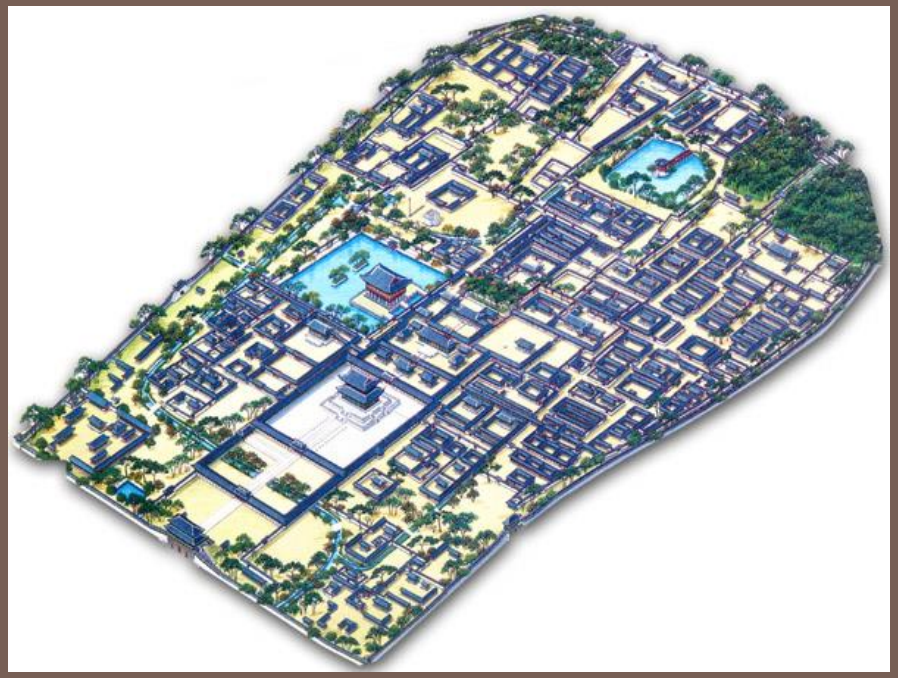
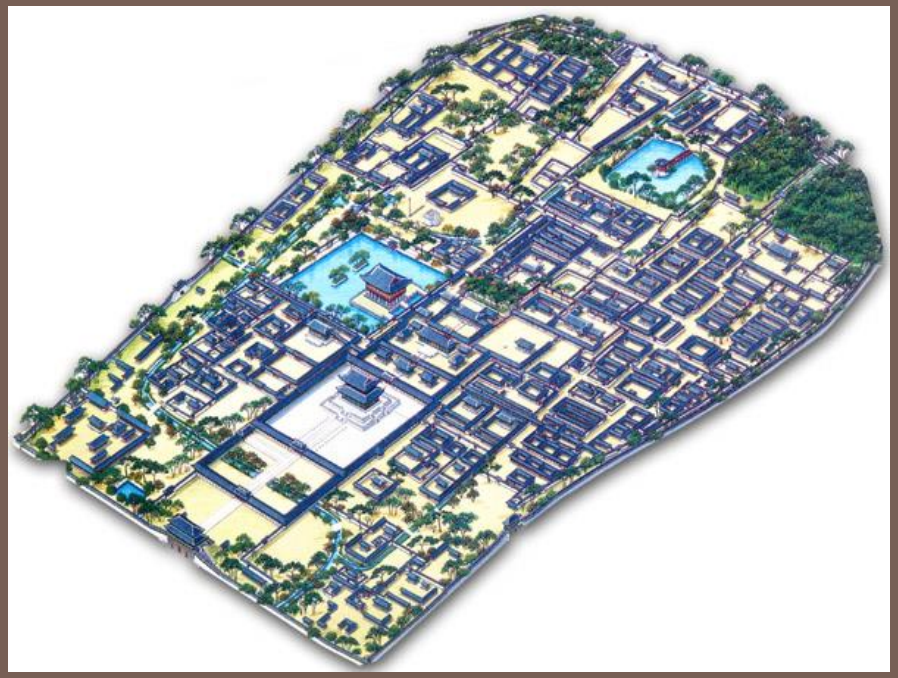
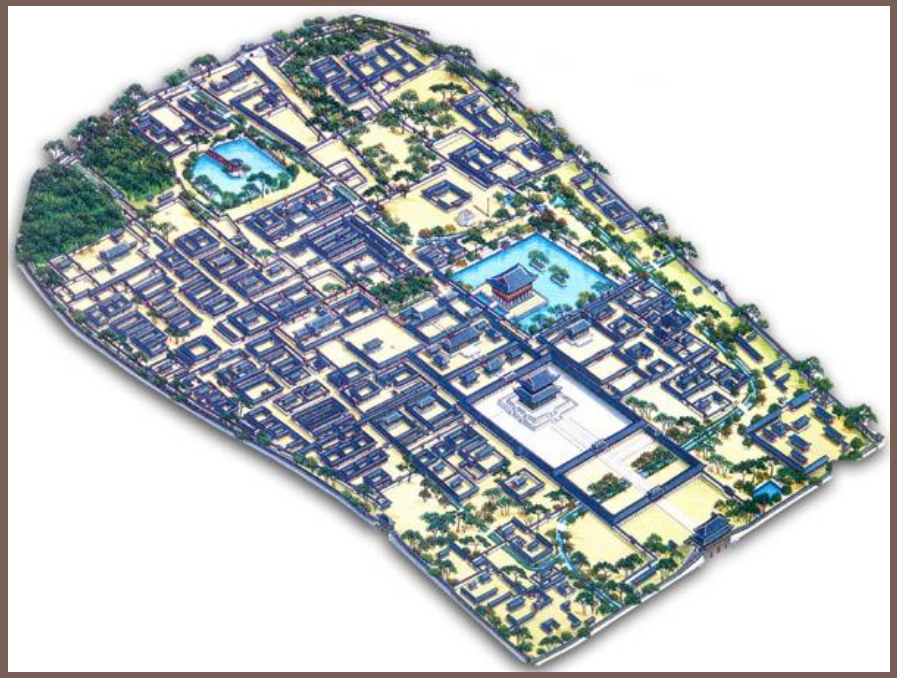
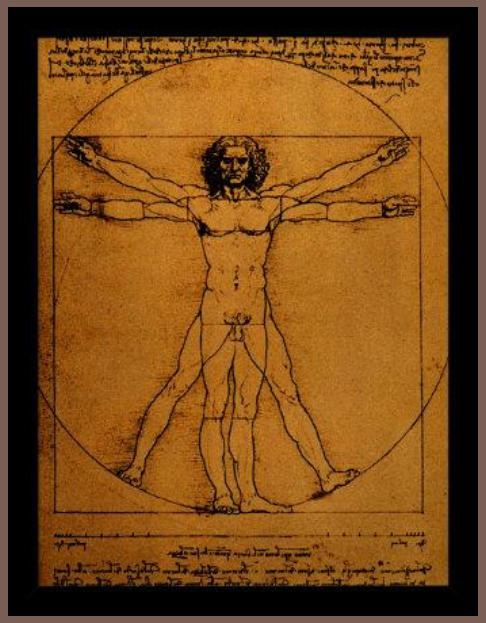


Symmetry and Group Theory

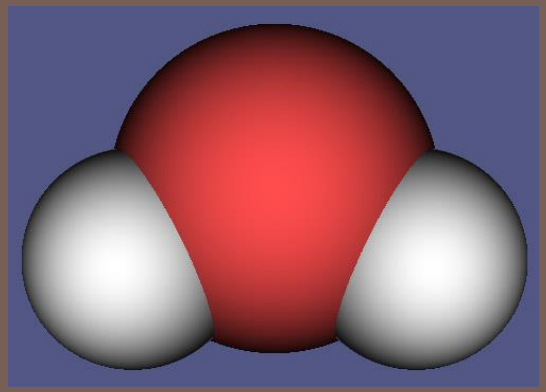


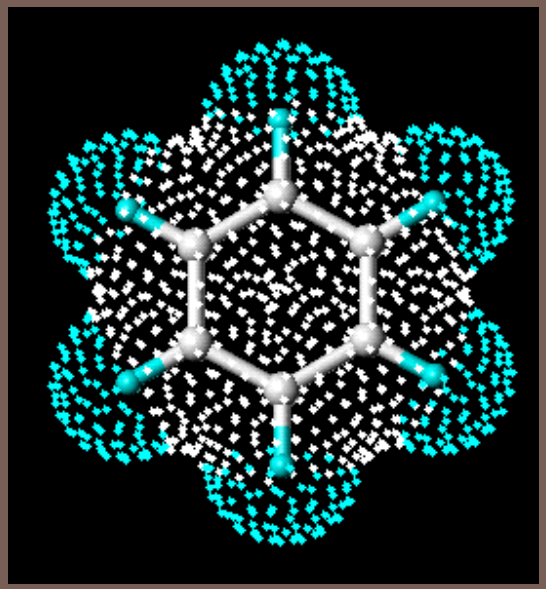


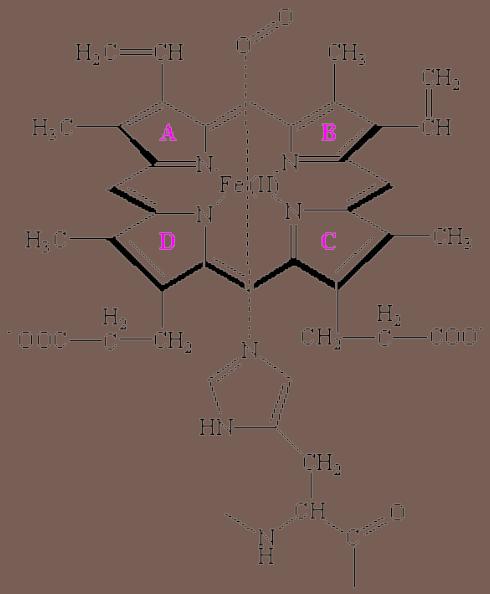
Symmetry and Group Theory

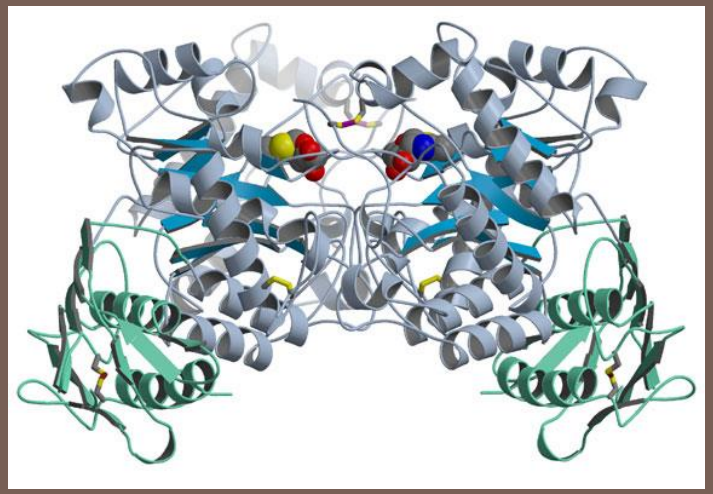


Symmetry and Group Theory





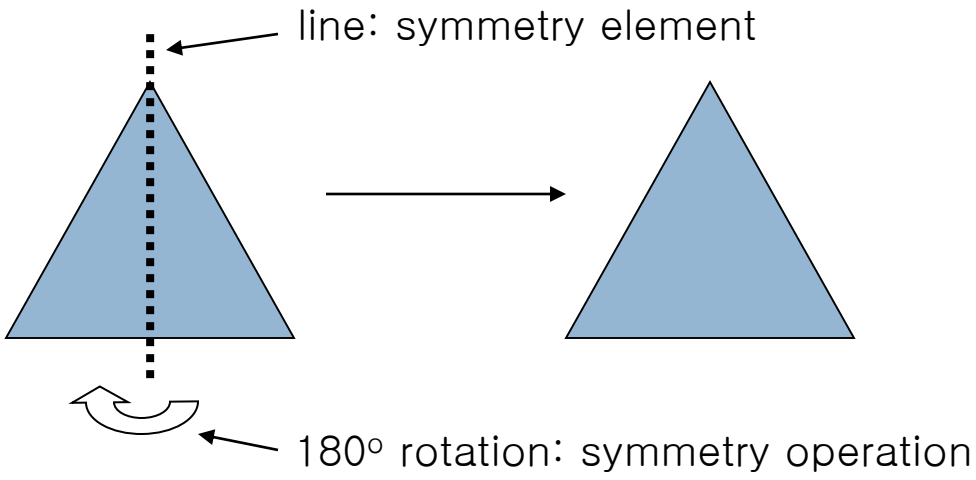




Symmetry and Group Theory

Symmetry Operation and Symmetry Elements

- **Symmetry Operation:** A well-defined, non-translational movement of an object that produces a new orientation that is **indistinguishable** from the original object.
- **Symmetry Element:** A point, line or plane about which the symmetry operation is performed.



Four kinds of Symmetry Elements and Symmetry Operations Required in Specifying Molecular Symmetry

- Proper (rotation) axis (C_n)
- Mirror plane (σ)
- Center of symmetry or center of inversion (*i*)
- Improper (rotation) axis (S_n)

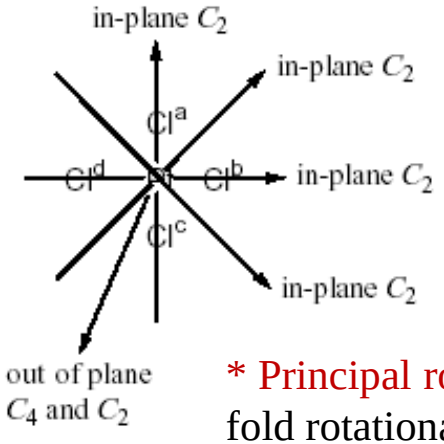
Four kinds of Symmetry Elements and Symmetry Operations Required in Specifying Molecular Symmetry (1)

- **Proper (rotation) axis (C_n):**

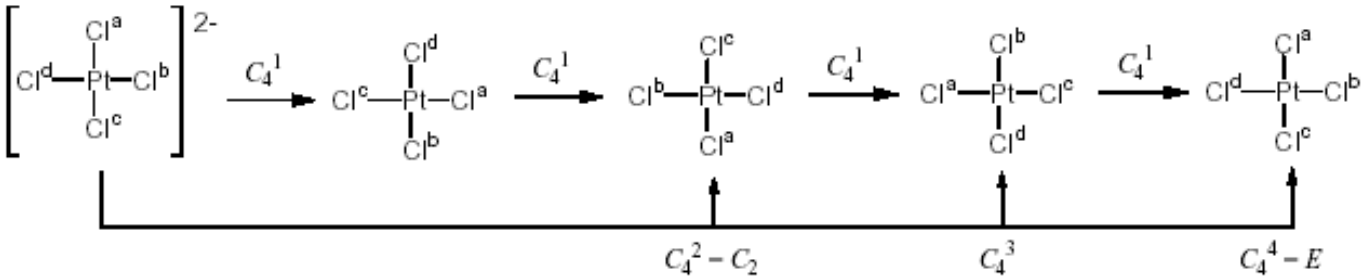
  Rotation about C_n axis by $2\pi/n$

  n-fold symmetry axis.

  A C_n axis generates n operations.



* Principal rotational axis: highest-fold rotational axis. If more than one principal axes exist, any one can be the principal axis.



*1: E : Identity (x1) *2: Right-handed rotation

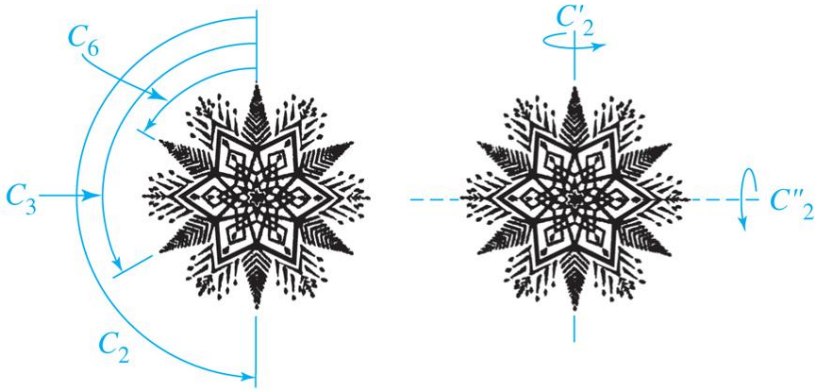
Four kinds of Symmetry Elements and Symmetry Operations Required in Specifying Molecular Symmetry (1)

- **Proper (rotation) axis (C_n):**

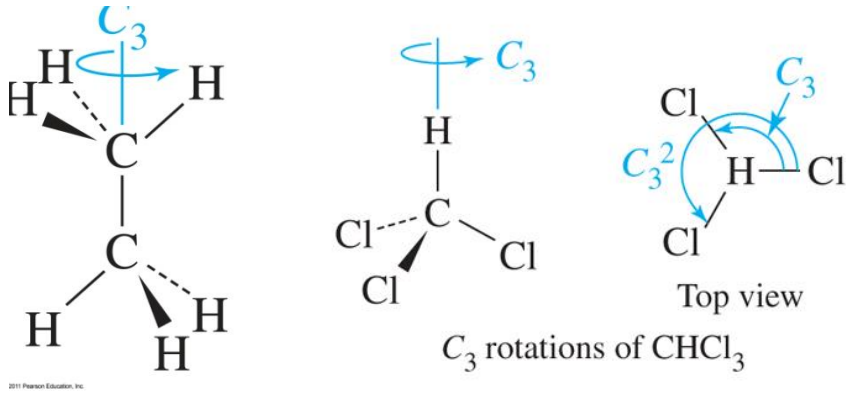
  Rotation about C_n axis by $2\pi/n$

  n-fold symmetry axis.

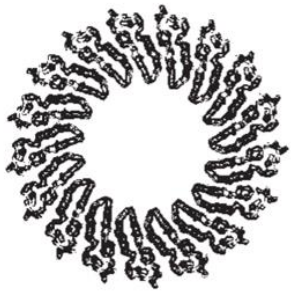
  A C_n axis generates n operations.



C_2, C_3 and C_6 rotations of a snowflake design



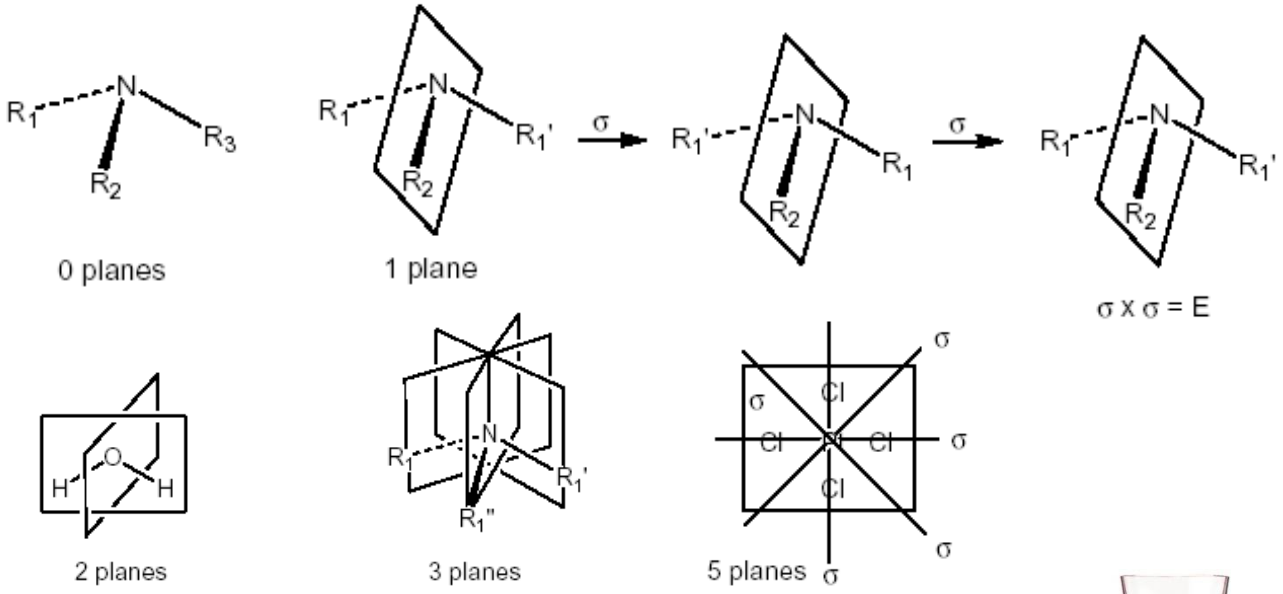
C_3 rotations of $CHCl_3$



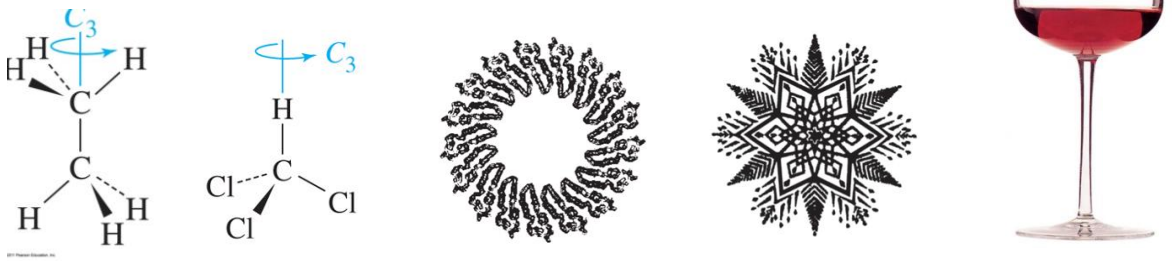
Cross section of protein disk of tobacco mosaic virus

Four kinds of Symmetry Elements and Symmetry Operations Required in Specifying Molecular Symmetry (2)

- **Mirror plane (σ):** Reflection about the σ plane

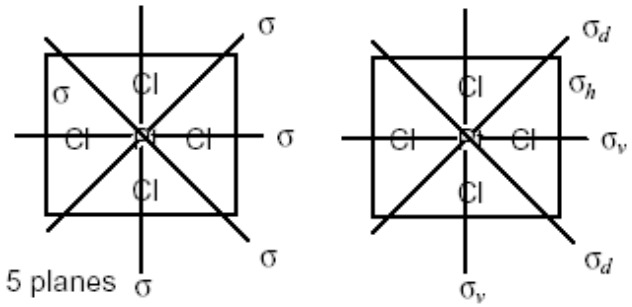


How many mirror planes ?



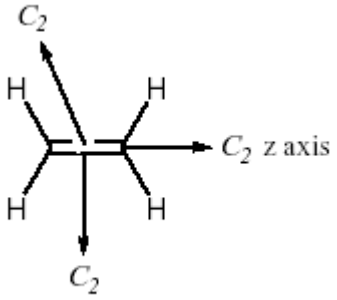
Four kinds of Symmetry Elements and Symmetry Operations Required in Specifying Molecular Symmetry (2)

- **Mirror plane (σ):** Reflection about the σ plane



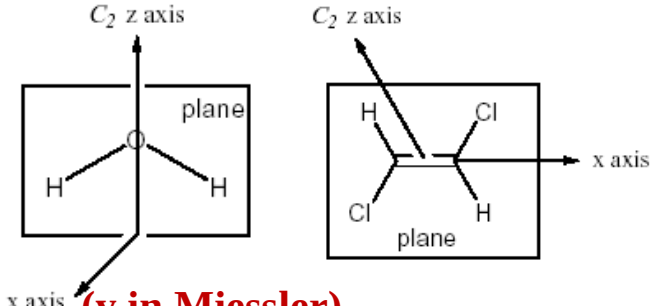
***σ_h :** mirror planes perpendicular to the principal axis.
σ_v :** mirror planes containing the principal axis ***Unless it is **σ_d**.
***σ_d :** mirror planes bisecting x, y, or z axis or bisecting C_2 axes perpendicular to the principal axis.

How to define molecular axes (x, y, z)?



1. The principal axis is the z axis.

2. If there are more than one possible principal axis, then the one that connects the most atoms is the z axis.



(y in Miessler)

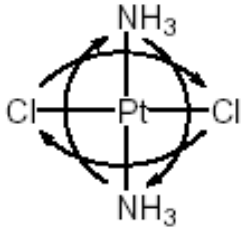
3. If the molecule is planar, then the z axis is the principal axis in that plane. The x axis is perpendicular to that plane.

4. If a molecule is planar and the z axis is perpendicular to that plane, then the x axis is the one that connects the most number of atoms. **(Actually, 3, 4 are arbitrary.)**

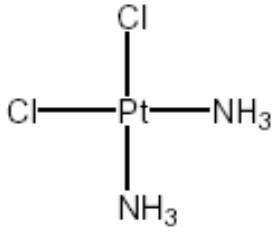
Four kinds of Symmetry Elements and Symmetry Operations Required in Specifying Molecular Symmetry (3)

- **Center of symmetry or center of inversion (*i*) :** Inversion of all objects through the center.

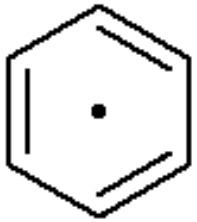
i is Pt atom.



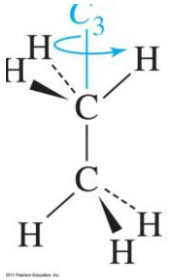
trans
inversion center



cis
no inversion

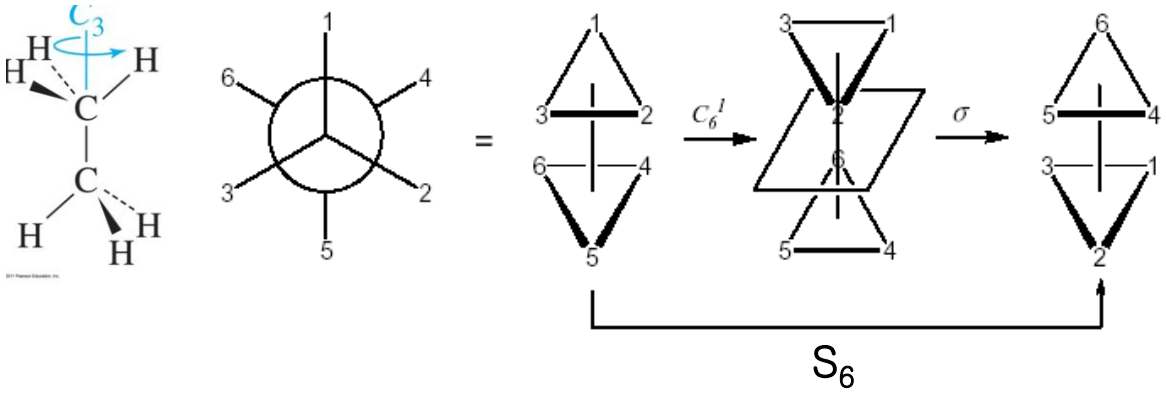


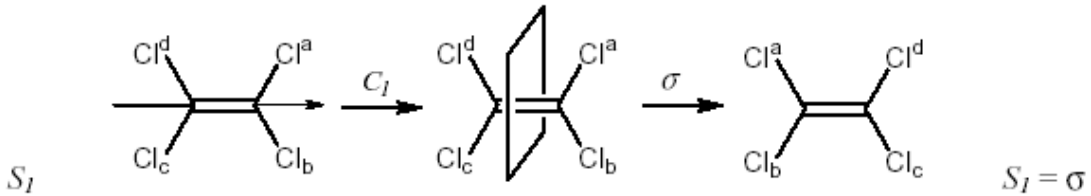
i is a point in space.

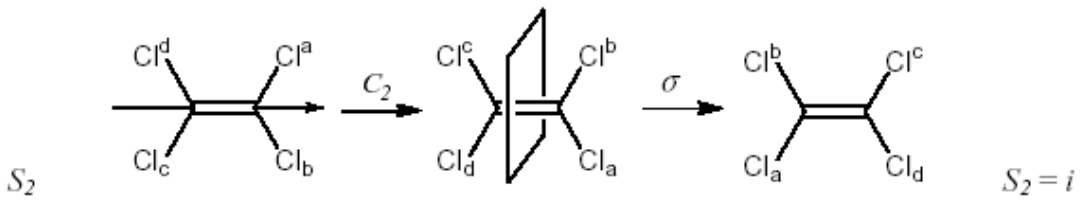


Four kinds of Symmetry Elements and Symmetry Operations Required in Specifying Molecular Symmetry (4)

- **Improper (rotation) axis (S_n) :** Rotation about an axis by $2\pi/n$ followed by a reflection through a plane perpendicular to that axis or *vice versa*.



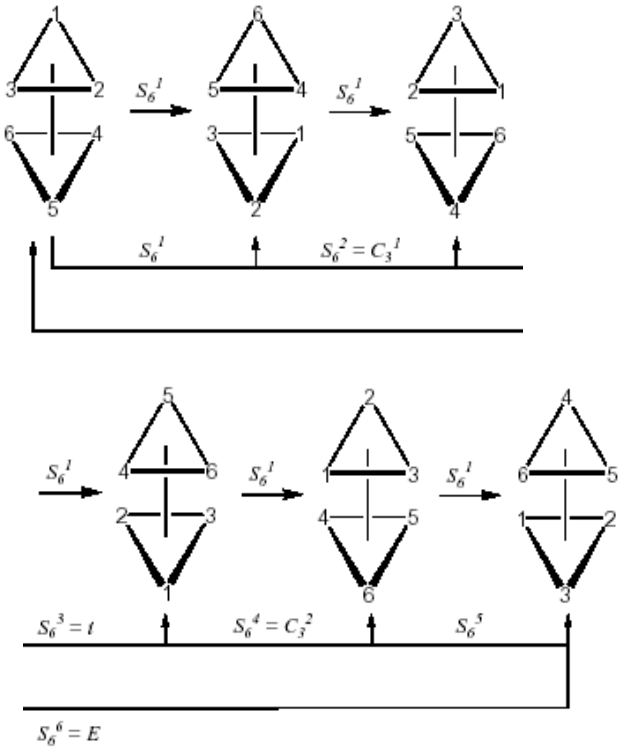




Four kinds of Symmetry Elements and Symmetry Operations Required in Specifying Molecular Symmetry (4)

- **Improper (rotation) axis (S_n) :** Rotation about an axis by $2\pi/n$ followed by a reflection through a plane perpendicular to that axis or *vice versa*.

  S_n generates n operations for even n and 2n operations for odd n.



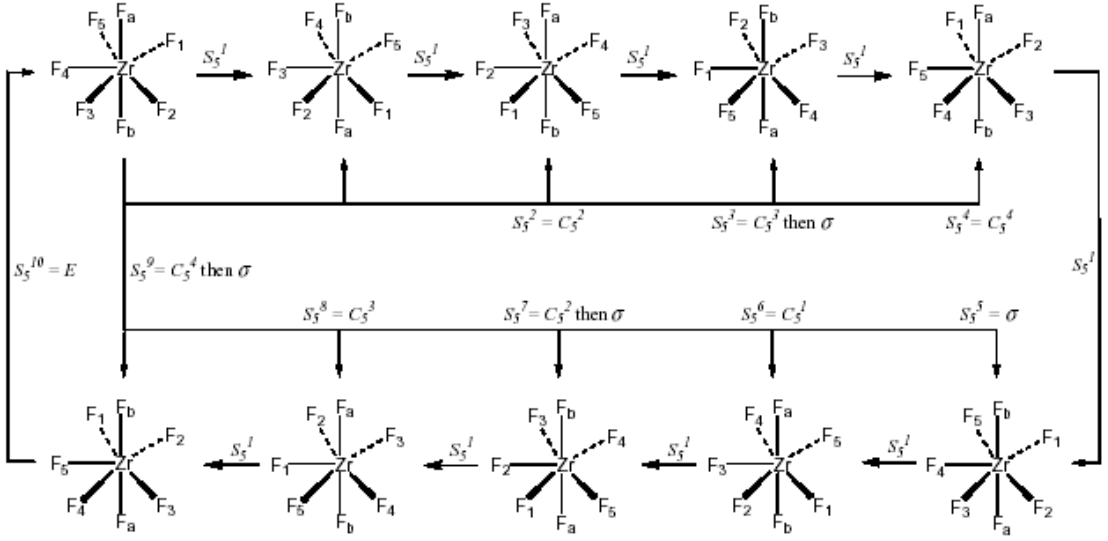
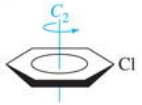
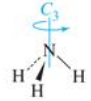
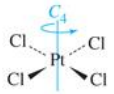
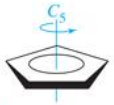
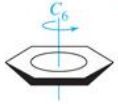
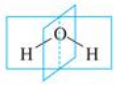
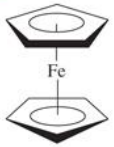
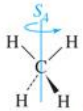
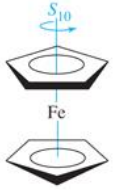
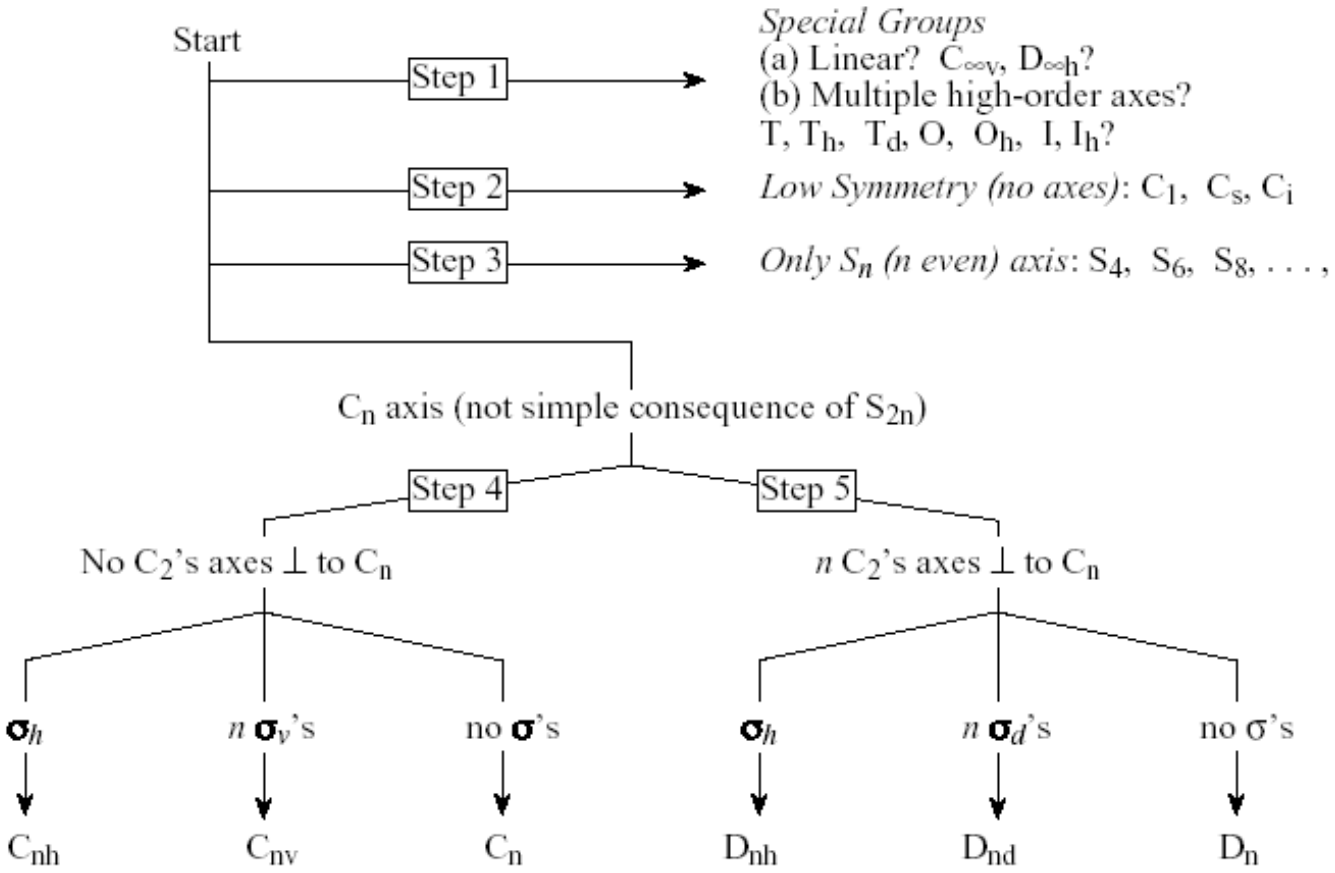


TABLE 4.1 Summary Table of Symmetry Elements and Operations

Symmetry Operation	Symmetry Element	Operation	Examples
Identity, E	None	All atoms unshifted	CHFClBr 
Rotation, C_2	Rotation axis	Rotation by $360°/n$	*p*-dichlorobenzene 
C_3			NH_3 
C_4			$[PtCl_4]^{2-}$ 
C_5			Cyclopentadienyl group 
C_6			Benzene 
Reflection, σ	Mirror plane	Reflection through a mirror plane	H_2O 
Inversion, i	Inversion center (point)	Inversion through the center	Ferrocene (staggered) 
Rotation-reflection, S_4	Rotation-reflection axis (improper axis)	Rotation by $360°/n$, followed by reflection in the plane perpendicular to the rotation axis	CH_4 
S_6			Ethane (staggered) 
S_{10}			Ferrocene (staggered) 

Point Groups



Point Groups

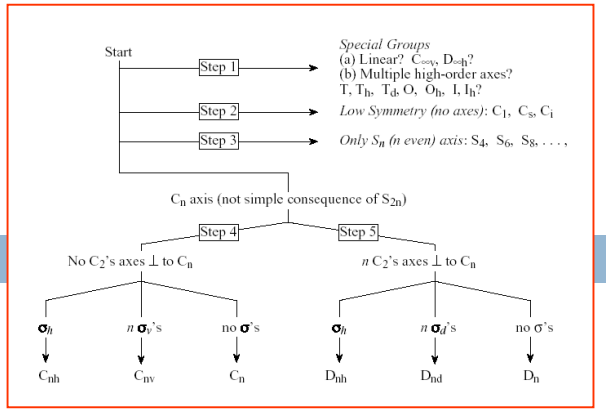
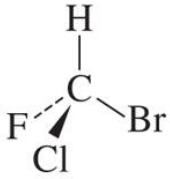
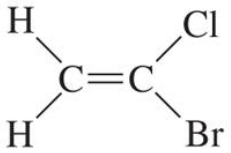
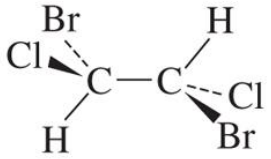
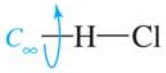
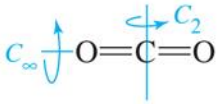
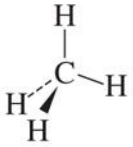
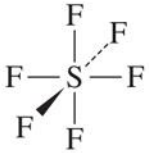
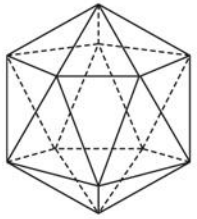


TABLE 4.2 Groups of Low Symmetry

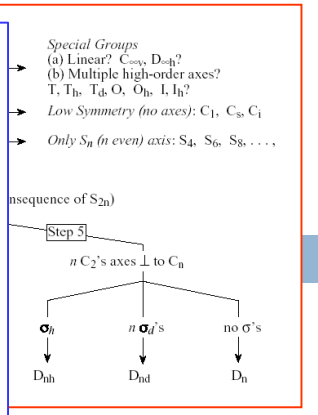
Group	Symmetry	Examples	
C_1	No symmetry other than the identity operation	CHFClBr	
C_s	Only one mirror plane	$H_2C{=}CClBr$	
C_i	Only an inversion center; few molecular examples	HClBrC—CHClBr (staggered conformation)	

Poi

TABLE 4.3 Groups of High Symmetry

Group	Description	Examples
$C_{\infty v}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.	
$D_{\infty h}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular C_2 axes, a perpendicular reflection plane, and an inversion center.	
T_d	Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d planes. They have no C_4 axes.	
O_h	These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four C_3 rotations, three C_4 rotations, and an inversion.	
I_h	Icosahedral structures are best recognized by their six C_5 axes, as well as many other symmetry operations—120 in all.	 $B_{12}H_{12}^{2-}$ with BH at each vertex of an icosahedron

In addition, there are four other groups, *T*, T_h, *O*, and *I*, which are rarely seen in nature. These groups are discussed at the end of this section.



Point Groups

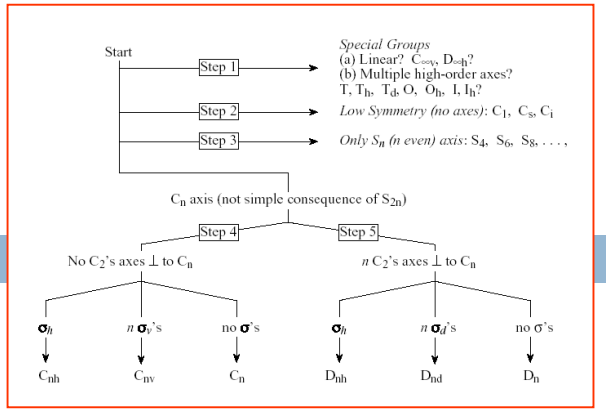
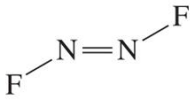
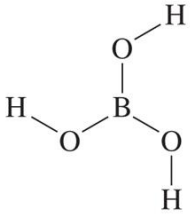
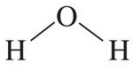


TABLE 4.4 Further Examples of *C* and *D* Point Groups

General Label	Point Group and Example		
C_{nh}	C_{2h}	difluorodiazene	
	C_{3h}	$B(OH)_3$, planar	
C_{nv}	C_{2v}	H_2O	

Point Groups

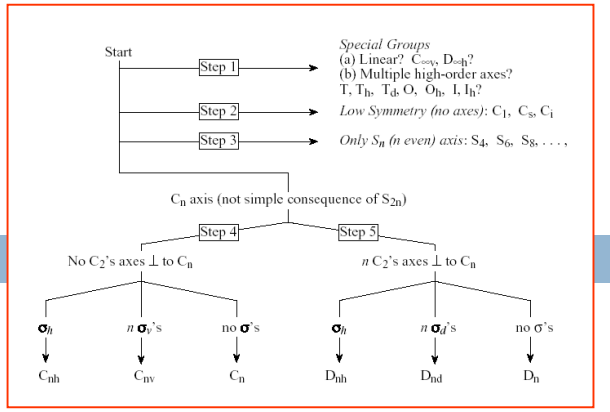
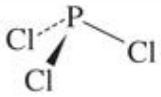
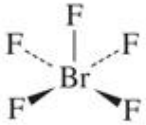
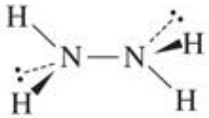
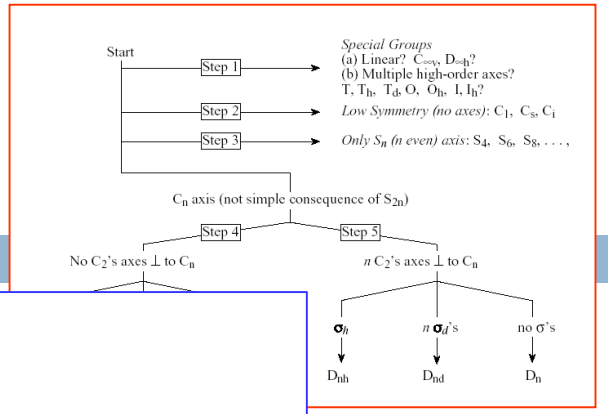
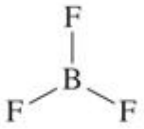
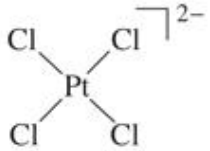
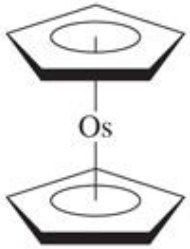
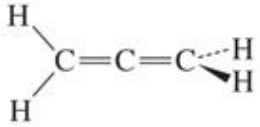


TABLE 4.4 Further Examples of *C* and *D* Point Groups—continued

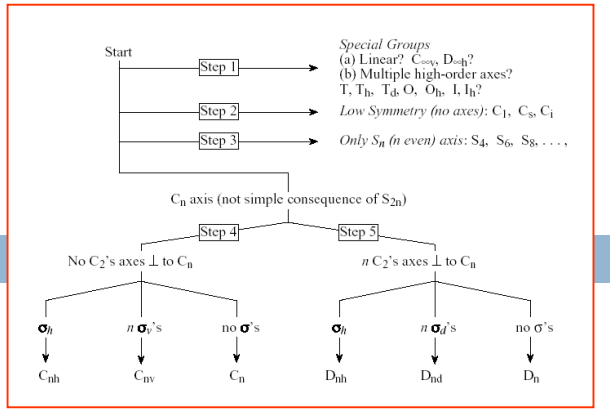
General Label	Point Group	Example	
	C_{3v}	PCl_3	
	C_{4v}	BrF_5 (square pyramid)	
	$C_{\infty v}$	HF, CO, HCN	
C_n	C_2	N_2H_4, which has a *gauche* conformation	
	C_3	$P(C_6H_5)_3$, which is like a three-bladed propeller distorted out of the planar shape by a lone pair on the P	

Point Groups

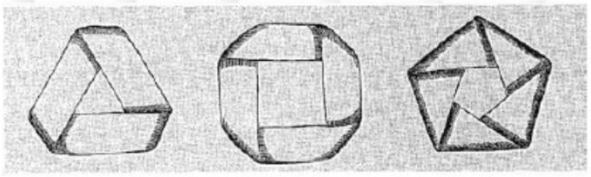


D_{nh}	D_{3h}	BF_3	
	D_{4h}	$PtCl_4^{2-}$	
	D_{5h}	$Os(C_5H_5)_2$ (eclipsed)	
	D_{6h}	benzene	
	$D_{\infty h}$	F_2, N_2	
		acetylene (C_2H_2)	
D_{nd}	D_{2d}	$H_2C=C=CH_2$, allene	

Point Groups



ihren zwei Grenzlinien hat. — Man kann aber auch, dafern das eine Paar paralleler Kanten AA' und BB' gegen das andere AB und $A'B'$ hinreichend gross ist, A' mit B, und B' mit A zur Coincidenz bringen, indem man zuvor, das eine Ende AB des Streifens festhaltend, das andere Ende $A'B'$ um die Längenaxe des Streifens halb herumdreht, als wodurch $A'B'$ mit BA einerlei Richtung erhält. Die nach der letztgedachten Coincidenz entstandene Fläche hat nur Eine Grenzlinie, nämlich die aus den jetzt gebogenen und in A und B', sowie in B und A' an einander grenzenden Linien AA' und BB' zusammengesetzte. Auch hat diese Fläche nur Eine Seite; denn wenn man sie — um dieses noch auf andere Weise vorstellig zu machen — von einer beliebigen Stelle aus mit einer Farbe zu überstreichen anfängt und damit fortfährt, ohne mit dem Pinsel über die Grenzlinie hinaus auf die andere Seite überzugehen, so werden nichtsdestoweniger zuletzt an jeder Stelle die zwei daselbst einander gegenüberliegenden Seiten der Fläche gefärbt seyn.

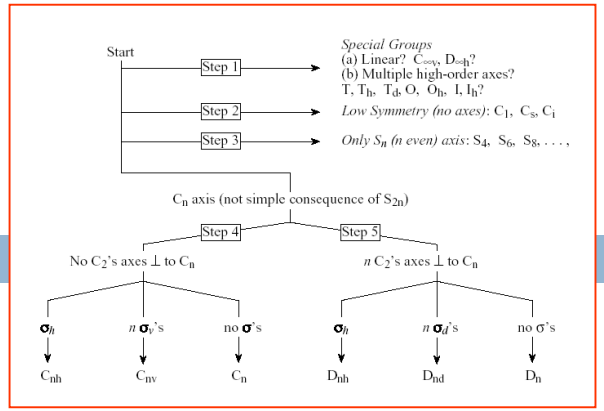


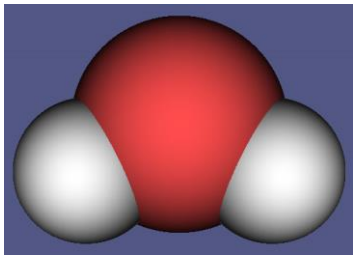
August Ferdinand Möbius
1790-1866

"Zur Theorie der Polyeder und der Elementarverwandschaft", diaria Mathematica, Mobius, A. F. 1858.

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	−1	z, R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

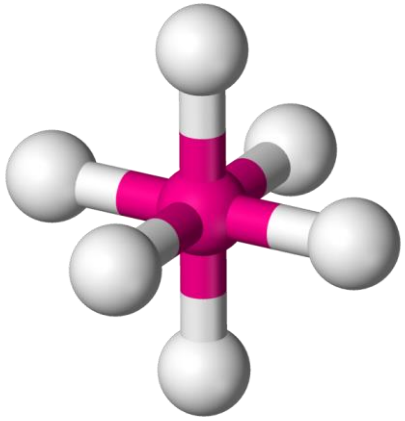
Point Groups



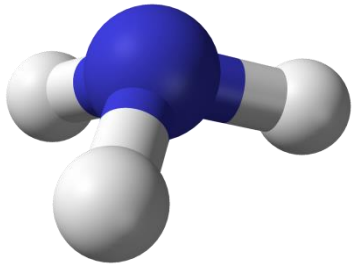


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1
E_g	2	−1	0	0	2	2	0	−1	2	0
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1
E_u	2	−1	0	0	2	−2	0	1	−2	0
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1

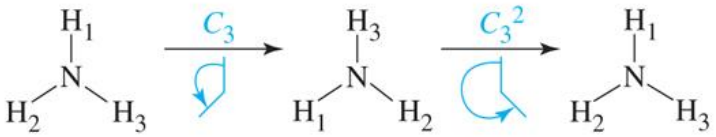
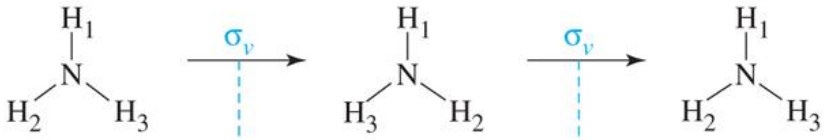
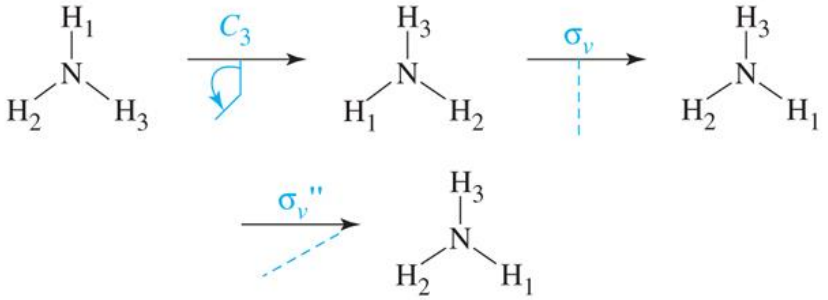


C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0



Properties and Representations of Groups

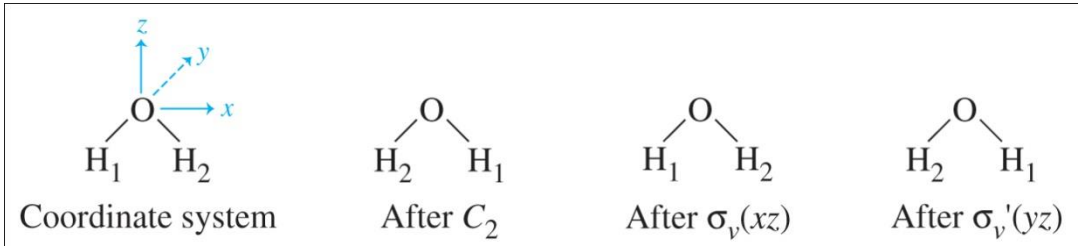
Properties of a Group

Property of Group	Examples from Point Group
1. Each group must contain an **identity** operation that commutes (in other words, $EA = AE$) with all other members of the group and leaves them unchanged ($EA = AE = A$).	C_{3v} molecules (and *all* molecules) contain the identity operation E.
2. Each operation must have an **inverse** that, when combined with the operation, yields the identity operation (sometimes a symmetry operation may be its own inverse). *Note:* By convention, we perform combined symmetry operations *from right to left* as written.	 $C_3^2 C_3 = E$ (C_3 and C_3^2 are inverses of each other)
	 $\sigma_v\sigma_v = E$ (mirror planes are shown as dashed lines; σ_v is its own inverse)
3. The product of any two group operations must also be a member of the group. This includes the product of any operation with itself.	 $\sigma_v C_3$ has the same overall effect as σ_v'', therefore we write $\sigma_v C_3 = \sigma_v''$. It can be shown that the products of any two operations in C_{3v} are also members of C_{3v}.
4. The associative property of combination must hold. In other words, $A(BC) = (AB)C$.	$C_3(\sigma_v \sigma_v') = (C_3 \sigma_v)\sigma_v'$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

Properties and Representations of Groups

Matrix Representations of Symmetry Operations



$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = E \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

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

$$E : \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = C_2 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

$$C_2 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

$$C_2 : \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \sigma_v(xz) \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

$$\sigma_v(xz) \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

$$\sigma_v(xz) : \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

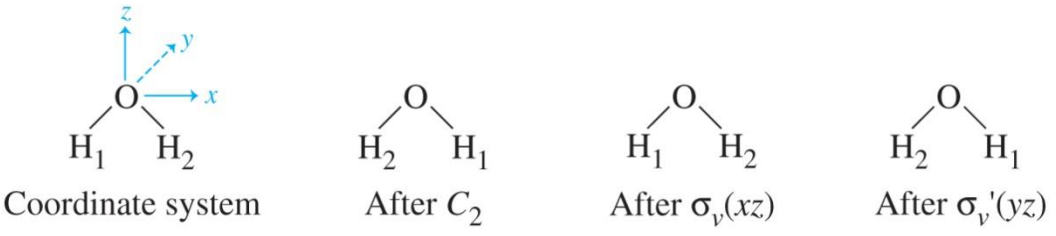
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \sigma'_v(yz) \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

$$\sigma'_v(yz) \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

$$\sigma'_v(yz) : \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Properties and Representations of Groups

Character Tables



Schoenfliers Symbol of the Point Group

Symmetry Operations (*R*)

Order of the Group = Σ(# of Operations)

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

Symmetry Types of the Irreducible representations

Classes (# of classes = # of symmetry types)

Irreducible Representations (Γ)

Characters (χ)

Character : Numerical representation of the operation (Extent of originality after the operation)

$$C_2 z = z = [1]z,\ \sigma_v(xz)R_z = -R_z = [-1]R_z,\ \sigma'_v(yz)yz = yz = [1]yz$$

$$C_2 z = z = [1]z, C_2 x^2 = x^2 = [1]x^2,\ C_2(x^2 + y^2 - z^2) = x^2 + y^2 - z^2 = [1](x^2 + y^2 - z^2)$$

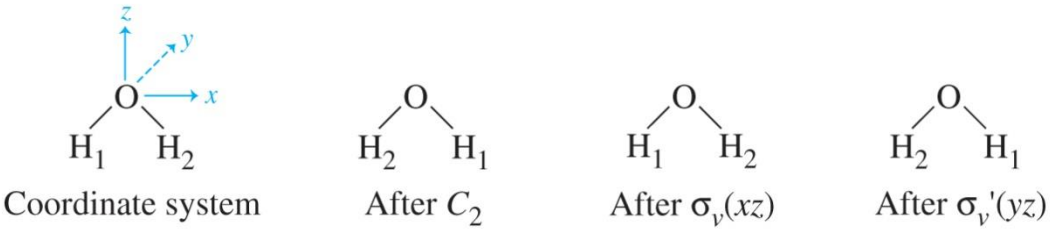
$$C_2 p_x = -p_x = [-1]p_x,\ \sigma_v(xz)d_{xy} = -d_{xy} = [-1]d_{xy},\ \sigma'_v(yz)d_{yz} = d_{yz} = [1]d_{yz},\ \sigma_v(xz)s = s = [1]s,\ \sigma'_v(yz)d_{z^2} = d_{z^2} = [1]d_{z^2}$$

Properties and Representations of Groups

Character Tables

Characters (χ)

Character : Numerical representation of the operation (Extent of originality after the operation)



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

Γ 3 −1 1 1

reducible representation (= A_1+B_1+B_2)

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = E \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

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

$$E: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\chi(E) = Tr(E) = 3$$

$$E: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi(E) = Tr(E) = 3$$

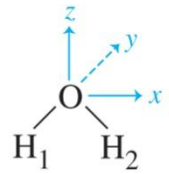
$$C_2: \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi(C_2) = Tr(C_2) = -1$$

$$\sigma_v(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi(\sigma_v) = Tr(\sigma_v) = 1$$

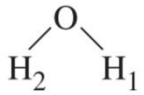
$$\sigma'_v(yz): \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi(\sigma'_v) = Tr(\sigma'_v) = 1$$

Properties and Representations of Groups

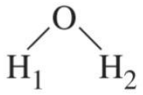
Character Tables



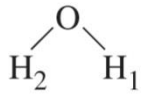
Coordinate system



After C_2



After $\sigma_v(xz)$



After $\sigma_v'(yz)$

Matrix Representations (Reducible)

$$E:\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} \quad C_2:\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix} \quad \sigma_v(xz):\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix} \quad \sigma_v'(yz):\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

Characters of Matrix Representations

3	−1	1	1

Block Diagonalized Matrices

$$\begin{bmatrix}[1]&0&0\\0&[1]&0\\0&0&[1]\end{bmatrix} \quad \begin{bmatrix}[-1]&0&0\\0&[-1]&0\\0&0&[1]\end{bmatrix} \quad \begin{bmatrix}[1]&0&0\\0&[-1]&0\\0&0&[1]\end{bmatrix} \quad \begin{bmatrix}[-1]&0&0\\0&[1]&0\\0&0&[1]\end{bmatrix}$$

Irreducible Representations

E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Coordinate Used
1	−1	1	−1	x
1	−1	−1	1	y
1	1	1	1	z
3	−1	1	1	

(= A_1+B_1+B_2)

Character Table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Matching Functions	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

* The biggest possible values of χ is 3.

Properties and Representations of Groups

Character Tables

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

TABLE 4.7 Properties of Characters of Irreducible Representations in Point Groups

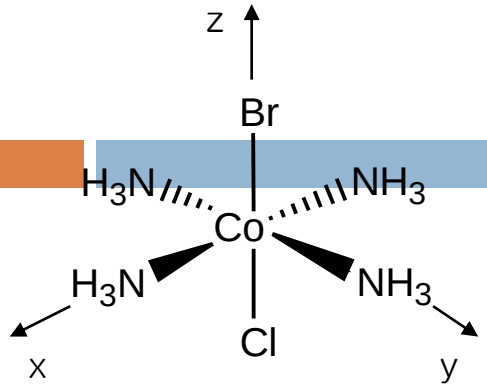
Property	Example: C_{2v}
1. The total number of symmetry operations in the group is called the **order (*h*)**. To determine the order of a group, simply total the number of symmetry operations listed in the top row of the character table.	Order = 4 four symmetry operations: E, C_2, $\sigma_v(xz)$, and $\sigma_v'(yz)$
2. Symmetry operations are arranged in **classes**. All operations in a class have identical characters for their transformation matrices and are grouped in the same column in character tables.	Each symmetry operation is in a separate class; therefore, there are four columns in the character table.
3. The number of irreducible representations equals the number of classes. This means that character tables have the same number of rows and columns (they are square).	Because there are four classes, there must also be four irreducible representations—and there are.

Great Orthogonality Theorem

4. The sum of the squares of the **dimensions** (characters under E) of each of the irreducible representations equals the order of the group. $h = \sum_i [\chi_i(E)]^2$	$1^2 + 1^2 + 1^2 + 1^2 = 4 = h$, the order of the group.
5. For any irreducible representation, the sum of the squares of the characters multiplied by the number of operations in the class (see Table 4.8 for an example), equals the order of the group. $h = \sum_R [\chi_i(\mathbf{R})]^2$	For A_2, $1^2 + 1^2 + (-1)^2 + (-1)^2 = 4 = h$. Each operation is its own class in this group.
6. Irreducible representations are **orthogonal** to each other. The sum of the products of the characters, multiplied together for each class, for any pair of irreducible representations is 0. $\sum_R \chi_i(\mathbf{R})\chi_j(\mathbf{R}) = 0, \text{when } i \neq j$ Taking any pair of irreducible representations, multiplying together the characters for each class, multiplying by the number of operations in the class (see Table 4.8 for an example), and adding the products gives zero.	B_1 and B_2 are orthogonal: $(1)(1) + (-1)(-1) + (1)(-1) + (-1)(1) = 0$ $E \quad C_2 \quad \sigma_v(xz) \quad \sigma_v'(yz)$ Each operation is its own class in this group.
7. A **totally symmetric representation**, with characters of 1 for all operations, is included in all groups.	C_{2v} has A_1, in which all characters = 1.

Properties and Representations of Groups

Character Tables



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

$Ez = z$
$C_4z = z$
$C_2z = z$
$\sigma_v z = z$
$\sigma_d z = z$

$Ex = x$ $\quad Ey = y$
$C_4x = y$ $\quad C_4y = -x$
$C_2x = -x$ $\quad C_2y = -y$
$\sigma_v x = x$ $\quad \sigma_v y = -y$
$\sigma_d x = y$ $\quad \sigma_d y = x$

x, y are interconvertable.
degenerate

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = E\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix} \qquad \chi(\mathrm{E}) = 2$$

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = C_4\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} y \\ -x \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix} \qquad \chi(C_4) = 0$$

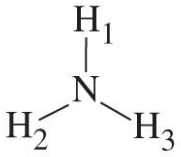
$$\begin{bmatrix} x' \\ y' \end{bmatrix} = C_2\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -x \\ -y \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix} \qquad \chi(C_2) = -2$$

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \sigma_v\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x \\ -y \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix} \qquad \chi(\sigma_v) = 0$$

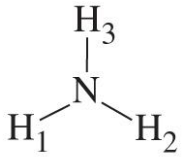
$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \sigma_d\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} y \\ x \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix} \qquad \chi(\sigma_d) = 0$$

Properties and Representations of Groups

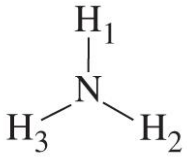
Character Tables



NH_3 after E

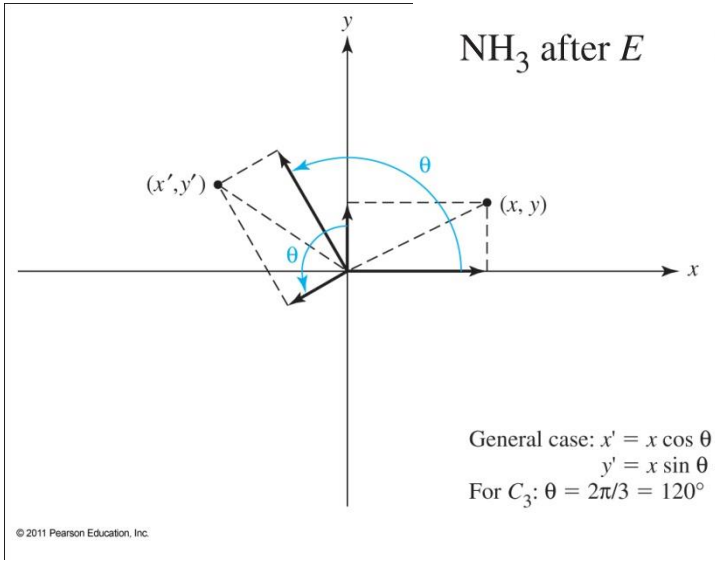


NH_3 after C_3



NH_3 after $\sigma_v\,(yz)$

C_{3v}



General case: $x' = x\cos\theta - y\sin\theta$
$y' = x\sin\theta + y\cos\theta$
For C_3: $\theta = 2\pi/3 = 120°$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = C_3 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x\cos\theta - y\sin\theta \\ x\sin\theta + y\cos\theta \\ z \end{bmatrix} = \begin{bmatrix} x\cos\frac{2\pi}{3} - y\sin\frac{2\pi}{3} \\ x\sin\frac{2\pi}{3} + y\cos\frac{2\pi}{3} \\ z \end{bmatrix}$$

$$C_3 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} & 0 \\ \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = E \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

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

$$E : \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \sigma_v(xz) \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

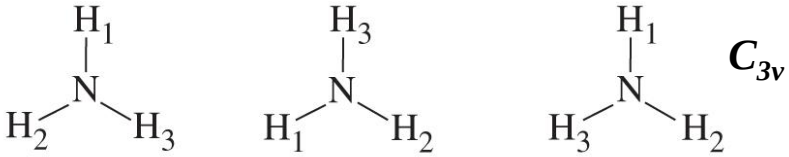
$$\sigma_v(xz) \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

$$\sigma_v(xz) : \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_3 : \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Properties and Representations of Groups

Character Tables



C_{3v}

NH_3 after E NH_3 after C_3 NH_3 after σ_v (yz)

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

$$E: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3: \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(xz): \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

block diagonalized

x, y are degenerated.

TABLE 4.9 Properties of the Characters for the C_{3v} Point Group

Property	C_{3v} Example
1. Order	6 (6 symmetry operations)
2. Classes	3 classes: E; $2C_3$ (= C_3, C_3^2); $3\sigma_v$ (= σ_v, σ_v', σ_v'')
3. Number of irreducible representations	3 (A_1, A_2, E)
4. Sum of squares of dimensions equals the order of the group	$1^2 + 1^2 + 2^2 = 6$
5. Sum of squares of characters multiplied by the number of operations in each class equals the order of the group	E $2C_3$ $3\sigma_v$ A_1: $1^2 + 2(1)^2 + 3(1)^2 = 6$ A_2: $1^2 + 2(1)^2 + 3(-1)^2 = 6$ E: $2^2 + 2(-1)^2 + 3(0)^2 = 6$ (Multiply the squares by the number of symmetry operations in each class.)
6. Orthogonal representations	The sum of the products of any two representations multiplied by the number of operations in each class equals 0. Example of $A_2 \times E$: $(1)(2) + 2(1)(-1) + 3(-1)(0) = 0$
7. Totally symmetric representation	A_1, with all characters = 1

Properties and Representations of Groups

Character Tables

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

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

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	−1	z, R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1
E_g	2	0	−2	0	0	2	0	−2	0	0
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1
E_u	2	0	−2	0	0	−2	0	2	0	0

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	2
A_1'	1	1	1	1	1	1	
A_2'	1	1	1	−1	1	1	
E_1'	2	$2\cos 72°$	$2\cos 144°$	0	2	$2\cos 72°$	2 c
E_2'	2	$2\cos 144°$	$2\cos 72°$	0	2	$2\cos 144°$	2 c
A_1''	1	1	1	1	−1	−1	
A_2''	1	1	1	−1	−1	−1	
E_1''	2	$2\cos 72°$	$2\cos 144°$	0	−2	$-2\cos 72°$	−2 c
E_2''	2	$2\cos 144°$	$2\cos 72°$	0	−2	$-2\cos 144°$	−2 cos 72 0

Symmetry Labels

1. Degeneracies — Symmetry Labels
   - 1 — A : symmetric about C_n ($\chi(C_n) = 1$)
     B : antisymmetric about C_n ($\chi(C_n) = -1$)
   - 2 — E
   - 3 — T

2. Subscript labels — Meanings
   - 1 — symmetric about $C_2(\perp C_n)$, ($\chi(C_2) = 1$)
   - 2 — antisymmetric about $C_2(\perp C_n)$, ($\chi(C_2) = -1$)

3. Subscript labels (when no $C_2(\perp C_n)$ — Meanings
   - 1 — symmetric about σ_v, ($\chi(\sigma_v) = 1$)
   - 2 — antisymmetric about σ_v, ($\chi(\sigma_v) = -1$)

4. Subscript labels — Meanings
   - g — symmetric about i, ($\chi(i) = 1$)
   - u — antisymmetric about i, ($\chi(i) = -1$)

5. Superscript labels — Meanings
   - ' — symmetric about σ_h, ($\chi(\sigma_h) = 1$)
   - " — antisymmetric about σ_h, ($\chi(\sigma_h) = -1$)

Applications of Symmetry

Polarity

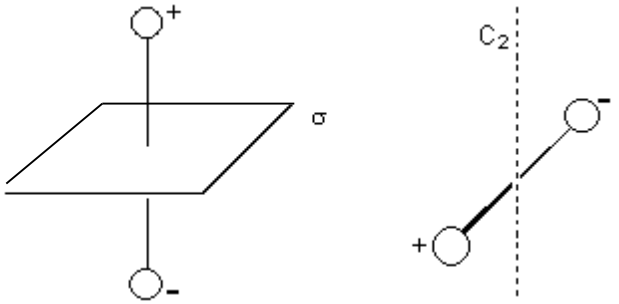
Polar molecule: a molecule with a permanent electric dipole moment.

A molecule with a center of inversion (*i*) cannot have a permanent dipole.

A molecule cannot have a permanent dipole perpendicular to any mirror plane.

A molecule cannot have a permanent dipole perpendicular to any axis of symmetry.

Therefore, molecules having both a C_n axis and a perpendicular C_2 axis or σ_h cannot have a dipole in any direction. $\Rightarrow$ Molecules belonging to any C_{nh}, *D*, *T*, *O* or *I* groups cannot have permanent dipole moment.



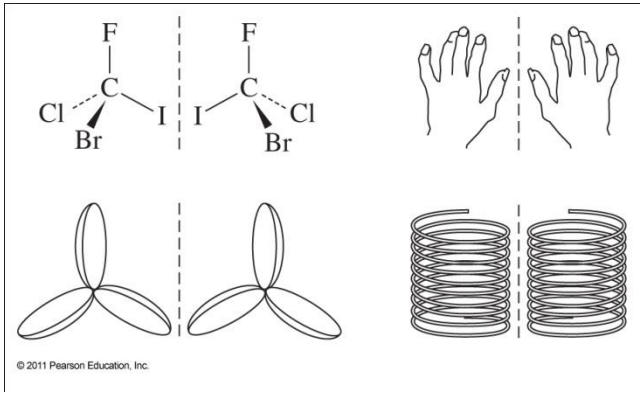
Applications of Symmetry

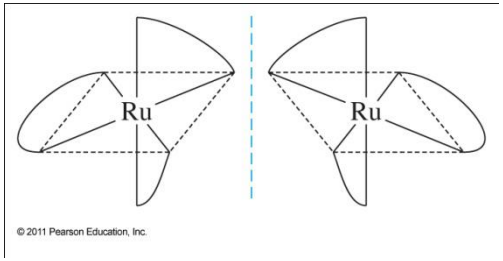
Chirality

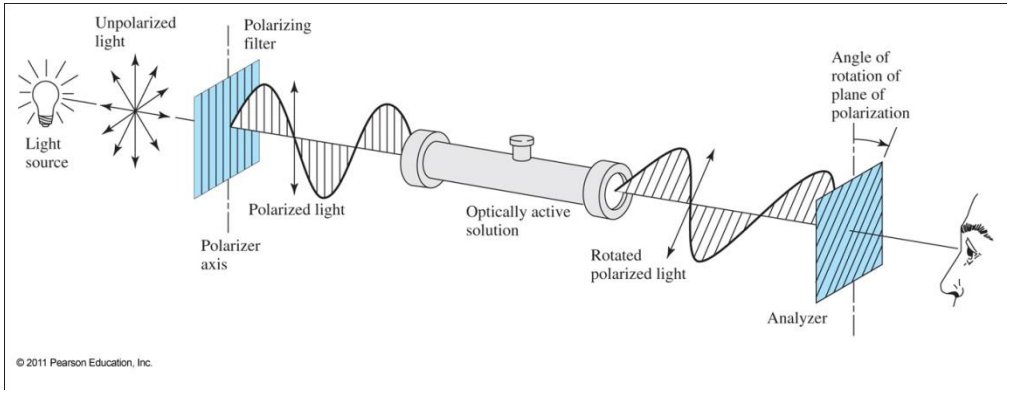
A **chiral molecule** is a molecule that is distinguished from its mirror image in the same way that left and right hands are distinguishable.

A molecule that has no axis of improper rotation (S_n) is chiral.

S_n: including $S_1 = \sigma$ and $S_2 = i$

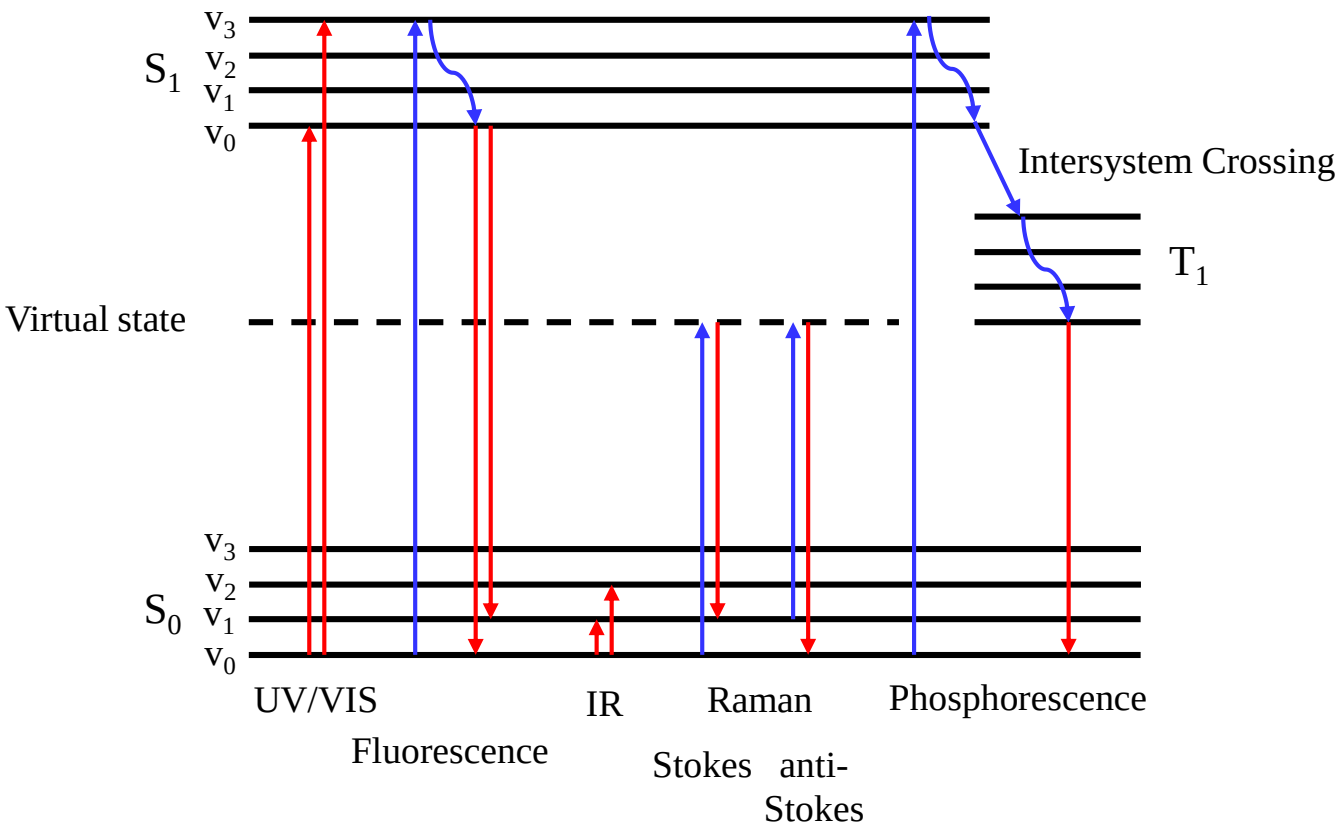






Applications of Symmetry

Molecular Spectroscopies



Applications of Symmetry

Molecular Vibrations

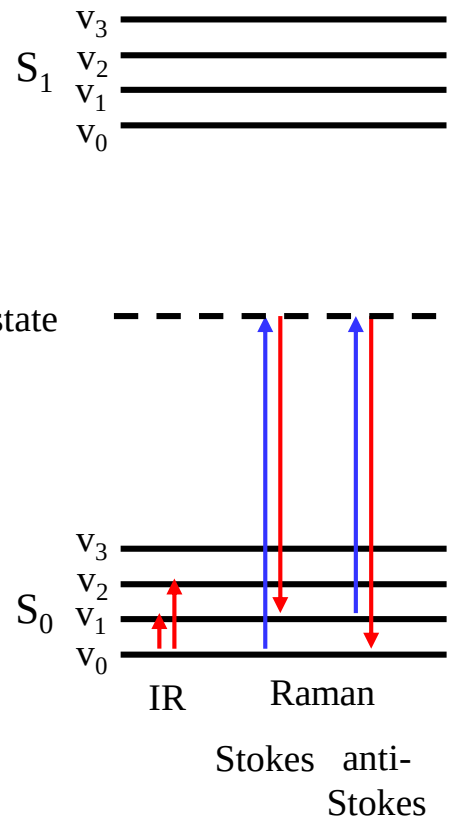


TABLE 4.10 Degrees of Freedom

Number of Atoms	Total Degrees of Freedom	Translational Modes	Rotational Modes	Vibrational Modes
N (linear)	3*N*	3	2	3*N* − 5
3 (HCN)	9	3	2	4
N (nonlinear)	3*N*	3	3	3*N* − 6
3 (H_2O)	9	3	3	3

IR-active: when there is a change in dipole moment in a molecule as it vibrates

Raman-active: when there is a change in polarizability a molecule as it vibrates

Applications of Symmetry

Molecular Vibrations

Water

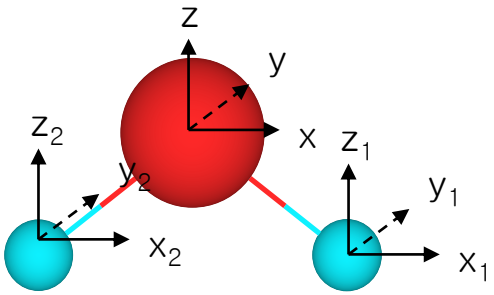


TABLE 4.10 Degrees of Freedom

Number of Atoms	Total Degrees of Freedom	Translational Modes	Rotational Modes	Vibrational Modes
N (linear)	3*N*	3	2	3*N* − 5
3 (HCN)	9	3	2	4
N (nonlinear)	3*N*	3	3	3*N* − 6
3 (H_2O)	9	3	3	3

H_2O

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz
Γ	9	−1	3	1		

$$n_{A_1} = \frac{1}{4}[1\cdot1\cdot9 + 1\cdot1\cdot(-1) + 1\cdot1\cdot3 + 1\cdot1\cdot1] = 3$$

$$n_{A_2} = \frac{1}{4}[1\cdot1\cdot9 + 1\cdot1\cdot(-1) + 1\cdot(-1)\cdot3 + 1\cdot(-1)\cdot1] = 1$$

$$n_{B_1} = \frac{1}{4}[1\cdot1\cdot9 + 1\cdot(-1)\cdot(-1) + 1\cdot1\cdot3 + 1\cdot(-1)\cdot1] = 3$$

$$n_{B_2} = \frac{1}{4}[1\cdot1\cdot9 + 1\cdot(-1)\cdot(-1) + 1\cdot(-1)\cdot3 + 1\cdot1\cdot1] = 2$$

(Little) Orthogonality Theorem

$$n_i = \frac{1}{h}\sum_R g(R)\chi_i(R)\chi_\Gamma(R)$$

$$\Gamma = 3A_1 + A_2 + 3B_1 + 2B_2$$

$$\Gamma_{trans} = A_1 + B_1 + B_2$$

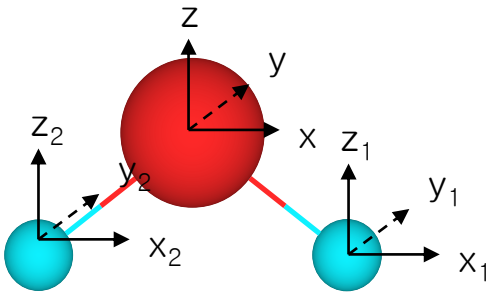
$$\Gamma_{rot} = A_2 + B_1 + B_2$$

$$\Gamma_{vib} = 2A_1 + B_1$$

Applications of Symmetry

Molecular Vibrations

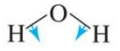
Water



H_2O

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz
Γ	9	−1	3	1	IR active	Raman active

TABLE 4.12 The Vibrational Modes of Water

A_1		Symmetric stretch: change in dipole moment; more distance between positive hydrogens and negative oxygen *IR active*
B_1		Antisymmetric stretch: change in dipole moment; change in distances between positive hydrogens and negative oxygen *IR active*
A_1		Symmetric bend: change in dipole moment; angle between H—O vectors changes *IR active*

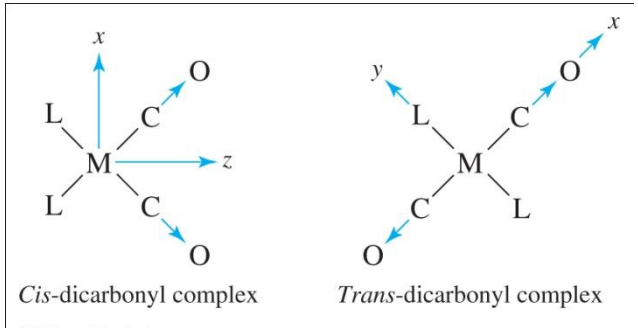
Both IR and Raman active

$$\Gamma_{vib} = 2A_1 + B_1$$

Applications of Symmetry

Molecular Vibrations

Selected Vibrational Modes



Cis-dicarbonyl complex

Trans-dicarbonyl complex

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

$\Gamma_{\nu(CO)}$ **2 0 2 0**

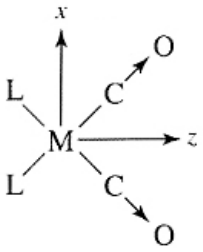
$\Gamma_{\nu(CO)} = A_1 + B_1$

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

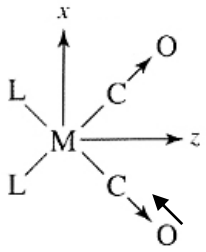
$\Gamma_{\nu(CO)}$ **2 0 0 2 0 2 2 0**

$\Gamma_{\nu(CO)} = A_g + B_{3u}$

A_1 :

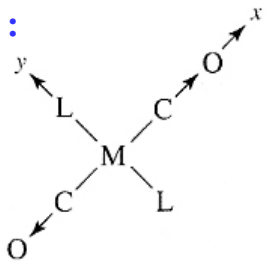


B_1 :



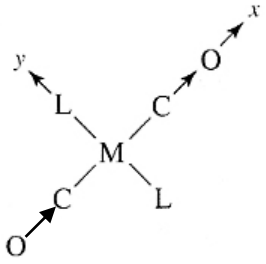
IR, Raman active

A_g :



Raman active

B_{3u} :



IR active

Applications of Symmetry

Molecular Vibrations

Selected Vibrational Modes

C_i	E	i		
A_g	1	1	R_x, R_y, R_z	x^2, y^2, z^2 xy, xz, yz
A_u	1	−1	x, y, z	

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	−1	1	1	−1	R_z	
E_g	2	−1	0	2	−1	0	(R_x, R_y)	(x^2-y^2, xy), (xz, yz)
A_{1u}	1	1	1	−1	−1	−1		
A_{2u}	1	1	−1	−1	−1	1	z	
E_u	2	−1	0	−2	1	0	(x, y)	

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Exclusion Rule : In a molecule with *i* symmetry element, IR-active and Raman -active vibrational modes are not coincident.