Symmetry Operations and Elements

- The goal for this section of the course is to understand how symmetry arguments can be applied to solve physical problems of chemical interest.
- To achieve this goal we must identify and catalogue the complete symmetry of a system and subsequently employ the mathematics of groups to simplify and solve the physical problem in question.
- A ***symmetry element is an imaginary geometrical construct*** about which a symmetry operation is performed.
- A ***symmetry operation is a movement of an object about a symmetry element*** such that the object's orientation and position before and after the operation are indistinguishable.
- A symmetry operation carries every point in the object into an ***equivalent point or the identical point*****.**

Point Group Symmetry

- All symmetry elements of a molecule pass through a central point within the molecule.
- The symmetry of a molecule or ion can be described in terms of the complete collection of symmetry operations it possesses.
- The total number of operations may be as few as one or as many as infinity. The more symmetry operations a molecule has, the higher its symmetry is.
- Regardless of the number of operations, all will be examples of only five types.

Operation	Element	Element Construct
Identity, E	The object	N/A
Proper rotation, C_n	Proper axis, Rotation axis	line
Reflection, σ	Mirror plane, Reflection plane	plane
Inversion, i	Inversion center, Center of symmetry	point
Rotation-reflection Improper rotation, S_n	Improper axis, alternating axis	line

The Identity Operation (*E*)

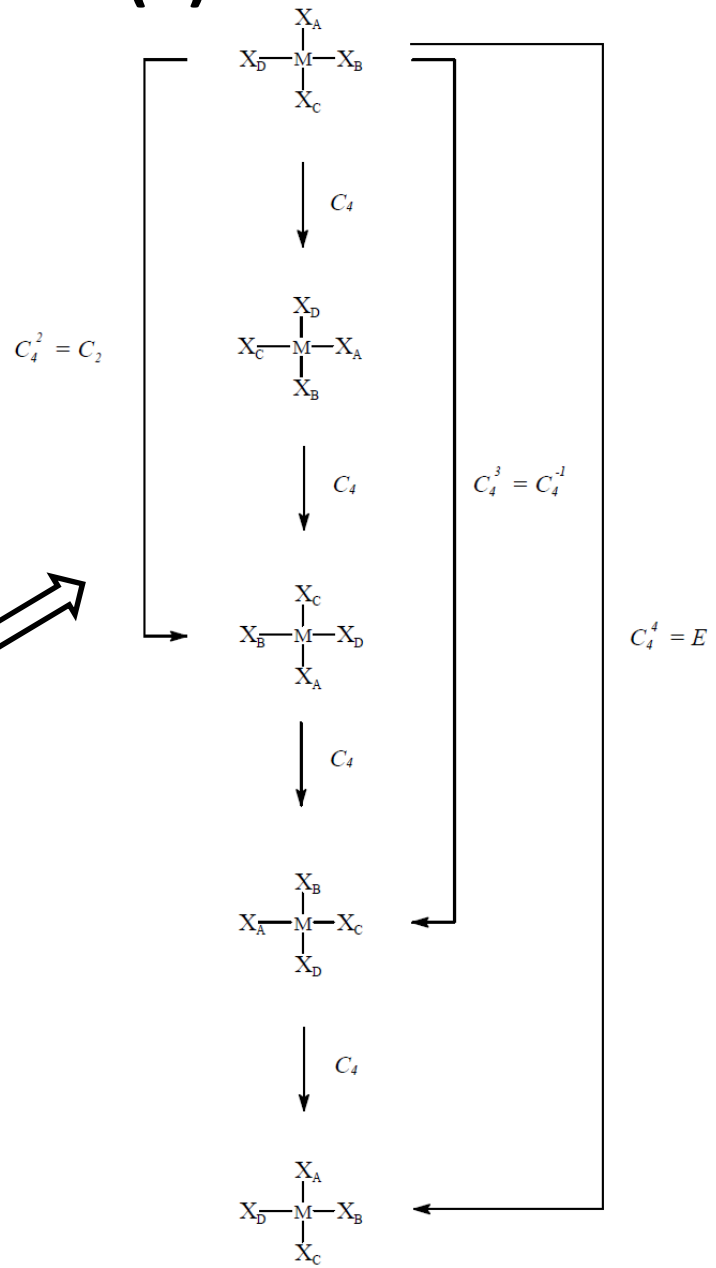
- The simplest of all symmetry operations is *identity*, given the symbol *E*.
- Every object possesses identity. If it possesses no other symmetry, the object is said to be *asymmetric*.
- As an operation, identity does nothing to the molecule. It exists for every object, because the object itself exists.
- The need for such an operation arises from the mathematical requirements of group theory.
- In addition, identity is often the result of carrying out a particular operation successively a certain number of times,

  i.e., if you keep doing the same operation repeatedly, eventually you may bring the object back to the identical (not simply equivalent) orientation from which was started.
- When identifying the result of multiple or compound symmetry operations they are designated by their most direct single equivalent.
- Thus, if a series of repeated operations carries the object back to its starting point, the result would be identified simply as identity.

The Rotation Operation (*C*)

- The operation of *rotation* is designated by the symbol C_n .
- If a molecule has rotational symmetry C_n , rotation by $2\pi/n = 360°/n$ brings the object into an equivalent position.
- The value of *n* is the ***order of an n-fold rotation*.**
- If the molecule has one or more rotational axes, the one with the highest value of *n* is the ***principal axis of rotation*.**
- Successive C_4 clockwise rotations of a planar MX_4 molecule about an axis perpendicular to the plane of the molecule ($X_A = X_B = X_C = X_D$).
- Multiple iterations are designated by a superscript,

  e.g. three successive C_4 rotations are identified as C_4^3
- The C_4^2 and C_4^4 operations are preferably identified as the simpler C_2 and *E* operations, respectively.



- There are four other C_2 axes in the place of the molecule.
- The C_2' and C_2'' axes of a planar MX_4 molecule.
- As these twofold axes are not collinear with the principal C_4 rotational axis they are distinguished by adding prime (‘) and double prime (‘’) to their symbols.
- Only two notations are needed for the four axes, because both C_2' axes are said to belong to the same *class*, while the two C_2'' axes belong to a separate class.

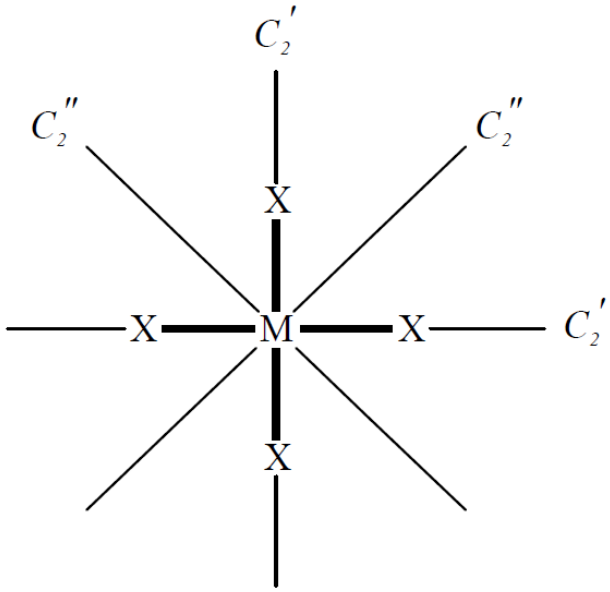
  i.e., both C_2' axes are geometrically equivalent to each other and distinct from C_2'' .

- In listing the complete set of symmetry operations for a molecule, operations of the same class are designated by a single notation preceded by a coefficient indicating the number of equivalent operations comprising the class.

  e.g. for the square planar structure here discussed of D_{4h} symmetry, the rotational operations grouped by class are

  $2C_4$ (C_4 and C_4^3), C_2 (collinear with C_4)

  $2C_2'$, and $2C_2''$.



The C_2' and C_2'' axes of a planar MX_4 molecule.

General Relationships for C_n

$$C_n^{\,n} = E$$

$$C_{2n}^{\,n} = C_2 \qquad (n = 2, 4, 6, 8\ldots\text{etc.})$$

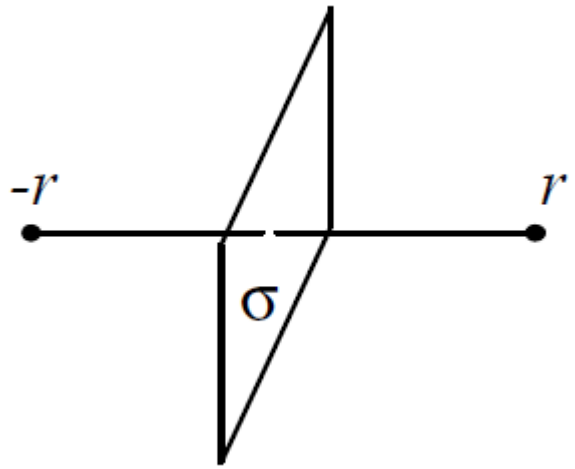
$$C_n^{\,m} = C_{n/m} \qquad (n/m = 2, 3, 4, 5\ldots\text{etc.})$$

$$C_n^{\,n+m} = C_n^{\,m} \qquad (m < n)$$

- *Every n-fold rotational axis has n–1 associated operations (excluding $C_n^{\,n} = E$).*
- Remember, the rotational operation $C_n^{\,m}$ *is* preferably identified as the simpler $C_{n/m}$ operation where *m/n* is an integer value.

The Reflection Operation (σ)

- The operation of *reflection* defines bilateral symmetry about a plane, called a *mirror plane* or *reflection plane*.
- For every point a distance r along a normal to a mirror plane there exists an equivalent point at –r.

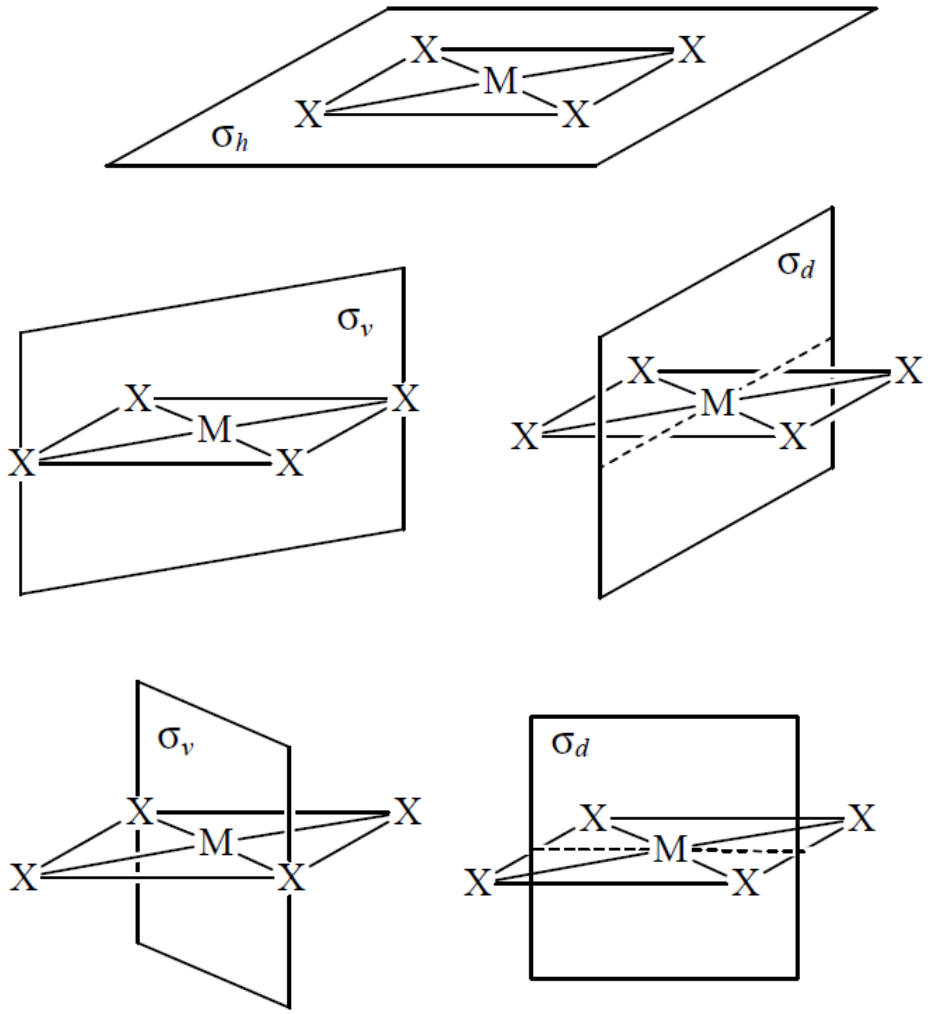


Two points, equidistant from a mirror plane σ, related by reflection.

- For a point (x,y,z), reflection across a mirror plane σ_{xy} takes the point into (x,y,–z).
- Each mirror plane has only one operation associated with it, since $\sigma_2 = E$.

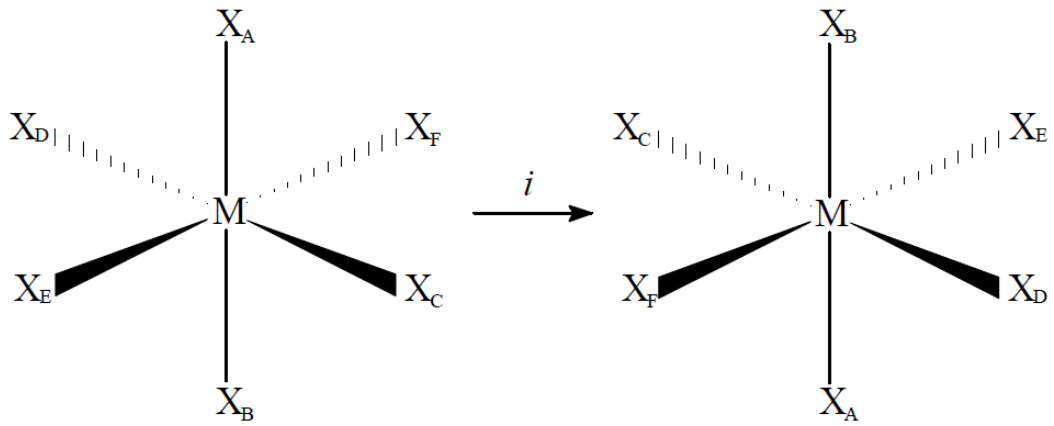
Horizontal, Vertical, and Dihedral Mirror Planes

- A σ_h plane is defined as perpendicular to the principal axis of rotation.
- If no principal axis of rotation exists, σ_h is defined as the plane of the molecule.
- σ_v and σ_d planes are defined so as to contain a principal axis of rotation and to be perpendicular to a σ_h plane.
- When both σ_v and σ_d planes occur in the same system, the distinction between the types is made by defining σ_v to contain the greater number of atoms or to contain a principal axis of a reference Cartesian coordinate system (x or y axis).
- Any σ_d planes typically will contain bond angle bisectors.
- The five mirror planes of a square planar molecule MX_4 are grouped into three classes (σ_h , $2\sigma_v$, $2\sigma_d$)



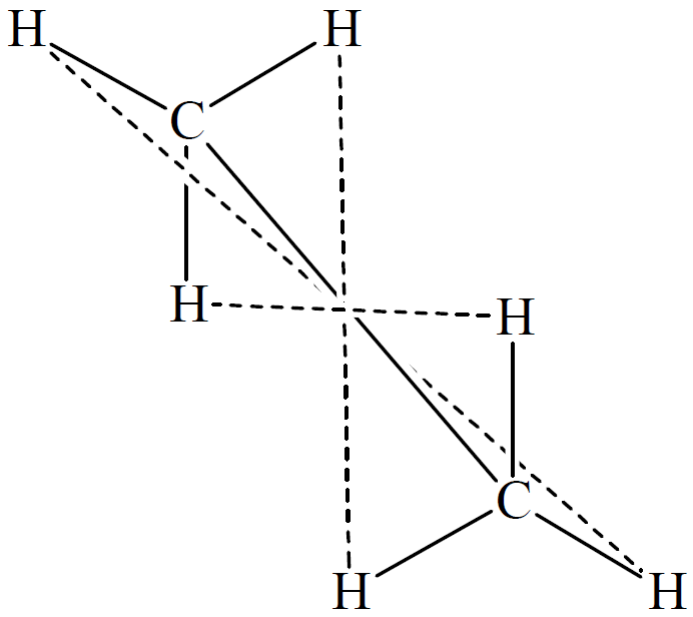
The Inversion Operation (*i*)

- The operation of *inversion* is defined relative to the central point within the molecule, through which all symmetry elements must pass (typically the origin of the Cartesian coordinate system).
- If inversion symmetry exists, for every point (x,y,z) there is an equivalent point (–x,–y,–z).
- Molecules or ions that have inversion symmetry are said to be *centrosymmetric*.
- Each inversion center has only one operation associated with it, since $i^2 = E$.



Effect of inversion (i) on an octahedral MX_6 molecule ($X_A = X_B = X_C = X_D = X_E = X_F$).

Inversion Center of Staggered Ethane



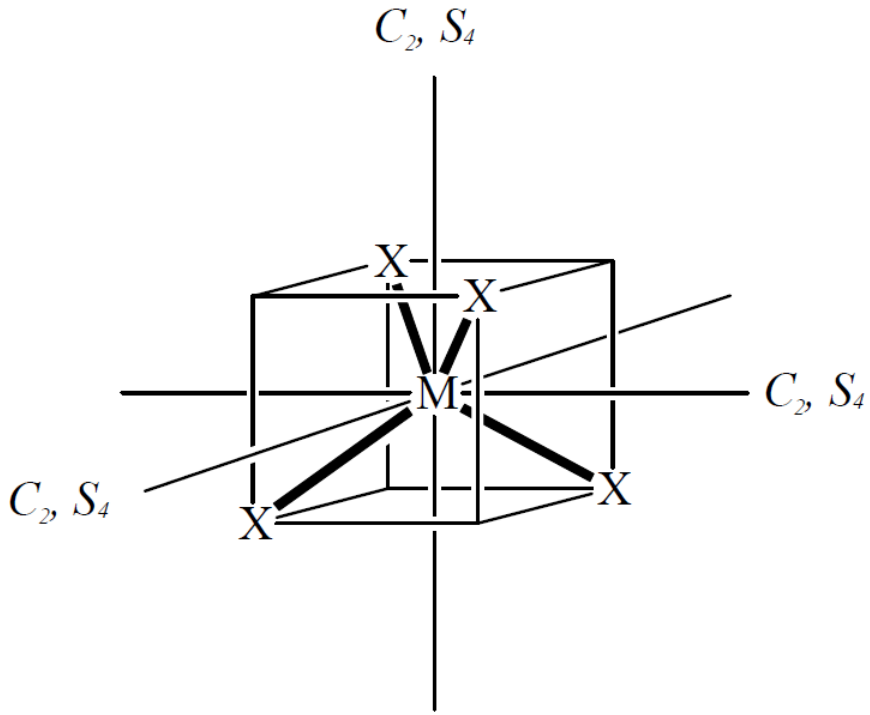
- Ethane in the staggered configuration. The inversion center is at the midpoint along the C-C bond. Hydrogen atoms related by inversion are connected by dotted lines, which intersect at the inversion center. The two carbon atoms are also related by inversion.

The Improper Rotation Operation (S_n)

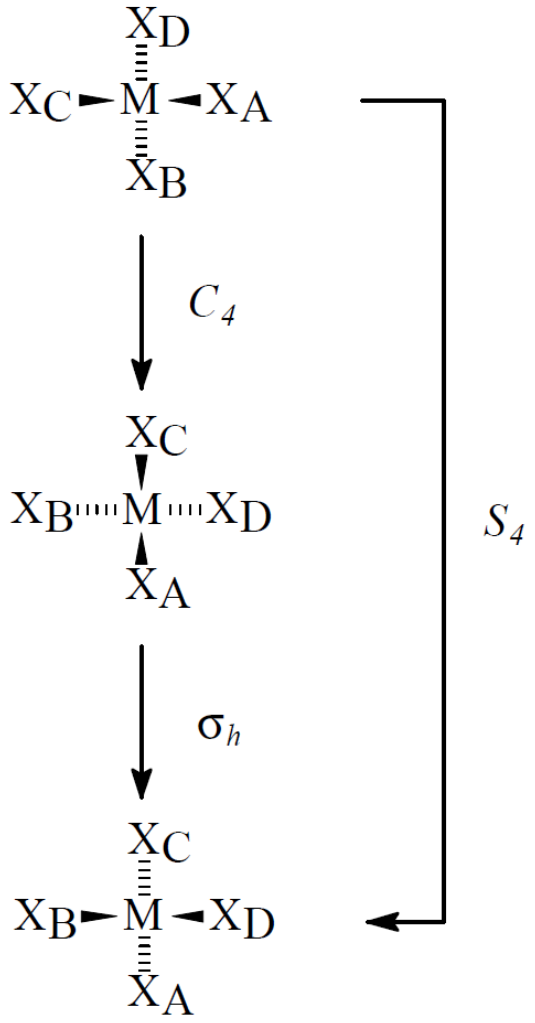
- The improper rotation operation S_n is also known as the *rotation-reflection* operation and as its name suggests is a compound operation.
- Rotation-reflection consists of a proper rotation followed by a reflection in a plane perpendicular to the axis of rotation.
- n refers to the improper rotation by $2\pi / n = 360° / n$.
- S_n exists if the movements C_n followed by σ_h (or vice versa) bring the object to an equivalent position.
- If both C_n and σ_h exist, then S_n must exist.

  e.g., S_4 collinear with C_4 in planar MX_4.
- Neither C_n nor σ_h need exist for S_n to exist.

  e.g., S_4 collinear with C_2 in tetrahedral MX_4.



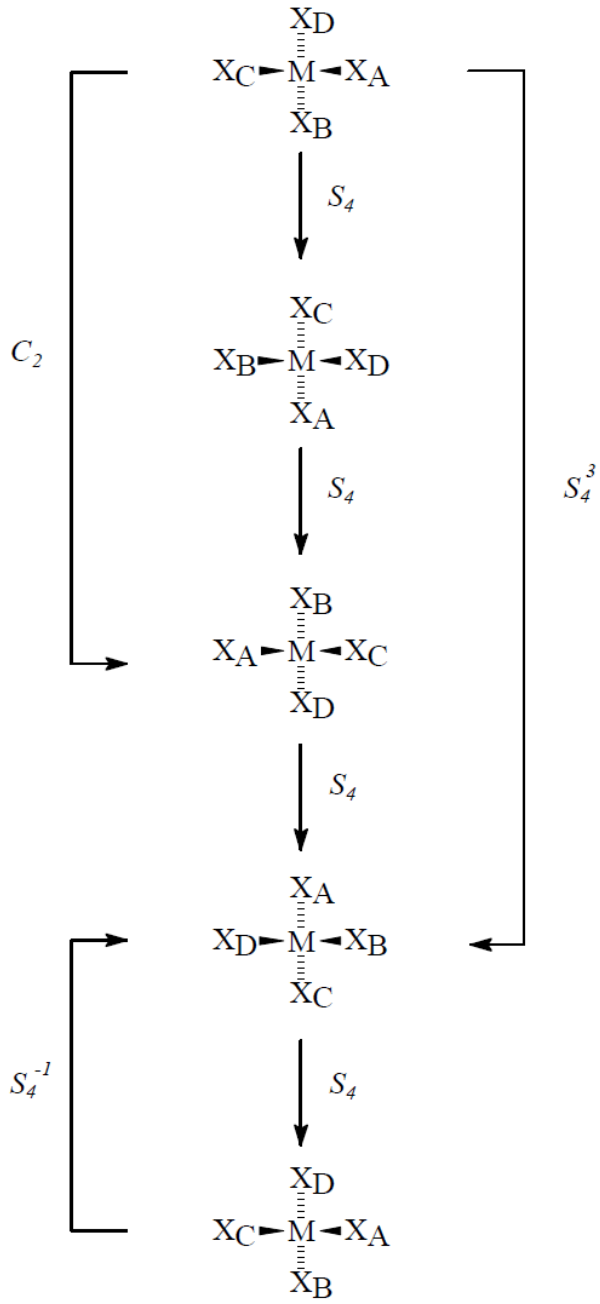
A tetrahedral MX_4 molecule inscribed in a cube.
A C_2 axis, collinear with an S_4 axis, passes through the centers of each pair of opposite cube faces and through the center of the molecule.
i.e., each axis bisects one of the M-X bonds.



S_4 improper rotation of a tetrahedral MX_4 molecule ($X_A = X_B = X_C = X_D$). The improper axis is perpendicular to the page. Rotation is arbitrarily taken in a clockwise direction. Note that neither C_4 nor σ_h are genuine symmetry operations of tetrahedral MX_4.

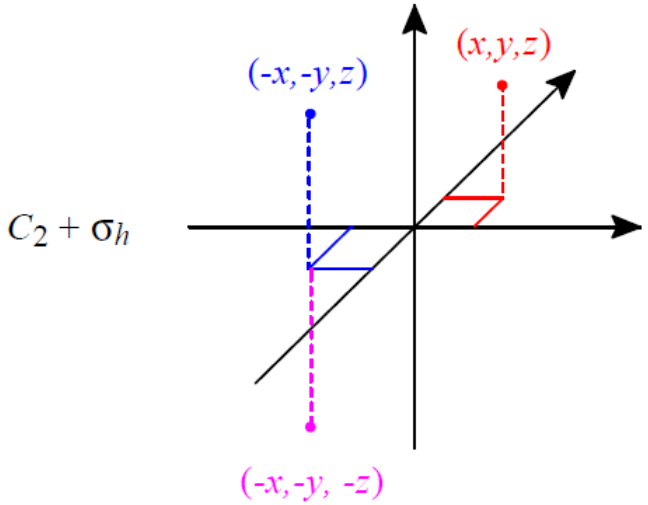
- Successive S_4 operations on a tetrahedral MX_4 molecule ($X_A = X_B = X_C = X_D$).
- Rotations are clockwise, except S_4^{-1}, which is equivalent to the clockwise operation S_4^3.
- Successively carrying out two S_4 operations is identical to the result of a single C_2 operation about the same axis

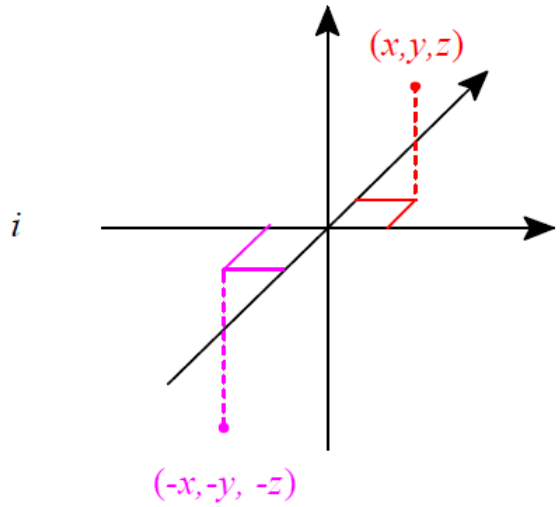
  i.e., $S_4^2 = C_2$
- Similarly, $S_4^4 = E$
- Thus, there are only two operations belonging to this class for the tetrahedral MX_4 molecule (S_4 and S_4^3) about this axis.
- In the highly symmetric tetrahedral system there are three equivalent and indistinguishable S_4 axes.
- Consequently, each axes gives rises to two S_4 operations resulting in a class designated as $6S_4$ ($3S_4 + 3S_4^3$)



Non-Genuine S_n *Operations:*

- $S_1 = \sigma$
- $S_2 = i$



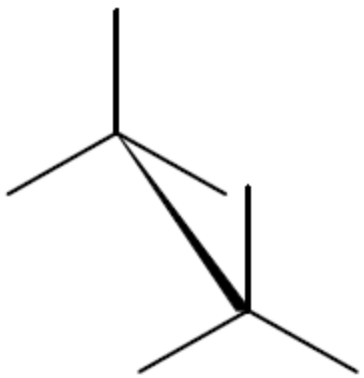


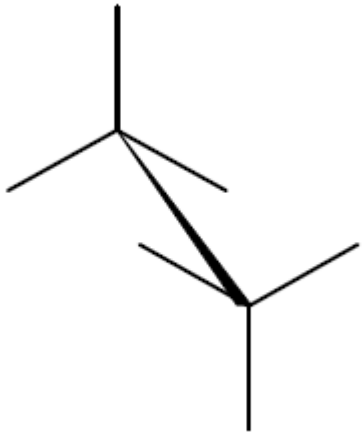
General Relations of S_n

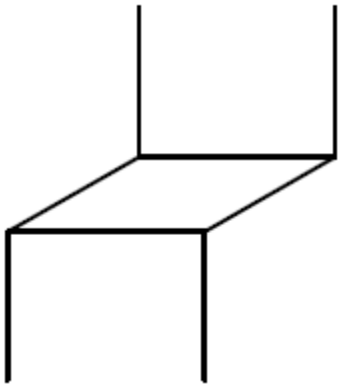
- Equivalences of successive S_n operations:
  - If n is even, $S_n^n = E$
  - If n is odd, $S_n^n = \sigma$ and $S_n^{2n} = E$
  - If m is even, $S_n^m = C_{nm}$ when $m < n$ and $S_n^m = C_n^{m-n}$ when $m > n$
  - If S_n with even n exists, then $C_{n/2}$ exists
  - If S_n with odd n exists, then both C_n and σ perpendicular to C_n exist.

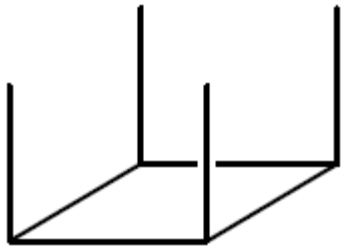
Examples

- Find all symmetry elements and operations in the following:









Examples

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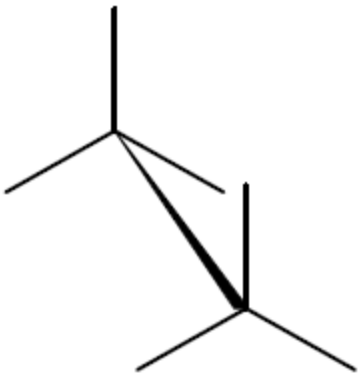
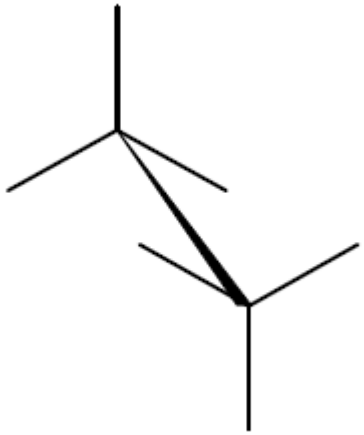
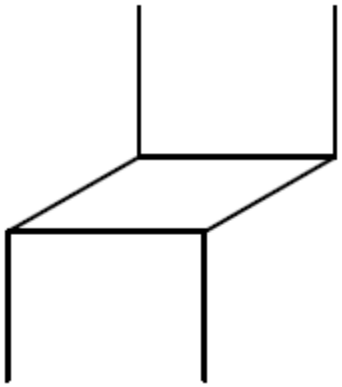


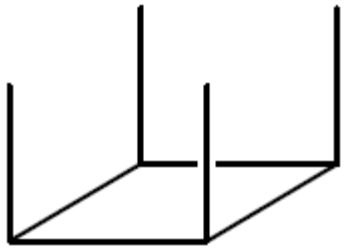
E, $2C_3$, $3\sigma_v$



E, i , $2C_3$, C_2 , $3\sigma_d$, σ_h , $2S_4$



E, i , C_2 , σ_h

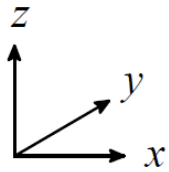


E, $2C_4$, C_2 , $2\sigma_v$, $2\sigma_d$

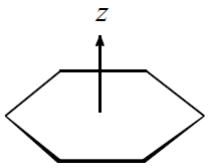
Defining the Coordinate System

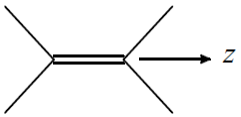
- Molecules are conventionally oriented relative to a right-hand Cartesian coordinate system:
- The following conventions of axis orientation are usually observed:

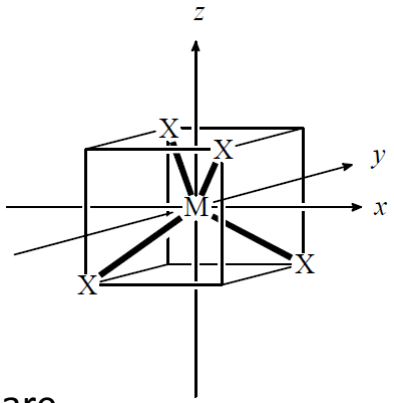
1. The *origin* of the coordinate system is located at the central atom or the center of the molecule.



2. The *z* axis is collinear with the highest-order rotational axis (the principal axis). If there are several highest order rotational axes, *z* is usually taken as the axis passing through the greatest number of atoms.



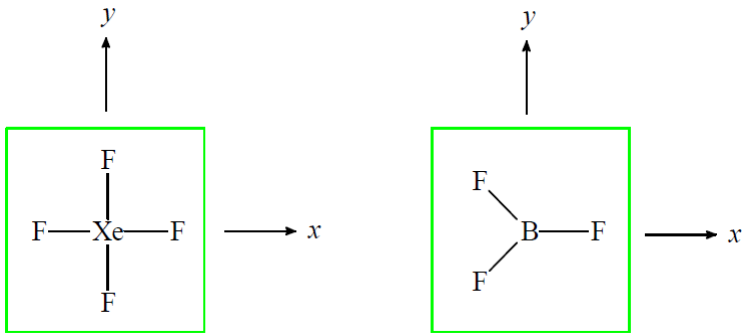




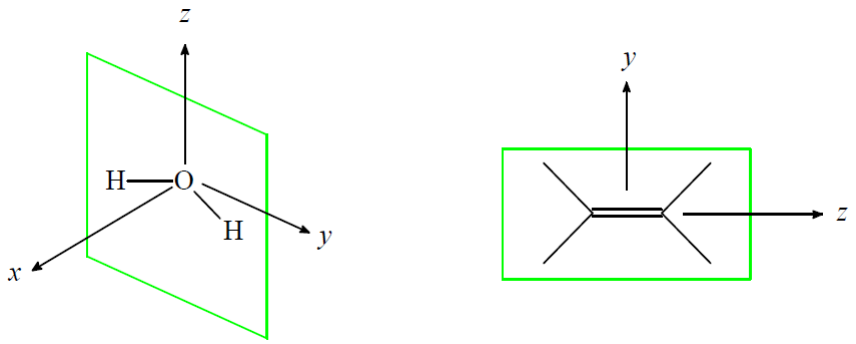
However, for a tetrahedral molecule, the *x*, *y*, and *z* axes are defined as collinear with the three C_2 axes (collinear with the three S_4 axes).

Defining the Coordinate System *(contd.)*

3. For planar molecules, if the *z* axis as defined above is perpendicular to the molecular plane, the *x* axis lies in the plane of the molecule and passes through the greatest number of atoms.

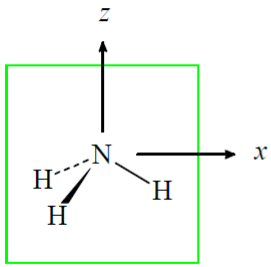


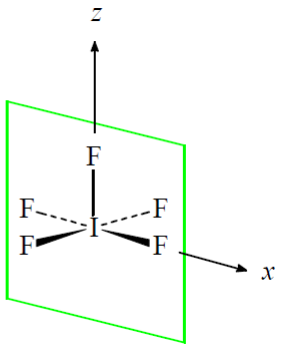
If the z axis lies in the plane of the molecule, then the *x* axis stands perpendicular to the plane.



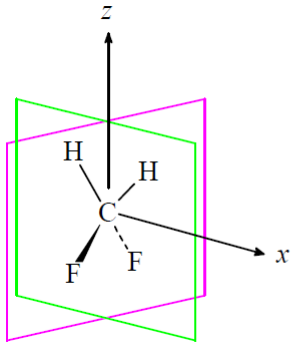
Defining the Coordinate System *(contd.)*

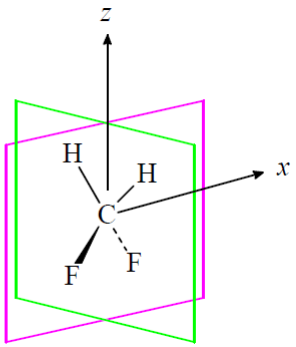
4. For non-planar molecules, once the *z* axis has been defined, the *x* axis is usually chosen so that the *xz* plane contains as many atoms as possible. If there are two or more such planes containing identical sets of atoms, any one may be taken as the *xz* plane.





Where a decision about the orientation of the *x* axis cannot be made on this basis, the distinction between *x* and *y* is usually not important or is not generally fixed by convention.





Combining Symmetry Operations (Multiplication)

- Multiplication of symmetry operations is the successive performance of two or more operations to achieve an orientation that could be reached by a single operation

  e.g., $i^2 = E$; $S_4 S_4 = S_4^2 = C_2$; $C_4 \sigma_h = S_4$ etc.

- The order in which successive different symmetry operations are performed can affect the result.

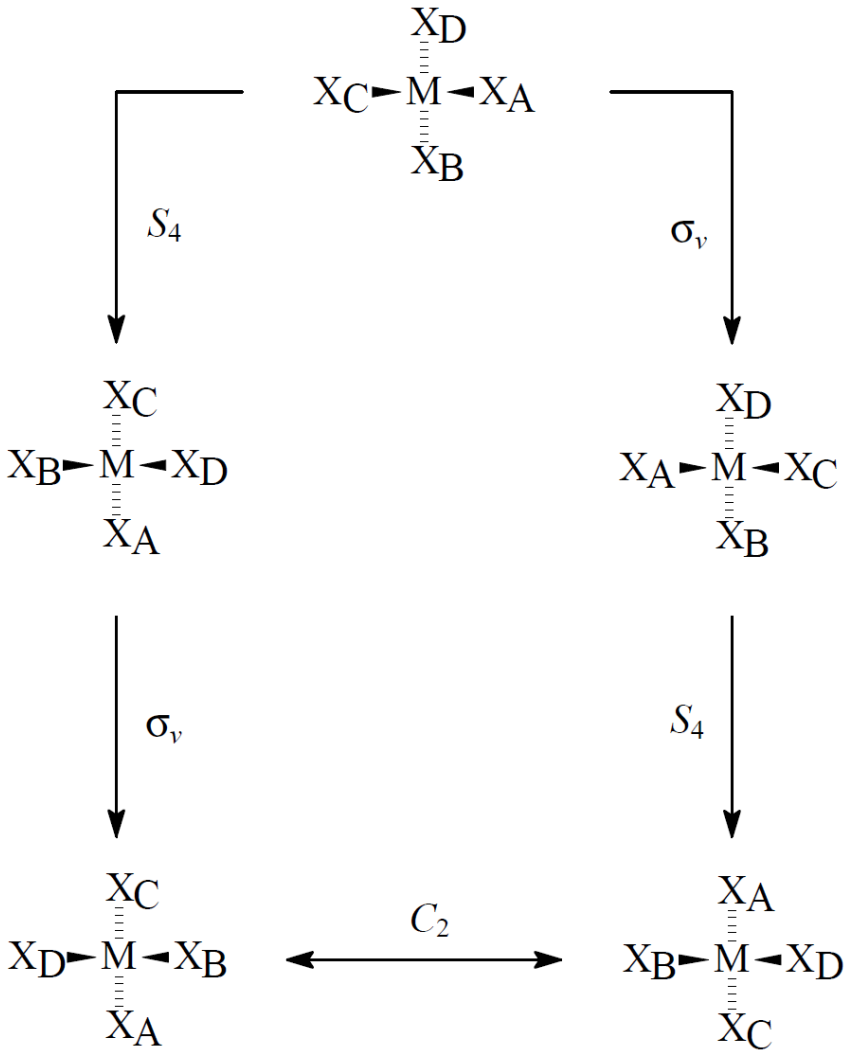
- ***Multiplication of symmetry operations is not commutative*** in general, although certain combinations may be.

- In writing multiplications of symmetry operation we use a "right-to-left" notation:

  - $BA = X$ "Doing A then B has the same result as the operation X."
  - We cannot assume that reversing the order will have the same result.
  - It may be that either $BA \neq AB$ or $BA = AB$.

- ***Multiplication of symmetry operations is associative:***

$$C(BA) = (CB)A$$

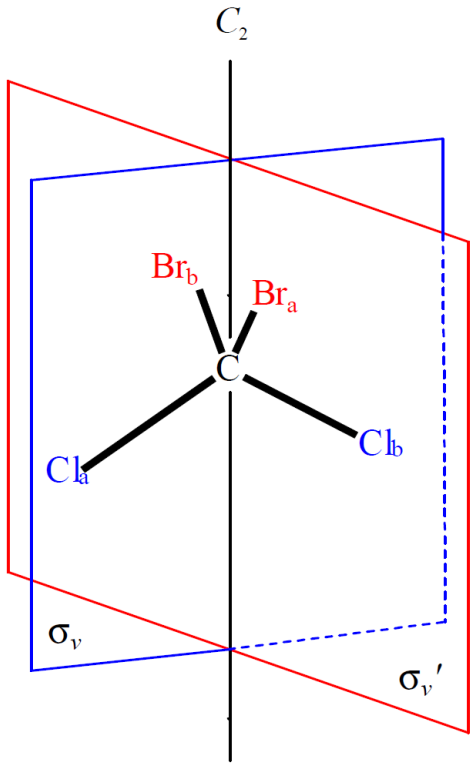


The order of performing S_4 and σ_v, shown here for a tetrahedral MX_4 molecule, affects the result. The final positions in each case are not the same, but they are related to each other by C_2.

$S_4 \sigma_v \neq \sigma_v S_4$ *but* $C_2 \sigma_v S_4 = S_4 \sigma_v$

- We will now consider the complete set of symmetry operations for a particular molecule and determine all the binary combinations of the symmetry operations it possesses.
- The symmetry elements of the CBr_2Cl_2 molecule are shown below. This molecule has a tetrahedral geometry

  Note: tetrahedral geometry does not automatically imply tetrahedral symmetry !



- The complete set of symmetry operations are *E*, C_2 , σ_v , σ_v‘

Point Groups of Molecules

- Chemists in general and spectroscopists in particular use the *Schönflies* notation.
- In contrast , crystallographers prefer to use the *Hermann-Mauguin* notation, which is best suited for designating the 32 crystallographic point groups and the space groups used to describe crystal structures.
- Familiar *Schönflies* labels and their corresponding *Hermann-Mauguin* notation are

Schönflies	Hermann-Mauguin
C_1	1
C_s	m
C_2	2
C_{2v}	mm
D_2	222
D_{3h}	$(3/m)mm$

- All of the chemically important point groups fall within one of four general categories:

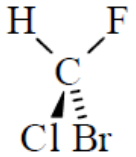
1. *Non-rotational*
2. *Single-axis rotational*
3. *Dihedral*
4. *Cubic*

Non-Rotational Point Groups

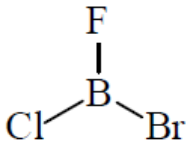
- With their low orders (h = 1,2) and lack of an axis of symmetry, the non-rotational point groups represent the lowest symmetry point groups.

Nonrotational Groups	
Symbol	Operations
C_1	E (asymmetric)
C_s	E, σ_h
C_i	E, i

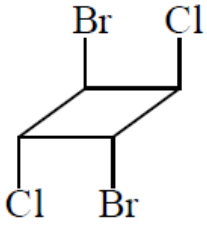
- C_1 is the point group of asymmetric molecules which only possess the identity element *E.*
- The C_s point group describes the symmetry of bilateral objects that lack any symmetry other than *E* and σ_h .
- The C_i point group is not commonly encountered as most molecules which posses the *i* element also possess other complimentary symmetry elements.



C_1



C_s



C_i

Single-Axis Rotational Point Groups

- The simplest family of this group are the C_n point groups, which consist of operations generated by an n-fold rotation C_n applied successively n times.
- These point groups are an example of the important *cyclic groups.*

Single-axis Groups		
Symbol	Operations	(n = 2, 3, ..., ∞)
C_n	$E, C_n, \ldots, C_n^{n-1}$	
C_{nv}	$E, C_n, \ldots, C_n^{n-1}, n\sigma_v$ (n/2 σ_v and n/2 σ_d if n even)	
C_{nh}	$E, C_n, \ldots, C_n^{n-1}, \sigma_h$	
S_{2n}	$E, S_{2n}, \ldots, S_{2n}^{2n-1}$	
$C_{\infty v}$	$E, C_\infty, \infty\sigma_v$	(noncentrosymmetric linear)

- A cyclic group of order h is generated by taking a single element X through all its powers up to $X_h = E$.

$$G = \{ X, X^2, \ldots, X^h = E \}$$

- All cyclic groups are Abelian, since all of their multiplications commute.
- The C_n and S_{2n} groups are cyclic groups; e.g.,

$$C_4 = \{ C_4, C_4^2, C_4^3, E \}$$

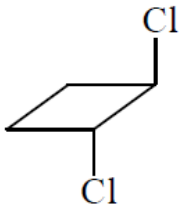
$$S_4 = \{ S_4, C_2, S_4^3, E \}$$

- The multiplication tables of cyclic groups "scroll" from row to row and column to column: e.g.,

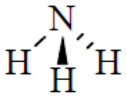
C_4	E	C_4	C_2	C_4^3
E	E	C_4	C_2	C_4^3
C_4	C_4	C_2	C_4^3	E
C_2	C_2	C_4^3	E	C_4
C_4^3	C_4^3	E	C_4	C_2

- To the rotations of the corresponding C_n groups the family of C_{nv} groups adds n vertical mirror planes, which intersect at the C_n axis.
- The point group $C_{\infty v}$, which has a infinite-fold C_∞ rotational axis, is an important member of this family. It is the point group of all non-centrosymmetric linear molecules.

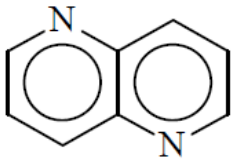
  e.g., H-Cl, C≡O.
- To generate any of the C_{nh} groups, we need only add a horizontal mirror plane to the series of C_n rotations of the appropriate cyclic C_n group.
- Since $C_n\sigma_h = S_n$ and $C_2\sigma_h = S_2 = i$, these groups also have n-fold improper axes when $n > 2$, and they are centrosymmetric when n is even.
- The S_{2n} series are not common.



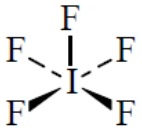
C_2



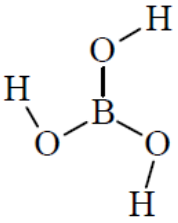
C_{3v}



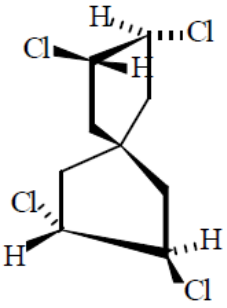
C_{2h}



C_{4v}



C_{3h}



S_4

Dihedral Point Groups

- The dihedral groups have *n* twofold axes perpendicular to the principal *n*-fold axis. These C_2 axes are called the *dihedral axes.*
- The number and arrangement of the dihedral axes are dictated by the *n*-fold order of the principal axis.

  e.g. the staggered conformation of ethane is of D_{3d} symmetry and possesses $3C_2$ dihedral axes.

Dihedral Groups		
Symbol	Operations	($n = 2, 3, \ldots, \infty$)
D_n	$E, C_n, \ldots, C_n^{n-1}, nC_2(\perp C_n)$	
D_{nd}	$E, C_n, \ldots, C_n^{n-1}, S_{2n}, \ldots, S_{2n}^{2n-1}, nC_2(\perp C_n), n\sigma_d$	
D_{nh}	$E, C_n, \ldots, C_n^{n-1}, nC_2(\perp C_n), \sigma_h, n\sigma_v$	
$D_{\infty h}$	$E, C_\infty, S_\infty, \infty C_2(\perp C_\infty), \infty\sigma_v, i$	(centrosymmetric linear)

- There are three families of dihedral groups: D_n , D_{nd} , D_{nh}

1) The D_n groups may be thought of as C_n groups to which n dihedral C_2 operations have been added.

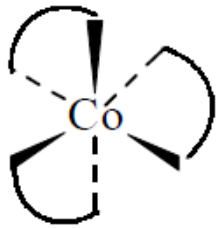
   Unlike the C_n groups, the D_n groups are not cyclic.

2) Similarly, the D_{nd} groups may be thought of as C_{nv} groups to which n dihedral C_2 operations have been added.

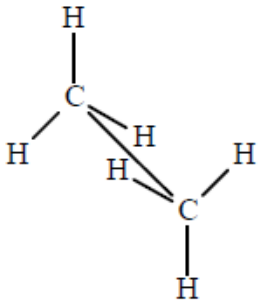
   In D_{nd} groups, the combination of rotational operations and vertical mirror reflections (σ_d) generates a series of S_{2n} operations about an axis collinear with the principal axis.

3) The D_{nh} groups may be thought of as C_{nh} groups to which n dihedral C_2 operations have been added.

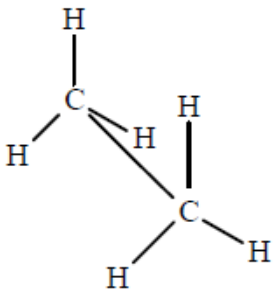
   Like the C_{nh} groups, the D_{nh} groups include n-fold improper axis when n>2 and are centrosymmetric.



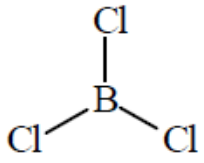
D_3



D_{3d}



D_{3h}

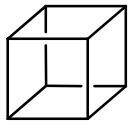


D_{3h}

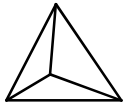
Cubic Point Groups

- The cubic groups are associated with polyhedra that are geometrically related to the cube.
- All are characterized by the presence of multiple, intersecting, high-order rotational axes.
- There are seven groups of this type, three of which are frequently encountered and highly relevant in chemistry

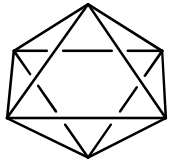
Cubic Groups	
Symbol	Operations
T_d	E, $4C_3$, $4C_3^2$, $3C_2$, $3S_4$, $3S_4^3$, $6\sigma_d$ (tetrahedron)
O_h	E, $4C_3$, $4C_3^2$, $6C_2$, $3C_4$, $3C_4^3$, $3C_2(=C_4^2)$, i, $3S_4$, $3S_4^3$, $4S_6$, $4S_6^5$, $3\sigma_h$, $6\sigma_d$ (octahedron)
I_h	E, $6C_5$, $6C_5^2$, $6C_5^3$, $6C_5^4$, $10C_3$, $10C_3^2$, $15C_2$, i, $6S_{10}$, $6S_{10}^3$, $6S_{10}^7$, $6S_{10}^9$, $10S_6$, $10S_6^5$, 15σ (icosahedron, dodecahedron)



Cube (O_h)



Tetrahedron (T_d)



Octahedron (O_h)

Icosahedron (I_h)

- The perfect tetrahedron defines the T_d group, comprised of the following 24 operations, listed by classes:

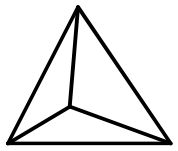
  $$E\ ,\ 8C_3\ (= 4C_3\ ,\ 4C_3^2\ ),\ 3C_2\ ,\ 6S_4\ (= 3S_4\ ,\ 3S_4^3\ ),\ 6\sigma_d$$

  with $h = 24$, T_d represents one of the higher symmetries encountered in chemistry.

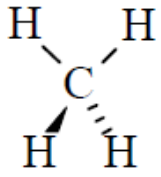
- A three-fold axis, generating the operations C_3 and C_3^2 , emerges from each of the four triangular faces of a tetrahedron.

- When a tetrahedron is inscribed inside a cube a C_2 axis collinear with the bisector of opposing bond angles emerges from each pair of apposite cube faces.

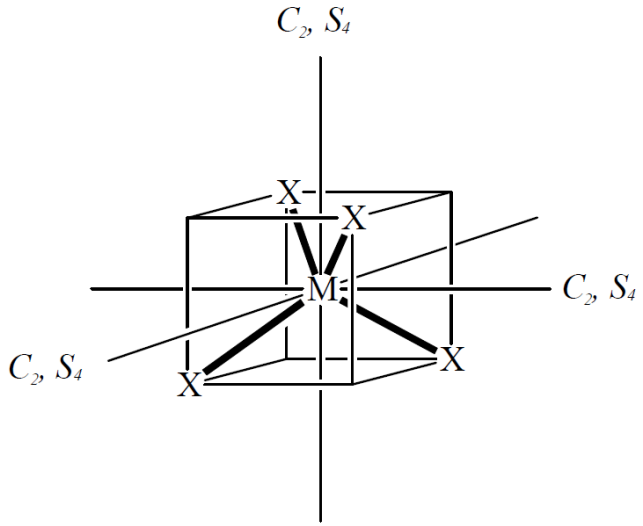
- Three S_4 axes, each associated with S_4 and S_4^3 operations, are each collinear with these C_2 axes.



Tetrahedron (T_d)



T_d

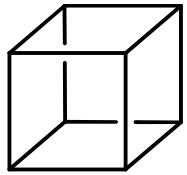


- The octahedron and cube both belong to the point group O_h , which is comprised of the following 48 operations (h = 48)

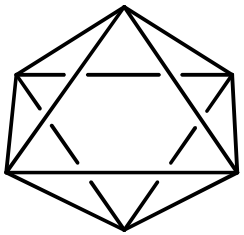
  E , $8C_3(= 4C_3 , 4C_3^2)$, $6C_4(= 3C_4 , 3C_4^3)$, $6C_2$, $3C_2(= 3C_4^2)$, i , $6S_4(= 3S_4 , 3S_4^3)$, $8S_6(= 4S_6 , 4S_6^5)$, $3\sigma_h(= \sigma_{xy} , \sigma_{yz} , \sigma_{xz})$, $6\sigma_d$

- In the octahedron a fourfold axis emerges from each pair of opposite apices, whereas a threefold axis emerges from each pair of opposite triangular faces.

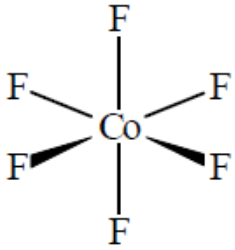
- In the cube, a fourfold axis emerges from each pair of opposite faces, whereas a threefold axis emerges from each pair of opposite corners, extending the diagonals of the cube.



Cube (O_h)



Octahedron (O_h)



O_h

- Both the regular icosahedron and dodecahedron belong to the point group I_h , composed of 120 symmetry operations

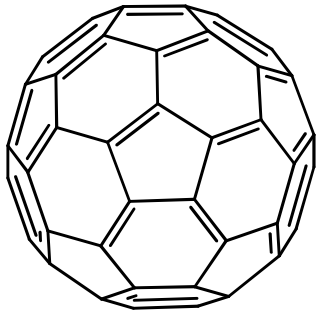
  E , $8C_3(= 4C_3 , 4C_3^2)$, $6C_4(= 3C_4 , 3C_4^3)$, $6C_2$, $3C_2(= 3C_4^2)$, i , $6S_4(= 3S_4 , 3S_4^3)$, $8S_6(= 4S_6 , 4S_6^5)$, $3\sigma_h(= \sigma_{xy} , \sigma_{yz} , \sigma_{xz})$, $6\sigma_d$

- Aside from the $C_{\infty v}$ and $D_{\infty h}$ point groups which have an order of $h = \infty$, I_h represents the highest symmetry one is likely to encounter in structural chemistry.

- Buckminsterfullerene C_{60} is an example of a high-order polyhedron with I_h symmetry.

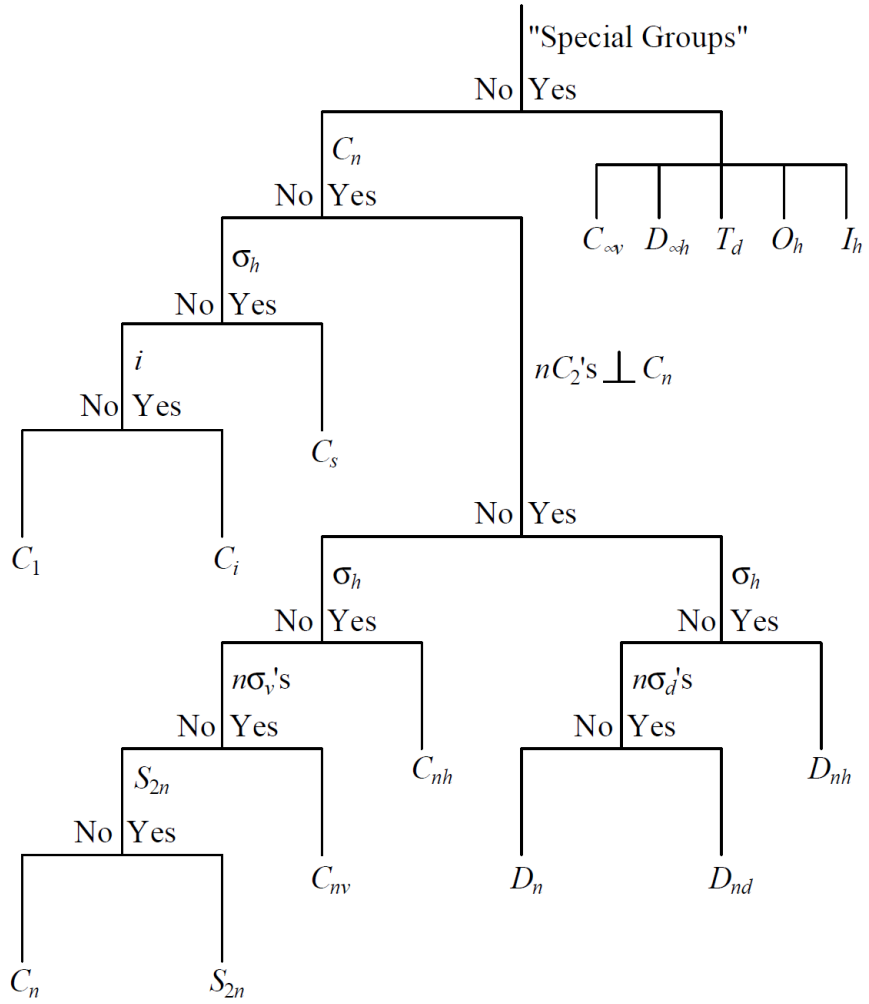
- A fivefold axis emerges from the face of each five-membered ring and a threefold axis emerges from the face of each six-membered ring.

Icosahedron (I_h)

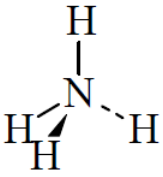


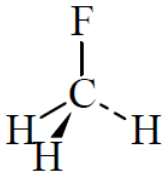
I_h

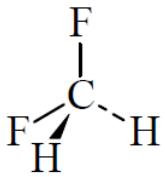
- In determining the point group of a structure we often ignore some of its symmetry elements which make up its group.
- The classification process only concentrates on finding the characteristic elements that uniquely define a group.

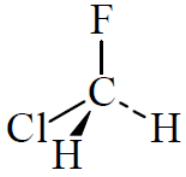


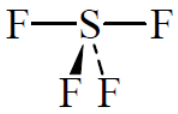
Flow chart for systematically determining the point group of a molecule.

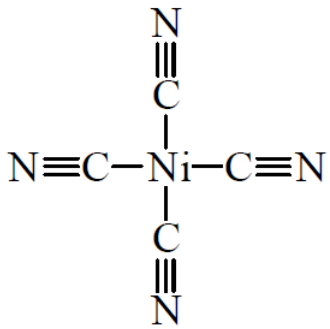


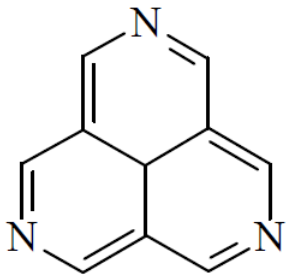


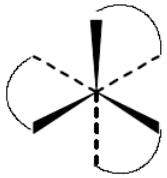


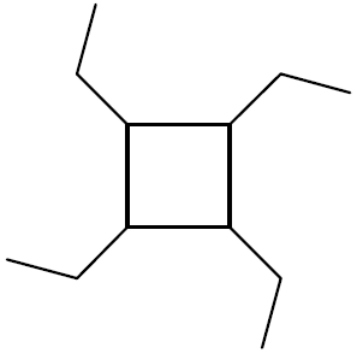




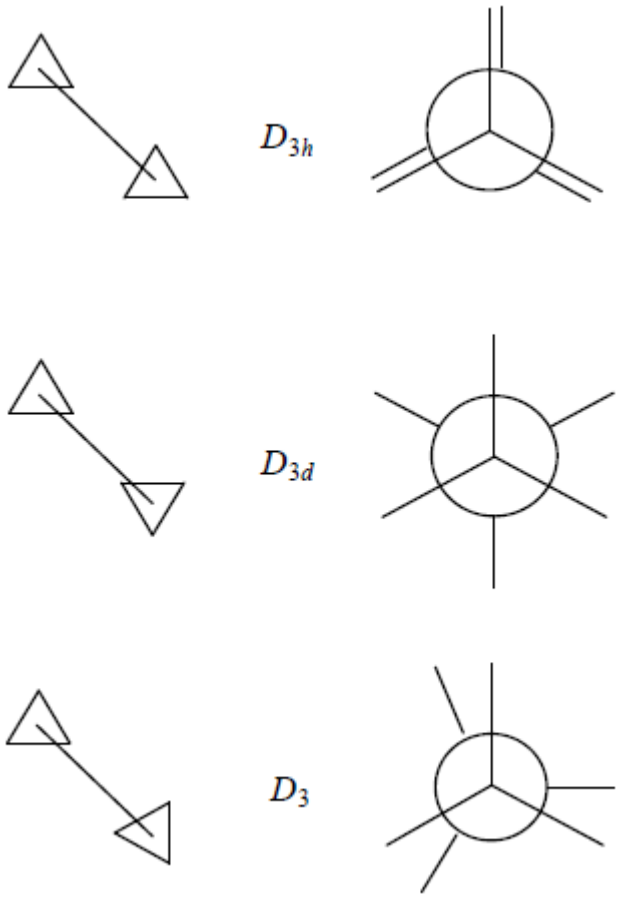








Examples for point group classification.

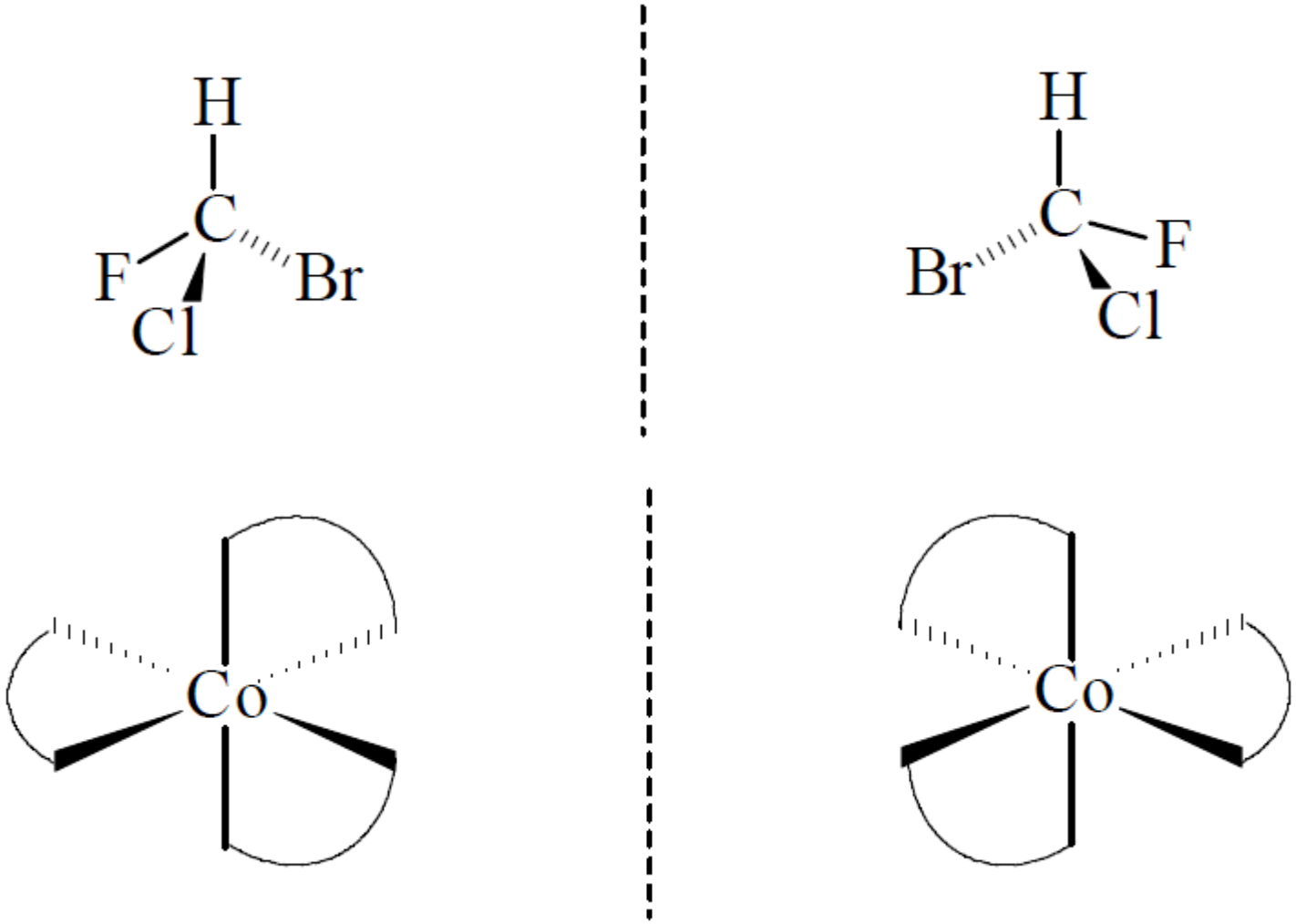


- Representations of the three conformations of ethane as two triangles separated along the C_3 axis. The corresponding Newman projections are shown on the right.

Optical Activity and Symmetry

- Chiral molecules can exist as enantiomers, which will rotate plane-polarized light in opposite directions.
- Chiral molecules are ***dissymmetric***, but not necessarily asymmetric (point group C_2).
- Asymmetric molecules are just the least symmetric among all dissymetric molecules.
- ***A molecule is dissymmetric and may be chiral either if it is asymmetric or if it has no other symmetry than proper rotation.***
- ***Dissymetric molecules can have proper rotations (C_n), but they cannot have any other symmetry.***
- Thus, chiral molecules belong to one of the following point groups:

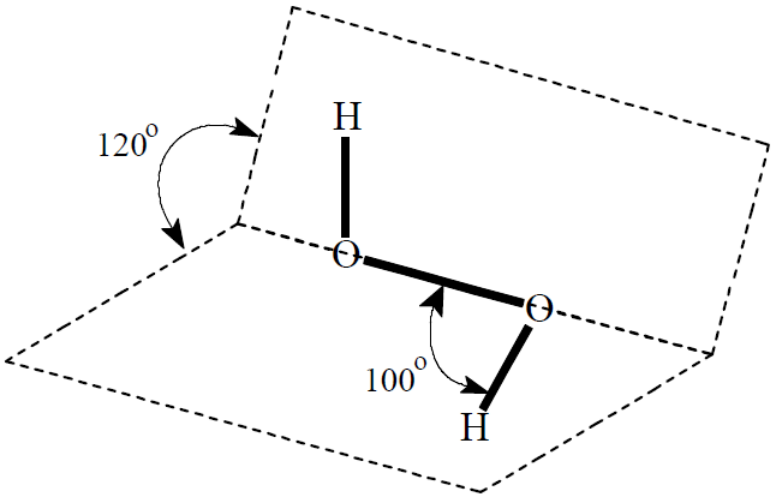
$$C_1 , C_n , D_n \ (T, O, I)$$



- Enantiomers of dissymetric species. CHFClBr (point group C_1) is asymmetric, but $[Co(en)_3]^{3+}$ (point group D_3) is not

Non-Chiral Dissymetric Molecules

- Sometimes, theoretically possible enantiomeric pairs do not exist, due to stereochemical non-rigidity.



- The structure of hydrogen peroxide (point group C_2)