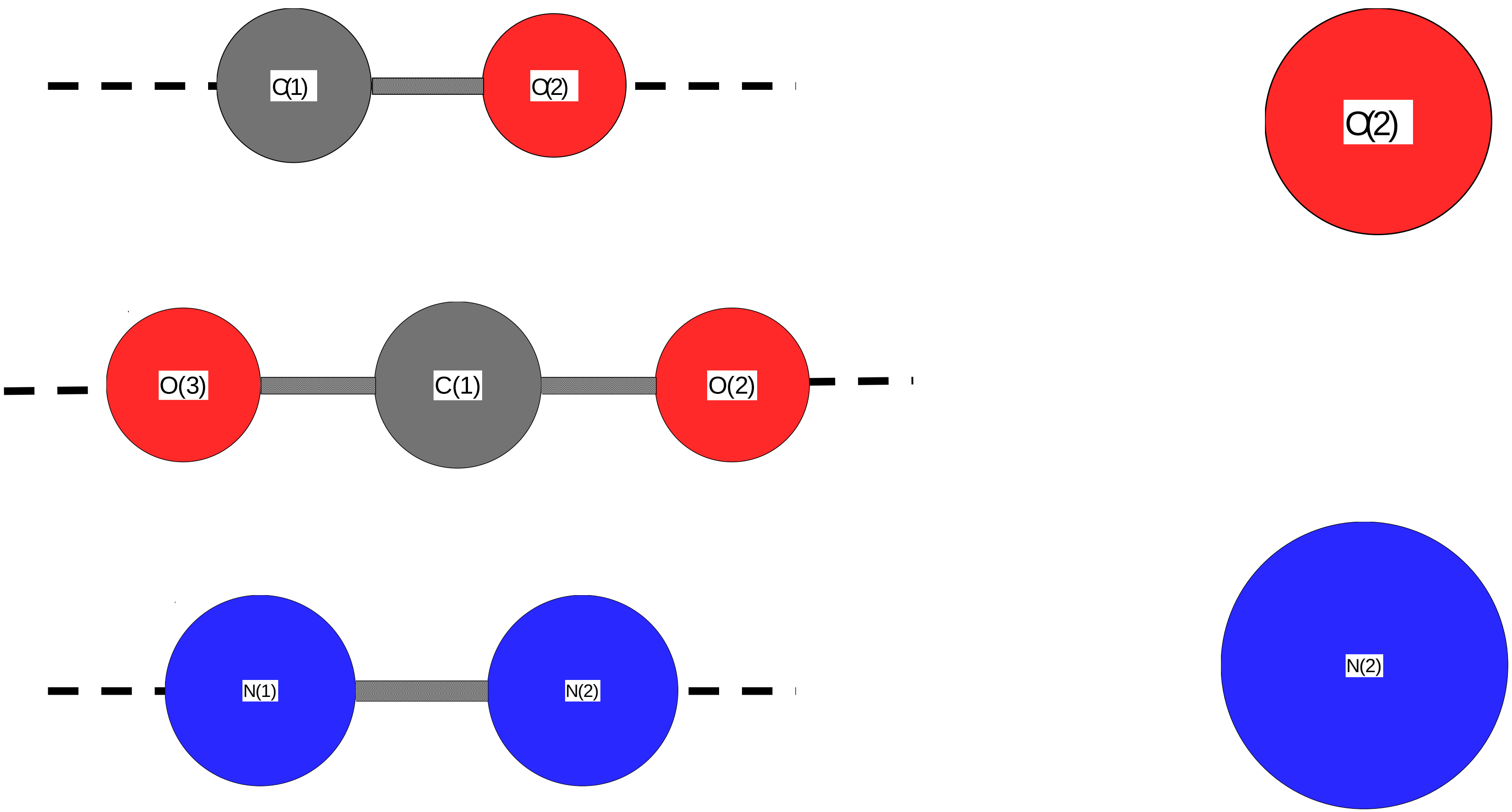
e.g. $C_4^2 = C_2^1$, $C_6^2 = C_3^1$, $C_6^3 = C_2^1$, etc. (identical to simplifying fractions)



Lecture 1 : Symmetry Elements and Symmetry Operation

Notes about rotation operations, C_n^m:

- Linear molecules have an infinite number of rotation axes C_∞ because any rotation on the molecular axis will give the same arrangement.



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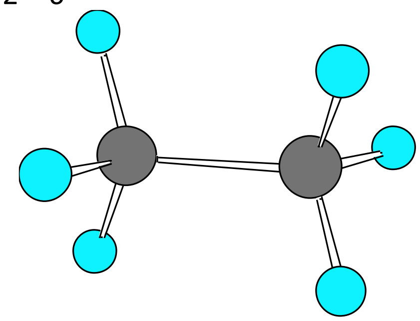
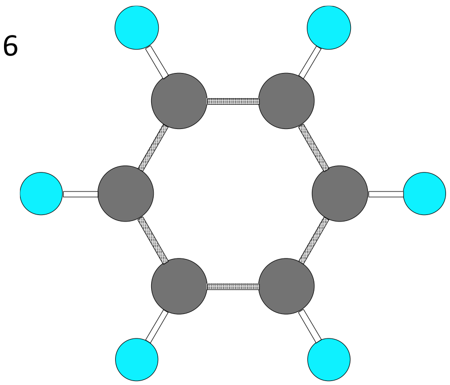
The *Principal axis* in an object is the highest order rotation axis. It is usually easy to identify the principle axis and this is typically assigned to the z-axis if we are using Cartesian coordinates.

Ethane, C_2H_6

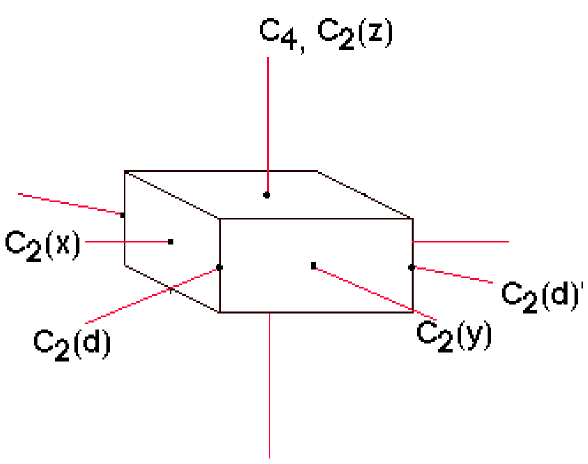


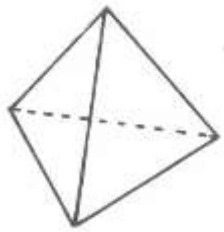
The principal axis is the three-fold axis containing the C-C bond.

Benzene, C_6H_6



The principal axis is the six-fold axis through the center of the ring.

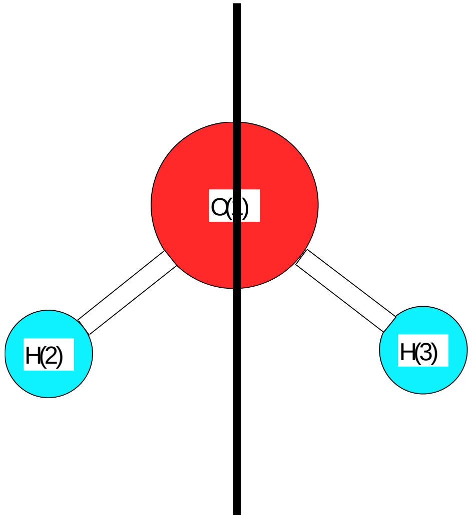




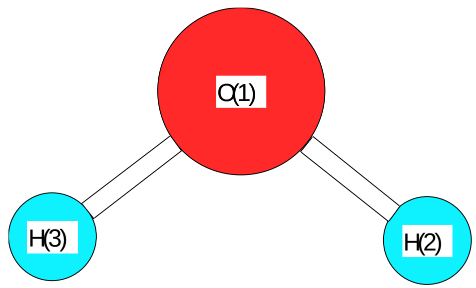
The principal axis in a tetrahedron is a three-fold axis going through one vertex and the center of the object.

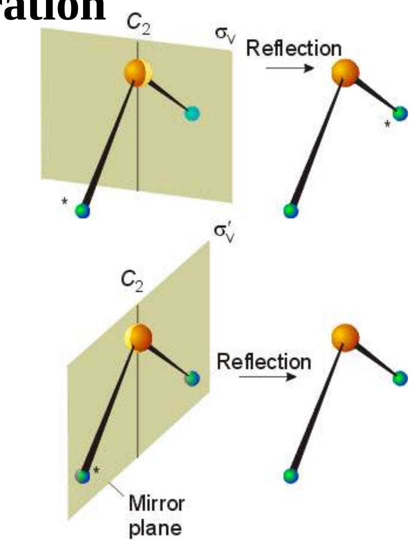
Lecture 1 : Symmetry Elements and Symmetry Operation

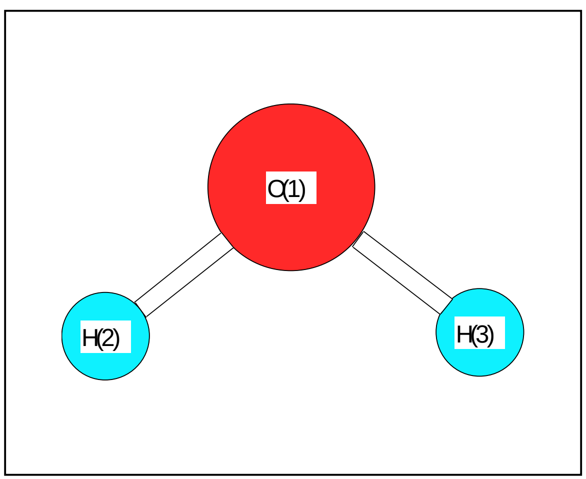
Reflection across a plane of symmetry, σ (mirror plane)



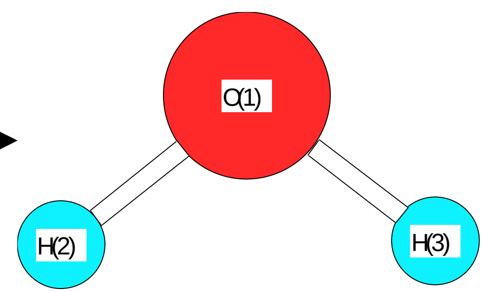
$\xrightarrow{\sigma_v}$

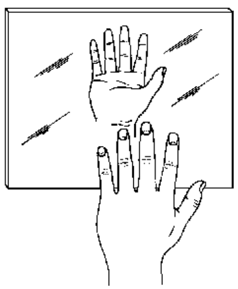






$\xrightarrow{\sigma_v}$



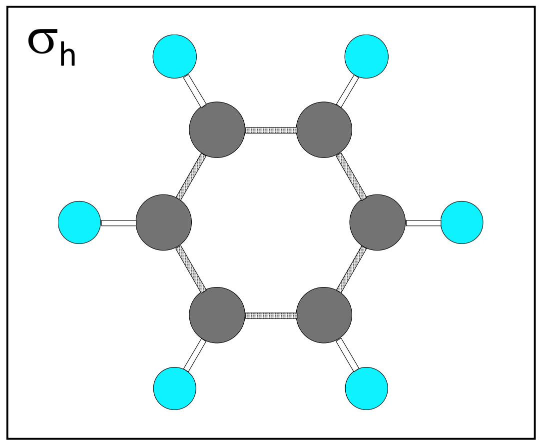


These mirror planes are called "vertical" mirror planes, σ_v, because they contain the principal axis. The reflection illustrated in the top diagram is through a mirror plane perpendicular to the plane of the water molecule. The plane shown on the bottom is in the same plane as the water molecule.

Handedness is changed by reflection!

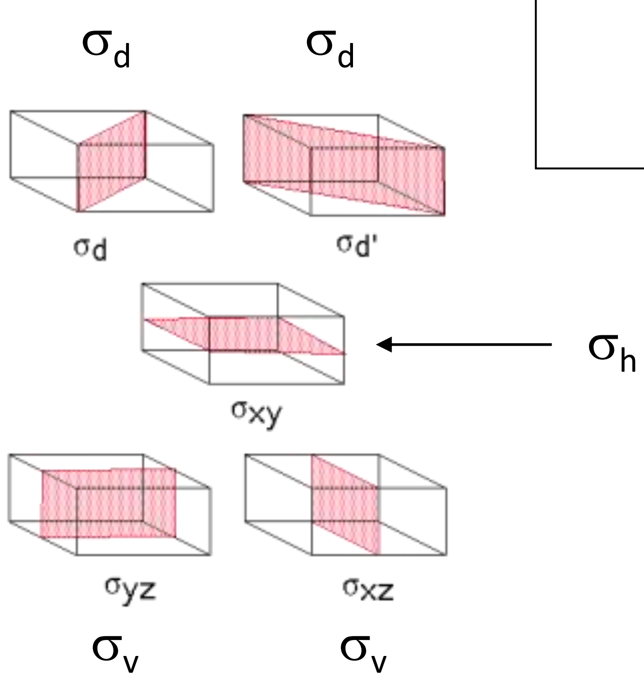
Notes about reflection operations:

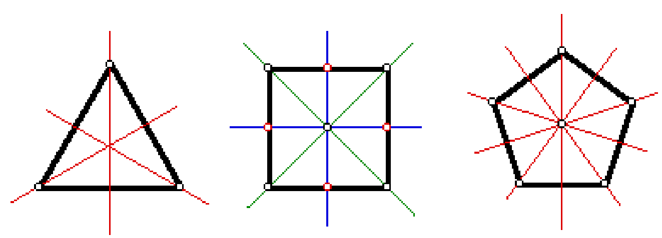
- A reflection operation exchanges one half of the object with the reflection of the other half.
- Reflection planes may be vertical, horizontal or dihedral (more on σ_d later).
- Two successive reflections are equivalent to the identity operation (nothing is moved).

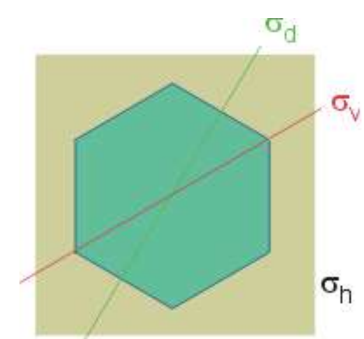


A “horizontal” mirror plane, σ_h, is perpendicular to the principal axis. This must be the xy-plane if the z-axis is the principal axis.

In benzene, the σ_h is in the plane of the molecule – it “reflects” each atom onto itself.







Vertical and dihedral mirror planes of geometric shapes.

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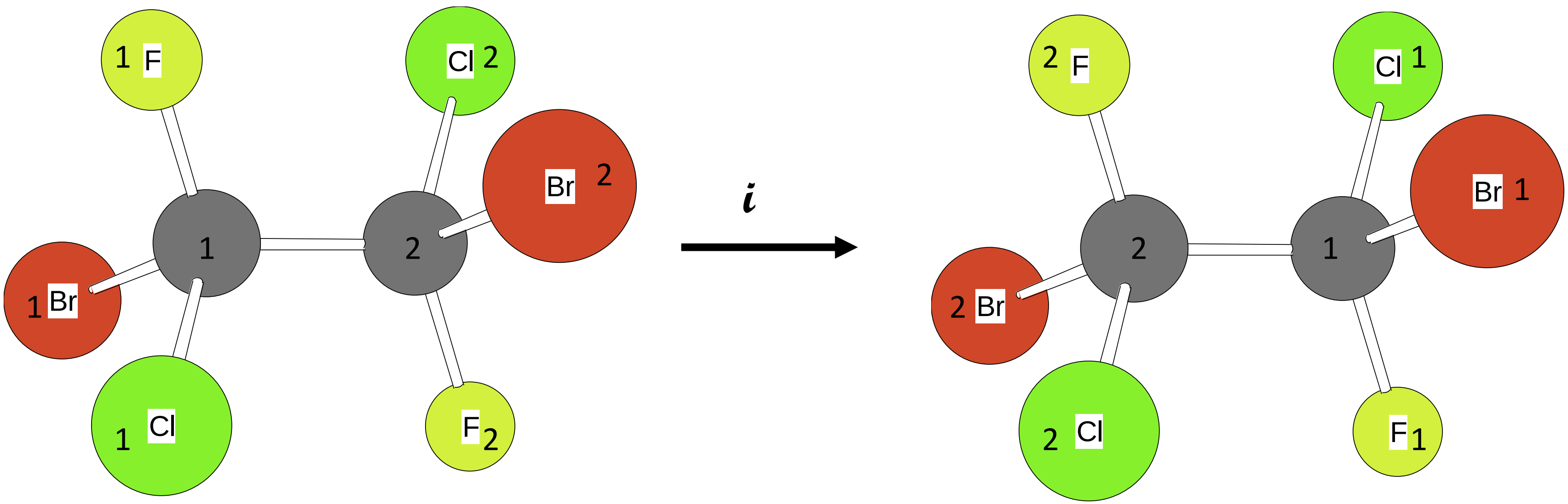
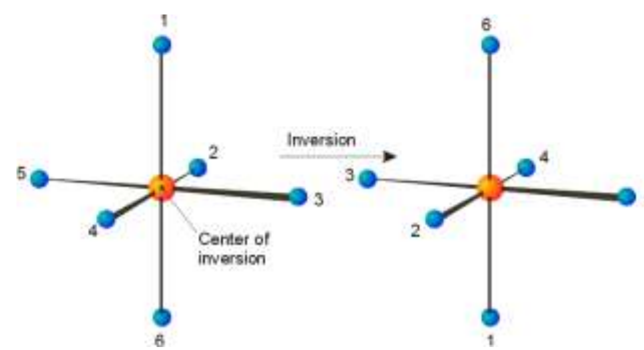
Inversion and centers of symmetry, i (inversion centers)

In this operation, every part of the object is reflected through the inversion center, which must be at the center of mass of the object.

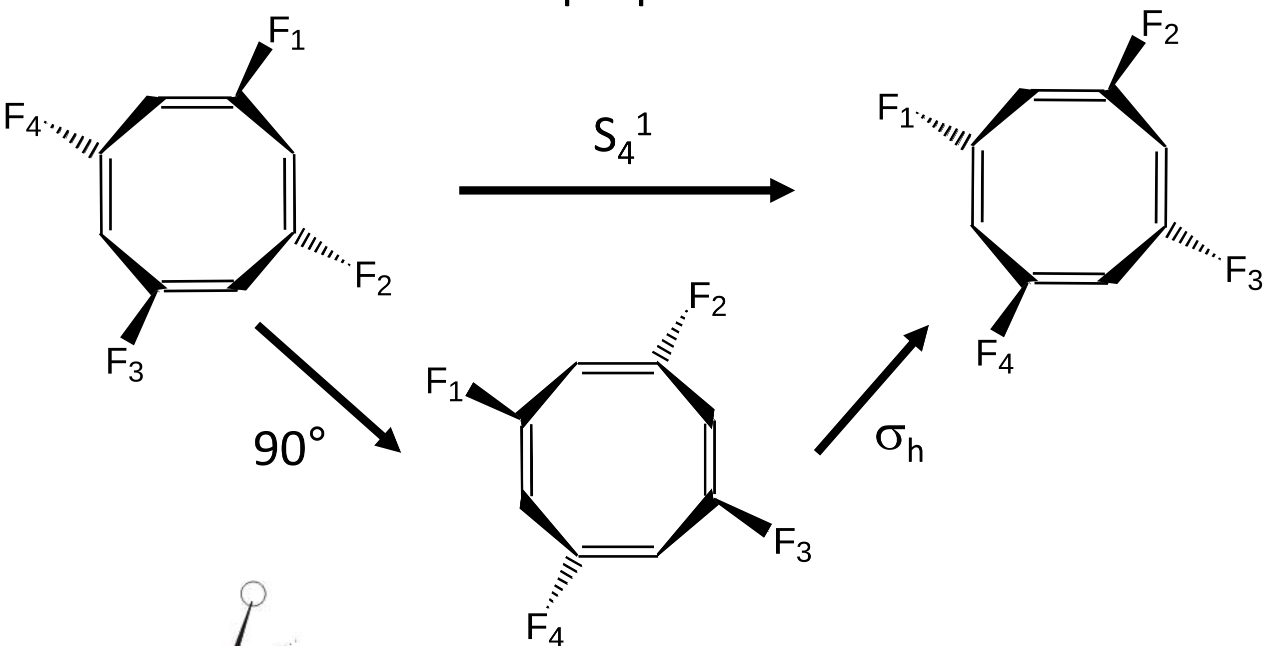


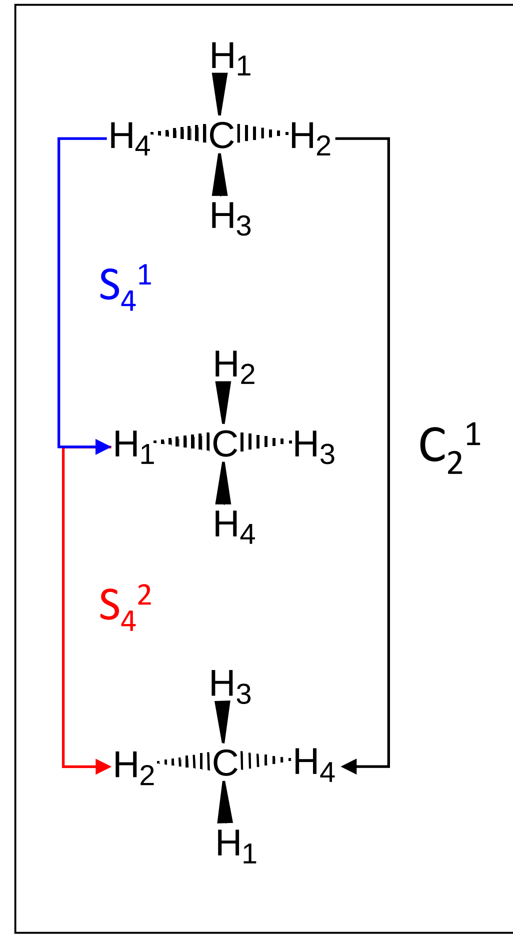
$$[x, y, z] \xrightarrow{i} [-x, -y, -z]$$

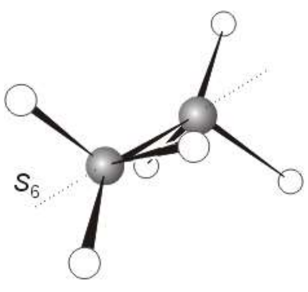


We will not consider the matrix approach to each of the symmetry operations in this course but it is particularly helpful for understanding what the inversion operation does. The inversion operation takes a point or object at [x, y, z] to [-x, -y, -z].

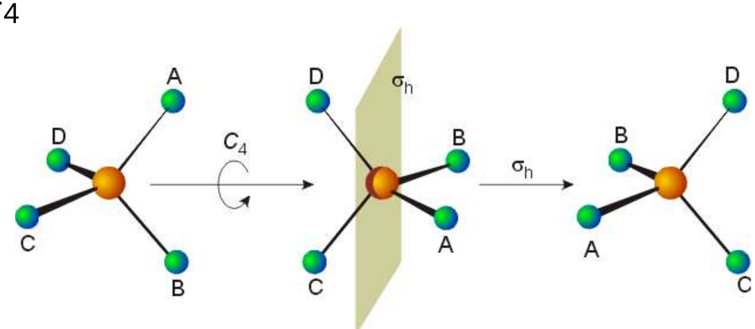
n-fold improper rotation, S_n^m (associated with an improper rotation axis or a rotation-reflection axis) This operation involves a rotation of 360°/n followed by a reflection perpendicular to the axis. It is a single operation and is labeled in the same manner as "proper" rotations.





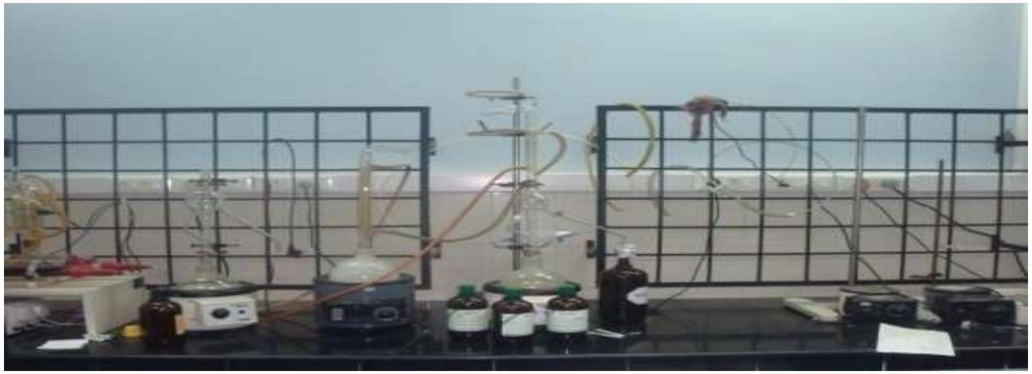


1 S_6 axis



Note that: $S_1 = \sigma$, $S_2 = \boldsymbol{i}$, and sometimes $S_{2n} = C_n$ (e.g. in box) this makes more sense when you examine the matrices that describe the operations.

Thank You



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