

SYMMETRY IN CHEMISTRY

Professor MANOJ K. MISHRA

CHEMISTRY DEPARTMENT

IIT BOMBAY

ACKNOWLEDGEMENT:

Professor David A. Micha

Professor F. A. Cotton

WHY SYMMETRY ?

$$H\psi = E\psi$$

For H - atom: $H(\vec{r}) \psi_{n,l,m,m_s}(\vec{r}) = E_n \psi_{n,l,m,m_s}(\vec{r})$

$$CSCO = [H, l^2, l_z, s^2, s_z] \text{ i.e. } [H, l^2] = 0, \text{ etc}$$

$$[H, l^2] = 0 \Rightarrow H l^2 = l^2 H$$

Each member of the CSCO labels, ψ

$$H \rightarrow n, \quad l^2 \rightarrow l, \quad l_z \rightarrow m, \quad s^2 \rightarrow s = \frac{1}{2}, \quad s_z = m_s = \pm \frac{1}{2} \alpha/\beta$$

$$\text{and } \int \psi_{n'l'm's'}^* \psi_{nlmms} d\tau = \delta_{nn'} \delta_{ll'} \delta_{mm'} \delta_{ms ms'}$$

For molecules: Symmetry operation $\mathbf{R} \in CSCO$

$$[H, R] = 0 \Rightarrow HR = RH \text{ or } R^{-1}HR = H$$

H is INVARIANT under \mathbf{R} (by definition too)

H $\psi = \mathbf{E}\psi$ gives ψ^Γ where Γ incorporates the effect of $\forall R \in CSCO$

$$\int \psi^{\Gamma\alpha} \psi^{\Gamma\beta} d\tau = \delta_{\alpha\beta}$$

e.g. for NH₃: C_{3v} {A₁A₂ E}

$$\psi_{NH_3}^{electronic} = \psi_{NH_3}^{A_1}, \psi_{NH_3}^{A_2}, \psi_{NH_3}^E,$$

$$NH_3 \text{ normal modes} = A_1 \oplus A_2 \oplus E$$

NH₃ rotation or translation **MUST** be *A₁, A₂ or E!*

NO ESCAPING SYMMETRY!

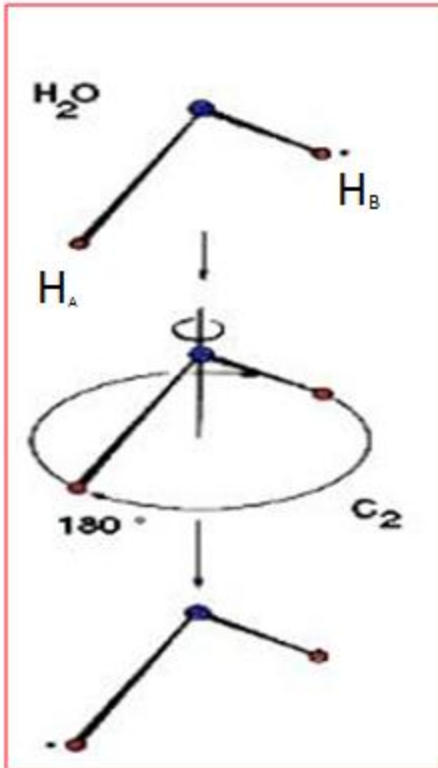
Molecular Symmetry

(Ref.: Inorganic chemistry by Shirver, Atkins & Longford, ELBS)

One aspect of the shape of a molecule is its symmetry (we define technical meaning of this term in a moment) and the systematic treatment and symmetry uses group theory. This is a rich and powerful subject, by will confine our use of it at this stage to classifying molecules and draw some general conclusions about their properties.

❖ An introduction to symmetry analysis

❖ Our initial aim is to define the symmetry of molecules much more precisely than we have done so far, and to provide a notational scheme that confirms their symmetry. In subsequent chapters we extend the material present here to applications in bonding and spectroscopy, and it will become that symmetry analysis is one of the most pervasive techniques in inorganic chemistry.



❖ Symmetry operations and elements

A fundamental concept of group theory is the symmetry operation. It is an action, such as a rotation through a certain angle, that leave molecules apparently unchanged. An example is the rotation of H_2O molecule by 180° (but not any smaller angle) around the bisector of HOH angle. Associated with each symmetry operation there is a symmetry element; this is a point, a line, or a plane with respect to which symmetry operation is performed. The most important symmetry operation and their corresponding elements are listed in table 2.6.

All operations leaves at least one point of the molecule unmoved, just as rotation of a sphere leaves its center unmoved. Hence they are operations of point-group symmetry. The identity operation E leaves whole molecule unchanged.

Fig.2.5. An H_2O molecule may be rotated through any angle about the bisector of the HOH bond angle, but only a rotation of 180° , C_2 , leaves it apparently unchanged.

The rotation of an H₂O molecule by 180° (n = 2) around a line bisect the HOH angle is a symmetry operation, so the H₂O molecule possess two-fold rotation axis C₂ (fig. 2.5). In general, an n-fold rotation symmetry operation if the molecule appears unchanged after rotation 360°/n. The corresponding symmetry element is a line, the n-fold rotational axis C_n, about which the rotation is performed. The triangular pyramid NH₃ molecule has a three-fold rotation axes, denoted C₃, but there are operations associated with it, one a rotation by 120° and the other a rotation through twice this angle (Fig. 2.6). The two operations are denoted C₃ and C₃². We do not need to consider C₃³, a rotation through 3x 120° = 360°, since it is equivalent to the identity.

Table 2.6. Important symmetry operations and symmetry elements

Symmetry element	Symmetry operation	Symbol
	Identity*	<i>E</i>
N-fold symmetry axis	Rotation by 2π/n	<i>C_n</i>
Mirror plane	Reflection	<i>σ</i>
Center of inversion	Inversion	<i>i</i>
N-fold axis of improper rotation‡	Rotation by 2π/n followed by reflection perpendicular to rotation axis	<i>S_n</i>

*The symmetry element can be thought of as the molecule as a whole.

‡Note the equivalences $S_1 = \sigma$ and $S_2 = i$.

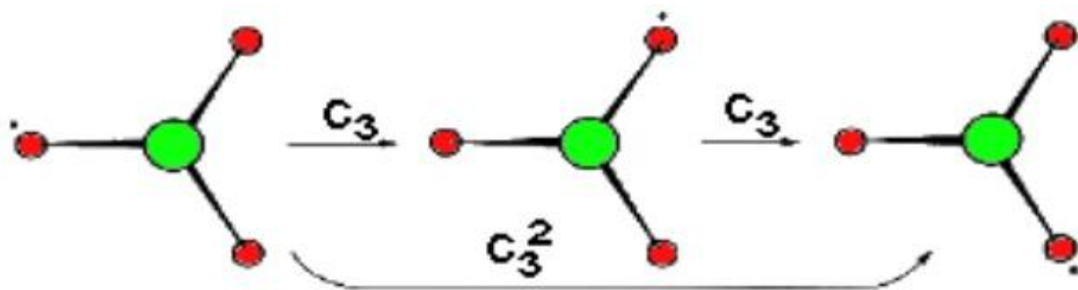


Fig. 2.6. A three-fold rotation and the corresponding C_3 axis in NH_3 . There are two rotations associated with this axis. One through 120° (C_3) and the other through 240° (C_3^2).

The reflection of an H_2O molecule in either of the two planes shown in Fig. 2.7 is a symmetry operation: corresponding symmetry element is a mirror plane σ . The H_2O molecule has two mirror planes which intersect at the bisector of the HOH angle. Because the planes are vertical (in the sense of being parallel to the rotational axis of the molecule), they are labeled σ_v and σ_v' . The C_6H_6 molecule has a mirror plane σ_h in the plane of the molecule.

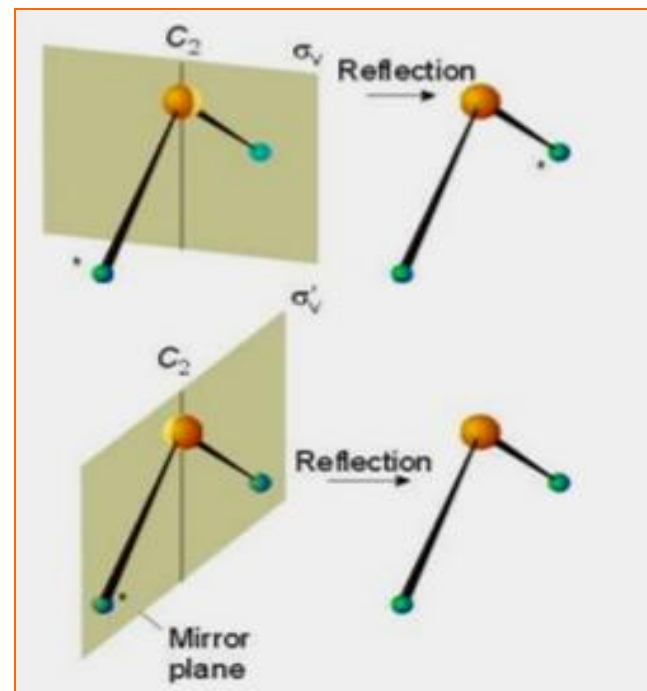


Fig. 2.7. The two vertical mirror planes σ_v and σ_v' in H_2O and the corresponding operations. Both planes cut through the C_2 axis.

The 'h' signifies that the plane is horizontal in the sense that the principal rotational axis of the molecule is perpendicular to it. This molecule also has two more sets of three mirror planes that intersect the six-fold axis (Fig. 2.8). In such cases, the members of one set are called vertical and the members of the other are called dihedral. The symmetry elements (and the associated operations) are denoted σ_v and σ_d respectively.

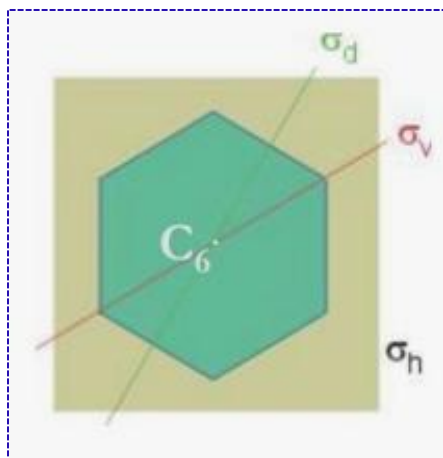


Fig. 2.8. Some of the symmetry elements of the benzene ring. There is one horizontal reflection plane (σ_h) and two sets of vertical reflection plane (σ_v and σ_d); one example of each is shown.

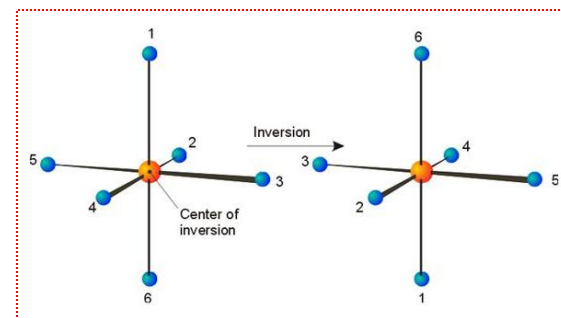


Fig. 2.9. The inversion operation and the center of inversion (i) in SF_6

The inversion operation consists of imagining that each point of the molecules is taken through a single center and projected an equal distance on the other side (Fig. 2.9). The symmetry element is the center of inversion (i), the point through which projection is made. An N_2 molecule has a center of inversion midway between the two nitrogen nuclei. The H_2O molecule does not possess this element, but a benzene molecule and a sulfur hexafluoride molecule both do. In due course we shall see the importance of recognizing that an octahedron has a center of inversion but that a tetrahedron does not.

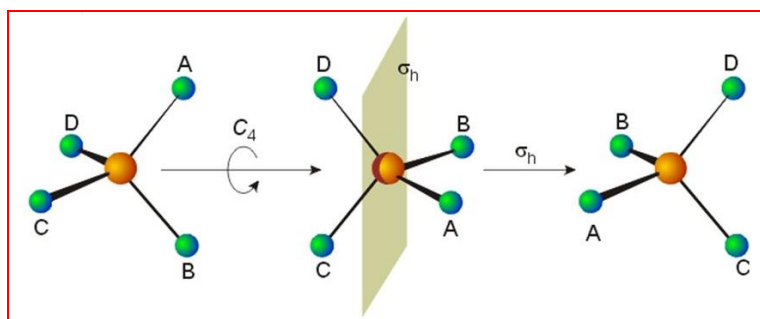


Fig. 2.10 A four fold axis of improper rotation S_4 in the CH_4 molecule A=1, B=2, C=3, &D=4.

The operation of improper rotation is composite: it consist of a rotation followed by a reflection in the plane perpendicular to the axis of rotation. Fig. 2.10 shows a fourfold improper rotation of a tetrahedral CH_4 molecule: in this case, the operation consists of a 90° rotation about an axis bisecting two HCH bond angles followed by a reflection through a plane perpendicular to the rotation axis.

Neither the operation C_4 nor the reflection σ_h alone is a symmetry operation for CH_4 , but their products $C_4 \times \sigma_h$ is a symmetry operation, the improper rotation S_4 . The symmetry element, the improper rotation axis S_n (S_4 in the example), is the corresponding combination of an n -fold rotational axis and a perpendicular to the mirror plane. The only S_n axes that exist are those for $n = 1$ and $n = 2, 4, 6, \dots$. Moreover, S_1 is equivalent to a horizontal reflection σ_h and S_2 is equivalent to the inversion (i) (Fig. 2.11).

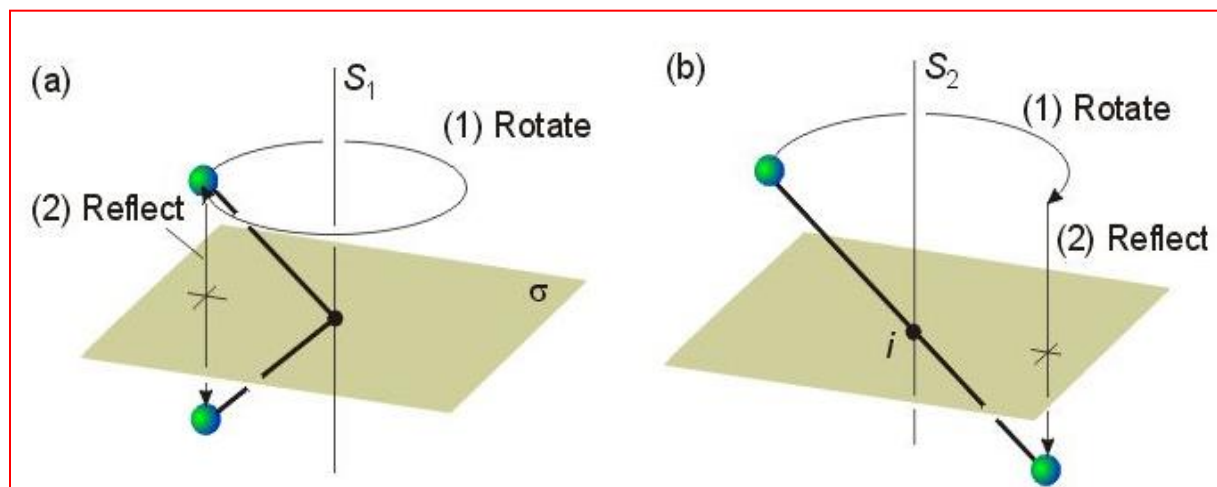


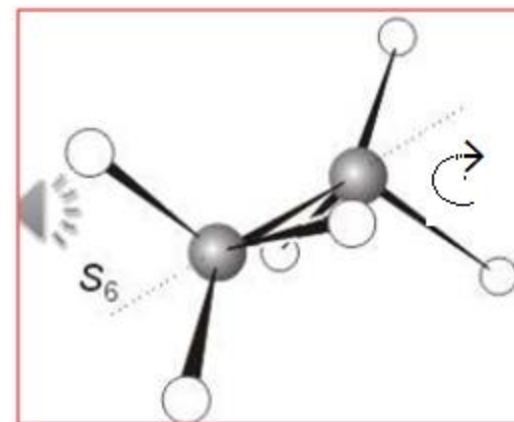
Fig. 2.11 (a) An S_1 axis is equivalent to a mirror plane and (b) an S_2 axis is equivalent to a center of inversion.

Example 2.6: Identifying a symmetry element

Q. Which conformation of CH_3CH_3 molecule has an S_6 axis ?

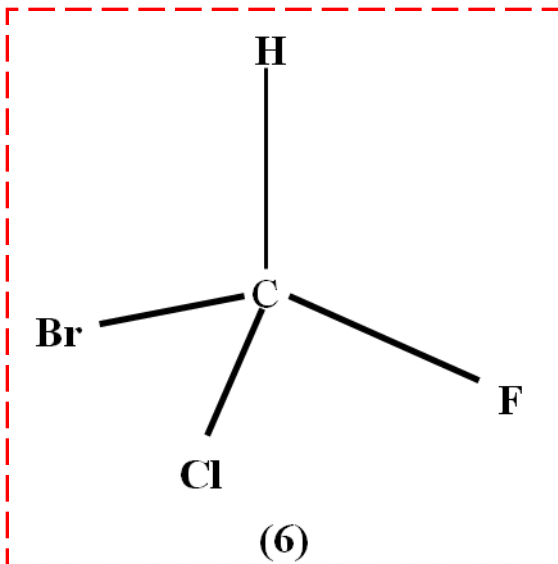
Answer: We need to find a conformation that leaves the molecule looking the same after a 60° rotation followed by a reflection in a plane perpendicular to that axis. The conformation and axis are shown in (5); this is the staggered conformation of the molecule, and also the one of lowest energy.

Exercise: Identify a C_3 axis of an NH_4^+ ion. How many of these axes are there in the ion?



The point groups of molecules

The symmetry elements possessed by molecules determine the point group to which they belong. Assigning a molecule to a particular group depends on making a list of symmetry elements it possesses and then comparing it with the list that is characteristic of each point group.



For example, if a molecule has only the identity element (CHBrClF is an example), we list its elements as E and look for the group that has only this one. In fact, the group called C_1 is the group with only the element E , so the CHBrClF (6) molecule belongs to that group. The molecule CH_2BrCl belongs to a slightly richer group: it has the elements E (all groups have that element) and a mirror plane. The group of elements E, σ is called C_s , so the CH_2BrCl molecule belongs to that group. This process can be continued, with molecules being assigned to the group that matches the symmetry elements they possess. Some of the more common groups and their names are listed in Table 2.7. Assigning a molecule to its group depends on listing the symmetry elements it possesses and then referring to the table. However, it is often easier to work through the tree in Fig. 2.12 and to arrive at the correct point group by answering the questions at each decision point on the correct point on the chart. (Note that we need to be careful to distinguish the names of the groups, C_2 , and so on. From the symbols for the symmetry elements, such as C_2 , and the corresponding operations, also C_2 . The context will always make it clear what interpretation is intended.)

Table 2.7: The composition of some common groups

Point group	Symmetry elements	Examples
C_1	E	SiBrClFI
C_2	E, C_2	H_2O_2
C_s	E, σ	NHF_2
C_{2v}	E, C_2 , $2\sigma_v$	H_2O , SO_2Cl_2
C_{3v}	E, C_2 , $3\sigma_v$	NH_3 , PCl_3 , $POCl_3$
$C_{\infty v}$	E, C_{∞}	CO, HCl, OCS
D_{2h}	E, $3C_2$, $2\sigma_v$, σ_h , i	N_2O_4 , B_2H_6
D_{3h}	E, C_3 , $3C_2$, $3\sigma_v$, σ_h	BF_3 , PCl_5
D_{4h}	E, C_4 , C_2 , i, S_4 , σ_h ,	XeF_4 , trans- MA_4B_2
$D_{\infty h}$	E, C_{∞} , $\infty\sigma_v$,	H_2 , CO_2 , C_2H_2
T_d	E, $3C_2$, $4C_3$, 6σ , $3S_4$	CH_4 , $SiCl_4$
O_h	E, $6C_2$, $4C_3$, $4S_6$, $3S_4$, i,	SF_6

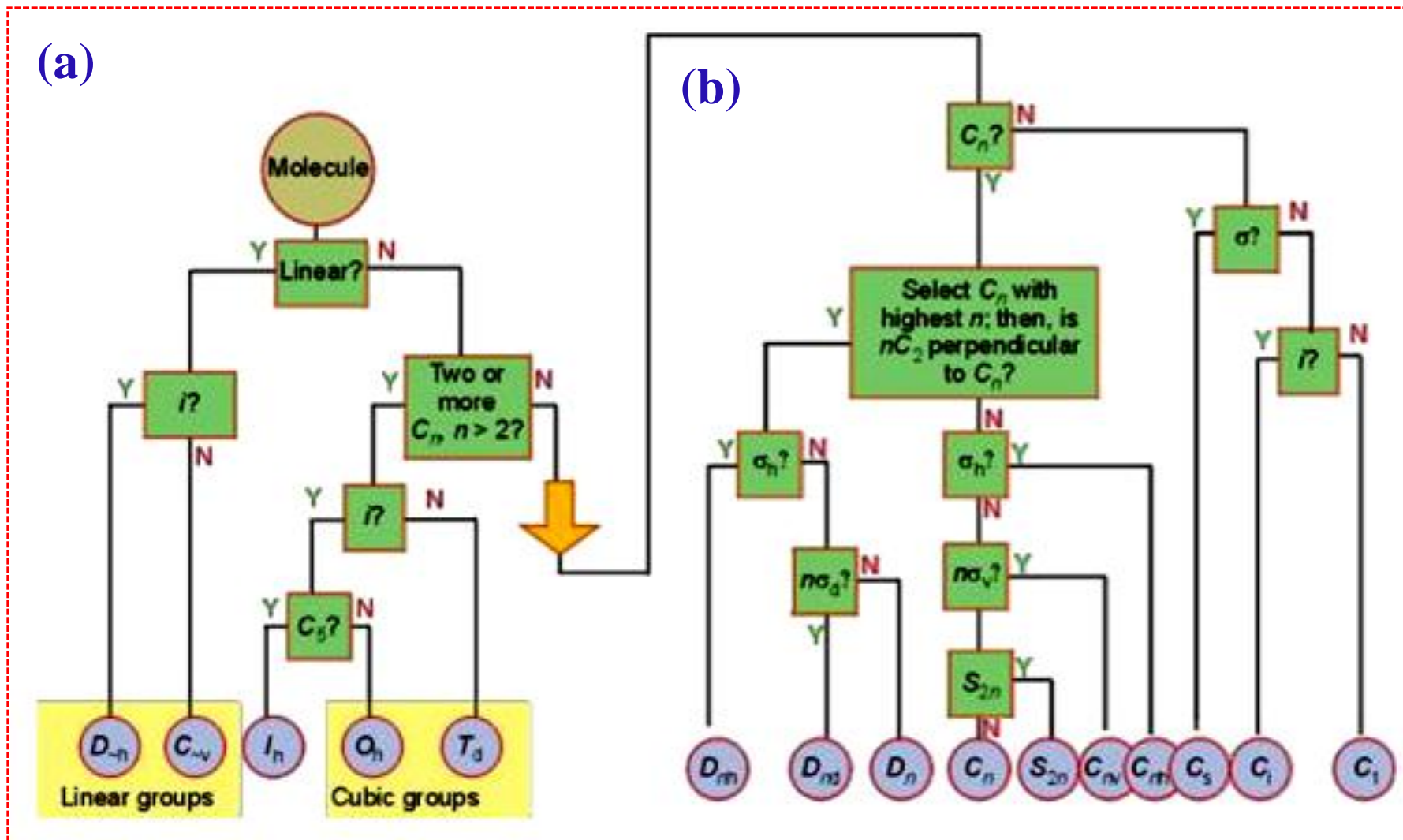


Fig. 2.12: The decision tree for identifying a molecular point group. After passing through part (a), go to part (b) if necessary.

Example 2.7: Identifying the point group of a molecule

To what point groups do H₂O and NH₃ belong?

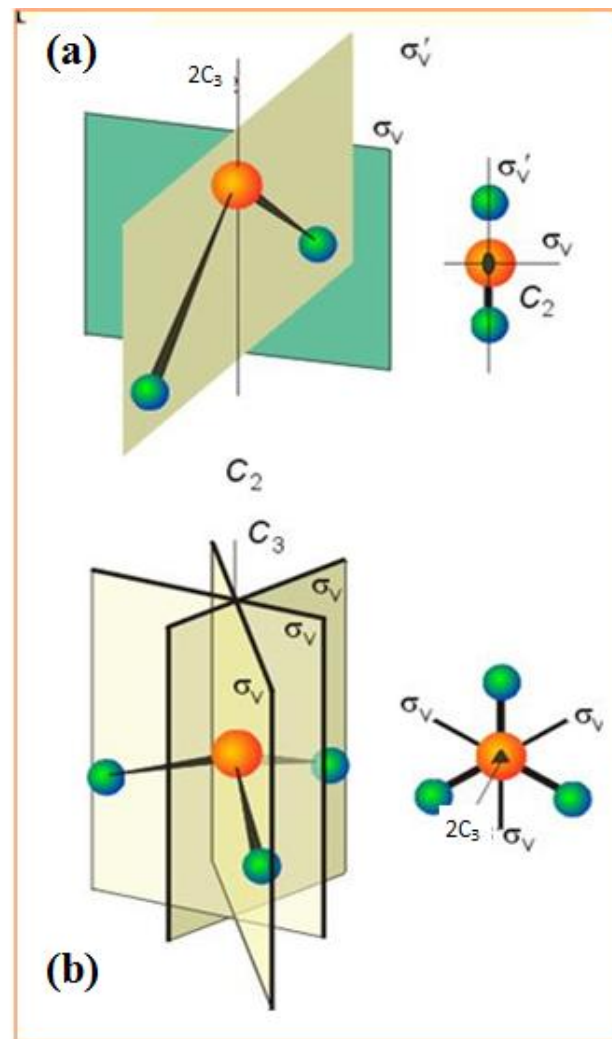
Answer: The symmetry elements are shown in Fig. 2.13.

(a) H₂O possesses the identity (*E*), a two fold rotation axis (*C*₂), and two vertical mirror planes (2*σ*_v). The set of elements (*E*, *C*₂, 2*σ*_v) corresponds to the group *C*_{2v}.

(b) NH₃ possesses the identity (*E*), a three fold rotation axes (*C*₃), and three vertical mirror planes (3*σ*_v). The set of elements (*E*, *C*₃, 3*σ*_v) corresponds to the group *C*_{3v}.

Exercise: Identify the point groups of (a) BF₃, a trigonal planar molecule and *D*_{3h} (b) the tetrahedral SO₄²⁻ ion (*T*_d).

Fig. 2.13: The symmetry elements of (a) H₂O and (b) NH₃. The diagrams on the right are views from above and summarize the diagrams to their left.



Linear molecules with a center of symmetry (H_2 , CO_2 , C_2H_2 ,) (7) belong to the point group $D_{\infty h}$. A molecule that is linear but has no center of symmetry (HCl , OCS , NNO ,) (8) belongs to the point group $C_{\infty v}$.

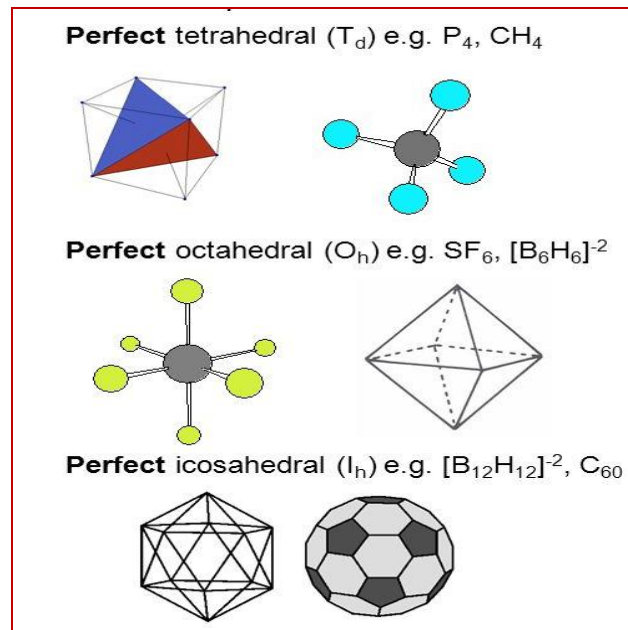
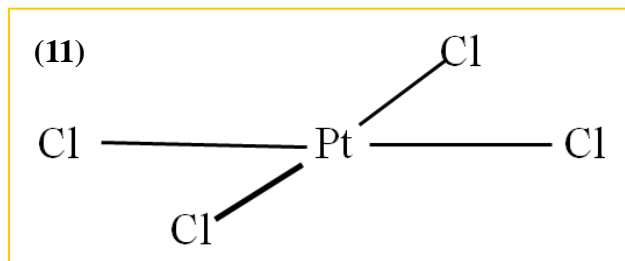
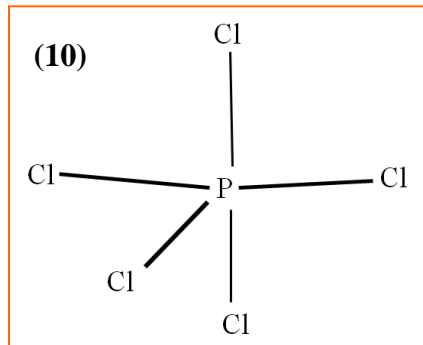
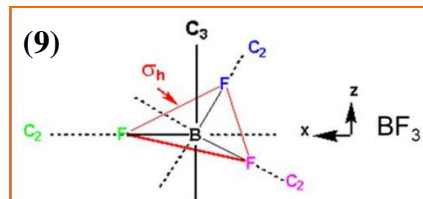
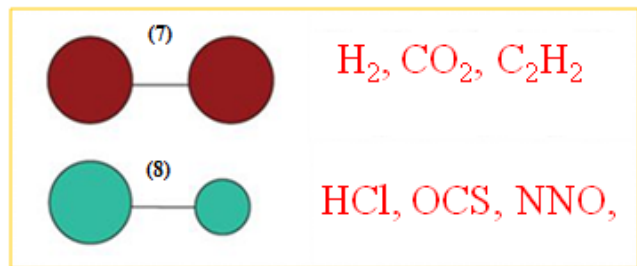
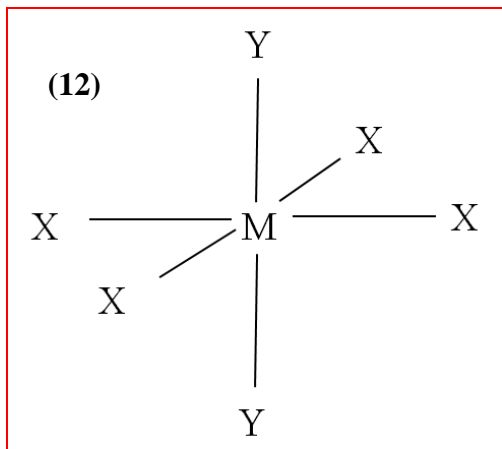
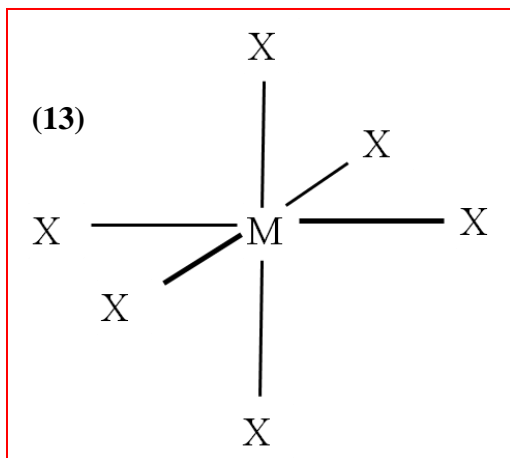


Fig. 2.14: shapes with the symmetries of the groups (a) T_d (b) O_h and (c) I_h . They are all closely related to the symmetries of a cube.

Tetrahedral (T_d) and octahedral (O_h) molecules (Fig. 2.14), which are of great importance in coordination chemistry, have more than one principal axis of symmetry: a tetrahedral CH_4 molecule, for instance, has four C_3 axes, one along each C-H bond. A closely related group, the icosahedral group (I_h) characteristic of the icosahedron (Fig. 2.14c), is important for boron compounds. The three groups are quite easy to recognize: a regular tetrahedron has four equilateral triangles for its faces, an octahedron has eight, and an icosahedron has 20.



For our present purposes, the most important groups are C_{2v} and C_{3v} and the tetrahedral and octahedral groups. We shall also sometimes encounter $C_{\infty v}$ and $D_{\infty h}$ for linear molecules, D_{3h} for trigonal planar molecules (such as BF_3 , 9) and trigonal bipyramidal molecules such as PCl_5 , 10), and D_{4h} for square-planar molecules (11) and octahedral molecules with two substituents opposite to each other, as in (12). This last example shows that the point group classification of molecule is more precise than the casual use of the term octahedral or tetrahedral. For instance, a molecule may loosely be called octahedral even if it has six different groups attached to the central atom. However, it only belongs to the octahedral point group O_h , if all six groups are identical (13)



GROUP

Consider a set $S = \{A, B, C, D, E, F\}$

The set S is classified as a GROUP (iff)

1. Identity element E is in this set i.e. $\exists E \ni EA = AE = A \forall A \in S$

2. $\forall A \in S \exists A^{-1} \ni AA^{-1} = A^{-1}A = E \& A^{-1} \in S$

3. If $A \& B \in S \& AB = C \& BA = D$

then $C \& D$ must also be $\in S$

i.e. S is CLOSED under multiplication

4. Association Law holds, i.e. $A(BC) = (AB)C$

Order: The number of elements in a group (G) is called the **ORDER** of the group.

e.g., if S is a Group, its order $h = 6$

Subgroup: If a smaller sub set of elements of a Group fulfills all the group requirements (1-4 above), then, this subset is called a **SUBGROUP** of that Group.

CLASS: For $A \& B \in G$, if $\exists X \in G$

$$\ni A = X^{-1}BX$$

Then $A \& B$ are said to belong to the same **CLASS**

GROUP MULTIPLICATION TABLE

Operation A

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

$$\left. \begin{array}{l} A = \sigma_v \\ B = \sigma_v' \end{array} \right\} \rightarrow AB = C_2 = BA$$

$$E(x, y, z) = (x, y, z)$$

$$C_p(r, \theta, z) = (r, \theta + \frac{2\pi}{p}, z)$$

$$\sigma_{xz}(x, y, z) = (x, -y, z)$$

$$i(x, y, z) = (-x, -y, -z)$$

-
- (i) C_{2v} is ABELIAN
 - (ii) 4 classes
 - (iii) 4 irreps
 - (iv) Subgroups
 $\{EC_2\}$ $\{E, \sigma_v\}$
 $\&\{E, \sigma_v'\}$

$C_3\sigma_1 \neq \sigma_1 C_3$

C_{3v}	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^2	E

- (i) C_{3v} is not abelian
- (ii) 3 Classes $\{E\}, \{C_3, C_3^2\}, \{\sigma_1, \sigma_2, \sigma_3\}$
- (iii) 3 irreps
- (iv) 4 subgroups $\{E, C_3, C_3^2\}, \{E, \sigma_1\}, \{E, \sigma_2\}$ & $\{E, \sigma_3\}$

of irreps

$$\sum_{i=1} l_i^2 = h$$

Each irrep furnishes l_i^2 vectors

ABELIAN GROUP

If $\forall A, B \in G : AB = BA$ then G is Abelian.

For an Abelian group EACH element is in a CLASS by ITSELF.

Proof: $X^{-1}AX = X^{-1}XA = A$

$\therefore A$ is in a class by itself

Illustration : $C_{2v} \{E, C_2, \sigma_v(xz), \sigma_v^1(yz)\}$

$$E(x, y, z) = (x, y, z)$$

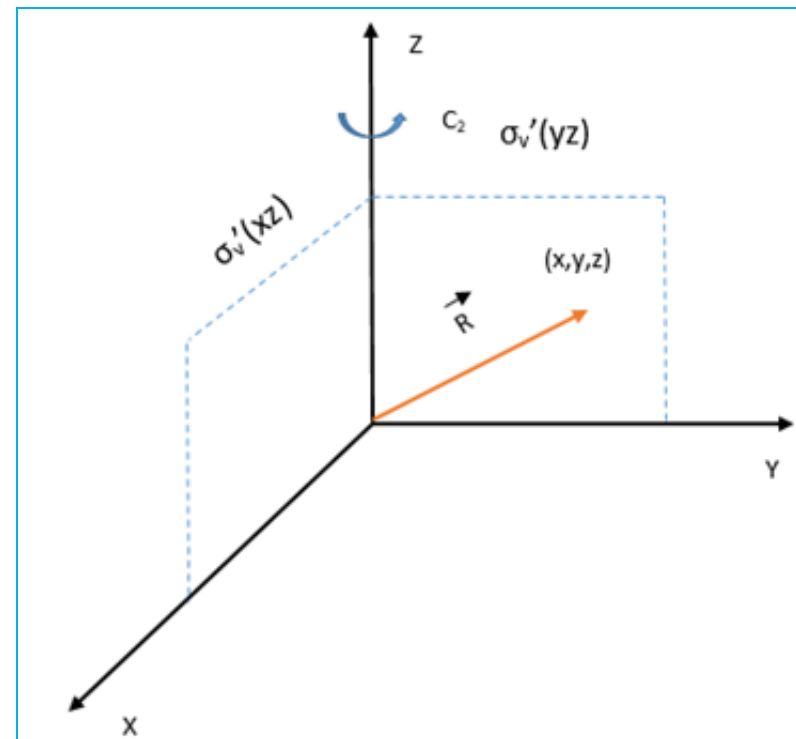
$$C_2(x, y, z) = (-x, -y, z)$$

$$\sigma_v(x, y, z) = (x, -y, z)$$

$$\sigma_v^1(x, y, z) = (-x, y, z)$$

$$\begin{aligned} C_2\sigma_v(x, y, z) &= C_2\{\sigma_v(x, y, z)\} \\ &= C_2(x, -y, z) \\ &= (-x, y, z) \\ &= \sigma_v^1(x, y, z) \end{aligned}$$

$$\therefore C_2\sigma_v = \sigma_v^1$$



Similarly, $\sigma_v C_2 (x, y, z) = \sigma_v (-x, -y, z) = (-x, y, z) = \sigma_v^{-1} (x, y, z)$

or $\sigma_v C_2 = \sigma_v^{-1} = C_2 \sigma_v$

$\therefore \sigma_v C_2 = C_2 \sigma_v$

Similarly, $C_2 \sigma_v^{-1} = \sigma_v^{-1} C_2 = \sigma_v$ and $\sigma_v \sigma_v^{-1} = \sigma_v^{-1} \sigma_v = C_2$

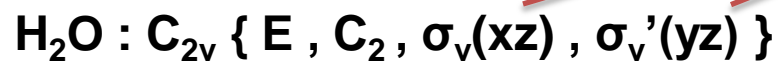
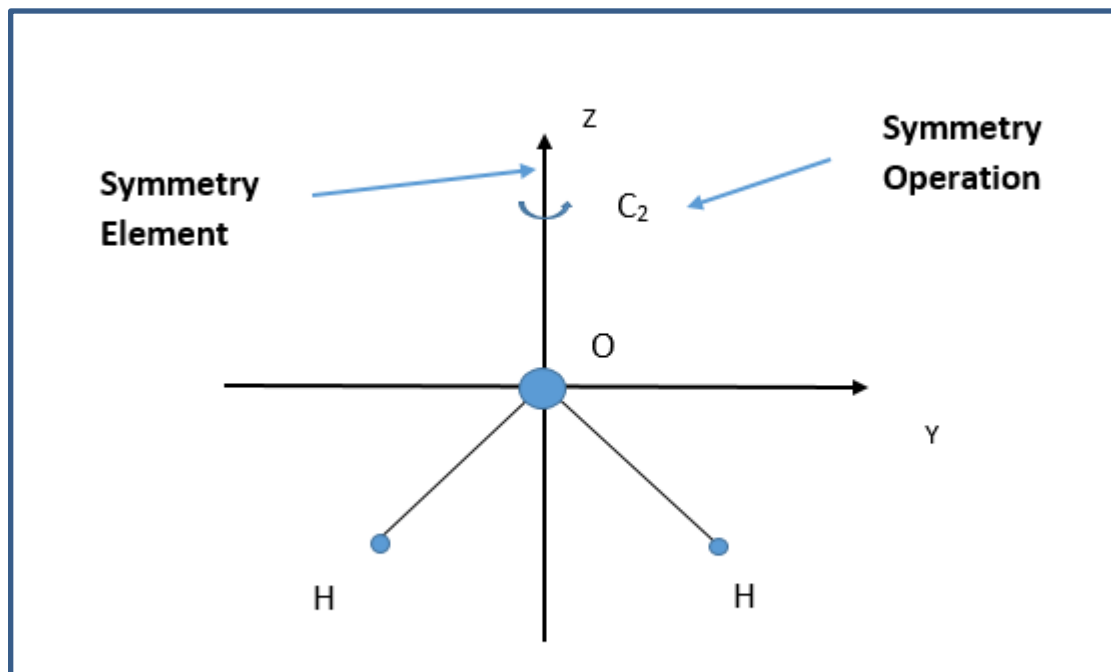
→(SHOW)←

$\therefore C_{2v}$ is ABELIAN. Is every element in a class by itself?

$C_2^2 (x, y, z) = C_2 C_2 (x, y, z) = C_2 (-x, -y, z) = (x, y, z) = E (x, y, z)$

$\therefore C_2 C_2 = E \Rightarrow C_2^{-1} = C_2$

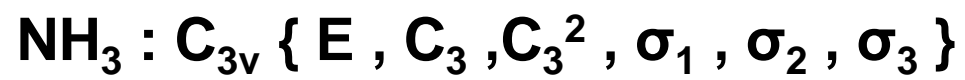
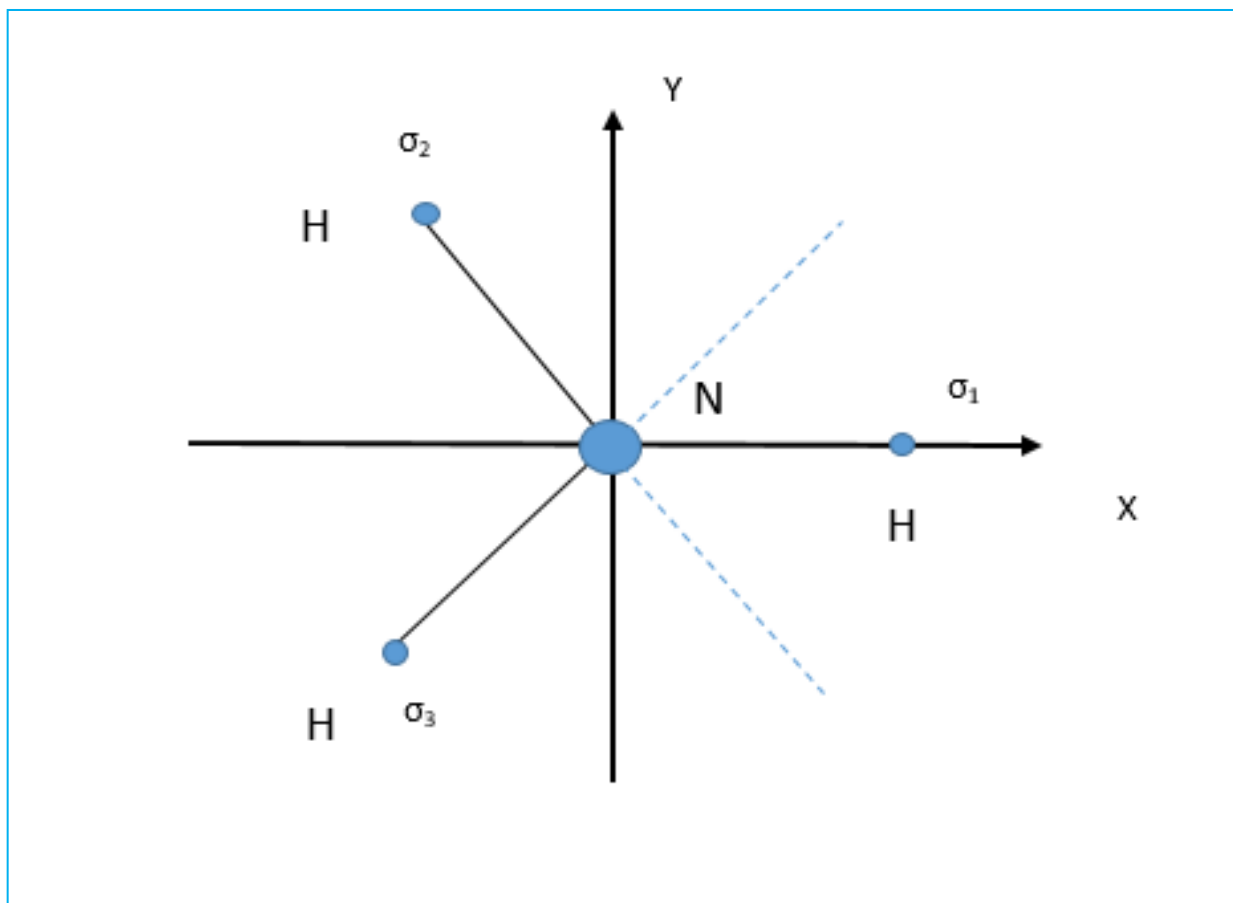
SIMILARLY $\sigma_v^{-1} = \sigma_v$ & $(\sigma_v^{-1})^{-1} = \sigma_v^{-1}$ →(SHOW)←

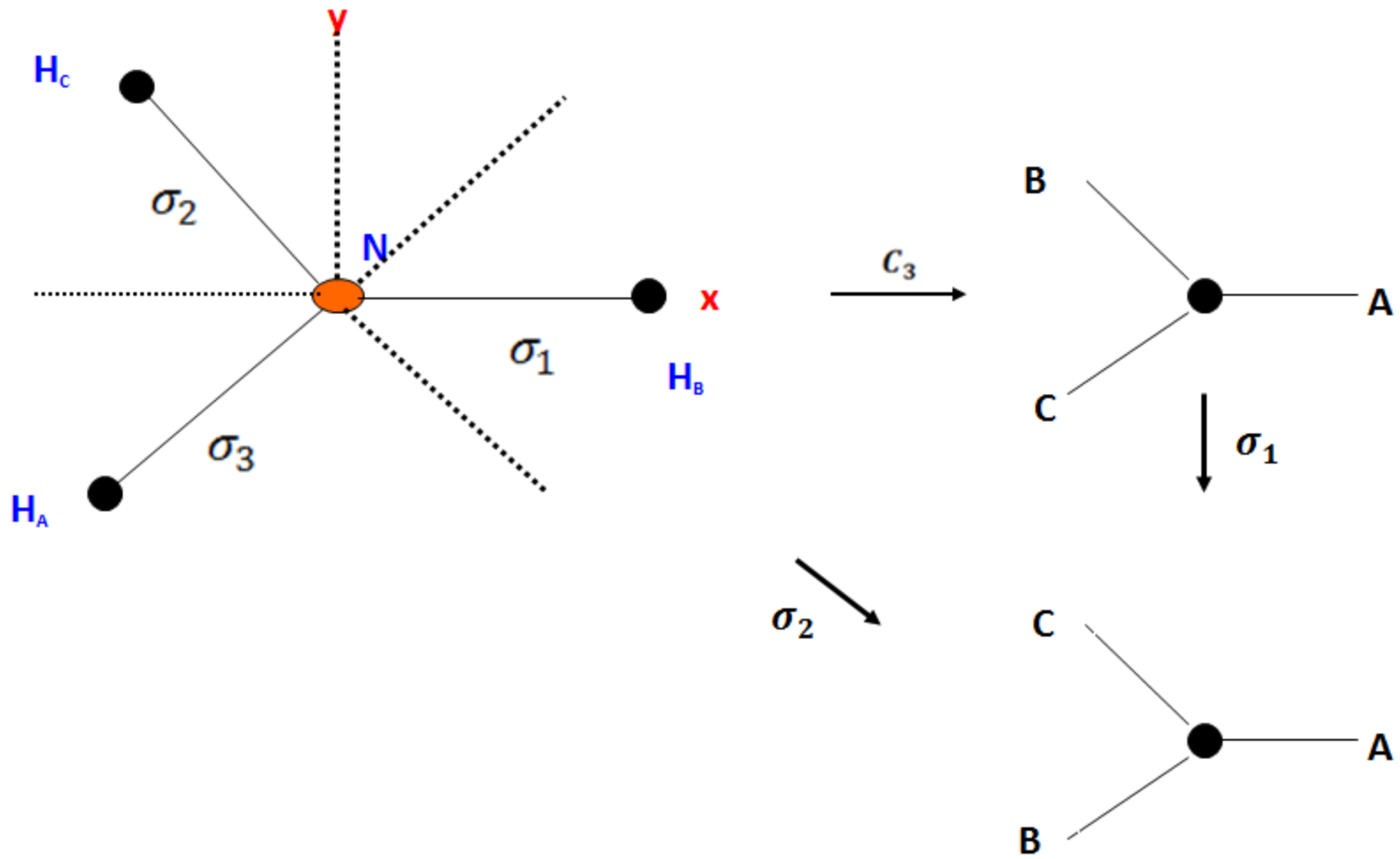


Symmetry Point Group

Symmetry Operation

Symmetry Element





$$\Rightarrow \begin{matrix} \sigma_1 C_3 = \sigma_2 \\ C_3 \sigma_1 = \sigma_3 \end{matrix} \Rightarrow C_{3v} \text{ is not abelian.}$$

Representation:

Consider the following set of simultaneous equations.

$$C_1 = a_{11} b_1 + a_{12} b_2 + a_{13} b_3 + \dots \quad (1)$$

$$C_2 = a_{21} b_1 + a_{22} b_2 + a_{23} b_3 + \dots \quad (2)$$

$$C_3 = a_{31} b_1 + a_{32} b_2 + a_{33} b_3 + \dots \quad (3)$$

Using matrix notation

$$\begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix}$$

or $C = A b$

or in operative form

$$\begin{array}{ccc} \rightarrow & & \rightarrow \\ C & = & A b \end{array}$$

Or the matrix representation of any operator A can be constructed by examining its effect on a vector and using equation (1)...(3) e.g.,

$$C_2(x, y, z) = (-x, -y, +z)$$

$$-x = (-1)x + 0y + 0z$$

$$-y = 0x + (-1)y + 0z$$

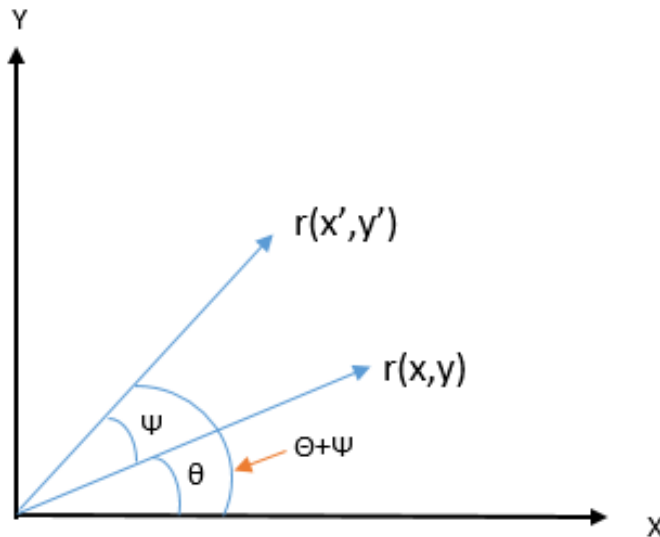
$$+z = 0x + 0y + 1z$$

$$\text{or } C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

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

$$\& \text{Tr}(C_2) = (-1) + (-1) + 1 = -1$$

Representation of Rotation Operation



$$x^1 = r \cos (\theta + \Psi) = r \underbrace{\cos \theta}_{x} \underbrace{\cos \Psi - \sin \theta \sin \Psi}_{y}$$

or $x^1 = \cos \Psi x - \sin \Psi y$, Similarly,

$$y^1 = r \sin (\theta + \Psi) = r \underbrace{\sin \theta \cos \Psi + \cos \theta \sin \Psi}_{y}$$

or, $y^1 = \sin \Psi x + \cos \Psi y$

$$\text{or, } \begin{bmatrix} x^1 \\ y^1 \end{bmatrix} = \begin{bmatrix} \cos \Psi & -\sin \Psi \\ \sin \Psi & \cos \Psi \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

$$\& \text{ Since } \begin{bmatrix} x^1 \\ y^1 \end{bmatrix} = R_2(\Psi) \begin{bmatrix} x \\ y \end{bmatrix}$$

$$R_2(\Psi) = \begin{bmatrix} \cos \Psi & -\sin \Psi \\ \sin \Psi & \cos \Psi \end{bmatrix}$$

$$C_2 = R_z(180^\circ) = \begin{bmatrix} \cos 180^\circ & -\sin 180^\circ \\ \sin 180^\circ & \cos 180^\circ \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = R_2(120^\circ) = \begin{bmatrix} -Y_2 & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -Y_2 \end{bmatrix}$$

GROUP REPRESENTATION

C_{2v}	E	C_2	σ_v	σ_v^1	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_2, xy
B_1	1	-1	1	-1	X, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz

$$C_3 = \hat{R}_z(120^\circ) = \begin{bmatrix} \cos 120^\circ & -\sin 120^\circ \\ \sin 120^\circ & \cos 120^\circ \end{bmatrix}$$

$$C_3^t = \begin{bmatrix} \cos 120^\circ & \sin 120^\circ \\ -\sin 120^\circ & \cos 120^\circ \end{bmatrix} \quad C_3 C_3^t = C_3^t C_3 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

C_{3v}	E	C_3	C_3^2	σ_1	σ_2	σ_3	
A_1	1	1	1	1	1	1	
A_2	1	1	1	-1	-1	-1	
E	1 0 0 1	$-\frac{1}{2}$ $-\frac{\sqrt{3}}{2}$ $\frac{\sqrt{3}}{2}$ $-\frac{1}{2}$	C_3^t	1 0 0 -1	$C_3\sigma_1$	$C_3^2\sigma_1$	
$\chi(E)$	2	-1	-1	0	0	0	

REPRESENTATIONS ARE NOT UNIQUE

If $\Gamma(R)$ is a representation $\forall R \in G$, so is

$$\Gamma^\beta(R) = \beta^{-1} \Gamma(R) \beta \quad \forall R \in G \text{ since}$$

$$\Gamma^\beta(R) \Gamma^\beta(S) = \beta \Gamma(R) \beta \beta^{-1} \Gamma(S) \beta$$

$$= \beta^{-1} \Gamma(R) \Gamma(S) \beta = \beta^{-1} \Gamma(RS) = \Gamma^\beta(RS)$$

Representations are NOT UNIQUE indeed! VARI! With β !!

However, Trace or character of a matrix A,

$$\text{Tr} (A) = \sum_i A_{ii}$$

is invariant i.e.

$$\begin{aligned} \text{Tr} (\beta^{-1} A \beta) &= \sum_i (\beta^{-1} A \beta)_{ii} = \sum_i \sum_k \sum_l \beta_{ik}^{-1} A_{kl} \beta_{li} \\ &= \sum_k \sum_l A_{kl} \sum_i \beta_{li} \beta_{ik}^{-1} \\ &= \sum_k \sum_l A_{kl} (\beta \beta^{-1})_{lk} = \sum_k \sum_l A_{kl} \delta_{lk} \\ &= \sum_k \sum_l A_{kl} \delta_{lk} \\ &= \sum_k A_{kk} = \sum_i A_{ii} \end{aligned}$$

i.e. **CHARACTER** of representations is invariant and we should be decline with character tables and not Representation Tables.

Let us collect the character for each representation in a six dimensional (component) vector for C_{3v} i.e.

$$\chi (A_1) = (1, 1, 1, 1, 1, 1)$$

$$\chi (A_2) = (1, 1, 1, -1, -1, -1)$$

& $\chi (E) = (2, -1, -1, 0, 0, 0)$

Notice that $\chi^E(C_3) = \chi^E(C_3^2)$ same for A_1 & A_2 .

i.e. $\chi^i(C_3) = \chi^i(\chi^{-1}C_3\chi)$ i.e. character is a Class property.

Similarly, $\chi^i(\sigma_1) = \chi^i(\sigma_2) = \chi^i(\sigma_3)$ for all imeps, can be easily verified that

$$\sum_{R \in C_{3v}} \chi^i(R) \chi^j(R) = h \delta_{ij}$$

where i & j are irrep labels and h is the order of the group for C_{3v} , $h = 6$.

Since reduction of a matrix is through similarity transform which presents character

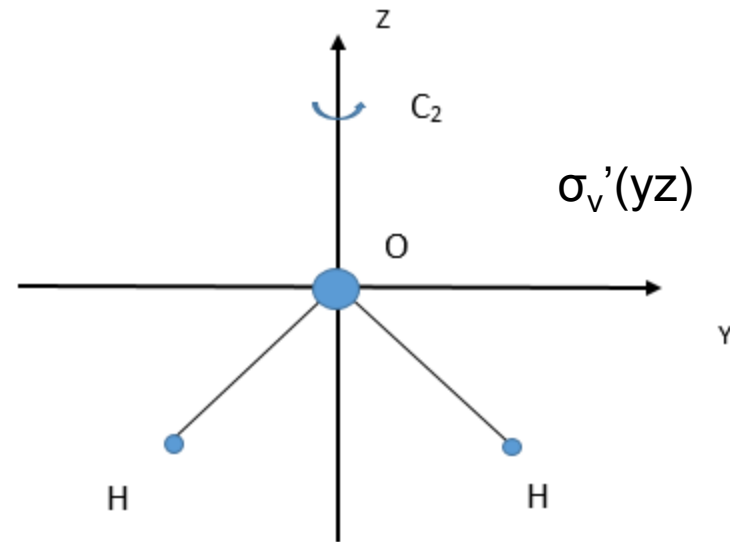
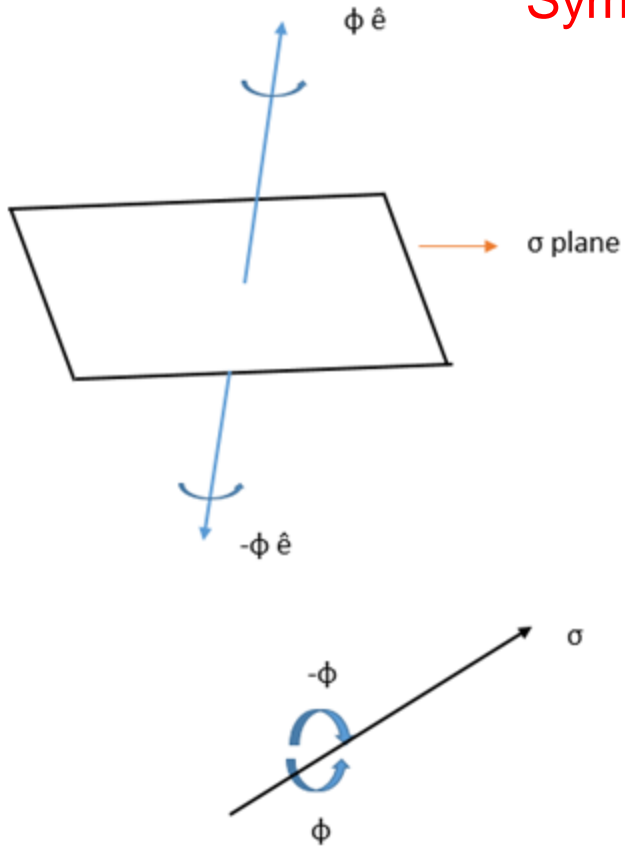
$$\chi^{red}(R) = \sum_j^{irreps} a_j \chi^j(R)$$

$$\begin{aligned} \Rightarrow \sum_R \chi^{red}(R) \chi^i(R) &= \sum_R \sum_j a_j \chi^j(R) \chi^i(R) \\ &= \sum_j a_j \sum_R \chi^j(R) \chi^i(R) \\ &= \sum_j a_j \delta_{ij} \end{aligned}$$

or

$$a_i = \frac{1}{h} \sum_R \chi^{red}(R) \chi^i(R)$$

Symmetry type of R_x , R_y , R_z



$$\hat{C}_2 R_z = +1 R_z \Rightarrow R_z \in A_1 \text{ or } A_2$$

$$\hat{\sigma}_v R_z = -1 R_z \Rightarrow R_z \in A_2$$

$$\hat{C}_2 R_y = -1 R_y \Rightarrow R_y \in B_1 \text{ or } B_2$$

$$\hat{\sigma}_v^1 R_y = -1 R_y \Rightarrow R_y \in B_1$$

Similarly, $R_x \in B_2$

Labels for IRREPS:

1. An One-dimensional irrep is given the symbol A or B.

2. A if $\chi(C_x) = +1$

B if $\chi(C_x) = -1$

3. Subscripts may be applied as follows:

(i) There are σ_v or σ_x plane then

1 if $\chi(\sigma) = +1$

2 if $\chi(\sigma) = -1$

(ii) If there is i then

g if $\chi(i) = +1$

u if $\chi(i) = -1$

4. Superscripts ' when $\sigma_h \in$ symmetry point group

(i) if $\chi(\sigma_h) = +1$

(ii) if $\chi(\sigma_h) = -1$

5. Two-dimensional irrep is given the symbol E.

6. Three-dimensional irrep is given the symbol T, etc.

$$\int^\lambda f_i^* f_j^\sigma d\tau = 0 \text{ unless } \lambda \otimes \sigma = A_1 \text{ or } A_1 \in \lambda \otimes \sigma$$

Where λ & σ are the irrep labels for f_i & f_j respectively.

Proof:

Let λ & σ be irreps of dimension 1

$$\text{i.e. } \chi^\lambda(R) = \pm 1 \forall R \in G$$

$$\& \chi^\tau(R) = \pm 1 \forall R \in G$$

$$S_{ij} = \int^\lambda f_i^* f_j^\sigma d\tau = \text{a number}$$

$$= \text{Totally symmetric}$$

$$\text{i.e. } R S_{ij} = +1 S_{ij} \forall R \in G$$

but,

$$R S_{ij} = \int R^\lambda f_i^* R f_j^\sigma d\tau = \chi^\lambda(R)^* \chi^\sigma(R) S_{ij}$$

$$= -S_{ij} \text{ for some } R \text{ unless } \lambda = \sigma$$

i.e. if $\lambda \neq \sigma$

$$\text{R } S_{ij} = -S_{ij} = S_{ij} = 0$$

\therefore for $S_{ij} \neq 0$ $\lambda = \sigma$ & $\lambda \otimes \sigma = A_1$ is required.

In general,

$$\int \phi_i^* \hat{O} \phi_j d\tau \neq 0$$

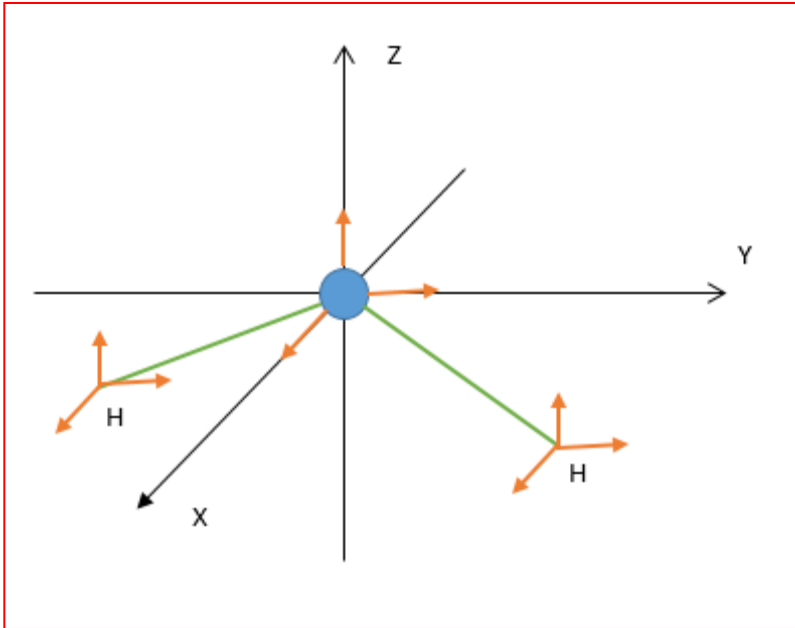
Iff

$$\mathbf{A}_1 \in \Gamma_i \otimes \Gamma_o \otimes \Gamma_j$$

i.e. if $\Gamma_o = \mathbf{A}_1$
then,

$$\mathbf{A}_1 \in \Gamma_i \otimes \Gamma_j$$

Vibrational Modes of H₂O



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

CONSTRUCT A REPRESENTATION IN THE BASIS OF CARTESIAN DISPLACEMENTS

() FOR EACH ATOM.

$$\chi(E) = 9$$

$$\chi(C_2) = -1$$

$$\chi(\sigma_{xz}) = 1$$

$$\chi(\sigma_{yz}) = 3$$

$$a_i = \frac{1}{h} \sum_{R \in C_{2v}} \chi(R) * \chi(R)$$

$$a_{A_1} = \frac{1}{4} * [9 - 1 + 1 + 3] = 3$$

$$a_{A_2} = 1, a_{B_1} = 2, a_{B_2} = 3$$

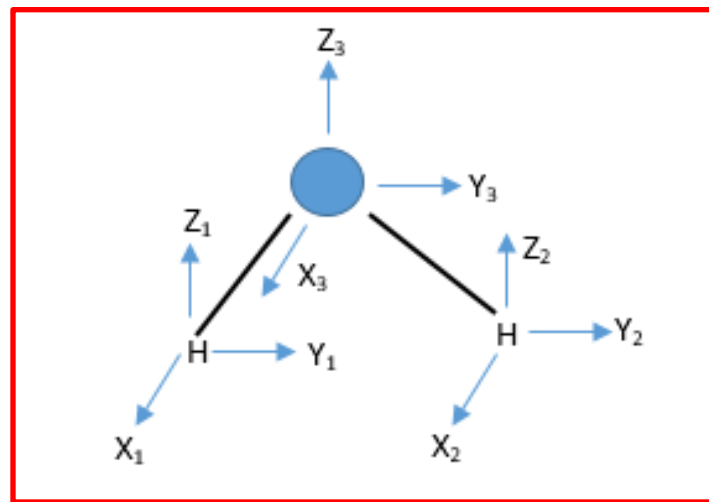
$$\begin{aligned} \therefore \quad \text{Total Modes (T + R + V)} &= 3A_1 + 3B_2 + 2B_1 + 1A_2 \\ \text{Translational Modes} &: x \rightarrow B_1, y \rightarrow B_2, z \rightarrow A_1 \\ \text{Rotational Modes} &: R_x \rightarrow B_2, R_y \rightarrow B_1, R_z \rightarrow A_2 \\ \text{Vibrational Modes} &= \text{Total} - \text{Rot} - \text{Trans} \end{aligned}$$

$$= (3A_1 + 3B_2 + 2B_1 + 1A_2) - (2B_1 + 2B_2 + 1A_1 + 1A_2)$$

$$= 1B_2 + 2A_1$$

i.e. H₂O has 2a₁, type and 1b₂ type

NORMAL MODES OF VIBRATION.



$$\begin{aligned}
 EX_1 &= X_1 &= 1X_1 + 0Y_1 + 0Z_1 + 0X_2 + 0Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 0Z_3 \\
 EY_1 &= Y_1 &= 0X_1 + 1Y_1 + 0Z_1 + 0X_2 + 0Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 0Z_3 \\
 EZ_1 &= Z_1 &= 0X_1 + 0Y_1 + 1Z_1 + 0X_2 + 0Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 0Z_3
 \end{aligned}$$

$$\text{OR } E \begin{pmatrix} X_1 \\ Y_1 \\ Z_1 \\ X_2 \\ Y_2 \\ Z_2 \\ X_3 \\ Y_3 \\ Z_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X_1 \\ Y_1 \\ Z_1 \\ X_2 \\ Y_2 \\ Z_2 \\ X_3 \\ Y_3 \\ Z_3 \end{pmatrix}$$

$$E_i \chi(E) = 9$$

$$4 = I_{9 \times 9}$$

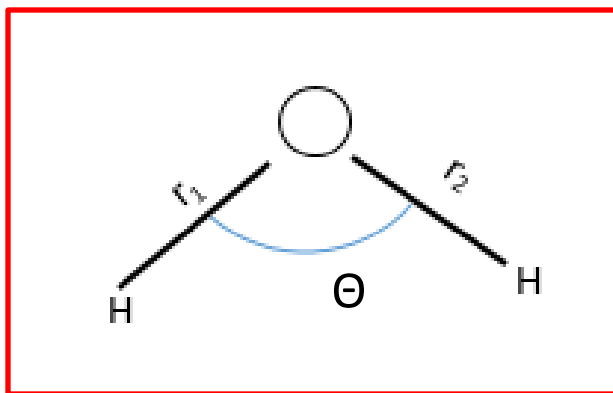
$$\begin{aligned}
C_2 X_1 &= -X_2 &= 0X_1 + 0Y_1 + 0Z_1 - 1X_2 + 0Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 0Z_3 \\
C_2 Y_1 &= -Y_2 &= 0X_1 + 0Y_1 + 0Z_1 + 0X_2 - 1Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 0Z_3 \\
C_2 Z_1 &= Z_2 &= 0X_1 + 0Y_1 + 0Z_1 + 0X_2 + 0Y_2 + 1Z_2 + 0X_3 + 0Y_3 + 0Z_3 \\
C_2 X_2 &= -X_1 &= -1X_1 + 0Y_1 + 0Z_1 + 0X_2 + 0Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 0Z_3 \\
C_2 Y_2 &= -Y_1 &= 0X_1 - 1Y_1 + 0Z_1 + 0X_2 + 0Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 0Z_3 \\
C_2 Z_2 &= Z_1 &= 0X_1 + 0Y_1 + 1Z_1 + 0X_2 + 0Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 0Z_3 \\
C_2 X_3 &= -X_3 &= 0X_1 + 0Y_1 + 0Z_1 + 0X_2 + 0Y_2 + 0Z_2 - 1X_3 + 0Y_3 + 0Z_3 \\
C_2 Y_3 &= -Y_3 &= 0X_1 + 0Y_1 + 0Z_1 + 0X_2 + 0Y_2 + 0Z_2 + 0X_3 - 1Y_3 + 0Z_3 \\
C_2 Z_3 &= +Z_3 &= 0X_1 + 0Y_1 + 0Z_1 + 0X_2 + 0Y_2 + 0Z_2 + 0X_3 + 0Y_3 + 1Z_3
\end{aligned}$$

Or,

$$C_2 = \begin{pmatrix}
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & +1 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & +1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & +1
\end{pmatrix}$$

$$\chi(C_2) = -1 + (-1) + 1 = -1$$

WHAT KIND OF DISPLACEMENT PATTERNS DO THESE VIBRATIONAL MODES REPRESENT?

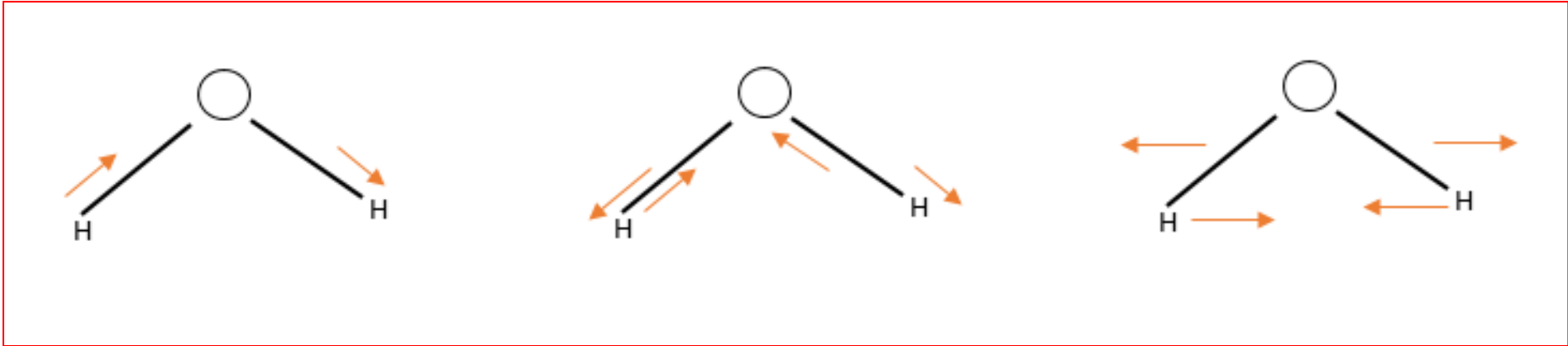


$$\Theta \in A_1$$

representation using r_1 and r_2 ,

$\chi(E)$	=	2	a_{A1}	=	1	$(r_1 + r_2)$
$\chi(C_2)$	=	0	a_{A2}	=	0	
$\chi(\sigma_v)$	=	0	a_{B1}	=	0	
$\chi(\sigma_v^1)$	=	2	a_{B2}	=	1	$(r_1 - r_2)$

∴ 1 Symmetric ($r_1 + r_2$) STRETCH
 1 Antisymmetric ($r_1 - r_2$) STRETCH
 and, 1 Symmetric (θ) BEND



$$V_{B_2^s} > V_{A_1^s} > V_{A_1^b}$$

WHICH OF THESE MODES ARE IR/RAMAN ACTIVE?

Symmetry type of q_j mode



$$IR: \int \psi_{\circ}^{A_1}(q_j) x(\text{or } y \text{ or } z) \psi_1(q_j) d\tau \neq 0$$



symmetry type of q_j mode

Raman:

$$\int \psi_{\circ}^{A_1}(q_j) xy (\text{or other tensor products } xz, yz, x^2, y^2, z^2 \text{ etc.}) \psi_1(q_j) d\tau \neq 0$$

∴ ALL THREE MODES ARE IR ACTIVE

and, also ALL THREE MODES ARE RAMAN ACTIVE.

H₂O: Is transition from $\Psi_{a_1} \rightarrow \Psi_{b_2}$ allowed?

WHAT is the polarization of the emitted light ?

$$\mu_z : \int \psi_{a_1} z \psi_{b_2} d\tau$$

$$\mu_x : \int \psi_{a_1} x \psi_{b_2} d\tau$$

$$\mu_y : \int \psi_{a_1} y \psi_{b_2} d\tau$$

$$z \rightarrow A_1 \quad \mu_z = 0$$

$$x \rightarrow B_1 \quad \mu_x = 0$$

$$y \rightarrow B_2 \quad \mu_y \neq 0$$

∴ TRANSITION $\Psi_{a_1} \rightarrow \Psi_{b_2}$ is ALLOWED and will be POLARIZED in Y DIRECTION

SYMMETRY IN QUANTUM CHEMISTRY

$$H\psi = E\psi; \psi = \sum_{i=1}^N C_i \phi_i \text{ LCAO - MO}$$

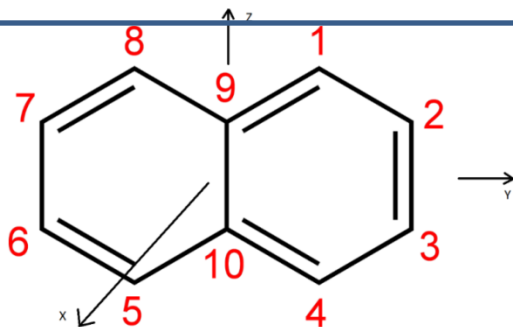
Leads to $\mathbb{H} \mathbb{C} = \mathbb{S} \mathbb{C} E$ e.g. HF or Huckel etc.

$$\mathbb{H} = \{H_{ij} = \langle \phi_i | \mathbb{H} | \phi_j \rangle\} N \times N$$

$$\mathbb{S} = \{S_{ij} = \langle \phi_i | \phi_j \rangle\} N \times N$$

$$\text{SALC } \chi^p = \sum_j C_j^p \phi_j; \langle \chi^p | \chi^q \rangle = \delta_{pq}; \langle \chi_p | \mathbb{H} | \chi_q \rangle = \delta_{pq}$$

\therefore $N \times N$ \mathbb{H} gets block diagonalised e.g., for $C_{10} H_8$.



Naphthalene:

D_{2h} {E, $C_2(x)$, $C_2(y)$, $C_2(z)$, i, $\sigma(xy)$, $\sigma(xz)$, $\sigma(yz)$ }

10 P_{Π}

\mathbb{H} & \mathbb{S} are 10 x 10 UNDOABLE by HAND.

$\Phi_1, \Phi_4, \Phi_5, \Phi_8$

$A_u, B_{1u}, B_{2g}, B_{3g}$

$\Phi_2, \Phi_3, \Phi_6, \Phi_7$

$A_u, B_{1u}, B_{2g}, B_{3g}$

Φ_9, Φ_{10}

B_{1u}, B_{3g}

SALC: A_u 2×2

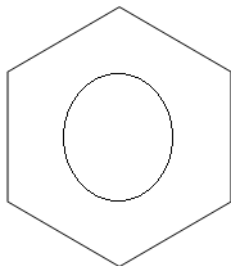
B_{1u} 3×3

B_{2g} 2×2

B_{3g} 3×3

EACH BLOCK CAN BE SOLVED SEPARATELY BY HAND.

QUALITATIVE MO THEORY



BENZENE

D_{6h}

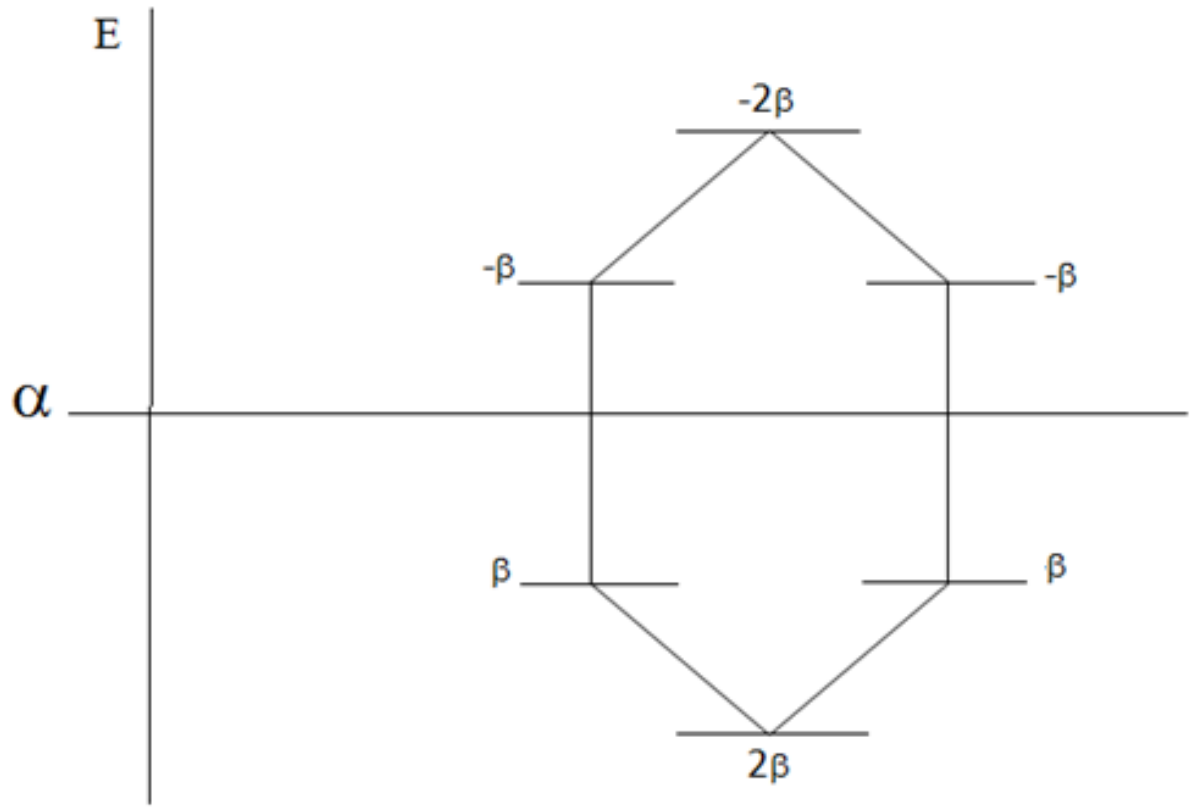
$$\hat{P}^\mu = \frac{l_\mu}{h} \sum_{R \in D_{6h}} \chi^\mu(R) \hat{R}$$

on $6 p_\pi$ AOs as basis – $A_2 \oplus B_2 \oplus E_1 \oplus E_2$

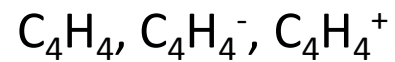
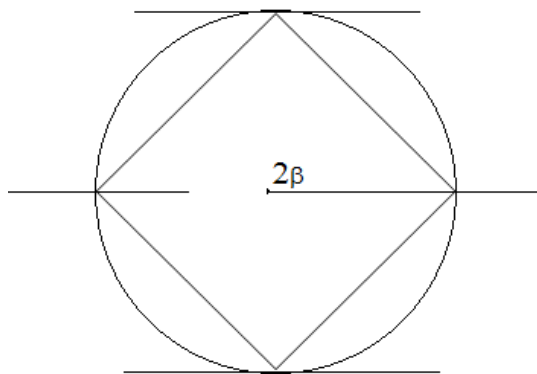
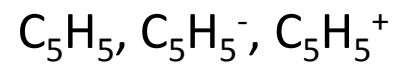
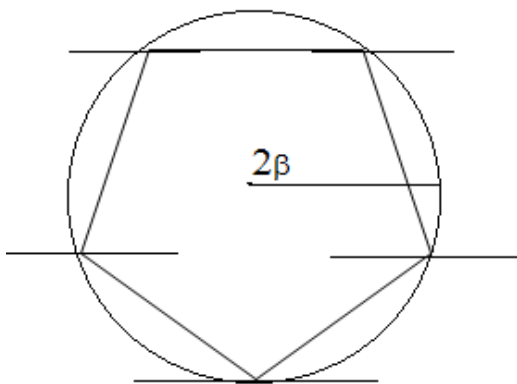
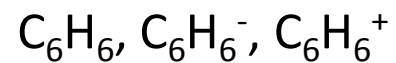
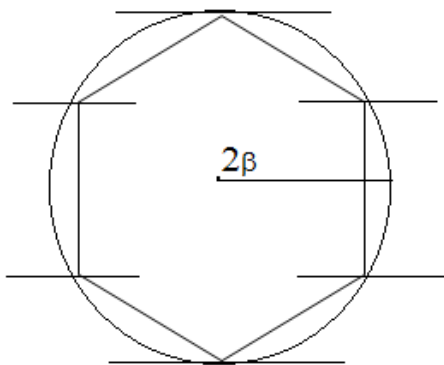
Set up Huckel Hamiltonian Matrix

$$\begin{vmatrix} x+2 & & & & & \\ & x-2 & & & & \\ & & x+1 & & & \\ (1) & & & x+1 & & \\ & & & & x-1 & \\ & & & & & x-1 \end{vmatrix} = 0,$$

$$x = \frac{\alpha - E}{\beta}$$

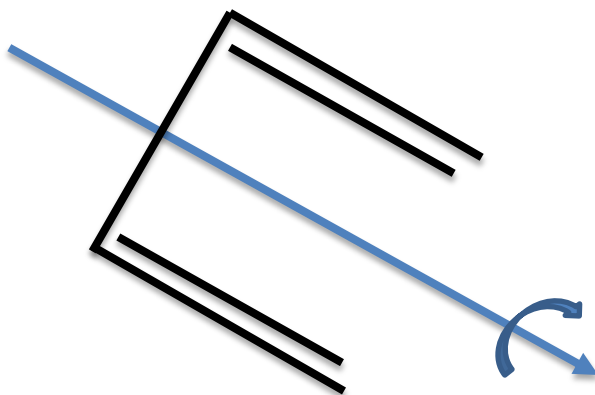


SYMMETRY OF ENERGY LEVELS IN HMO THEORY



CONSERVATION OF ORBITAL SYMMETRY WOODWARD-HOFFMANN RULES

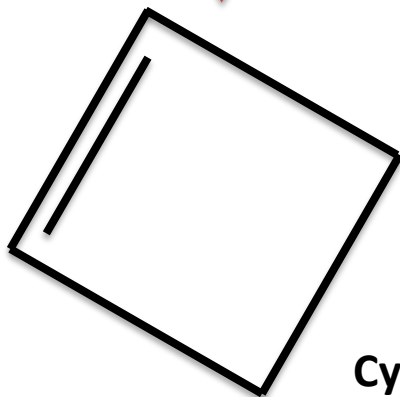
APPLICATION TO CYCLIZATION OF 1-3 CIS BUTADIENE TO CYCLOBUTENE



C_2, σ_V containing C_2

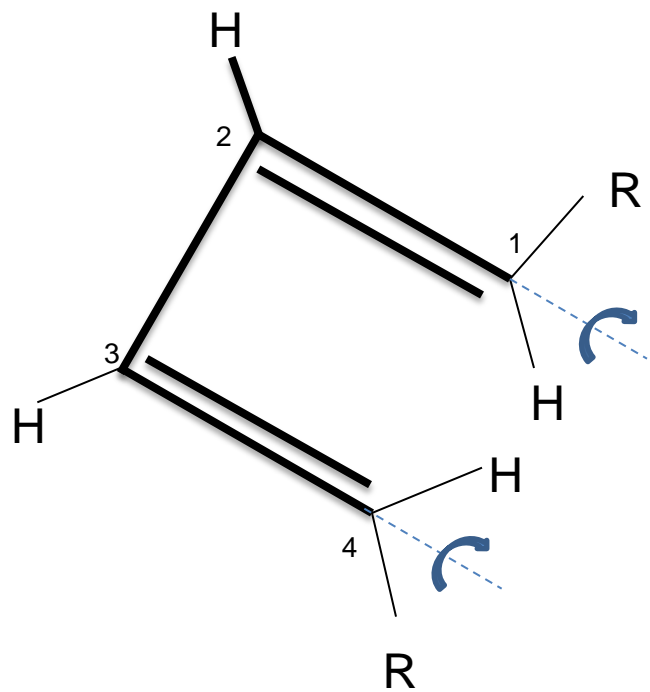
σ_V^1 (plane of molecule)

Butadiene



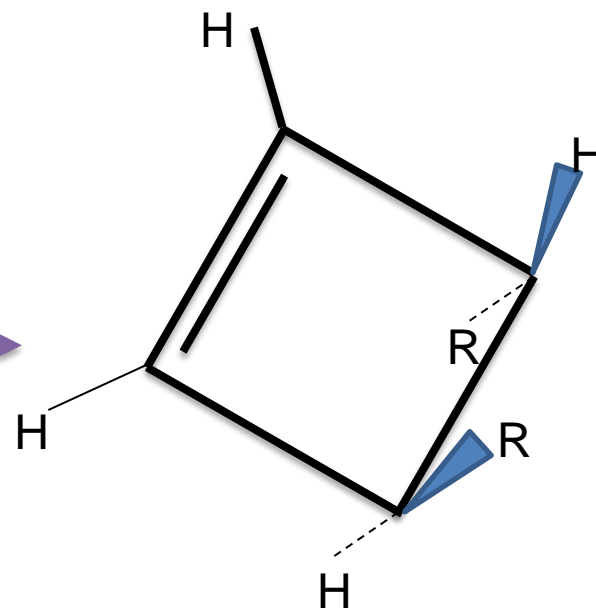
Cyclobutene

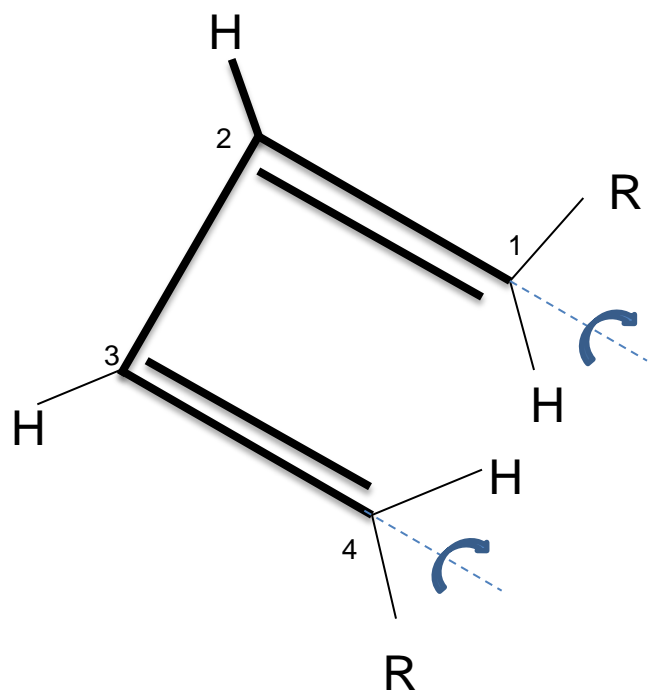
Same symmetry elements as for Butadiene



con-rotatory

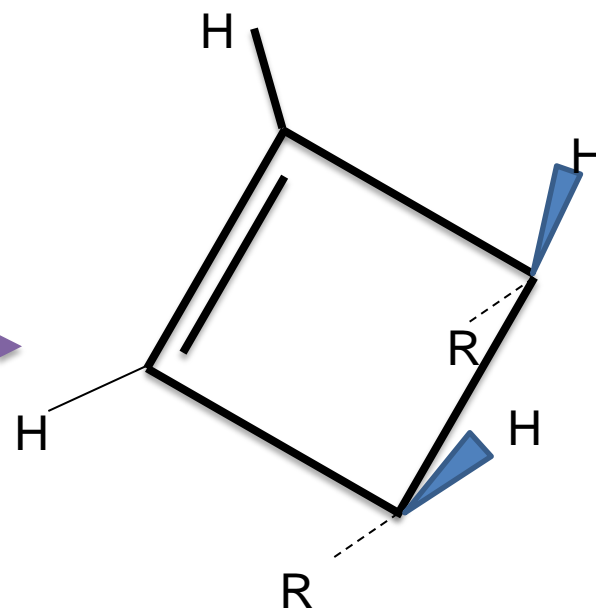
C_2 survives
 σ_v & σ_v' don't

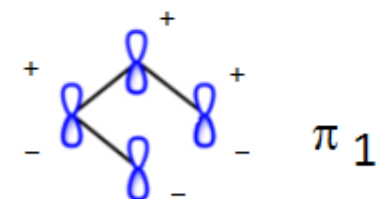
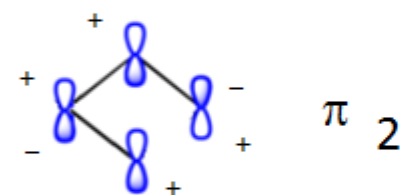
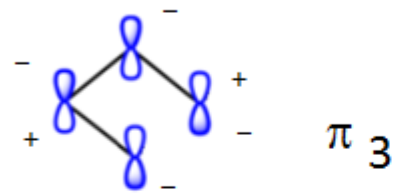
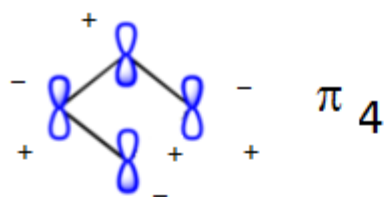




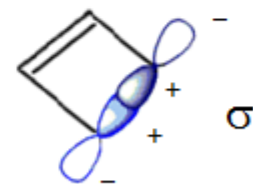
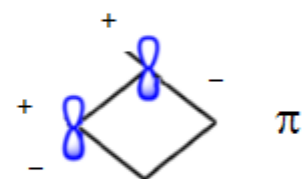
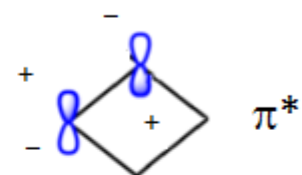
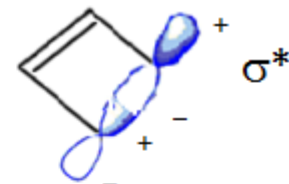
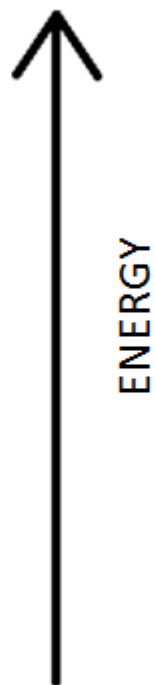
dis-rotatory

σ_v survives
 C_2 & σ_v' don't





Butadiene



Cyclobutene

Cyclobutene

dis

Butadiene

con

Cyclobutene

σ_v

C_2

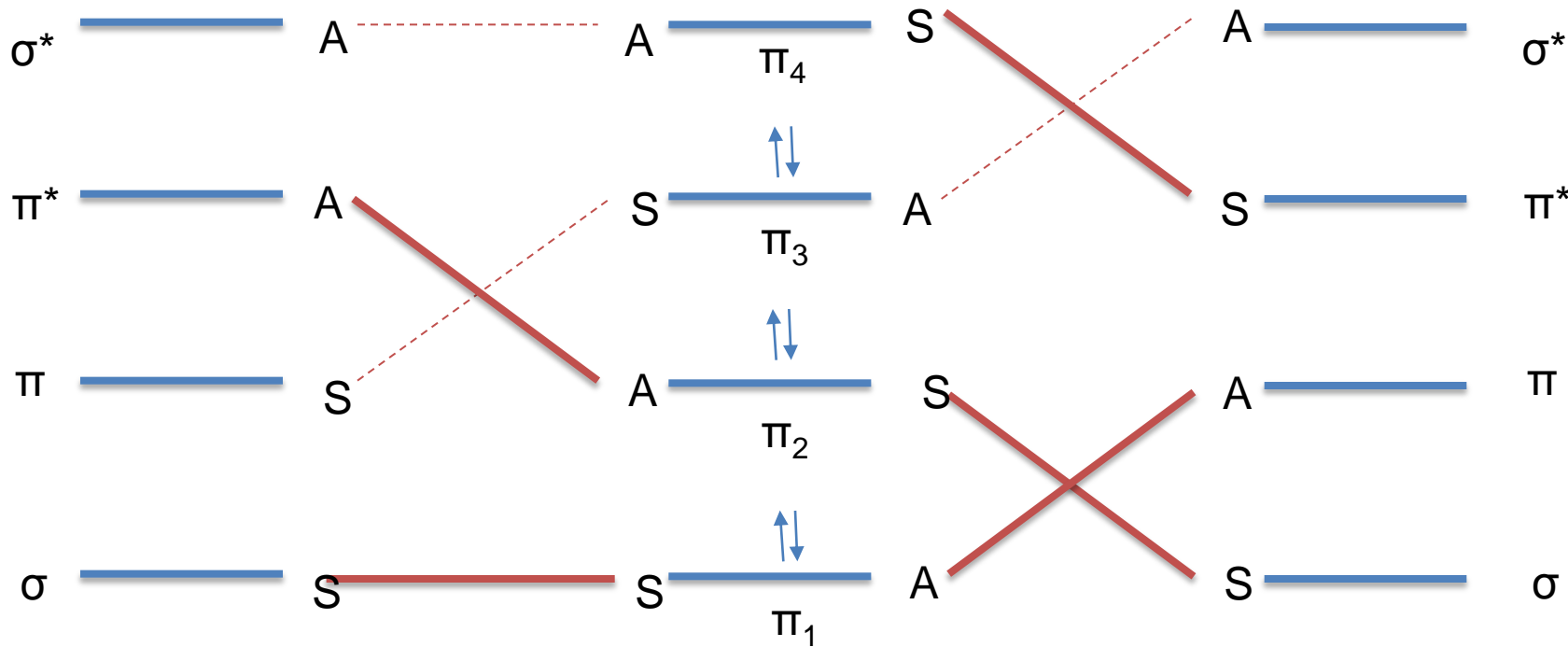


Photo chemically Allowed

Thermally Allowed

Thermally disallowed

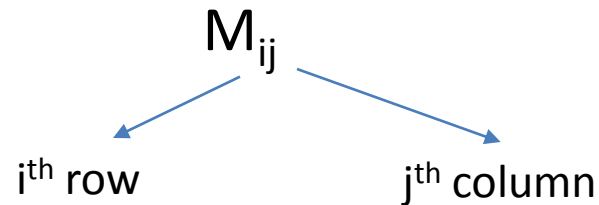
Why not $\pi_1^{(S)}$ with $\pi^{(S)}$ _{cyclo}

Because of Non-crossing Rule

MATRICES

$$\mathbf{M} = \begin{pmatrix} M_{11} & M_{12} & \dots & M_{1n} \\ M_{21} & M_{22} & \dots & M_{2n} \\ \dots & \dots & \dots & \dots \\ M_{n1} & M_{n2} & \dots & M_{nn} \end{pmatrix}$$

Square M contains n^2 elements



$$\mathbf{M} + \mathbf{N} = \mathbf{P}$$

$$\Rightarrow P_{ij} = M_{ij} + N_{ij}$$

$$\mathbf{M} \mathbf{N} = \mathbf{P}$$

$$\Rightarrow P_{ij} = \sum_k M_{ik} N_{kj}$$

Let $M = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}$ and, $N = \begin{bmatrix} 5 & 6 \\ 7 & 8 \end{bmatrix}$

$$M + N = \begin{bmatrix} 6 & 8 \\ 10 & 12 \end{bmatrix}$$

$$MN = P = \begin{bmatrix} 19 & 22 \\ 43 & 50 \end{bmatrix}$$

$NM \neq MN$

$$NM = \begin{bmatrix} 23 & 34 \\ 31 & 46 \end{bmatrix}$$

Matrices are the operators.

SPECIAL NAME MATRICES

(i) DIAGONAL MATRIX: -

$$M_{ij} = 0 \text{ if } i \neq j$$

i.e. $M = \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix}$ is diagonal but $\begin{bmatrix} 0 & 1 \\ 2 & 0 \end{bmatrix}$ is not.

(ii) THE UNIT MATRIX IS A DIAGONAL MATRIX

$$I \text{ or } I_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

3 dimensional unit matrix

$$I M = M$$

(iii) THE TRANSPOSE OF A MATRIX $M = M^t$ or \tilde{M}

$$\tilde{M}_{ij} = M_{ji}$$

Thus if

$$M = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix} ; \quad M^t = \begin{bmatrix} 1 & 3 \\ 2 & 4 \end{bmatrix}$$

If $M = M^t$ then M is symmetric.

(iv) THE INVERSE OF A MATRIX M IS WRITTEN AS M^{-1}

$$M M^{-1} = M^{-1} M = I$$

$$M^{-1} = \tilde{M}' / \det M \quad (' \text{ for co-factor})$$

i.e. for inverse to $\exists \det (M) \neq 0$.

**THANK YOU FOR
YOUR PATIENCE**