UNIT 2 SYMMETRY OF MOLECULES

Structure

2.1   INTRODUCTION

The molecules with different structures show different reactivity pattern and molecular spectra. The question arises, "is there any way to relate structure, spectra and reactivity?". Such a relationship could help us both in understanding the nature of known substances and in predicting the properties of new ones. In this unit, we are going to discuss symmetry aspects of molecules and, we will indicate how symmetry could relate structure (or shape) to spectra (or to many of the physical properties).

In Unit 3 of CHE-01 (Atoms and Molecules) course, we have discussed

● the way of writing the Lewis structures of molecules (and ions) and

● predicting their shapes on the basis of valence shell electron pair repulsion theory.

As a continuation of the same, we shall relate shape of a molecule and symmetry aspects in this unit. We shall show how to classify molecules as point groups based on symmetry. We shall state the uses of point group classification in understanding the physical properties such as dipole moment, optical rotation and spectra. Some of the aspects of symmetry are covered under group theory in the Appendix part of this unit. We shall also indicate the uses of group theory in understanding the chemistry of molecules. In this unit, we shall attempt a qualitative treatment of molecular symmetry and group theory.

Objectives

After studying this unit, you should be able to:

● define symmetry elements and symmetry operations,

● state the list of symmetry elements in simple molecules,

● identify the point group of a molecule from the list of its symmetry elements, and

● state the implications of molecular symmetry.

2.2 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

It is worth recapitulating valence shell electron pair repulsion theory which has been discussed in Unit 3 of CHE-01 course. The VSEPR theory helps us to explain the shapes and bond angles of molecules in relation to the number of shared and lone electron pairs around the central atoms.

We present in Table 2.1 the shapes of different molecules and ions according to VSEPR theory.

Table 2.1: Number of Electron Pairs in the Valence Shell of the Central Atom, and shape of Molecule or Ion.

No. of Electron Pairs				
Total	Bond pairs	Lone pairs	Shape	Examples
2	2	0	linear	$HgCl_2$, $BeCl_2$
3	3	0	triangular planar	BF_3, BCl_3, CO_3^{2-}, NO_3^-
3	2	1	angular	$SnCl_2$(gas), NO_2^-, $ClNO$
4	4	0	tetrahedral	CH_4, BF_4^-, NH_4^+
4	3	1	trigonal pyramidal	NH_3, PF_3
4	2	2	angular	H_2O, ICl_2^+, NH_2^-
5	5	0	trigonal bipyramidal	PCl_5(gas), $SnCl_5^-$
5	4	1	see-saw	$TeCl_4$, IF_4^+, SF_4
5	3	2	T-shaped	ClF_3, BrF_3
5	2	3	linear	XeF_2, ICl_2^-
6	6	0	octahedral	SF_6, PF_6^-
6	5	1	square pyramidal	IF_5, SbF_5^{2-}
6	4	2	square planar	BrF_4^-, XeF_4

SAQ 1

Using VSEPR theory, predict the shape of PCl_3. Draw its structure.

....

....

....

2.3 SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

In the last section, we saw how molecules can be classified on the basis of shape. It is better to classify the molecules based on their symmetry aspects. This could help us to understand the molecular properties such as dipole moment, optical activity and

spectral characteristics. Before trying to classify molecules on the basis of symmetry, we must understand the terms, symmetry elements and symmetry operations.

Symmetry operation is the movement of an object such that it leaves the object looking the same. A symmetry operation brings the molecule into the equivalent or identical configuration. You can understand the words 'equivalent' and 'identical' configurations by using a cardboard which is shaped like an equilateral triangle (Fig. 2.1a). You label the three vertices of the triangle as 1, 2 and 3. Rotation of the triangular cardboard through 120° $(2\pi/3)$ and 240° $(4\pi/3)$ in the anticlockwise direction gives rise to equivalent configurations i.e., each configuration is indistinguishable from the original configuration (Figs. 2.1 b and c) whereas the rotation through 360° (2π) results in an identical configuration (Fig. 2.1 d). In equivalent configuration, the positions of the atoms in space *are similar* to those in the original configuration, i.e., before applying symmetry operation. In identical configuration, the positions of the atoms *are the same* as before applying symmetry operation. (Compare Figs. 2.1a and d).
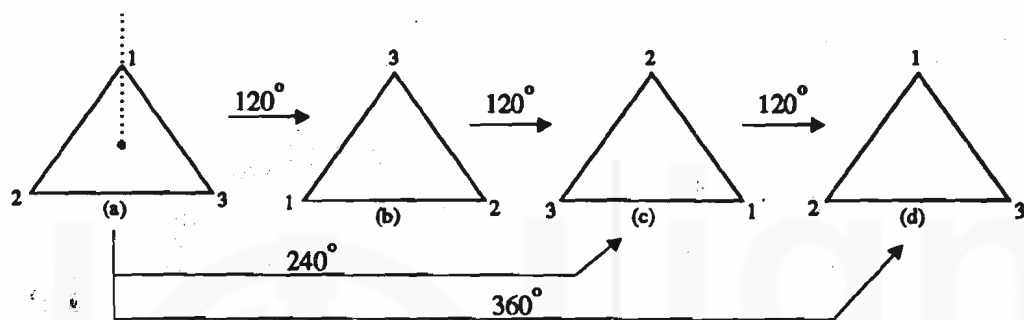

Fig. 2.1: (a)   The configuration before rotation; the dotted line shows the axis of rotation in a direction perpendicular to the plane of the molecule.

(b)   and (c) equivalent configurations (after anticlockwise rotation through 120° $(2\pi/3)$ and 240° $(4\pi/3)$.

(d)   identical configuration (after rotation through 360° (2π)).

Similarly, reflection once across a plane passing through equilateral triangle type molecule can give rise to equivalent configuration, while another reflection through the same plane gives rise to identical configuration. For instance, imagine a perpendicular plane passing through vertex 1 of the equilateral triangle-shaped cardboard. This perpendicular plane is shown as a dotted line in Figs. 2.2 a and b. Reflection through this plane once results in equivalent configuration, Fig. 2.2b. Another reflection through this plane results in an identical configuration, Fig. 2.2c.

Rotation through 120° once, twice and thrice can be denoted by C_3^1, C_3^2 and C_3^3; C_3 also represents threefold axis of rotation. We shall discuss this in a detailed way in the next section.
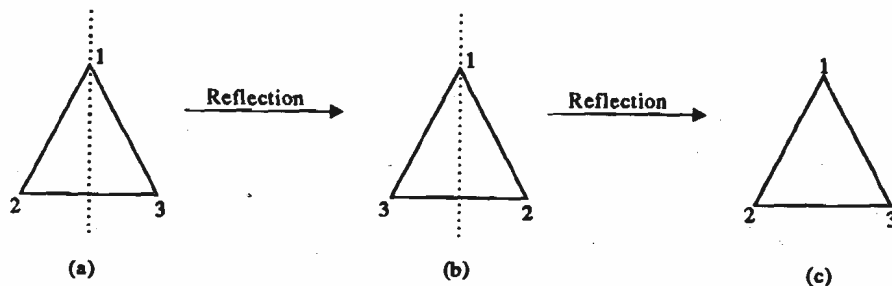

Fig. 2.2: a)   The configuration before reflection.

b)   The equivalent configuration resulting from reflection through a perpendicular plane (shown as dotted line passing through the vertex 1).

c)   The identical configuration resulting from another reflection through the same plane.

39

The symmetry element is a line or
a plane or a point whereas the
symmetry operation is the
operation performed to bring the
object into an equivalent
configuration.

So far we have seen rotation about an axis and reflection across a plane which are two
of the five symmetry operations. All the symmetry operations are listed in Table 2.2.
Corresponding to each symmetry operation, there is a symmetry element. **The
symmetry element is a line or a plane or a point with respect to which the symmetry
operation is performed.** The symmetry element is a geometrical property which is said
to generate the operation. Table 2.2 lists the various symmetry elements and symmetry
operations.

Table 2.2: List of Symmetry Elements and Symmetry Operations

S. No.	Symmetry Element	Symmetry Operation
1.	n-fold axis of symmetry or proper axis of symmetry (C_n)	Rotation once or several times by an angle (equal to $360°/n$ or $2\pi/n$) about the axis; n must be an integer.
2.	Plane of symmetry (σ)	Reflection plane passing through the molecule
3.	Axis of improper rotation or alternating axis of symmetry or rotary-reflection axis (S_n)	Rotation about an axis by an angle $360°/n$ or $2\pi/n$ followed by reflection in a plane perpendicular to the axis of rotation
4.	Centre of symmetry (i)	Inversion of all atoms through the centre of symmetry
5.	Identity element (E)	Doing nothing to the object

We will be using the same
symbols for each pair of symmetry
elements and symmetry
operations. These symbols are
indicated within brackets under
the column 'Symmetry element' in
Table 2.2.

The crystal symmetry includes
translational symmetry whereas
molecular symmetry does not
include it.

At least one point in the molecule should be unaffected by all the symmetry
operations. Also, all the symmetry operations possible for a molecule must intersect at
this point. Thus, the symmetry operation should not lead to translational motion of the
molecule in the space. This is the basic difference between the molecular symmetry
and crystal symmetry.

This aspect will be made more clear in Sec. 2.9 where we shall distinguish between
molecular point groups and crystallographic space groups. We shall explain the
symmetry operations and symmetry elements in a detailed way in the sections to follow.

SAQ 2

Draw a square and label the corners 1, 2, 3 and 4. Also through diagrams indicate the
equivalent configurations and the identical configuration arising out of rotation
through 90° successively four times through an axis perpendicular to the square
surface.

....

....

....

2.4 ROTATION ABOUT AN AXIS OF SYMMETRY

The n-fold axis of symmetry (or the proper axis of symmetry) is a line about which a
molecule is to be rotated through $360°/n$ (or $2\pi/n$ or α) to obtain an equivalent
configuration. The symbol for n-fold axis of symmetry is C_n. The subscript 'n' in C_n is
called order of an axis which can be defined through Eq. 2.1.

$$\text{Order of axis} = n = \frac{360°}{\text{Minimum angle of rotation } (\alpha) \text{ for obtaining equivalent configuration}} \qquad ...(2.1)$$

In the case of water molecule, rotation through 180° (= 360°/2) results in an equivalent configuration.

Hence, $\qquad n = \dfrac{360°}{180°} = 2$

i.e., H_2O molecule has a twofold axis of rotation (C_2 axis). C_2 axis of H_2O is illustrated in Fig. 2.3 along with the rotation through C_2 axis once (C_2^1) and twice (C_2^2); C_2^1 stands for 180° rotation once and C_2^2 stands for 180° rotation twice. The twofold axis of water is on the same plane as the oxygen and hydrogen atoms.
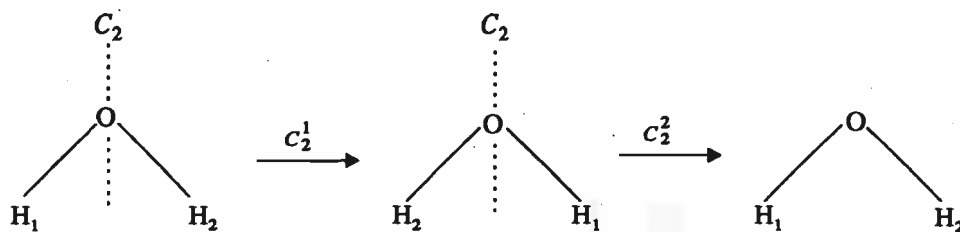

The subscripts 1 or 2 are used to indicate the interchanging of the hydrogen atoms.

Fig. 2.3: Twofold axis C_2 in water molecule; the effect of one C_2 rotation (C_2^1) is shown by interchange of H_1 and H_2 atoms. Application of C_2 twice (C_2^2) brings the molecule to identical configuration as indicated by the position of H_1 on the left side and H_2 on the right side.

In general a *n*-fold axis of symmetry (C_n) gives rise to $C_n^1, C_n^2, ... C_n^n$ operations, and,

$$C_n^n = E \qquad ...(2.2)$$

For C_2 rotation,

$$\alpha = \frac{2\pi}{2}$$
$$= 180°$$

where E refers to identity operation. Identity operation means doing nothing to the molecule and after performing an identity operation, the molecule regains identical configuration. A rotation through 360° (C_n^n) is an instance of identity operation.

Note that C_n^n means *n* times rotation about C_n axis. We shall see shortly other ways of carrying out identity operation.

Note that as per Eq. 2.2 in H_2O molecule, rotation through C_2 axis twice leads to identical configuration.

i.e., $\qquad C_2^1 C_2^1 = C_2^2 = E$

The rotation operation by $2\pi/n \ (= \alpha)$ is denoted as $C\ (\alpha)$.

The presence of C_3 axis in NH_3 can be understood on the basis of the fact that rotation through 120° about this axis results in an equivalent configuration. Using Eq. 2.1,

$$n = \frac{360°}{120°} = 3$$

The C_3 axis of NH_3 is shown in Fig. 2.4a.

The rotations through 120°, 240°, and 360° are denoted by the symbols C_3^1, C_3^2 and C_3^3, respectively. The operations C_3^1 and C_3^2 lead to equivalent configurations while C_3^3 leads to identical configuration. The equilateral triangle formed by joining the positions of three H atoms can be used to represent the effect of successive rotations by 120° three

The rotations, C_3^1, C_3^2 and C_3^3 in NH_3 and BF_3 can be explained using the figures given below. As far as NH_3 molecule is concerned, it must be realised that the three vertices of the equilateral triangle represent the three hydrogen atoms of NH_3 while nitrogen atom is above the plane of equilateral triangle so that the shape of the molecule is trigonal pyramidal. In case of BF_3, the three vertices of the equilateral triangle represent the three flourine atoms and the boron atom is also in the plane of this triangle in keeping with the triangular planar shape of BF_3 molecule.
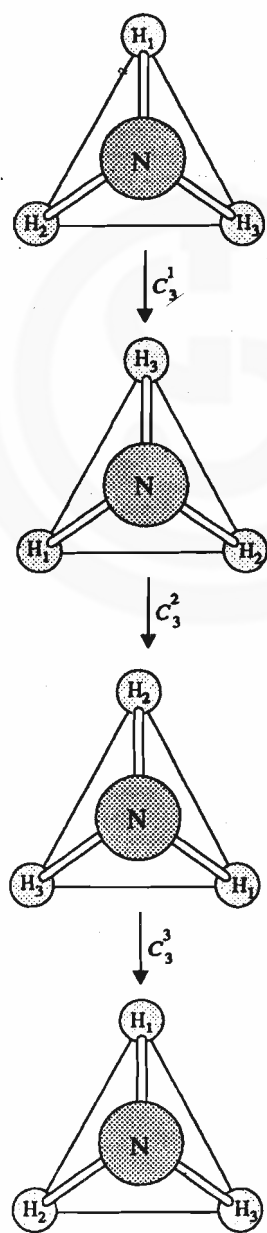
times. For this, use Figs. 2.1 a-d; Figs. 2.1 b, c and d are the results of C_3^1, C_3^2 and C_3^3 operations. You can understand these operations using the figures given in the margin.

In other words, a threefold axis of symmetry gives rise to three operations, C_3^1, C_3^2 and C_3^3.

Also $$C_3^1 C_3^1 = C_3^2 \qquad \qquad ...(2.3)$$

i.e., rotation through 240° is equivalent to rotation through 120° twice.

Further, $$C_3^2 C_3^1 = C_3^3 = E \qquad \qquad ...(2.4)$$

i.e., a rotation by 240° after a rotation through 120° is equal to rotation by 120° three times (C_3^3) or rotation by 360°. The operation C_3^3 is equivalent to identity operation, E.

The difference between the trigonal pyramidal molecule NH_3 and planar molecule BF_3 can be seen from the fact that these two molecules have different numbers of axes of symmetry. For example, NH_3 has only a threefold axis of symmetry but BF_3 has one threefold axis of symmetry (perpendicular to the plane of the molecule and passing through atom B) and three twofold axes of symmetry. Each C_2 axis in BF_3 is along one of the B − F bonds (Figs. 2.5 a-b). Thus, the three C_2 axes are perpendicular to C_3 axis in BF_3.

Let us examine benzene molecule. Benzene has one C_6 axis (perpendicular to the molecular plane) and six C_2 axes (Figs. 2.6 a-b). Three of the C_2 axes pass through the mid points of the opposite and parallel sides of the hexagon (i.e., in between C − C bonds) while three others pass through the opposite corners of the hexagon (i.e., along C − H bonds). Hence in benzene, the six C_2 axes are perpendicular to C_6 axis.

If a molecule has many C_n axes of different orders, then the axis with the highest order is called the principal axis of the molecule. Thus, the C_3 axis in BF_3 is its principal axis. Benzene has C_6 axis as its principal axis.

(a)

(b)

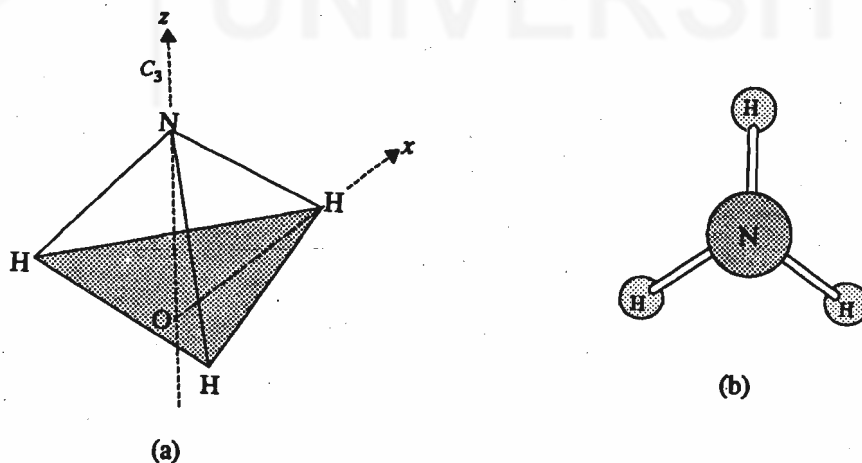**Fig.2.4:** (a) The shape of NH_3 molecule—trigonal pyramidal; point O lies in the xy plane (shown as shaded area) and on the z axis which is C_3 axis passing through nitrogen atom. The three hydrogen atoms form an equilateral triangle in the xy plane.

(b) The top view of NH_3 molecule which is used in drawing the figures given at the margin to denote C_3^1, C_3^2 and C_3^3 operations.
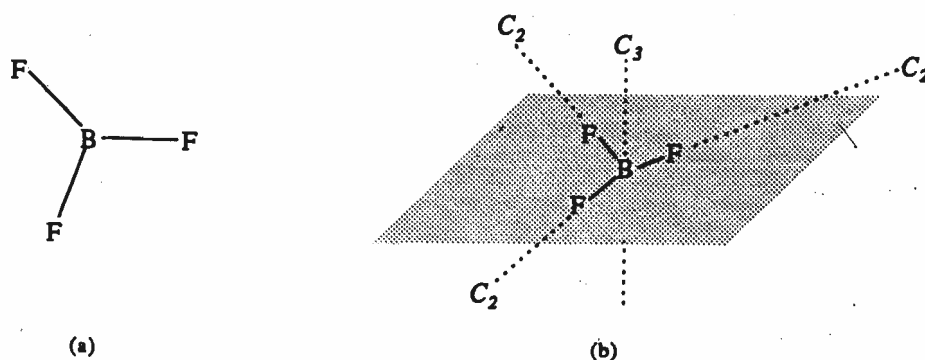
(a)

(b)

Fig. 2.5:   (a)   The shape of BF_3 molecule — triangular planar

(b)   Threefold axis of symmetry in BF_3; it is perpendicular to the molecular plane. The molecular plane is shown by the shaded area. Each B — F bond is also a twofold axis of symmetry. All the three C_2 axes are in the molecular plane.
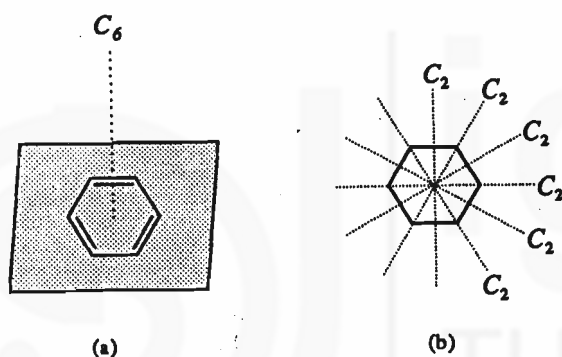

(a)

(b)

Fig. 2.6:   (a) C_6 in benzene; it is perpendicular to the molecular plane (shown as shaded area)

(b)   The three C_2 axes along opposite C—H bonds and three C_2 axes in between parallel C — C bonds.

Since $n = 2\pi/\alpha$, n tends to infinity as α tends to zero. Also note that α is a continuous angle variable.

Linear molecules such as H_2, HCl, CO_2, COS, etc. have C_∞ axis along their molecular axes since rotation through even any small angle gives rise to an equivalent configuration. In other words, the angle of rotation for obtaining equivalent configuration is infinitesimally small (i.e., $\alpha \rightarrow 0$) for linear molecules such that application of Eq. 2.1 leads to the conclusion that $n = \infty$.

Using the above ideas, answer the following SAQs.

SAQ 3

You have predicted the shape of PCl_3 in SAQ 1. Name the axis of symmetry in PCl_3.

....

....

....

SAQ 4

State the symbols for the operations of six successive rotations through C_6 axis.

....

....

....

2.5 REFLECTION IN A PLANE OF SYMMETRY

A plane bisects the object under consideration so that one half of the object on one side of the plane is the mirror image of the half on the other side. If the plane contains the principal axis, it is called the vertical plane and is denoted by σ_v. H_2O has two vertical planes of symmetry (σ_v and σ_v' -Figs. 2.7. a and b) while NH_3 has three vertical planes of symmetry σ_v, σ_v' and σ_v'' (Fig. 2.8).

A vertical plane passes through principal axis. Hence σ_v and σ_v' in H_2O are vertical planes.
A horizontal plane (σ_h) is perpendicular to the principal axis.

(a)

(b)
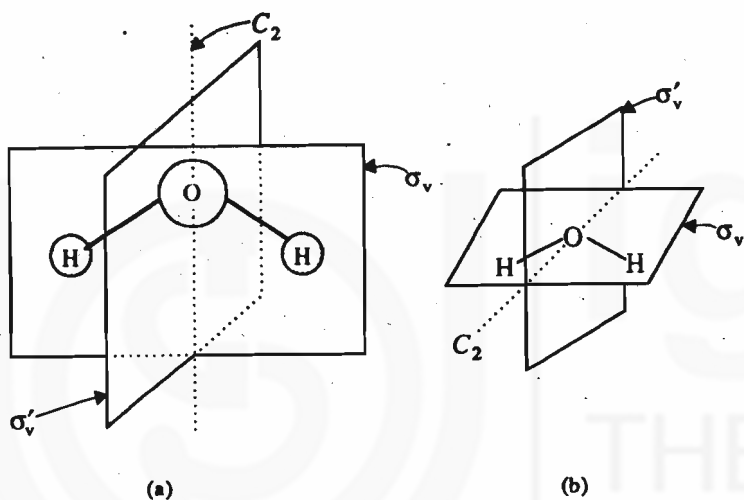
Fig. 2.7: a) Two vertical planes of symmetry (σ_v and σ_v') in water.

b) σ_v plane is differently shown so that it is easier to visualise the two planes.
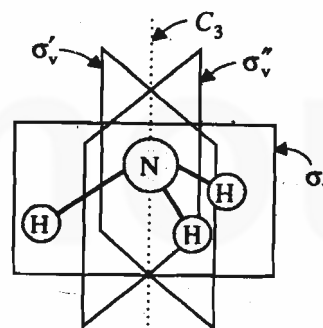
Fig. 2.8: The three vertical planes of symmetry in NH_3 (σ_v, σ_v' and σ_v''); each vertical plane of symmetry encloses one N—H bond also.

The terms 'conformation' and 'configuration' have to be properly understood. Various conformations of a molecule result due to rotation about C—C bond through different angles. For instance, ethane has two well known conformations, eclipsed and staggered. For a better understanding of the term, conformation, refer to Sec. 3.7 of Unit 3 of Block 1 of Organic Chemistry (CHE-05) course.

The term 'configuration' refers to a particular spatial arrangement of atoms in a molecule. The optical isomers and geometrical isomers come under this category. In this context, you may refer to Sec. 2.2 of Unit 2 of Block 1 of Organic Chemistry course.

When the plane of symmetry is perpendicular to the principal axis, it is called the horizontal plane, and, is denoted by σ_h. For instance, the plane containing all the six carbon atoms and six hydrogen atoms in benzene is the horizontal plane, since it is perpendicular to the (C_6) principal axis.

Again let us examine the simple cases of NH_3 and BF_3. The fact that their shapes are different is shown up by the presence of different types of planes of symmetry. Thus, both these molecules have three vertical planes of symmetry. In addition to these, the planar molecule, BF_3, has a horizontal plane of symmetry but not NH_3 (which is pyramidal).

We shall also examine another type of plane of symmetry which is known as dihedral plane and is denoted by σ_d. A dihedral plane must be,

i)   vertical (i.e., must contain the principal axis) and

ii)   bisect the angle between two C_2 axes which are themselves perpendicular to the principal axis.

For instance, the staggered form of ethane (Fig. 2.9a) has three dihedral planes. Each dihedral plane contains the C_3 axis (which is the principal axis) and intersects two mutually perpendicular C_2 axis. One of the three dihedral planes is shown in Fig. 2.9b.
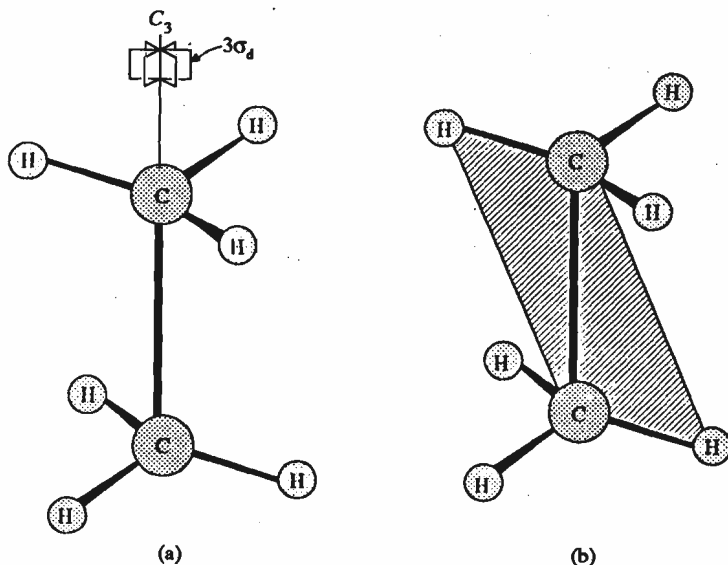

Fig. 2.9: (a) The staggered conformation of ethane. It has three σ_d planes and each σ_d plane contains C — C bond and a pair of C — H bonds.

b) One of the dihedral planes shown by the shaded portion.

The operation of reflection of same type (viz. vertical, horizontal or dihedral) conducted twice across a plane leads to identity operation:

i.e.,
$$\left.\begin{aligned} \sigma_v\,\sigma_v &= E \\ \sigma_h\,\sigma_h &= E \\ \sigma_d\,\sigma_d &= E \end{aligned}\right\} \qquad ...(2.5)$$

Having studied the above, answer the following SAQs.

SAQ 5

Name the planes of symmetry in PCl_3. For its structure, refer to SAQ 1.

....

....

....

SAQ 6

$SOCl_2$ is pyramidal in shape. It has a plane of symmetry. Identify the atoms on this plane.

Hint: There is a simple restriction on the planes of symmetry. A plane must either pass through an atom or else that type of atom must occur in pairs being placed symmetrically on either side of the plane.
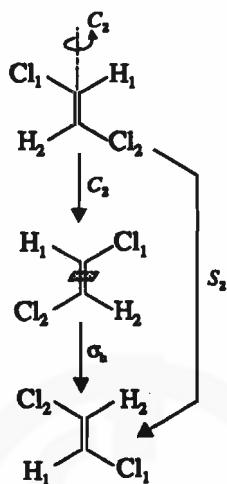
....

....

....

2.6 IMPROPER ROTATION ABOUT AN AXIS OF IMPROPER ROTATION

In the Appendix part, we shall discuss the importance of combining operations such as in Eq. 2.6.

In *trans*-dichloroethylene, S_2 being equivalent to C_2 operation followed by σ_h can be shown as follows:

An n-fold improper rotation consists of n-fold rotation followed by a horizontal reflection. Improper rotation about an axis is also known as rotary-reflection operation. Such an axis is called rotary-reflection axis or alternating axis of symmetry or improper axis of symmetry (S_n).

To cite an example, the staggered conformation of ethane has improper axis of order $6(S_6)$. To illustrate this fact, the rotation of the staggered conformation of ethane by $60°$ (C_6) followed by reflection through the horizontal plane (σ_h) has been shown in Fig. 2.10. You can see from this figure that C_6 followed by σ_h which is equivalent to S_6 leads to an equivalent configuration.

i.e., $$\sigma_h C_6 = S_6 \qquad \qquad ...(2.6)$$

To understand the displacement of particular hydrogen or chlorine atoms, the subscripts 1 and 2 are used. Also note that S_2 is equivalent to i, the inversion operation, which we shall discuss in the next section.
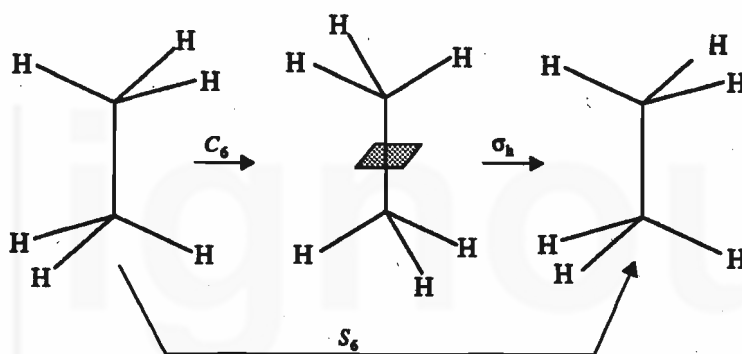

Fig. 2.10: S_6 in staggered conformation of ethane shown in terms of C_6 and σ_h.

The presence of improper axis of symmetry in a molecule may seem difficult to identify. But it is useful for deciding whether a molecule is optically active or not. This aspect will be made clear in Subsec. 2.10.2 of this unit. Your understanding of this section can be verified by answering the following SAQ.

SAQ 7

The staggered conformation of ethane has S_6 axis. What do you mean by this?

....

....

....

2.7 INVERSION THROUGH CENTRE OF SYMMETRY

Inversion is the process of drawing a line from any point through the centre of the molecule to an equal distance on the other side from the centre to arrive at an equivalent point. The centre of the molecule which generates inversion is called the centre of symmetry or the inversion centre (i).

All homonuclear diatomic molecules (e.g., H_2, N_2, etc.) possess the centre of symmetry. Also CO_2, C_2H_4 (Fig. 2.11), C_6H_6, SF_6 and the staggered conformation of ethane possess centre of symmetry.

H_2O, NH_3, BF_3 and CH_4 do not possess centre of symmetry. In Sec. 6.6.3 of Unit 6 of Atoms and Molecules course, we have indicated that the presence of centre of symmetry in a molecule leads to zero dipole moment for the molecule. We will recall this idea in Sec. 2.10.1 of this Unit. Similar to reflection, the operation of inversion conducted twice through the centre of symmetry leads to identity operation.

$$i.i = E \qquad \qquad ...(2.7)$$

Answer the following SAQ.

SAQ 8

What do you think could be the dipole moment of benzene? State the reason.

....

....

....

Fig. 2.11: The dot represents the centre of symmetry in ethylene.

Note that i is a special case of improper rotation, when the angle of rotation is 180° ($\alpha = 2\pi/2 = \pi$).

Also $\sigma_h C_2 = S_2 = i$

This relationship has been illustrated using *trans*-dichloroethylene in the previous section.

2.8 IDENTITY

The operation of identity (E) consists of doing nothing. The corresponding element is the entire object. All molecules possess identity element. One reason for its inclusion is that some molecules (e.g., CHFClBr, Fig. 2.12) have only this symmetry element; another reason is connected with one of the fundamental aspects of group theory (which we shall mention in the Appendix of this unit). We have already mentioned the relationships of rotation, reflection and inversion with identity operation through Eqs. 2.2, 2.5 and 2.7.
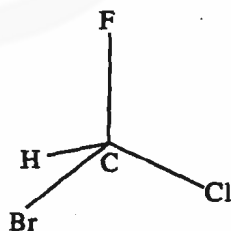

Fig. 2.13: Quinoline

Fig. 2.12: CHFClBr which has only identity as the element of symmetry.

So far, we discussed in detail the symmetry elements and symmetry operations. In the next section, let us see how the molecules can be classified according to symmetry.

Fig. 2.14: *meso*-tartaric acid

2.9 POINT GROUPS OF MOLECULES

Point groups of molecules are classes of molecules which have same list of symmetry elements. Thus, CH_4 and CCl_4, have same list of symmetry elements and, belong to the same point group, and, are different from the point group to which H_2O belongs. The classification of molecules into point groups is of help in understanding the spectral characteristics, dipole moment values etc. of molecules.
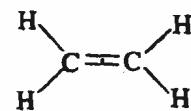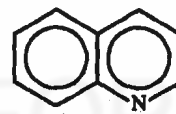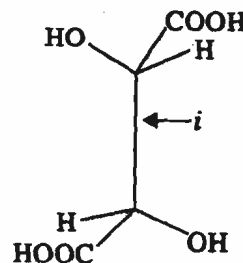
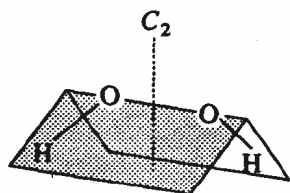The method of identifying point groups of molecules has been discussed in the Appendix.

Fig. 2.15: H_2O_2 (partially opened book configuration)

Note that all dihedral groups have a C_n axis and nC_2 axes perpendicular to C_n axis. The dihedral groups mentioned in Table 2.3 are $D_3, D_{3h}, D_{6h}, D_{3d}$ and $D_{\infty h}$.
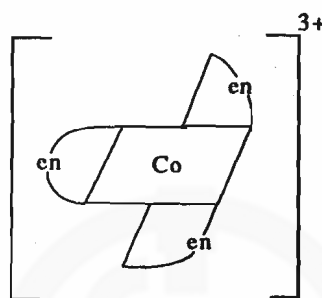

Fig. 2.16: $[Co(en)_3]^{3+}$ ion; en stands for ethylene diamine
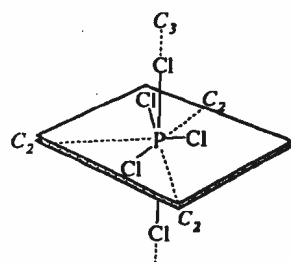

Fig. 2.17: PCl_5: note that the vertical Cl-P-Cl bonds constitute C_3 axis.

A group is called a cubic group, if it has many C_n axes of order greater than 2. The important cubic groups are T_d and O_h.

A molecular group is called a point group because one point in the molecule remains fixed under all the symmetry operations in the molecule. All the symmetry elements of a molecule intersect at this point. We may note that crystals have an additional element of symmetry known as translational symmetry, wherein symmetry arises from the translational motion of crystals through space. The crystals are classified into **space groups**. We are not going to discuss crystallographic symmetry in this unit.

The point group of a molecule can be denoted by a specific symbol. There are two kinds of notations, one devised by Schoenflies and, the other, by Hermann and Mauguin. The Schoenflies notation is more common for the discussion of molecular symmetry and the Hermann − Mauguin symbolism is exclusively used for the discussion of crystal symmetry. In Table 2.3, we shall give the Schoenflies notation for some of the point groups.

Table 2.3: Schoenflies Notation for Some Point Groups.

Schoenflies notation	Symmetry elements	Examples
C_1	E	CHFClBr
C_s	σ and E	Quinoline (Fig. 2.13)
$C_i (S_2)$	i and E	*meso*-tartaric acid (Fig. 2.14)
C_2	C_2 and E	H_2O_2 (partially opened book configuration (Fig. 2.15)).
C_{2v}	$C_2, 2\sigma_v$ and E	H_2O and SO_2
C_{3v}	$2C_3, 3\sigma_v$ and E	NH_3 and $CHCl_3$
$C_{\infty v}$	$2C_\infty, \infty\sigma_v$ and E	Linear molecules without centre of symmetry such as CO, OCS and HBr
C_{2h}	C_2, σ_h, i and E	*trans*-1,2-dichloroethylene
D_3	$C_3, 3C_2$ and E	$[Co(en)_3]^{3+}$ (Fig. 2.16)
D_{3h}	$2C_3, 3C_2, \sigma_h, 3\sigma_v, 2S_3$ and E	BF_3, PCl_5 (Fig.2.17) and eclipsed form of ethane
D_{6h}	$2C_6, 2C_3, 6C_2, \sigma_h, 3\sigma_v, 3\sigma_d, 2S_3, 2S_6, i$ and E	C_6H_6
$D_{\infty h}$	$2C_\infty, \infty C_2, \infty\sigma_v, \sigma_h, 2S_\infty, i$ and E	All linear molecules with centre of symmetry such as H_2, Cl_2 and C_2H_2
D_{3d}	$2C_3, 3C_2, 3\sigma_d, i, 2S_6$ and E	Staggered form of ethane
T_d	$8C_3, 3C_2, 6S_4, 6\sigma_d$ and E	CCl_4 and CH_4 (Fig. 2.18)
O_h	$6C_4, 8C_3, 6C_2, 3\sigma_h, 6S_4, 8S_6, 6\sigma_d, i$ and E	SF_6 (Fig. 2.19)
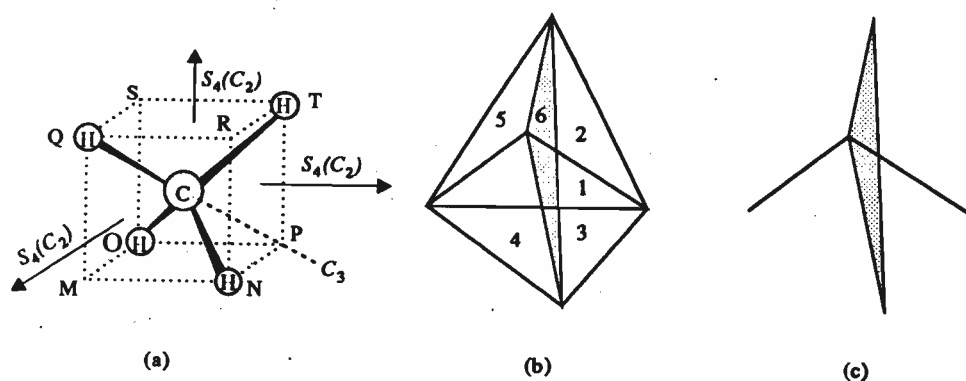
Fig. 2.18: a) Methane belonging to T_d group; the three cartesian axes serve as three C_2 (and also S_4) axes. The four C_3 axes are along the four C—H bonds (these C_3 axes are also the body diagonals—MT, NS, OR and QP); one of the C_3 axes (QP) is shown.

   b) You can make six triangular planes in a tetrahedron by combining any two corners with the centre; do not confuse these six planes with four faces of the tetrahedron which are obtained by joining any three corners only. These six planes are $6\sigma_d$ for CH_4; each of the σ_d passes through the carbon and two hydrogen atoms and relates the other two hydrogen atoms as a mirror image of each other.
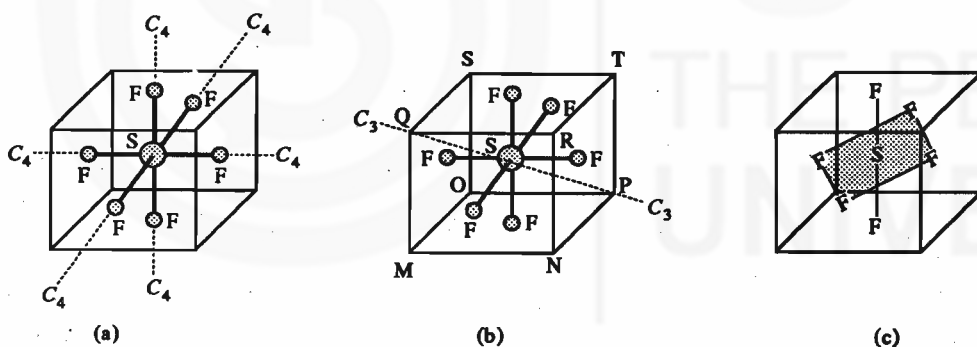
   c) One of the six dihedral planes (σ_d).

Fig. 2.19: SF_6 with O_h point group symmetry; SF_6 is shown inside the cube.

   (a) Each F—S—F linear arrangement is a C_4 axis; the three C_4 axes are at right angles to each other

   (b) Four C_3 axes are located along the body diagonals (MT, NS, OR and QP) of the cube; one of the C_3 axes (QP) is shown.

   (c) One of the three σ_h planes is shown by the shaded area; each σ_h plane comprises of two diagonal units of F—S—F; other symmetry elements are not shown.

Using the above materials, answer the following SAQ.

SAQ 9

Using your answers for SAQs 1, 3 and 5, identify the point group of PCl_3.

....

....

....

2.10 SOME IMPLICATIONS OF MOLECULAR SYMMETRY

The examination of molecules with respect to symmetry aspects could lead us to many useful conclusions. We shall examine a few of them.

2.10.1 Dipole Moment and Molecular Symmetry

Dipole moment is a vector quantity as defined in Sec. 6.4 of Unit 6 of CHE-01 (Atoms and Molecules) course. It has both direction and magnitude. The symmetry operation allowed for a molecule should not affect the direction or magnitude of the dipole moment vector. In other words, the dipole moment vector should be invariant and must be contained in each of the symmetry elements of the molecule. As a result of this, **only molecules belonging to the groups C_n, C_{nv} and C_s may have dipole moment.**

The statement that the dipole moment vector should be invariant (or totally symmetric) with respect to symmetry operations will be used in defining the allowed transitions in the Appendix of this unit.

Let us illustrate this using H_2O molecule. As explained in the Appendix of Unit 6 of CHE-01 course, the direction of the resultant dipole moment vector in H_2O (indicated by $\updownarrow$ sign) is as shown in Fig. 2.20a.

You try C_2, σ_v or σ_v' operation (using Fig. 2.20b) through diagrams such as Fig. 2.3 and verify the fact that the dipole moment vector remains invariant after each symmetry operation.

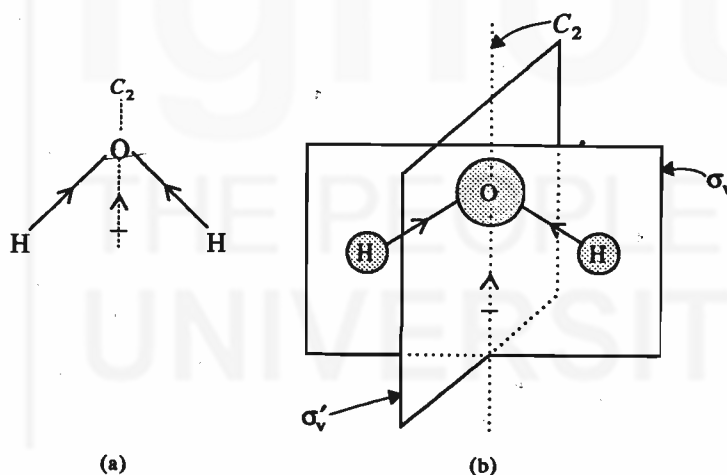(a)   (b)

Fig. 2.20: Illustration of the fact that each of the symmetry elements of water contains the dipole moment vector. It is worth recollecting that H_2O has E, C_2 and $2\sigma_v$ as symmetry elements.

a) H→—O stands for O—H bond moment and $\updownarrow$ stands for the direction of the resultant dipole moment vector. Note that the dipole moment vector lies along the C_2 axis.

b) Both σ_v and σ_v' planes contain the dipole moment vector. (b) is drawn to show that σ_v, σ_v' and C_2 contain the dipole moment vector.

Note that molecular symmetry is a theoretical concept. Experimental quantities such as dipole moment or absorption frequencies (obtained from spectral measurements) help us in confirming the theoretical aspects such as symmetry of a molecule.

As shown in Fig. 2.20 a-b, the symmetry elements, C_2 axis and two σ_v planes, also contain the resultant dipole moment vector in H_2O molecule.

In molecules with the point groups such as C_{nh}, D_n, D_{nh}, etc., there are symmetry operations that correspond to turning the molecule upside down. This would reverse the direction of the dipole moment vector which is not allowed. Hence, the molecules belonging to the point groups such as C_{nh}, D_{nh} etc. cannot have dipole moment. Use Table 2.3 and see how many of the molecules possess dipole moment.

The presence or absence of dipole moment tells us about the symmetry of the molecule. We shall illustrate this taking two cases of triatomic molecules, H_2O and CO_2. H_2O has a dipole moment value of 6.14×10^{-30} C m. This confirms the bent structure of H_2O (as predicted by VSEPR theory in Sec. 2.2) and the fact that it could belong to the point group C_{2v} (a special case of C_{nv} which has permanent dipole moment).

CO_2 has zero dipole moment. This confirms the linear structure of CO_2 (as predicted by VSEPR theory) and the fact that it could belong to $D_{\infty h}$ point group.

It is worth recapitulating that the bent structure of H_2O and the linear structure of CO_2 have been explained in subsec. 6.6.3 of Unit 6 of CHE-01 (Atoms and Molecules) course based on $O-H$ and $C=O$ bond moments.

2.10.2 Symmetry and Optical Activity

In Sec. 6.10 of Unit 6 of CHE-01 course, we have explained the concept of optical activity. A molecule is optically active only if it could exist as separate left-and right-handed forms or mirror image isomers. Lactic acid (Fig. 2.21) is an example of an optically active molecule. From symmetry point of view, we can define optical acivity. A molecule is optically active only if it cannot be superimposed on its mirror image through improper rotation. Since a rotation about an axis followed by a reflection in a perpendicular plane (i.e., improper rotation) converts a right-handed object to a left-handed object, the presence of S_n axis indicates that a molecule cannot exist in separate left-and right-handed forms. This implies that any optically active molecule will not have an axis of improper rotation, S_n. It is important to check whether a molecule has S_n axis even in an implied way. For example, the molecules in the point group C_{nh} are not optically active, since these molecules have S_n axis as implied by the presence of both C_n axis and σ_h plane. All molecules with centre of symmetry are optically inactive. It is so since any molecule having the inversion centre possesses S_2 ; i is equivalent to C_2 followed by σ_h which is equivalent to S_2 as explained in Secs. 2.6 and 2.7.

Even if a molecule possesses only σ, then also it is optically inactive since σ is equal to S_1 [one full rotation of the molecule by 360° (C_1) through any axis, followed by reflection across a perpendicular plane]. Thus, fluorochloromethane (Fig. 2.22) which has σ is not optically active.

To sum up, molecules having improper rotation axes will not be optically active. For example, lactic acid belongs to C_1 and is optically active. Molecules having σ (i.e., S_1), i (i.e., S_2) or any other S_n are optically inactive.
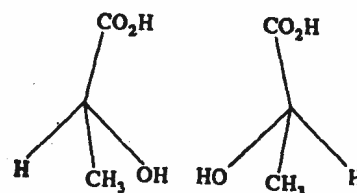

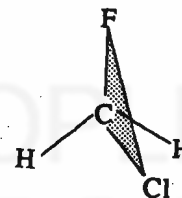Fig. 2.21: Lactic acid: the left-and right-handed forms (mirror images).

Fig. 2.22: σ plane in CH_2FCl encloses C, F and Cl.

2.10.3 Spectra and Molecular Symmetry

We can examine the microwave and infrared spectral characteristics of a molecule to understand the molecular symmetry or vice versa.

We shall see in Unit 3 of this course that only molecules having permanent dipole moment can give rise to pure rotational (or microwave) spectra. Thus, only molecules belonging to the point groups C_{nv} and C_s which have permanent dipole moment can exhibit pure rotational spectra. For example, CO ($C_{\infty v}$) and CH_3Cl (C_{3v}) can exhibit pure rotational spectra but not CO_2 ($D_{\infty h}$) and CCl_4 (T_d). The former two possess permanent dipole moment but not the latter two. This again could help us in confirming the point group classification of a molecule.

In Units 4 and 5 of this course, we shall see that for a molecule to give rise to vibrational spectra, one or more vibrations of a molecule must give rise to a dipole moment change. The vibration spectra could be understood using the symmetry aspects of a particular vibration of a molecule. The assignment of infrared spectral frequencies to the specific vibrations causing the absorption can be made using group theory. We shall discuss some of the aspects of group theory in the Appendix of this unit and in Units 5 and 6.

51

Answer the following SAQs.

SAQ 10

CH_2Cl_2 has the following symmetry elements:

E, C_2 and $2\sigma_v$

a) Identify the point group.

b) Will the molecule show permanent dipole moment?

....

....

....

SAQ 11

Both CO_2 and CO are linear. Which of the two can exhibit pure rotational spectra? State the reason.

....

....

....

SAQ 12

1-Bromo-1-chloroethane belongs to C_1 point group. Is this molecules optically active? State the reason.

....

....

....

2.11 SUMMARY

In this unit, we have discussed symmetry aspects of molecules. We have explained the Shoenflies system of point group classification. We have given examples for the point groups of molecules. These ideas should enable you to relate the Lewis structure of a molecule to its point group. In some of the units of this course, we shall be using symmetry aspects of a molecule for understanding the molecular spectra.

2.12 TERMINAL QUESTIONS

1. (a) Using VSEPR theory, find the shape of $XeOF_4$.

   Hints : Of the 8 electrons of Xe, 4 are involved in forming four Xe−F bonds; 2 electrons are involved in Xe→O bond which should be considered like a single covalent bond only. The other two electrons form a lone pair around Xe.

   (b) Draw its shape.

   (c) Name the principal axis of $XeOF_4$.

2. (a) Although $CHCl_3$ has tetrahedral structure, it has symmetry elements similar to NH_3. The C—H bond in $CHCl_3$ is a C_3 axis. There are three σ_v planes, each plane enclosing C—H bond and one C—Cl bond. Identify the point group of $CHCl_3$.

    (b) Can it have permanent dipole moment?

    (c) Can it exhibit pure rotational spectra?

    (d) Can it be optically active?

3. (a) $[PtCl_4]^{2-}$ has a square planar structure. State the name of the two proper axes of symmetry.

    (b) Does it have centre of symmetry?

    (c) Can it have permanent dipole moment?

4. (a) HBr is a linear molecule. State the name of the principal axis of symmetry in it.

    (b) State its planes of symmetry.

    (c) Name its point group.

    (d) Can it have permanent dipole moment?

    (e) Can it exhibit pure rotational spectra?

5. H_2O belongs to C_{2v} group. Name the symmetry elements in it.

6. (a) For PF_5, predict the shape using VSEPR theory.

    (b) State any three symmetry elements in it.

    (c) Identify its point group.

2.13 ANSWERS

Self Assessment Questions

1. The central atom phosphorus has three bond pairs and one lone pair. Hence, it is trigonal pyramidal.

2. Through drawings it can be established that the equivalent configurations arise thrice one after the other, and finally the identical configuration.

3. PCl_3 has C_3 axis.

4. $C_6^1, C_6^2, C_6^3, C_6^4, C_6^5$, and $C_6^6 (=E)$.

5. There are 3 σ_v planes in PCl_3. Each σ_v plane encloses one P—Cl bond.

6. The plane of symmetry in $SOCl_2$ must pass through sulphur and oxygen atoms since one atom each is present. The two chlorine atoms must lie on front and back sides of this plane.

7. Presence of S_6 axis indicates that rotation through 60° followed by reflection in a perpendicular plane leads to equivalent configuration.

8. The dipole moment of C_6H_6 is zero, since it has a centre of symmetry.

9. Using Table 2.3, it can be shown that PCl_3 belongs to C_{3v} point group.

10. a) C_{2v}

    b) The molecule can have permanent dipole moment, since its point group (C_{2v}) is one among the C_{nv} groups.

11. CO_2 belongs to $D_{\infty h}$ point group and does not have permanent dipole moment. Hence, it cannot exhibit pure rotational spectra. CO belongs to $C_{\infty v}$ point group
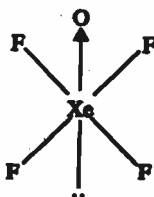
53
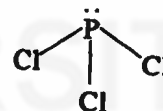
and has permanent dipole moment. Hence, it can exhibit pure rotational spectra.

(12)   1-bromo-1-chloroethane is optically active, since it does not have S_n axis.

Terminal Questions

1. (a) $XeOF_4$ is square pyramidal in shape.

    (b)

    (c) C_4

2. (a) C_{3v}

    (b)   It can have permanent dipole moment.

    (c)   It can exhibit pure rotational spectra.

    (d)   It cannot be optically active.

3. (a) C_2 and C_4

    (b)   It has centre of symmetry.

    (c)   It cannot have permanent dipole moment.

4. (a) C_∞

    (b) $\infty \, \sigma_v$

    (c) $C_{\infty v}$

    (d)   It can have permanent dipole moment.

    (e)   It can exhibit pure rotational spectra.

5. E, C_2 and $2\sigma_v$.

6. (a)   Trigonal bipyramidal

    (b) C_3, $3C_2$ (perpendicular to C_3) and σ_h

    (c) D_{3h}

2.14 APPENDIX

The Basic Aspects of Group Theory

The group theory is the mathematical method for dealing with the application of symmetry concepts to spectroscopy and molecular structure. We shall deal with the following aspects of group theory in this section:

    i)   The criteria of a group

    ii)   Character table of point groups

    iii)   Uses of character tables

The Criteria of Group

A group is a collection or a set of elements which should satisfy the five criteria mentioned below. The elements of a group are related to one another through a combination process. The elements of a group may be symmetry operations of a molecule or the real numbers ($-\infty$ to $+\infty$, inclusive of fractions). The combination process may be multiplication or addition. A group should satisfy the following five criteria:

1.   The product of two elements of a group gives another element of the group.

Example

If A and B are two elements of a group, then the combination, AB, leads to C, which is also an element of the group. The combination AB means, B is carried out first and then A. The combination AB need not always be equal to BA (BA means A is carried out first and then B). That is the order of combination is quite important. Those groups for which AB = BA are said to be *commutative or Abelian* groups; i.e., in Abelian groups, each element commutes with other elements of the group.

2.   An element combines with itself to form one of the elements of the group.

3.   Every group has one element which commutes with all the elements of the group to leave them unchanged. This element is called the identity element and is indicated by the symbol E.

Examples

   (a) $EA = AE = A$

   (b) $EB = BE = B$

4.   Every element has an inverse or reciprocal which also belongs to the group. The element and the inverse combine to give the identity element.

Examples

If A^{-1} is the inverse of A and, B^{-1} the inverse of B, we can write

$$AA^{-1} = A^{-1}A = E$$

$$BB^{-1} = B^{-1}B = E$$

5.   Every element of the group obeys the associative law of combination. If A, B and C are three elements of a group and the process of combination is multiplication, then the associative law tells us that

$$(AB)C = A(BC)$$

We can illustrate the criteria of groups using the symmetry operations of C_{2v} point group.

Example

The four symmetry operations of C_{2v} point group, E, $C_2(z)$, $\sigma_v (xz)$ and $\sigma_v' (yz)$ satisfy the criteria of group. Let us explain the significance of the operations, E, $C_2(z)$, $\sigma_v (xz)$ and $\sigma_v' (yz)$.

These operations can be understood using the following diagrams (Fig. A.1) where one has to observe how (i) the two hydrogen atoms 1 and 2 and (ii) the x, y and z coordinates of oxygen atom are affected by these operations.

Fig. A.1: E, $C_2(z)$, σ_v (xz) and σ_v' (yz) operations.
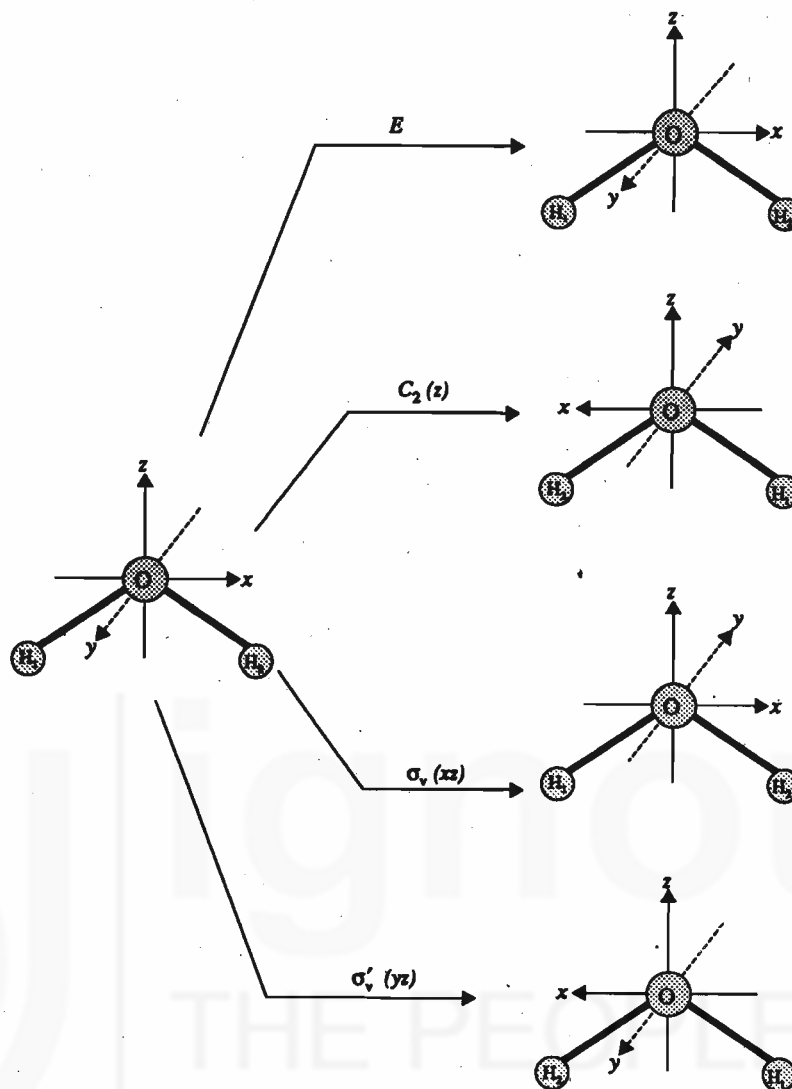
$C_2(z)$ means rotation through $180°$ around z-axis.

Note that C_2 operation is carried out around z-axis and it interchanges the positions of H_1 and H_2 atoms besides changing the x and y coordinates on oxygen atom. You can observe that the positions of the two hydrogen atoms and the coordinates of the oxygen atom remain the same as a result of E operation. But the σ_v (xz) operation changes the y coordinate of oxygen atom while retaining the x and z coordinates of oxygen atom and the positions of two hydrogen atoms. The operation σ_v' (yz) results in the change of positions of two hydrogen atoms and the x coordinate of the oxygen atom. Using the rules that define a group, we can construct the following multiplication table (Table A.1) for C_{2v} group.

The elements of a group are its constituents. The elements of the group discussed in this example are the symmetry operations such as reflection, rotation etc. These elements are not to be confused with symmetry elements such as plane of symmetry, axis of symmetry, etc.

Table A.1: Multiplication Table for C_{2v} group

	E	$C_2(z)$	$\sigma_v(xz)$	σ_v' (yz)
E	E	$C_2(z)$	$\sigma_v(xz)$	σ_v' (yz)
$C_2(z)$	$C_2(z)$	E	σ_v' (yz)	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	σ_v' (yz)	E	$C_2(z)$
σ_v' (yz)	σ_v' (yz)	$\sigma_v(xz)$	$C_2(z)$	E

Note that any particular symmetry operation appears only once in each column or each row. In order to verify the entries in Table A.1, you must remember the convention that the operation listed at the top of the table has to be carried out first followed by the operation listed at the left side. For example, the execution of operation $\sigma_v (xz)$ followed by the operation $C_2(z)$ gives rise to $\sigma_v' (yz)$. The sequence of carrying out the operations $\sigma_v (xz)$ and $C_2(z)$, and the resultant product, $\sigma_v' (yz)$ are represented by means of curved arrows I and II in Table A.1. The product of operations $\sigma_v (xz)$ and $C_2 (z)$ can be represented by Eq. A.1.

$$C_2 (z). \sigma_v (xz) = \sigma_v' (yz) \qquad \qquad ...(A.1)$$

Eq. A.1 can be understood using Fig. A.2; this helps in verifying the first of the criteria of a group stated above.
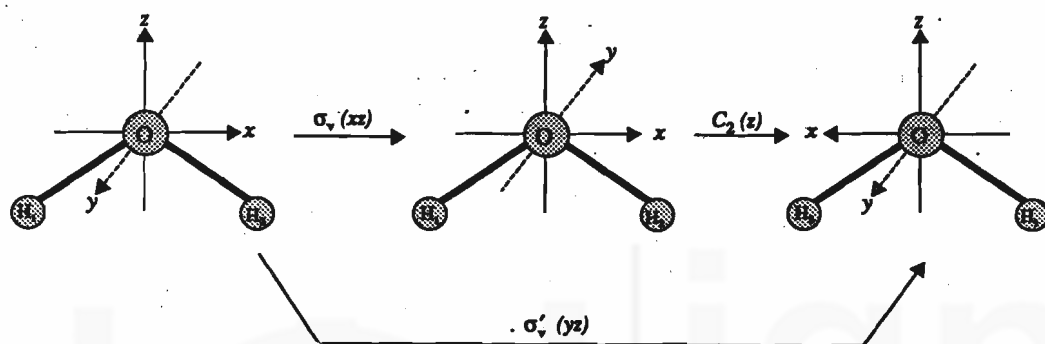

Fig. A.2: Illustration of Eq. A.1 $[C_2(z) \sigma_v(xz) = \sigma_v' (yz)]$.

You can verify the other four criteria of group using the symmetry operations of C_{2v} group. Note that in C_{2v} group, the inverse of each element (i.e., symmetry operation) is the element itself.

Thus, $[C_2 (z)]^{-1} = C_2 (z)$

$[\sigma_v (xz)]^{-1} = \sigma_v (xz)$

$[\sigma_v' (yz)]^{-1} = \sigma_v' (yz)$

These are characteristic of C_{2v} group. These relationships along with the fact that $E^{-1} = E$ should help you in verifying the entries in Table A.1 and also the fact that $\sigma_v (xz)$, $\sigma_v' (yz)$, $C_2 (z)$ and E form a group.

Next we shall devote our attention towards the formation of character table of C_{2v} point group. This could help us in studying some of the applications of group theory.

A matrix is a rectangular array of numbers or symbols for numbers, which may be combined with other such arrays according to certain rules. You go through Unit 13 of PMT Course or Unit 5 of MTE-04 Course for getting an elementary idea about matrices.

Character Table of Point Groups

The symmetry operations of a point group can be represented using a set of matrices. Each matrix is called a representative. The sum of the diagonal elements of a matrix is called its character. It is possible to reduce a matrix into smaller matrices known as irreducible matrices. A set of irreducible matrices corresponding to the symmetry operations of a point group is known as irreducible representation. Each irreducible representation describes the effect of symmetry operations on the directional properties such as translational coordinates (x, y, z) rotational coordinates (R_x, R_y, R_z) etc. It is possible to obtain useful information by listing the characters of all possible irreducible representations of a point group in a tablular form known as character table. The set of character values of each irreducible representation is denoted by the symbol τ.

We shall use a simple method to arrive at the character table of C_{2v} point group and then illustrate its uses. This can be done by seeing the effect of four symmetry operations of C_{2v} group on the signs of the lobes of p_x, p_y and p_z orbitals. If the signs of the lobes remain the same after performing a symmetry operation, the resulting change is represented by 1; on the other hand, if a symmetry operation changes the signs of the lobes, then it is represented by –1. In other words, the value of 1 signifies no change in signs of the lobes while a value of –1 signifies a change of sign.

### Effect of Symmetry Operations on p_x Orbital
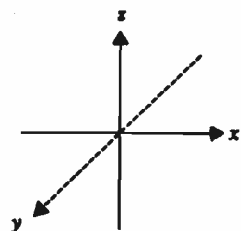
The signs of the lobes of p_x orbital remain the same after identity operation (E); so E can be represented by 1.
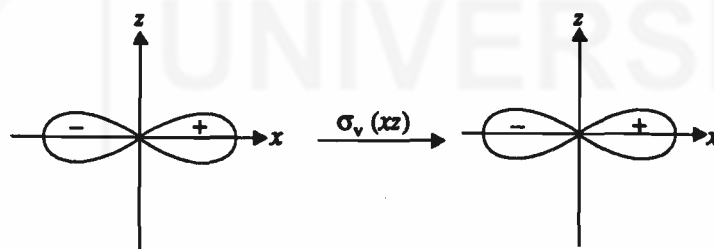
$$Ep_x = 1p_x$$

This can be understood since performance of identity operation means doing nothing.

The signs of the lobes of p_x orbital changes by C_2 operation (about the z axis) and hence, this operation can be represented by -1.
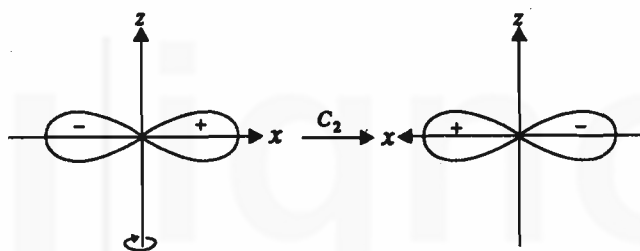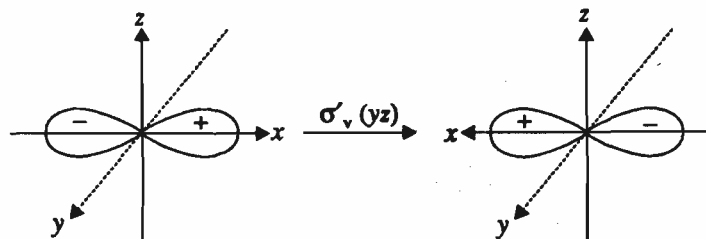

$$C_2 p_x = -1p_x$$

The signs of the lobes of p_x orbitals remain the same after reflection through σ_v (xz) plane while there is a change after reflection through σ_v' (yz) plane.

$$\sigma_v \ (xz) \ p_x = 1p_x$$

or σ_v (xz) can be represented by 1.

$$\sigma_v' \ (yz)p_x = -1p_x$$

or σ_v' (yz) can be represented by –1.

The four numbers corresponding to the operations E, C_2, σ_v (xz) and σ_v' (yz) on p_x orbital constitute a representation which we shall call τ_1 and denote as follows:

C_{2v}	E	C_2	σ_v (xz)	σ_v' (yz)	
τ_1	1	–1	1	–1	x

Effect of Symmetry Operations on p_y Orbital

If we proceed on similar lines, we can find out the four numbers corresponding to the four operations of C_{2v} group on p_y orbital and write τ_2 representation as shown below:

C_{2v}	E	C_2	σ_v (xz)	σ_v' (yz)	
τ_2	1	–1	–1	1	y

In other words, C_2 and σ_v (xz) result in changes of signs of the p_y lobes whereas E and σ_v' (yz) cause retention of signs.
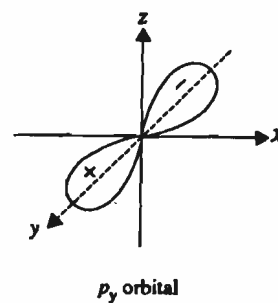
Effect of Symmetry Operations on p_z Orbital

By similar arguments, we can arrive at the decision that E, C_2, σ_v (xz) and σ_v' (yz) do not change the signs of p_z orbital. Each of the operations can be denoted by 1 only in the representation τ_3.

C_{2v}	E	C_2	σ_v (xz)	σ_v' (yz)	
τ_3	1	1	1	1	z

Effect of Symmetry Operations on Quadratic Coordinates

From the columnwise products of τ_1, τ_2 and τ_3, we can get the τ values for xy, yz, and xz as follows:

	E	C_2	σ_v (xz)	σ_v' (yz)
x (τ_1)	1	–1	1	–1
y (τ_2)	1	–1	–1	1
z (τ_3)	1	1	1	1
xy (τ_4)	1	1	–1	–1
yz (τ_2)	1	–1	–1	1
xz (τ_1)	1	–1	1	–1

Note that
i) $\tau_4 = \tau_1 \tau_2$
ii) $\tau_2 = \tau_2 \tau_3$
iii) $\tau_1 = \tau_1 \tau_3$

The representation (τ_4) for the operations on xy is different from the representations corresponding to the operations on x, y or z; but the representations for the operations on yz and xz are τ_2 and τ_1, respectively, which are same as for those on y and x.

You try columnwise products such as $\tau_1 \tau_1$ or $\tau_2 \tau_2$ or $\tau_3 \tau_3$ for obtaining representations corresponding to the effect of the four operations on x^2, y^2 and z^2. If you work out correctly, you should be able to prove that all these representations are the same, viz, τ_3, which is the representation corresponding to the effect of the four operations on z.

	E	C_2	σ_v (xz)	σ_v' (yz)
x^2 or y^2 or z^2 (τ_3)	1	1	1	1

Effect of Symmetry Operations on R_x, R_y and R_z

The symbols, R_x, R_y and R_z, denote the rotations around the x -, y - and z-axes.
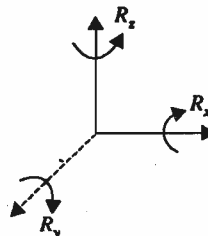
The molecule, H_2O, is in xz plane. The operation E on R_z leaves it unchanged. The operation C_2 around z-axis does not alter the direction of R_z rotation. Hence E and C_2 operations on R_z can be represented by 1. The operations, σ_v (xz) and σ_v' (yz), reverse the direction of R_z rotation, and hence, these two operations can be represented by -1.

$$ER_z \quad = \quad 1\,R_z$$

$$C_2R_z \quad = \quad 1\,R_z$$

$$\sigma_v\,(xz)R_z \quad = \quad -1\,R_z$$

$$\sigma_v'\,(yz)R_z \quad = \quad -1\,R_z$$

We can see that the representation corresponding to the effect of operations on R_z is same as τ_4.

	E	C_2	σ_v (xz)	σ_v' (yz)
R_z	1	1	-1	-1

Similarly the effect of the four symmetry operations on R_x and R_y can be stated through following representations:

	E	C_2	σ_v (xz)	σ_v' (yz)	
R_x	1	-1	-1	1	(τ_2)
R_y	1	-1	1	-1	(τ_1)

Thus we see that these are only four representations τ_1, τ_2, τ_3 and τ_4 for C_{2v} group. There are rules to give names to these representations which are known by the name, Mulliken notations. We shall not discuss these rules but use Mulliken notations of B_1, B_2, A_1 and A_2 for τ_1, τ_2, τ_3 and τ_4, respectively.

These four representations can be represented in a table called the character table of the C_{2v} group (Table A.2). Also, we would have arrived at the same table, had we started with the matrix representation of symmetry operations and proceeded to obtain the characters of irreducible representations.

The four rows of Table A.2 represent the sets of characters for the four irreducible representations of C_{2v} group.

Table A.2: Character Table of C_{2v}

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	xy	R_z
B_1	1	–1	1	–1	x, xz	R_y
B_2	1	–1	–1	1	y, yz	R_x

The value under E represents the dimensions of a representation. In C_{2v} group, all the four representations are one-dimensional and in each case, $E = 1$. Such representations are called non-degenerate representations. In these representations, the application of a symmetry operation does not interconvert one orbital into another; for instance, p_x, p_y and p_z belong to different representations, namely B_1, B_2 and A_1. Also, A_1 representation is said to be totally symmetric representation of C_{2v} point group since the character value is 1 for all the four symmetry operations.

> A_1 representation is said to be totally symmetric representation since any directional property belonging to A_1 representation of C_{2v} point group does not suffer sign change due to any of the symmetry operations.

The formation of character table for C_{3v} point group is more complicated and hence we shall only give its character table without much explanation (Table A.3).

Table A.3: Character Table for C_{3v} Group

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

The Mulliken notation of E is used for a representation, if the character value of 2 is observed for the identity operation, E. The representation E is two dimensional; this means x and y, R_x and R_y, xz and yz etc. which are all bracketed together are interconverted by a symmetry operation; i.e., those bracketed together are degenerate and hence have same energy.

Uses of Character Tables

We can make use of character tables to solve specific problems such as those given below:

1. Selection rules regarding the allowed transitions between energy levels in (atomic and) molecular spectra.

2. Symmetry species of vibrational modes in molecules.

3. Hybridisation schemes in molecules of specific geometry.

The second one will be explained in Units 5 and 6 and we shall not be discussing the third of the above. Let us now see how selection rules for transitions in the molecular spectra can be derived using character tables.

Selection Rules for the Allowed Spectral Transitions

The selection rules for the spectroscopic transitions throw light on the type of initial and final energy states for allowed spectral transitions. The selection rules specify the conditions for the allowed transitions in terms of changes in quantum numbers. Let us examine the first of the above two.

1. The Type of Initial and Final Energy States for Allowed Spectral Transitions

Let us first see how to decide whether a particular spectral transition is allowed or not. Let ψ_a and ψ_b be the wave functions of two energy states a and b, and M, the transition dipole moment operator for which the components are M_x, M_y and M_z. The transition **dipole moment** μ during the transitions between states a and b can be defined as

$$\mu = \int \psi_b \, M \, \psi_a \, d\tau \qquad ...(A.2)$$

where $d\tau$ is the volume element. The three components of transition dipole moment (μ_x, μ_y and μ_z) can be defined in terms of the components of dipole moment operator (M_x, M_y and M_z) along the three axes as follows:

$$\mu_x = \int \psi_b \, M_x \, \psi_a \, d\tau \qquad ...(A.3)$$

$$\mu_y = \int \psi_b \, M_y \, \psi_a \, d\tau \qquad ...(A.4)$$

$$\mu_z = \int \psi_b \, M_z \, \psi_a \, d\tau \qquad ...(A.5)$$

But

$$M_x = ex, \ M_y = ey \text{ and } M_z = ez \qquad ...(A.6)$$

where e is the electronic charge, and x, y and z are the cartesian coordinates.

Combining Eqs. A.3 to A.6,

$$\mu_x = e \int \psi_b \, x \, \psi_a \, d\tau \qquad ...(A.7)$$

$$\mu_y = e \int \psi_b \, y \, \psi_a \, d\tau \qquad ...(A.8)$$

$$\mu_z = e \int \psi_b \, z \, \psi_a \, d\tau \qquad ...(A.9)$$

For a spectral transition to occur from the state, a to b, atleast one of the components of μ (viz., μ_x, μ_y or μ_z) should be a finite quantity (i.e., should be nonzero). On the other hand, if all the components (μ_x, μ_y or μ_z) are zero, then the spectral transition is totally symmetry forbidden.

Further μ_x, μ_y or μ_z will be finite (i.e., nonzero), only if the product of the symmetry species of the functions, ψ_a and ψ_b, and the transition moment operator, M_x M_y or M_z (i.e., $\psi_b \, M_x \, \psi_a$, $\psi_b \, M_y \, \psi_a$ or $\psi_b \, M_z \, \psi_a$) is totally symmetric; for example, the product must belong to A_1 representation for the molecular point group C_{2v}. Since M_x, M_y and M_z transform like x, y and z coordinates, we can state that the transition moment integral will be nonzero, if the product of the symmetry species of the functions, ψ_b and ψ_a and the coordinates (x, y, z) is totally symmetric. Further, it can be shown that the symmetry species of the product, $\psi_b \, x \, \psi_a$, $\psi_b \, y \, \psi_a$ or $\psi_b \, z \, \psi_a$ will be totally symmetric, if the symmetry species of the product of the functions ψ_b and ψ_a is the same as that of x, y and z coordinates.

For example, let us examine whether the transition from the molecular state with symmetry of wave function (ψ_a) as A_1 to the state with symmetry of wave function (ψ_b) as B_1, is allowed for the molecules of C_{2v} group. From Table A.2, we know that x, y and z belong to B_1, B_2 and A_1 representations, respectively. Let us see whether any of the three products, $\psi_b \, x \, \psi_a$, $\psi_b \, y \, \psi_a$ or $\psi_b \, z \, \psi_a$ belongs to A_1 representation.

i) Representation of the product, $\psi_b \, x \, \psi_a$

Function	Symmetry species	Characters in four columns			
		E	C_2	$\sigma_v \, (xz)$	$\sigma_v' \, (yz)$
ψ_b	B_1	1	−1	1	−1
ψ_a	A_1	1	1	1	1
$\psi_b \, \psi_a$	B_1	1	−1	1	−1
x	B_1	1	−1	1	−1
$\psi_b \, \psi_a \, x$	A_1	1	1	1	1

You can see that the $\psi_b \psi_a$ product has the same representation as x. So $\psi_b \psi_a x$ (or $\psi_b x \psi_a$) is totally symmetric.

ii) Representation of the product, $\psi_b y \psi_a$

Function	Symmetry species	Characters in four columns			
		E	C_2	$\sigma_v (xz)$	$\sigma_v' (yz)$
ψ_b	B_1	1	−1	1	−1
ψ_a	A_1	1	1	1	1
$\psi_b \psi_a$	B_1	1	−1	1	−1
y	B_2	1	−1	−1	1
$\psi_b \psi_a y$	A_2	1	1	−1	−1

We can see that the symmetry species of the product, $\psi_b \psi_a$, is different from that of the y coordinate.

Hence, the product $\psi_b y \psi_a$ does not belong to A_1 representation.

iii) Representation of the product, $\psi_b z \psi_a$

Function	Symmetry species	Characters in four columns			
		E	C_2	$\sigma_v (xz)$	$\sigma_v'(yz)$
ψ_b	B_1	1	−1	1	−1
ψ_a	A_1	1	1	1	1
$\psi_b \psi_a$	B_1	1	−1	1	−1
z	A_1	1	1	1	1
$\psi_b \psi_a z$	B_1	1	−1	1	−1

Again $\psi_b \psi_a$ belongs to B_1 representation which is different from that of the z-coordinate. Hence, the product, $\psi_b \psi_a z$ also does not belong to totally symmetric representation.

Hence, we see that $\psi_b x \psi_a$ belongs to A_1 representation although $\psi_b y \psi_a$ and $\psi_b z \psi_a$ do not. Hence the x component of the transition dipole moment is non-zero. Therefore, we conclude that the transition $A_1 \longrightarrow B_1$ is allowed and is polarized in the x direction. By similar procedure, it can be shown that (i) the transitions $B_2 \longrightarrow A_2$ and $B_1 \longrightarrow A_2$ are allowed, the former being polarized in the x direction and the latter in the y direction and (ii) $A_1 \longrightarrow A_2$ and $B_1 \longrightarrow B_2$ transitions are not allowed.

Note that the transition moment has three components, μ_x, μ_y and μ_z. If only one, say, x component is different from zero, then the transition is said to be polarized in the x-direction. If two of the components, say, μ_x and μ_y are different from zero, then the transition is said to be polarized in the xy plane. If all the components (μ_x, μ_y and μ_z) are different from zero, then the transition is fully allowed. Similarly, if all the three components are zero, then transition is totally forbidden and its intensity is zero.

Specific Selection Rules

Further, a detailed study of the transition dipole moment leads to specific selection rules which state the conditions for the allowed transitions in terms of changes in quantum numbers. In Units 3 and 4, we shall study selection rules specific to rotation and vibration spectra.
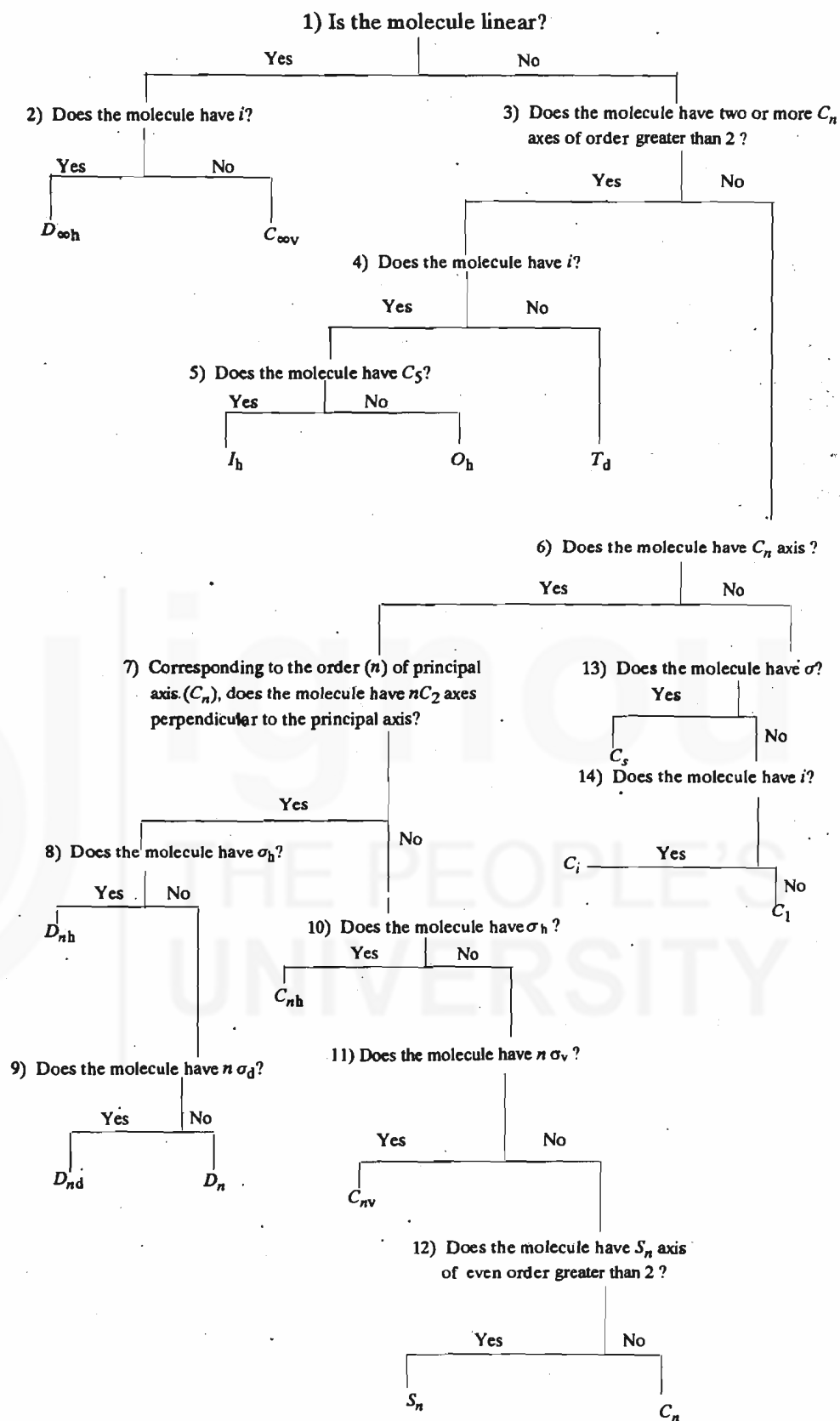
Next, let us discuss the method of identifying point groups of molecules.

Identification of Point Groups

It is possible to find out the point group of a molecule by knowing its shape and symmetry elements and, by using Table A.4.

Table A.4: Flow Chart for Identifying Point Groups.

1) Is the molecule linear?

    Yes   No

2) Does the molecule have i?   3) Does the molecule have two or more C_n axes of order greater than 2 ?

    Yes   No   Yes   No

$D_{\infty h}$ $C_{\infty v}$

4) Does the molecule have i?

    Yes   No

5) Does the molecule have C_5?

    Yes   No

I_h O_h T_d

6) Does the molecule have C_n axis ?

    Yes   No

7) Corresponding to the order (n) of principal axis (C_n), does the molecule have nC_2 axes perpendicular to the principal axis?   13) Does the molecule have σ?

         Yes

C_s No

14) Does the molecule have i?

    Yes   No

8) Does the molecule have σ_h? C_i Yes   No C_1

    Yes   No

D_{nh}

10) Does the molecule have σ_h ?

    Yes   No

C_{nh}

9) Does the molecule have $n\,\sigma_d$?   11) Does the molecule have $n\,\sigma_v$?

    Yes   No   Yes   No

D_{nd} D_n C_{nv}

12) Does the molecule have S_n axis of even order greater than 2 ?

    Yes   No

S_n C_n

Note that the questions in the flow chart given above are numbered. This is done for referring to the questions which are relevant for identifying the point group of a particular molecule.

For identifying the point groups, the following steps would be quite useful:

Step   i)   Find out the shape of the molecule; this can be done using Sec. 2.2 of this unit.

Step   ii)   List the symmetry elements in the molecule.

Step   iii)   Mark those questions from Table A.4 which are relevant to the symmetry elements of the molecule under consideration. Write down the answers and the inference. The answer to the last question gives the point group of the molecule.

Let us examine a few examples in the light of the steps mentioned above:

I H_2

Step   i) H_2 molecule has linear shape.

Step   ii) H_2 has the following symmetry elements:

$E, 2C_\infty, \infty C_2$ (perpendicular to C_∞), $\sigma_h, \infty\sigma_v, 2S_\infty$ and i

Step   iii)   The questions of Table A.4 relevant to this molecule are given below alongwith the answers:

1.   The molecule is linear (Proceed to question 2).

2. H_2 has i. The answer to this question indicates that the point group of H_2 is $D_{\infty h}$.

In short, all linear molecules with i such as acetylene, and homonuclear diatomic molecules belong to $D_{\infty h}$ point group.

II HCl

Step   i)   HCl molecule has linear shape.

Step   ii)   HCl has the following symmetry elements:

$E, 2C_\infty$ and $\infty \sigma_v$.

Step   iii)   The questions of Table A.4 relevant to this molecule are given below along with the answers:

1.   The molecule is linear (Proceed to question 2).

2.   HCl does not have i. Hence, the point group of HCl is $C_{\infty v}$.

Similarly, all linear molecules without i such as heteronuclear diatomic molecules belong to $C_{\infty v}$ point group.

III H_2O

Step   i) H_2O molecule has angular shape.

Step   ii) H_2O has the following symmetry elements:

$E, 2\sigma_v$ and C_2.

To predict the shape of the molecule, you may use Sec. 2.2 of this unit and Sec. 3.7 of Unit 3 of CHE-01 (Atoms and Molecules) course.

Note that in Step (ii), we have mentioned many symmetry elements for H_2 molecule. But in Step (iii), all these symmetry elements are not used for arriving at the point group of the molecule. Thus, the point group of a molecule can be found out by using a few symmetry elements only. While writing step (iii), follow Table A.4 carefully.

In each of the examples I to IV, we mention under step (iii) only relevant question numbers from Table A.4 along with answers. Thus, in Example III for H_2O, the relevant question numbers are 1, 3, 6, 7, 10 and 11. The "yes" or "no" part of the answer for each question can be inferred from the word in bold type. The answer to the last question gives the point group of the molecule.

65

Step iii) The questions of Table A.4 relevant to this molecule are given below along with the answers:

1. The molecule is **not** linear (Proceed to question 3).

3. The molecule does **not** have two or more C_n axes of order greater than 2 (Proceed to question 6).

6. The molecule has C_2 axis. (Proceed to question 7).

7. The molecule does **not** have two C_2 axes perpendicular to the principal axis (C_2). (Proceed to question 10).

10. The molecule does **not** have σ_h (Proceed to question 11).

11. The molecule **has** $2\sigma_v$. The last answer indicates that the point group of H_2O is C_{2v}.

SO_2 is another example belonging to C_{2v} point group.

IV NH_3

Step i) NH_3 molecule has trigonal pyramidal shape.

Step ii) NH_3 has the following symmetry elements:

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

Step iii) The questions of Table A.4 relevant to this molecule are given below along with the answers:

1. The molecule is **not** linear (Proceed to question 3).

3. The molecule does **not** have two or more C_n axes of order greater than 2 (Proceed to question 6).

6. The molecule **has** C_3 axis (Proceed to question 7).

7. The molecule does **not** have three C_2 axes perpendicular to C_3 axis (Proceed to question 10).

10. The molecule does **not** have σ_h (Proceed to question 11).

11. The molecule has $3\,\sigma_v$. Hence, the molecule belongs to C_{3v} point group.

As an exercise, you try to identify the point groups of BF_3 and C_6H_6.