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♣ Symmetry is everywhere, in **nature** and in **engineering achievements**.

♣ Nature loves symmetry

♣ Most objects found in nature have symmetry

♣ Symmetry is associated with beauty

Symmetry is when a shape looks identical to its original shape after being flipped or turned.

When applied to Chemistry, it can be used, for example

- ✓ *To predict whether or not a molecule has a dipole moment*
- ✓ *To predict if a molecule will show optical activity*
- ✓ *To derive selection rules for spectroscopic transitions*
- ✓ *To determine which AOs to be used to construct hybrid orbitals.*
- ✓ *To predict which molecular vibrations lead to IR spectra.*
- ✓ *To label and designate MOs*
- ✓ *Interpret electronic spectra*

Symmetry Elements & Operations

✓ *A **symmetry element** is a geometrical entity such as a line, a plane, or a point about which one can perform an operation of rotation, reflection, or inversion.*

✓ *A **symmetry operation** is movement of a molecule/object about a symmetry element such that resulting configuration is **indistinguishable** from the original.*

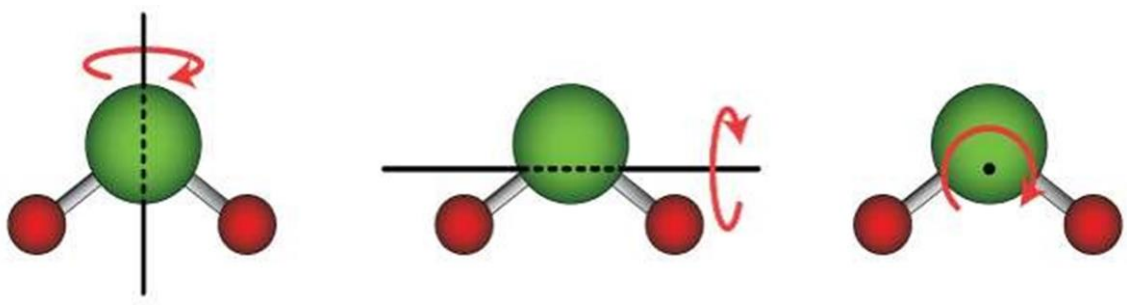
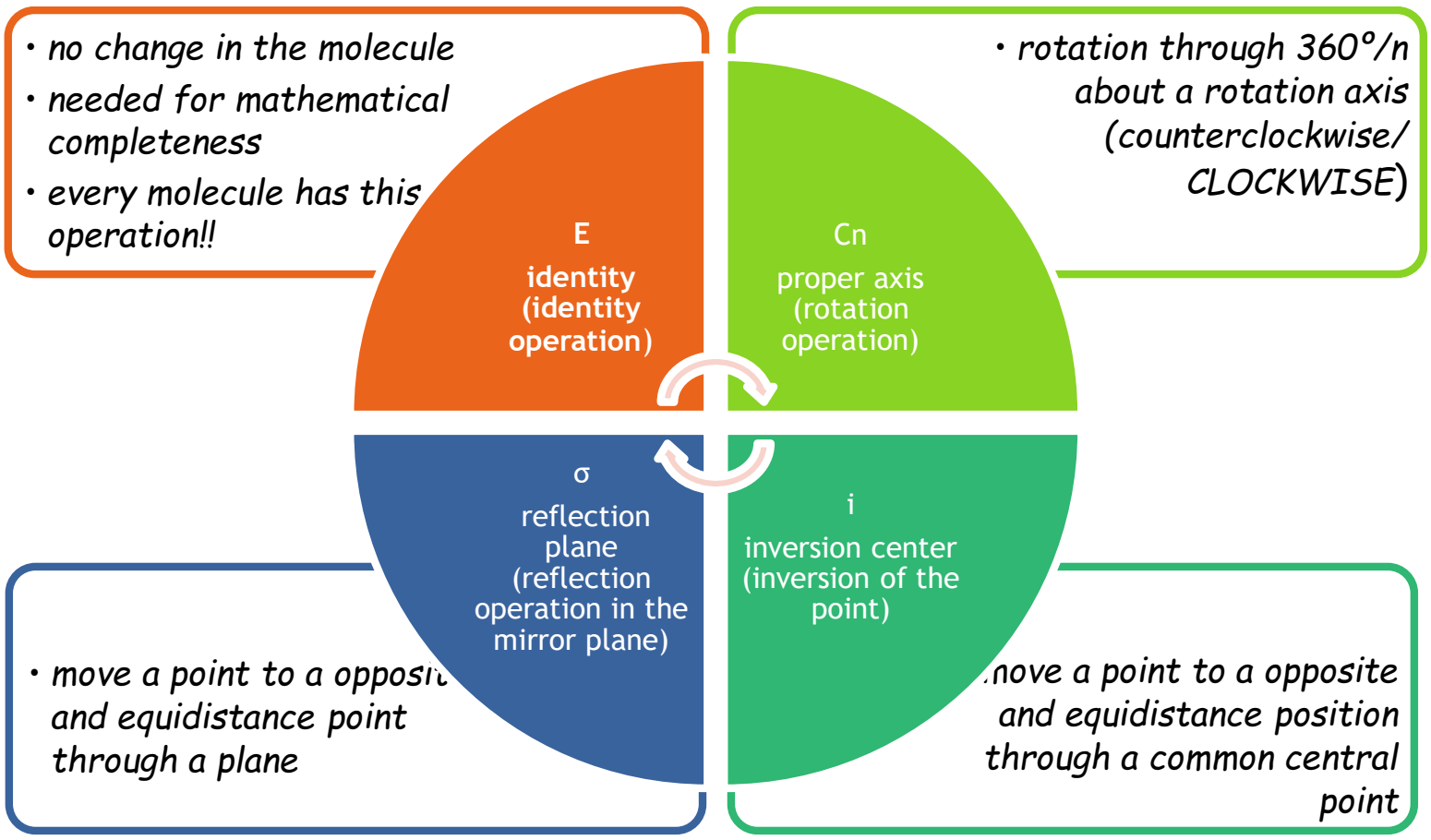
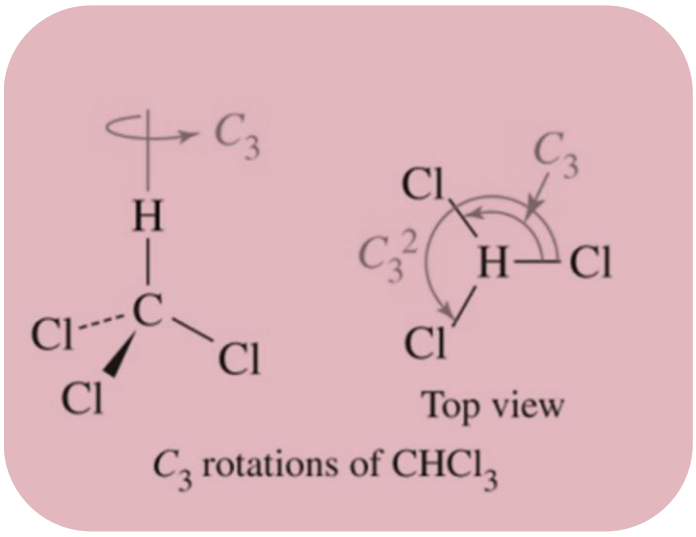


Table of Symmetry Elements and Symmetry Operations		
Elements	Symbols	Operations
Identity	***E***	Identity operation
Proper Axis	***Cn***	Rotation operation by 360°/*n*
Reflection Plane	***σ***	Reflection operation (in the plane)
Inversion Center	***i***	Inversion (of the point *x, y, x* to *-x, -y, -z)*
Improper Axis	***Sn***	Improper rotation (= rotation-reflection operation) 1. *Rotation by 360 °/n* *2. Reflection in plane perpendicular to rotation axis*



E: identity (identity operation)

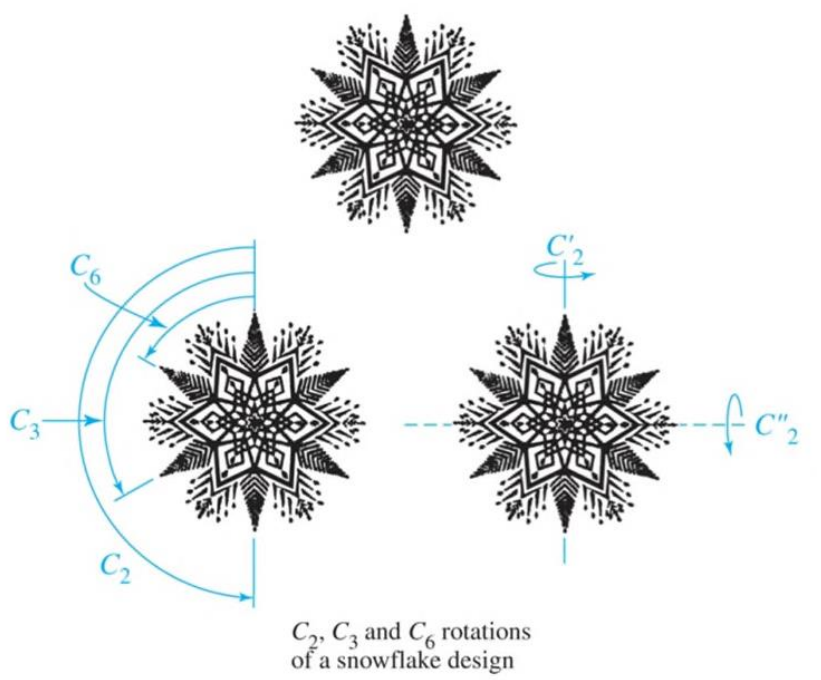
- ♣ *no change in the molecule*
- ♣ *needed for mathematical completeness*
- ♣ *every molecule has this operation!!*



C_3 rotations of $CHCl_3$

▪ **C_n: proper axis (rotation operation)**

- ♣ *Rotation through 360°/n about a rotation axis (clockwise: +)*
- ♣ *$CHCl_3$: threefold (C_3) axis*
- ♣ *Rotation axis → parallel to C-H axis*
- ♣ *C_3^1: rotation angle: 360°/3 = 120°*
- ♣ *C_3^2: two consecutive rotation → 360° x (2/3) = 240°*
- ♣ *$C_3^3 \equiv E$ (*E is included in all molecules!!)*



C_2, C_3 and C_6 rotations of a snowflake design

Rotation Angle	Symmetry Operation
60°	C_6
120°	C_3 ($\equiv C_6^2$)
180°	C_2 ($\equiv C_6^3$)
240°	C_3^2 ($\equiv C_6^4$)
300°	C_6^5
360°	E ($\equiv C_6^6$)

C_6: along the axis through the center of molecule

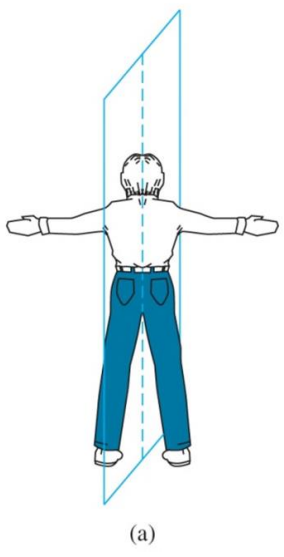
Principal axis (= highest order of rotation axis): *Cn* axis w/ the largest *n* value for snowflake →*C*6
principal axis →*z* axis in Cartesian coordinate

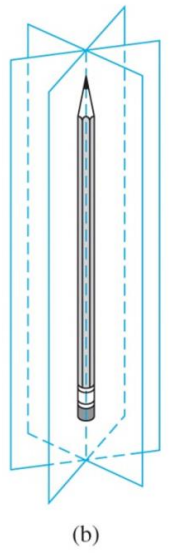
σ : reflection plane (reflection operation in the mirror plane)

♣ *Move a point to a opposite and equidistance point through a plane*

⇒ *e.g.) human body: one mirror plane switching left to right*

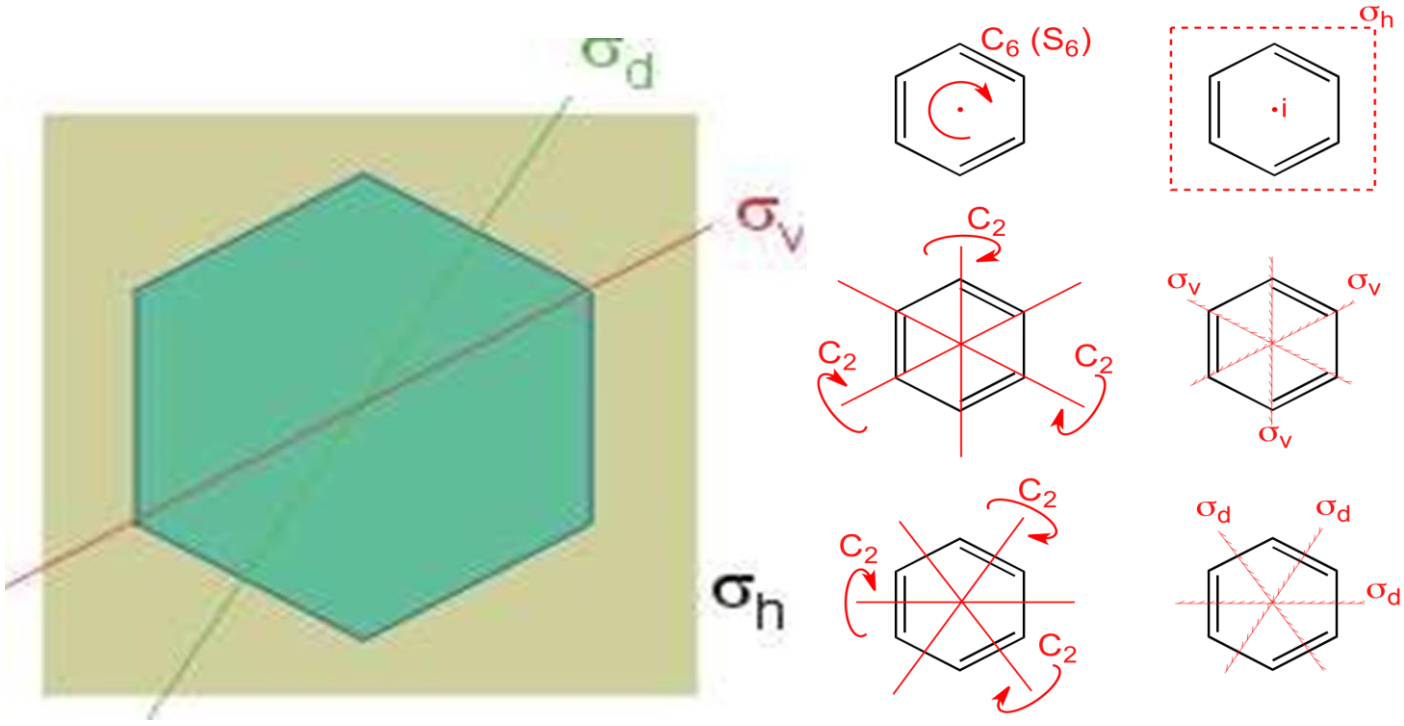
⇒ *round pencil: infinite # mirror planes at the center of the object (e.g. acetylene, CO_2)*


(a)


(b)

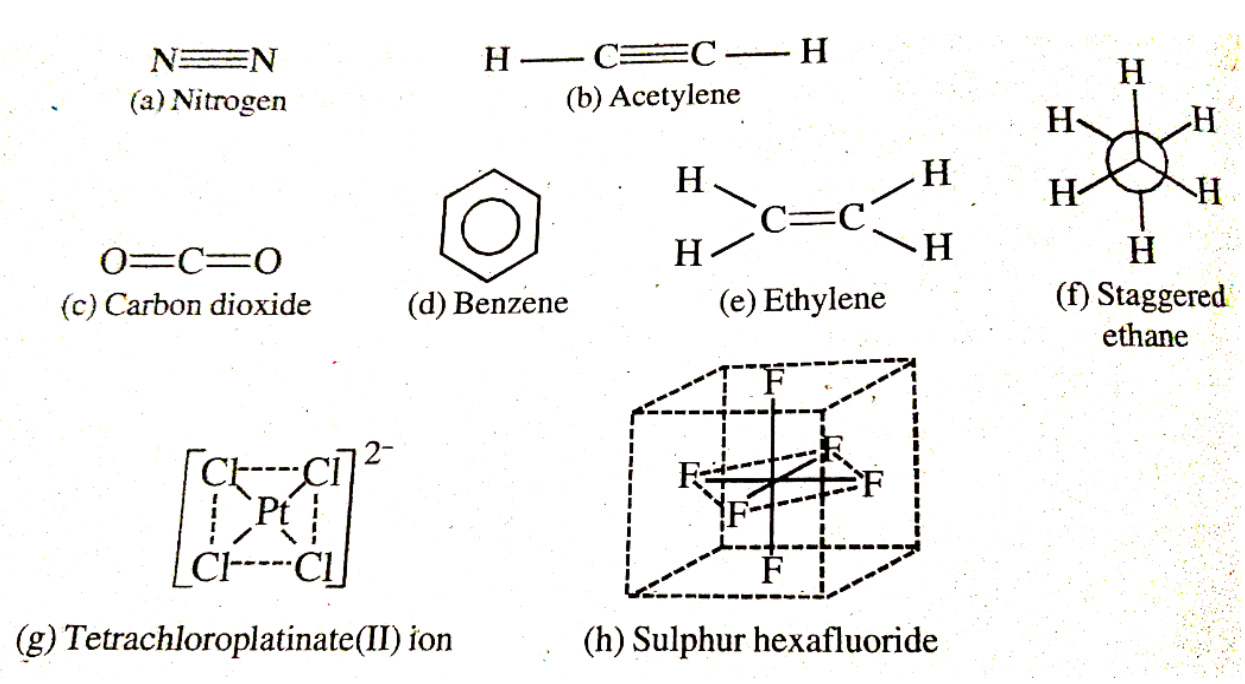
♣ *if perpendicular to the principal axis, → σ_h (horizontal)*

♣ *if contain the principal axis, → σ_v (vertical), σ_d (dihedral: Between two C_2 axis)*



i : inversion center (inversion of the point)

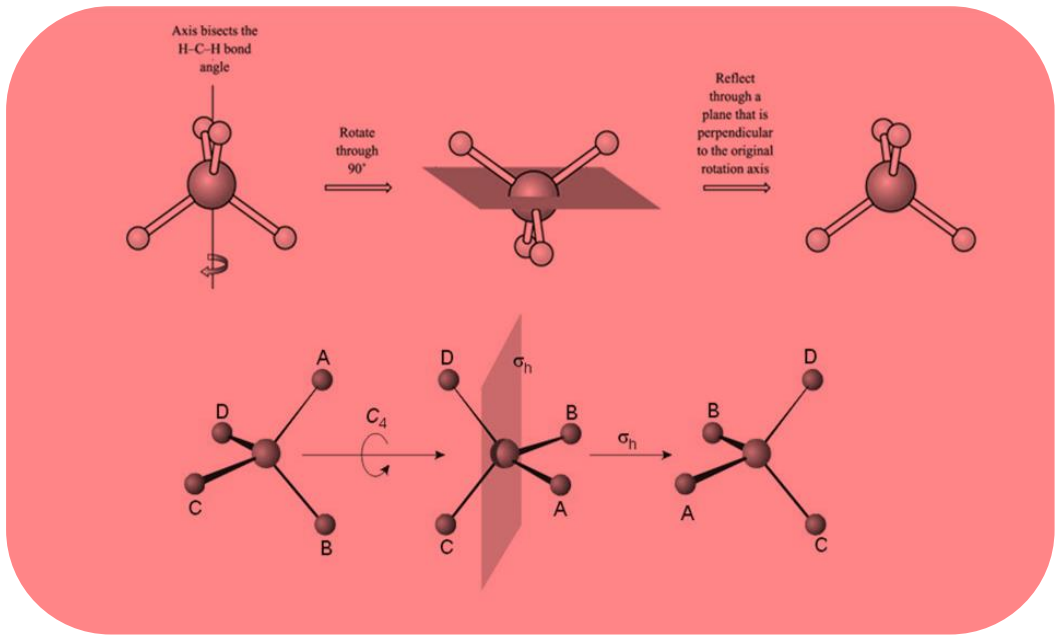
♣ *move a point to a opposite and equidistance position through a common central point*



S_n : improper axis (improper rotation, rotation-reflection operation)

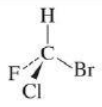
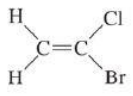
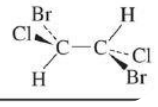
♣ *rotation by 360°/n + reflection through a perpendicular plane*

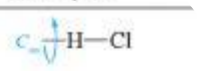
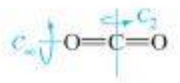
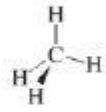
e.g.) methane → S_4 (x3) (through C & bisecting the angle b/w two H)



Classifications

I. Low symmetry: few or no symmetry operations

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)	

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

II. High symmetry: contain many symm.
Operations linear, tetrahedral, octahedral, icosahedral

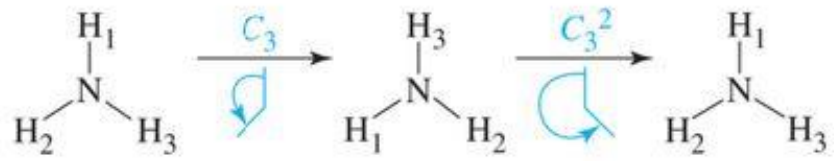
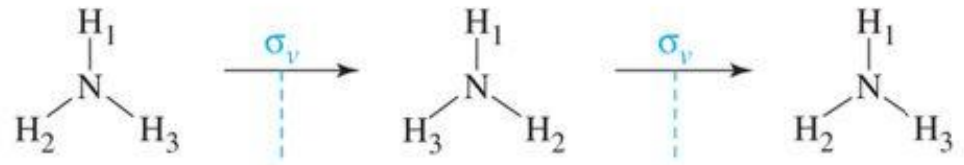
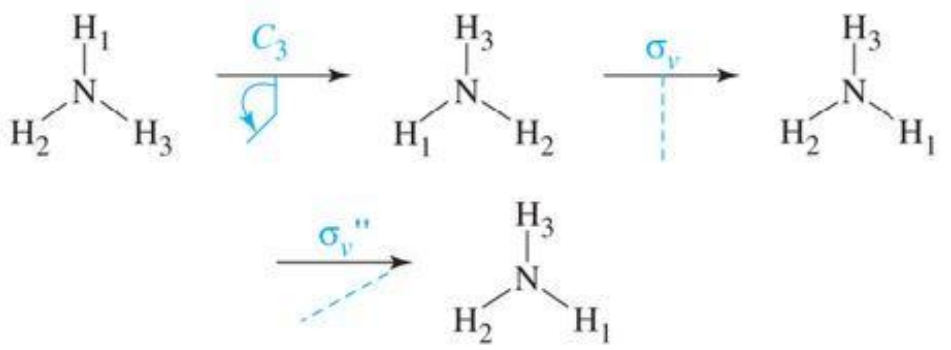
Point Groups

- *A **Point Group** describes all the symmetry operations that can be performed on a molecule that at least one point remain unmoved and results in a conformation indistinguishable from the original.*

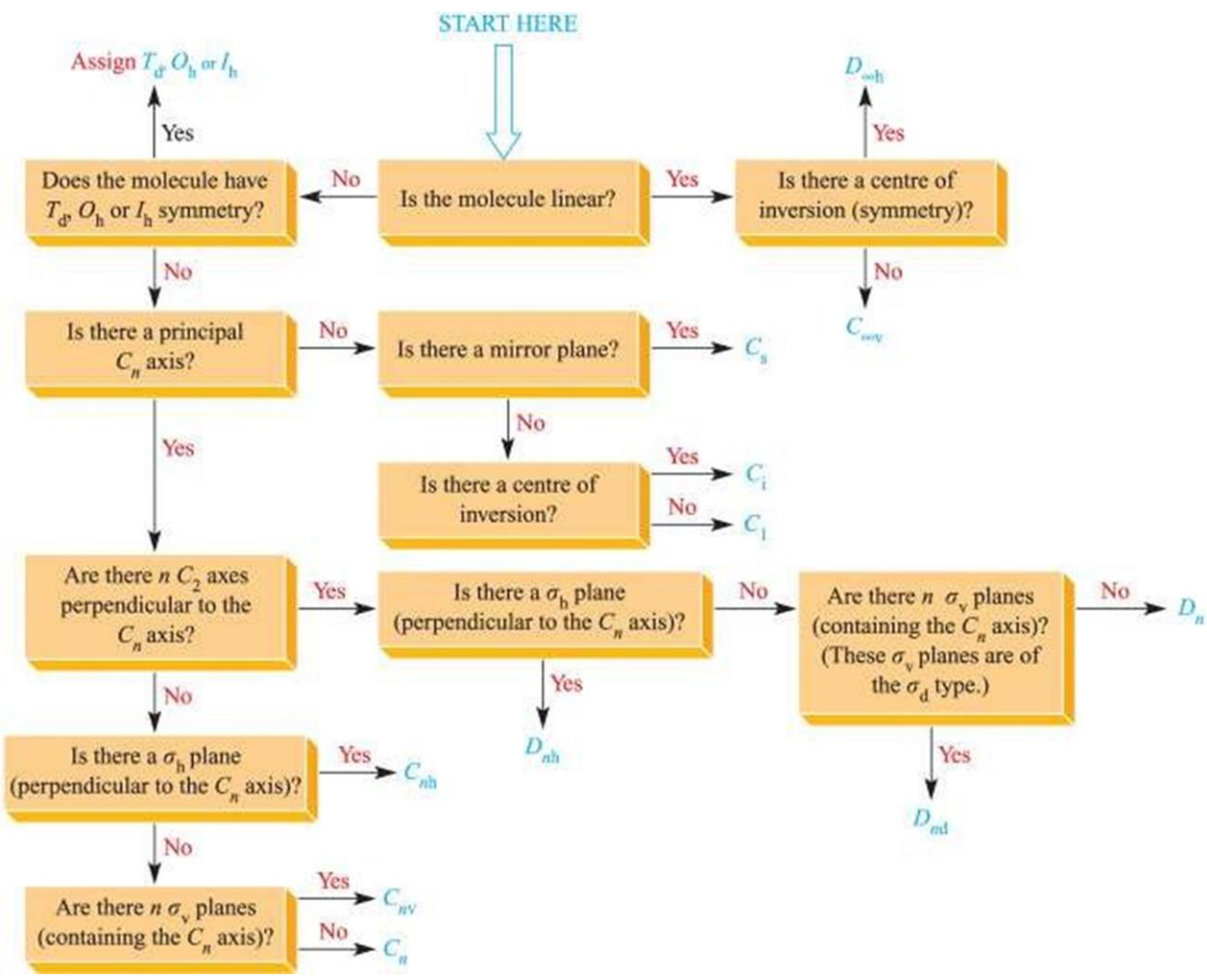
Conditions

⇒***Closure rule***
⇒***Identity rule***
⇒***Associative rule***
⇒***Inverse rule***

} Point 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 ($EA = AE = A$). Identity Rule	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. Inverse Rule	 $C_3^2 C_3 = E$ (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. Closure Rule	 $\sigma_v C_3$ 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, $A(BC) = (AB)C$. Associative Rule	$C_3(\sigma_v \sigma_v') = (C_3 \sigma_v)\sigma_v'$

Determination of Point Groups



Matrix Representations

H_2O: C_{2v} point group - E, C_2, $\sigma_v(xz)$, $\sigma_v'(yz)$

z axis — xz plane as the plane of molecule

: symmetry operation may be expressed as a transformation matrix

[new coordinates] = [transformation matrix] [old coordinates]

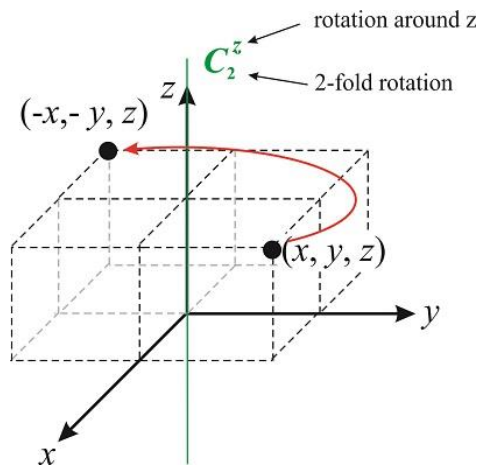
1) C_2:

$$\begin{cases} x' = \text{new } x = -x \\ y' = \text{new } y = -y \\ z' = \text{new } z = z \end{cases} \qquad \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

in matrix notation,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

$$\begin{pmatrix} \text{new} \\ \text{coordinates} \end{pmatrix} = \begin{pmatrix} \text{transformation} \\ \text{matrix} \end{pmatrix} \begin{pmatrix} \text{old} \\ \text{coordinates} \end{pmatrix} = \begin{pmatrix} \text{new coordinates} \\ \text{In terms of old} \end{pmatrix}$$



2) $\sigma_v(xz)$:

$$\begin{cases} x' = \text{new } x = x \\ y' = \text{new } y = -y \\ z' = \text{new } z = z \end{cases} \qquad \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

in matrix notation

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix}$$

$$R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The transformation matrices for the four symmetry operations.

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

Character: only for a square matrix

↳ the **sum of the # on the diagonal** from upper left to lower right

e.g.) for C_{2v} from the above operation

E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
3	-1	1	1

↳ **reducible** representation (Γ)

↳ can be reduced to **irreducible** representations

Reducible and irreducible representations

- **transformation matrix** is 'block diagonalized' → broken into smaller matrices along the diagonal

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

↑ **1x1 matrix** along the principal diagonal

- *x*, *y*, *z* coordinates are independent each other

each 1, 1 position → result of the ***x*** **coordinate**
each 2, 2 position → result of the ***y*** **coordinate**
each 3, 3 position → result of the ***z*** **coordinate**

four matrix elements for x → representation of the group
four matrix elements for y → representation of the group
four matrix elements for z → representation of the group

	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*
Γ	3	−1	1	1	

each row: **irreducible representation** → cannot simplified further

Σ of irreducible representation: **reducible representation**

Character Table:

- *A complete set of irreducible representations for a point group*
- *C_{2v} character table : the irreducible representations*

Point Group (I)	***Classes*** (III)		
IRs (II)	*Array of Characters* (IV)	*Translational and Rotational Functions* (V)	*Binomial and Polynomial Functions* (VI)

Deduction of Character Table:

The Great orthogonality theorem (GOT)

This Basic theorem is concerned with the elements of the matrices constituting irreducible representations of a group. All the properties and characters of a group representation can be derived this theorem.

Notations Used

Order of the group : h

Dimensions of i^{th} *&* j^{th} *rep:* l_i & l_j

Kronecker delta : δ_{ij} *it is equal to 1 when i = j and zero when 1* $\neq$ *j*

$\Gamma_i (R_{mn})$ $\rightarrow$ *The element in the* m^{th} *row and* n^{th} *column of the matrix corresponding to* i^{th} *irreducible representation*

For i^{th} & j^{th} *IR* Γ_i & Γ_j *of certain group, the terms of the related matrices should satisfy the equation*

$$\Sigma\, [\Gamma_i (R)_{mn}]\ \ [\Gamma_j (R)_{m'n'}]^* = h\ \ \delta_{ij}\delta_{mm'}\delta_{nn'}$$

It follows from the theorem that the sum over various operations, of the products of the elements of ***irreducible representations will be equal to zero***

1. *If the elements are chosen from different IRs(i.e., if i* $\neq$ *j).*
2. *If elements are chosen from different rows of same rep.(i.e., m* $\neq$*m')*
3. *If elements are chosen from different columns of the rep.(i.e., n* $\neq$*n')*

Five important rules about irreducible representations

1. The sum of the squares of the dimensions of the IRs of a group = the order of the group.

   $\Sigma li^2 = l_1^2 + l_2^2 + l_3^2 + \ldots\ldots\ldots\ldots = h.$

   Since the character of the identity element E is the same as the dimension of the IR, so the sum of the squares of the characters of E in a group = h.

   $\Sigma[\chi_i(E)\ ]^2 = h.$

2. The sum of the squares of the characters in any IR is equal to h.

   $\Sigma[\chi i(R)\ ]^2 = h.$

3. The characters of two different IRs are orthogonal.

   $\Sigma\ \chi_i(R)\ \chi_j(R) = 0$

4. In a given representation characters of the elements belonging to the same class are identical.

5. The No. of IRs =No. of classes.

Construction of C_{2V} character table.

There are 4 elements E, $C_2(z)$, $\sigma_v(xz)$, $\sigma_v'(yz)$. : *Each element is in a class by itself.*

Assumption 1: No. of IRs = No. of classes (Rule 5) = 4.

Let l_1, l_2, l_3 and l_4 are the dimensions of the four IRs, say Γ_1, Γ_2, Γ_3 & Γ_4 .

We know, $\Sigma l_i^2 = h$ (Rule-1) = 4.

i.e., $l_1^2+l_2^2+l_3^2+ l_4^2 = 4$.

Since l_i can't be zero or negative the only solution is

$l_1=l_2=l_3=l_4= 1$. i.e., all the IRs are 1D

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_1	1	1	1	1
Γ_2	1	a	b	c
Γ_3	1	d	e	f
Γ_4	1	g	k	m

Assumption 2: A totally symmetric representations with characters equals to 1 should be included in the group : *There would be one one 1D IR say Γ_1, which would be totally symmetric.*

Assumption 3: The sum of the squares of the dimensions of the IRs of a group = the order of the group.

$\Sigma[\chi_i(E)]^2 = h. = 4$

Γ_1 already satisfies this rule i.e., $1^2+1^2+1^2+1^2=4$.

For others we may write

$1^2+ a^2 + b^2 + c^2 = 4$

$1^2 + d^2 + e^2 + f^2 = 4$

$1^2 + g^2 + k^2 + m^2 = 4$

This is possible only if a , b, c .....have values either 1 or -1

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_1	1	1	1	1
Γ_2	1	a	b	c
Γ_3	1	d	e	f
Γ_4	1	g	k	m

Assumption 4: According to orthogonality rule

$\Sigma\, g_i\, \chi_i(R)\, \chi_j(R) = 0$ when $i \neq j$

So among Γ_2, Γ_3, & Γ_4 each has to be orthogonal to Γ_1

i.e., 1.1 + 1.a + 1.b + 1. c = 0

1.1 + 1.d + 1.e + 1. f = 0

1.1 + 1.g + 1.k + 1. m = 0

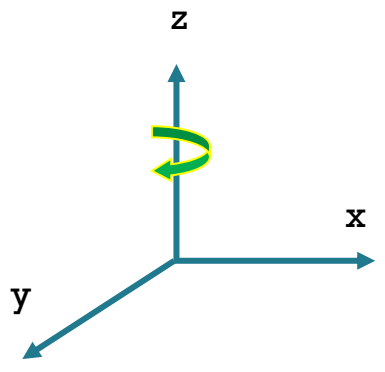
This is possible only if there are two +1 and two -1 in each of Γ_2, Γ_3, & Γ_4

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
x	1	-1	1	-1
y	1	-1	-1	1
z	1	1	1	1

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$	
Γ_1	1	1	1	1	z
Γ_2	1	1	-1	-1	
Γ_3	1	-1	1	-1	x
Γ_4	1	-1	-1	1	y

The R_x, R_y & R_z indicate the transformation of rotational motion of the molecule about x , y & z axis.



Let us find out the character of rotation R_z; the rotation may be represented by a curved. arrow about the z axis.

E - the arrow is unaffected character is 1

C_2 (z) - it is unaffected- character is 1

σ_v(xz) -the Left side of arrow move towards right side and vice-versa.
Hence the character is -1.

σ_v'(yz) – Same as σ_v(xz). So Character is -1.
1,1,-1,-1 is related to the IR Γ_2.

Similarly rotation about the x and y axis(Rx & Ry) transforms as Γ_4 & Γ_3 respectively.

C_{2v}	E	C_2(z)	σ_v(xz)	σ_v'(yz)	
Γ_1	1	1	1	1	z
Γ_2	1	1	-1	-1	Rz
Γ_3	1	-1	1	-1	X, Ry
Γ_4	1	-1	-1	1	Y, Rx

Binary products x, y & z including squares and their linear combinations

C_{2v}	E	C_2(z)	σ_v(xz)	σ_v'(yz)
x	1	-1	1	-1
y	1	-1	-1	1
z	1	1	1	1

C_{2v}	E	C_2(z)	σ_v(xz)	σ_v'(yz)		
Γ_1	1	1	1	1	z	x^2, y^2, z^2
Γ_2	1	1	-1	-1	Rz	xy
Γ_3	1	-1	1	-1	X, Ry	xz
Γ_4	1	-1	-1	1	Y, Rx	yz

C_{3v}

We know that $\sum[g_i\chi_i(R)]^2 = h = 6$.
Γ_1 already satisfy this rule → $1^2 + 2x1^2 + 3x1^2 = 6$.
For Γ_2 → $1^2 + 2a^2 + 3b^2 = 6$
To satisfy this a & b should be either 1 or -1.
According to Orthogonality rule,
i.e., $\sum g_i\chi_i(R)\ \chi_{j(R)} = 0$ when $i \neq j$
So for Γ_1 & Γ_2 → *1 x 1 + 2 x 1 x a + 3 x 1 x b = 0*
1 + 2a + 3b = 0
This would be possible only if value of a = 1 & b = -1

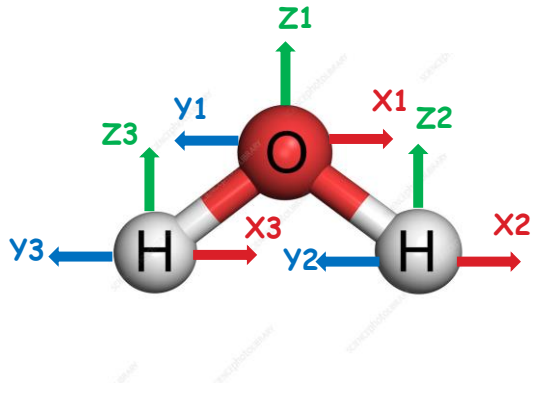
For Γ_1 & Γ_3 → *1 x 2 + 2 x 1 x c + 3 x 1 x d = 0*
2 + 2c + 3d = 0 ***2c + 3d = -2 .....(1)*** ***For Γ_2 & Γ_3 →*** *1x 2 + 2 x 1 x c + 3 x -1 x d = 0*
2 + 2c - 3d = 0 *2c – 3d = -2 .....(2)*
(1) + (2) *4c = -4 c = -1. Putting c = -1 in eqn (1) -2 + 3d = -2 3d = 0 d = 0*

C_{3v}	E	$2C_3$	$3\sigma_v$		
Γ_1	1	1	1	z	$x^2 + y^2$, z^2
Γ_2	1	1	-1	Rz	
Γ_3	2	-1	0	x, y, Rx, Ry	x^2-y^2, xy,xz,yz

C_3	E	C_3	C_3^2		
Γ_1	1	1	1	z, Rz	$x^2 + y^2$, z^2
Γ_2	1	ε	ε^*		
Γ_3	1	ε^*	ε		

Transition Probabilities of Infra Red & Raman Spectroscopy

- 3N Degrees of freedom
- 3 translation. } From Character Table
- 3 rotation.
- 3N-6 vibrational degrees of freedom.
- 3N-5 for linear molecule.
- Only Vibrations with change in dipole moment is infra red active.
- Raman activity is associated with polarization of molecule. Only vibrations which bring about change in polarization will be Raman active.



CALCULATION OF TOTAL CHARACTER.

The three degrees of freedom of each atom in a molecule may be represented by three mutually perpendicular arrows- x, y, & z.

These 3N vectors may be taken as the basis for evaluating the total character.

If we subtract the characters relating to the translational and rotational degrees of freedom from the above total character, we will get the character relating to vibrational degrees of freedom.

Take H2O as example.

Point group : C_{2v}

Elements : E, C_2, σ_v & σ_v'

The basis vectors are $x_1,y_1,z_1,x_2,y_2,z_2,x_3,y_3$ &z_3.

The transformation of these vectors give 9-D matrices.

During the operation the vectors x_1,y_1….changes to x_1',y_1'….

During the operation **E**, all the vectors are retained, i.e., $X_1'=x_1,y_1'=y_1$etc

$$\begin{bmatrix}1&0&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&0&1\end{bmatrix}\begin{bmatrix}x1\\y1\\z1\\x2\\y2\\z2\\x3\\y3\\z3\end{bmatrix}=\begin{bmatrix}x1'\\y1'\\z1'\\x2'\\y2'\\z2'\\x3'\\y3'\\z3'\end{bmatrix}$$

The operation σ_v' bring about the following changes

$x_1 \rightarrow -x_1'$; $y_1 \rightarrow y_1'$; $z_1 \rightarrow z_1'$; $x_2 \rightarrow -x_2'$; $y_2 \rightarrow y_2'$; $z_2 \rightarrow z_2'$; $x_3 \rightarrow -x_3'$; $y_3 \rightarrow y_3'$ and $z_3 \rightarrow z_3'$

$$\begin{bmatrix}-1&0&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&0&1\end{bmatrix}\begin{bmatrix}x1\\y1\\z1\\x2\\y2\\z2\\x3\\y3\\z3\end{bmatrix}=\begin{bmatrix}x1'\\y1'\\z1'\\x2'\\y2'\\z2'\\x3'\\y3'\\z3'\end{bmatrix}$$

The operation C_2 bring about the following changes

- $x_1 \rightarrow x_3'$; $y_1 \rightarrow -y_3'$; $z_1 \rightarrow z_3'$; $x_2 \rightarrow -x_2'$; $y_2 \rightarrow -y_2'$; $z_2 \rightarrow z_2'$; $x_3 \rightarrow -x_1'$; $y_3 \rightarrow -y_1'$ and $z_3 \rightarrow z_1'$

$$\begin{bmatrix}0&0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&0&1\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&-1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\-1&0&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\end{bmatrix}\begin{bmatrix}x1\\y1\\z1\\x2\\y2\\z2\\x3\\y3\\z3\end{bmatrix}=\begin{bmatrix}x1'\\y1'\\z1'\\x2'\\y2'\\z2'\\x3'\\y3'\\z3'\end{bmatrix}$$

The operation σ_v bring about the following changes

- $x_1 \rightarrow x_3'$; $y_1 \rightarrow -y_3'$; $z_1 \rightarrow z_3'$; $x_2 \rightarrow x_2'$; $y_2 \rightarrow -y_2'$; $z_2 \rightarrow z_2'$; $x_3 \rightarrow x_1'$; $y_3 \rightarrow -y_1'$ and $z_3 \rightarrow z_1'$

$$\begin{bmatrix}0&0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&0&1\\0&0&0&1&0&0&0&0&0\\0&0&0&0&-1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\1&0&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\end{bmatrix}\begin{bmatrix}x1\\y1\\z1\\x2\\y2\\z2\\x3\\y3\\z3\end{bmatrix}=\begin{bmatrix}x1'\\y1'\\z1'\\x2'\\y2'\\z2'\\x3'\\y3'\\z3'\end{bmatrix}$$

Reducible Representation-

- A representation of a symmetry operation of a group, which **CAN** be expressed in terms of a representation of lower dimension.
- **CAN** be broken down into a simpler form.
- Characters **CAN** be further diagonalized.
- Are composed of several irreducible representations.

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

Irreducible Representation-

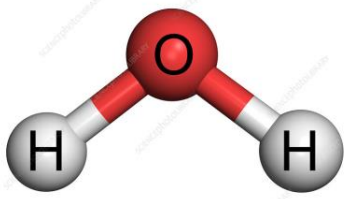
- A representation of a symmetry operation of a group, which **CANNOT** be expressed in terms of a representation of lower dimension.
- **CANNOT** be broken down into a simpler form.
- Characters **CANNOT** be further diagonalized.

Thus the total representation taking the nine vectors on the three atoms on the water as the basis.

C_{2v}	E	C_2	σ_v	σ_v'
Γ	9	-1	1	3

Another easy method to determine total character.

Only that atom which retain position contribute to total character. In such atoms, each vector which retain direction contribute 1 and each vector which reverse direction contribute -1.



C_{2v}	E	C_2	σ_v	σ_v'
NUSA	3	1	1	3
χ_{cart}	3	-1	1	1
$\Gamma_{cart\ (3N)}$	**9**	**-1**	**1**	**3**

REDUCTION FORMULA

$$n(i) = \frac{1}{h}\sum_R \chi_r(R)\,\chi_i(R)$$

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

$n_{(i)}$ = Number of times the ith irreducible representation occurs in the representation r that we are aiming to reduce.

h = Order of group

$\sum$ = This denotes a summation over all the operations R in the group. If there is more than one operation in a given class we must remember to include each operation in the summation.

$\chi_{r\,(R)}$ = Character of the reducible representation r under the symmetry operation R.

$\chi_{i\,(R)}$ = Character of the irreducible representation i under the symmetry operation R.

Reducible Representation

$\Gamma = A_1 + B_1 + B_2$

Irreducible Representations