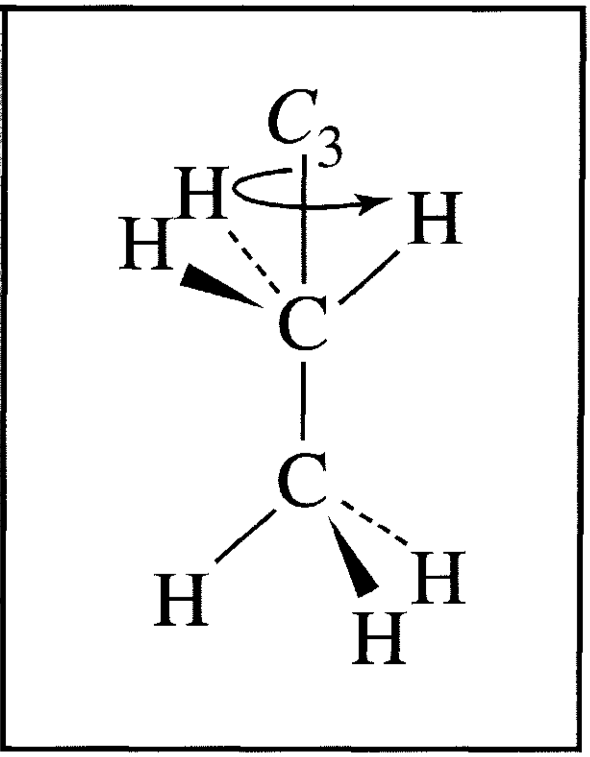
CHAPTER

4

Symmetry and Group Theory



Symmetry is a phenomenon of the natural world, as well as the world of human invention (Figure 4-1). In nature, many types of flowers and plants, snowflakes, insects, certain fruits and vegetables, and a wide variety of microscopic plants and animals exhibit characteristic symmetry. Many engineering achievements have a degree of symmetry that contributes to their esthetic appeal. Examples include cloverleaf intersections, the pyramids of ancient Egypt, and the Eiffel Tower.

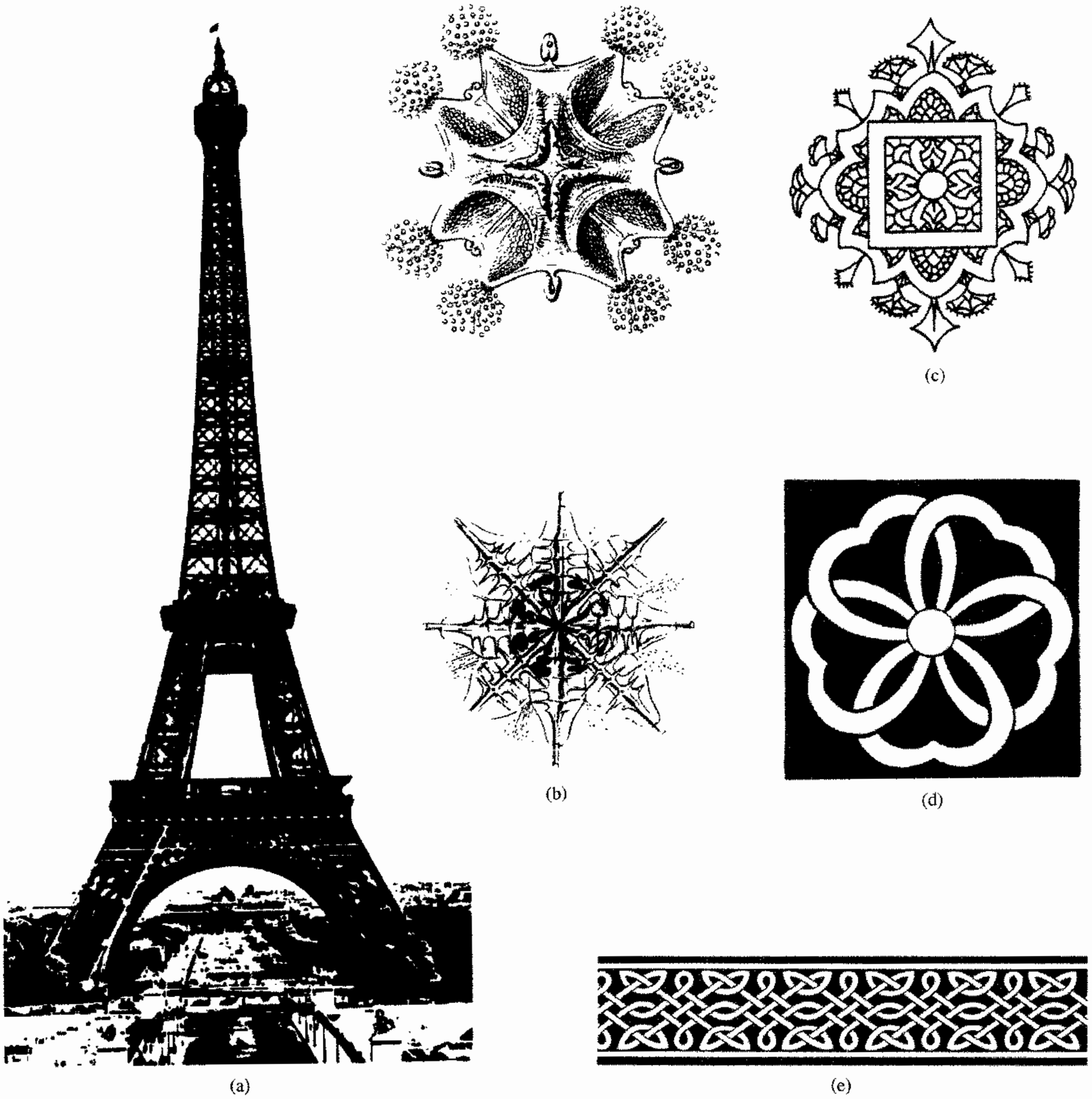
Symmetry concepts can be extremely useful in chemistry. By analyzing the symmetry of molecules, we can predict infrared spectra, describe the types of orbitals used in bonding, predict optical activity, interpret electronic spectra, and study a number of additional molecular properties. In this chapter, we first define symmetry very specifically in terms of five fundamental symmetry operations. We then describe how molecules can be classified on the basis of the types of symmetry they possess. We conclude with examples of how symmetry can be used to predict optical activity of molecules and to determine the number and types of infrared-active stretching vibrations.

In later chapters, symmetry will be a valuable tool in the construction of molecular orbitals (Chapters 5 and 10) and in the interpretation of electronic spectra of coordination compounds (Chapter 11) and vibrational spectra of organometallic compounds (Chapter 13).

A molecular model kit is a very useful study aid for this chapter, even for those who can visualize three-dimensional objects easily. We strongly encourage the use of such a kit.

4-1 SYMMETRY ELEMENTS AND OPERATIONS

All molecules can be described in terms of their symmetry, even if it is only to say they have none. Molecules or any other objects may contain **symmetry elements** such as mirror planes, axes of rotation, and inversion centers. The actual reflection, rotation, or inversion is called the **symmetry operation**. To contain a given symmetry element, a molecule must have exactly the same appearance after the operation as before. In other words, photographs of the molecule (if such photographs were possible!) taken from the same location before and after the symmetry operation would be indistinguishable. If a symmetry operation yields a molecule that can be distinguished from the original in



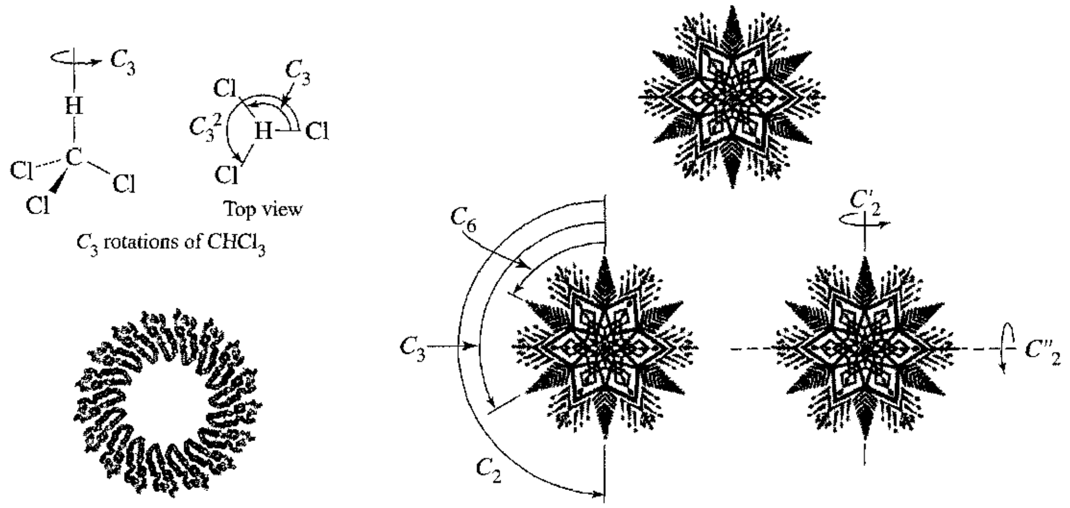
(a) (b) (c) (d) (e)

FIGURE 4-1 Symmetry in Nature, Art, and Architecture.

any way, then that operation is *not* a symmetry operation of the molecule. The examples in Figures 4-2 through 4-6 illustrate the possible types of molecular symmetry operations and elements.

The **identity operation** (***E***) causes no change in the molecule. It is included for mathematical completeness. An identity operation is characteristic of every molecule, even if it has no other symmetry.

The **rotation operation** (**C_n**) (also called **proper rotation**) is rotation through $360°/n$ about a rotation axis. We use counterclockwise rotation as a positive rotation. An example of a molecule having a threefold (C_3) axis is $CHCl_3$. The rotation axis is coincident with the C—H bond axis, and the rotation angle is $360°/3 = 120°$. Two C_3 operations may be performed consecutively to give a new rotation of 240°. The resulting



Cross section of protein disk of tobacco mosaic virus

C_2, C_3 and C_6 rotations of a snowflake design

FIGURE 4-2 Rotations. The cross section of the tobacco mosaic virus is a cover diagram from *Nature*, 1976, *259*. © **1976**, Macmillan Journals Ltd. Reproduced with permission of Aaron Klug.

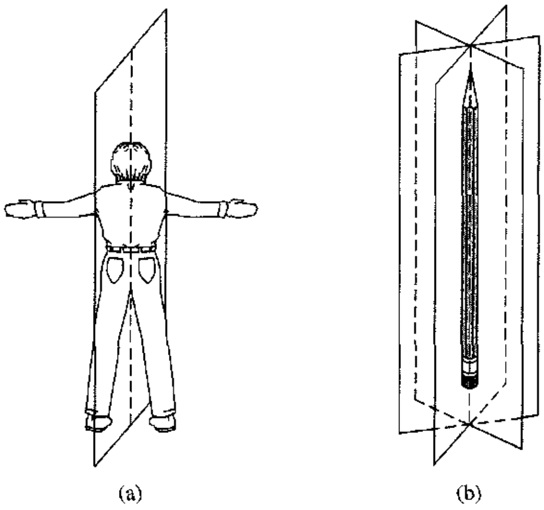
operation is designated C_3^2 and is also a symmetry operation of the molecule. Three successive C_3 operations are the same as the identity operation ($C_3^3 \equiv E$). The identity operation is included in all molecules. Many molecules and other objects have multiple rotation axes. Snowflakes are a case in point, with complex shapes that are nearly always hexagonal and nearly planar. The line through the center of the flake perpendicular to the plane of the flake contains a twofold (C_2) axis, a threefold (C_3) axis, and a sixfold (C_6) axis. Rotations by 240° (C_3^2) and 300° (C_6^5) are also symmetry operations of the snowflake.

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

There are also two sets of three C_2 axes in the plane of the snowflake, one set through opposite points and one through the cut-in regions between the points. One of each of these axes is shown in Figure 4-2. In molecules with more than one rotation axis, the C_n axis having the largest value of n is the **highest order rotation axis** or **principal axis**. The highest order rotation axis for a snowflake is the C_6 axis. (In assigning Cartesian coordinates, the highest order C_n axis is usually chosen as the z axis.) When necessary, the C_2 axes perpendicular to the principal axis are designated with primes; a single prime (C_2') indicates that the axis passes through several atoms of the molecule, whereas a double prime (C_2'') indicates that it passes between the outer atoms.

Finding rotation axes for some three-dimensional figures is more difficult, but the same in principle. Remember that nature is not always simple when it comes to symmetry—the protein disk of the tobacco mosaic virus has a 17-fold rotation axis!

In the **reflection operation** (σ) the molecule contains a mirror plane. If details such as hair style and location of internal organs are ignored, the human body has a left-right mirror plane, as in Figure 4-3. Many molecules have mirror planes, although they may not be immediately obvious. The reflection operation exchanges left and right, as if each point had moved perpendicularly through the plane to a position exactly as far from the plane as when it started. Linear objects such as a round wood pencil or molecules



(a) (b)

FIGURE 4-3 Reflections.

such as acetylene or carbon dioxide have an infinite number of mirror planes that include the center line of the object.

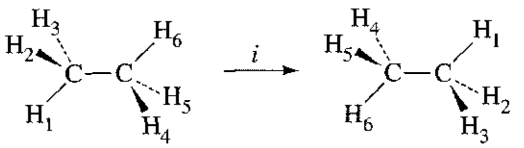
When the plane is perpendicular to the principal axis of rotation, it is called σ_h (horizontal). Other planes, which contain the principal axis of rotation, are labeled σ_v or σ_d.

Inversion (i) is a more complex operation. Each point moves through the center of the molecule to a position opposite the original position and as far from the central point as when it started.[1] An example of a molecule having a center of inversion is ethane in the staggered conformation, for which the inversion operation is shown in Figure 4-4.

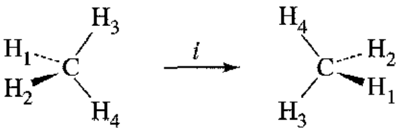
Many molecules that seem at first glance to have an inversion center do not; for example, methane and other tetrahedral molecules lack inversion symmetry. To see this, hold a methane model with two hydrogen atoms in the vertical plane on the right and two hydrogen atoms in the horizontal plane on the left, as in Figure 4-4. Inversion results in two hydrogen atoms in the horizontal plane on the right and two hydrogen atoms in the vertical plane on the left. Inversion is therefore *not* a symmetry operation of methane, because the orientation of the molecule following the i operation differs from the original orientation.

Squares, rectangles, parallelograms, rectangular solids, octahedra, and snowflakes have inversion centers; tetrahedra, triangles, and pentagons do not (Figure 4-5).

A **rotation-reflection operation (S_n)** (sometimes called **improper rotation**) requires rotation of 360°/n, followed by reflection through a plane perpendicular to the axis of rotation. In methane, for example, a line through the carbon and bisecting the



Center of inversion



No center of inversion

FIGURE 4-4 Inversion.

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[1] This operation must be distinguished from the inversion of a tetrahedral carbon in a bimolecular reaction, which is more like that of an umbrella in a high wind.

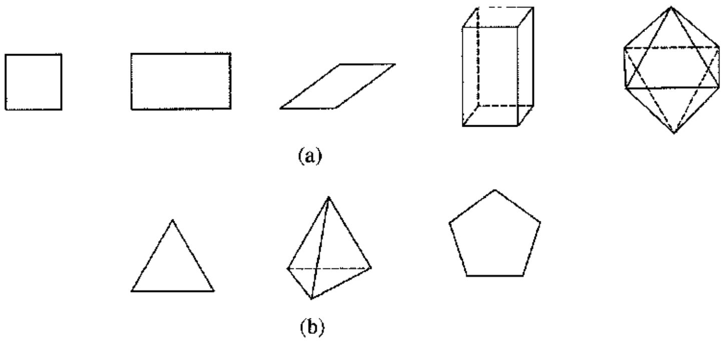


FIGURE 4-5 Figures (a) With and (b) Without Inversion Centers.

angle between two hydrogen atoms on each side is an S_4 axis. There are three such lines, for a total of three S_4 axes. The operation requires a 90° rotation of the molecule followed by reflection through the plane perpendicular to the axis of rotation. Two S_n operations in succession generate a $C_{n/2}$ operation. In methane, two S_4 operations generate a C_2. These operations are shown in Figure 4-6, along with a table of C and S equivalences for methane.

Molecules sometimes have an S_n axis that is coincident with a C_n axis. For example, in addition to the rotation axes described previously, snowflakes have S_2 ($\equiv i$), S_3, and S_6 axes coincident with the C_6 axis. Molecules may also have S_{2n} axes coincident with C_n; methane is an example, with S_4 axes coincident with C_2 axes, as shown in Figure 4-6.

Note that an S_2 operation is the same as inversion; an S_1 operation is the same as a reflection plane. The i and σ notations are preferred in these cases. Symmetry elements and operations are summarized in Table 4-1.

Rotation Angle	*Symmetry Operation*
90°	S_4
180°	C_2 ($\equiv S_4^2$)
270°	S_4^3
360°	E ($\equiv S_4^4$)

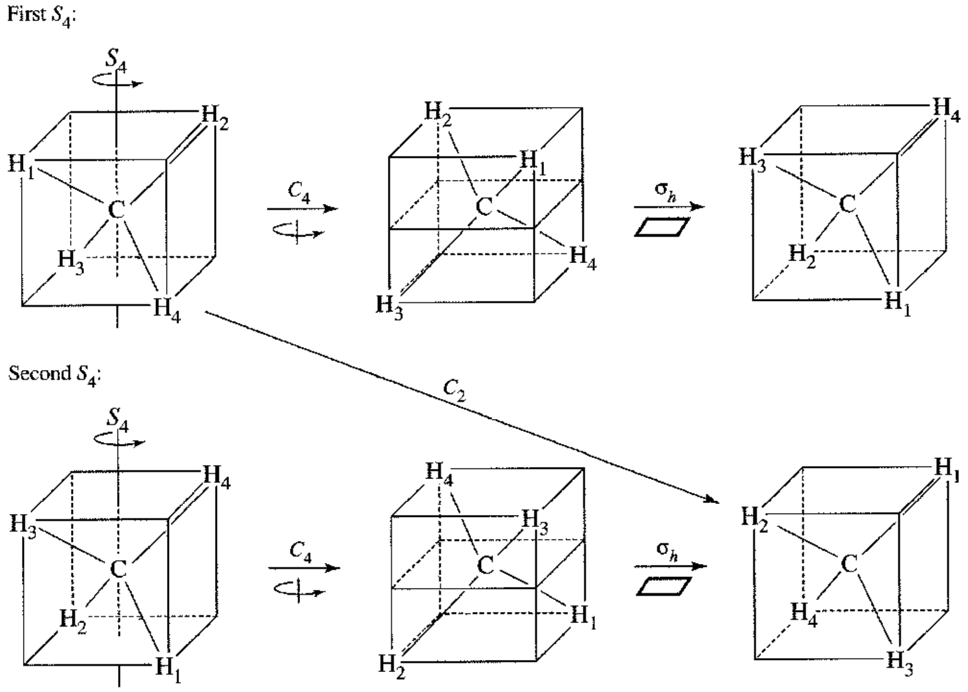
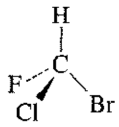
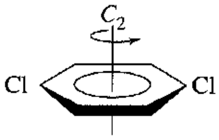
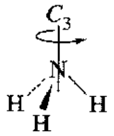
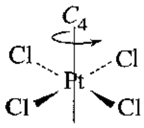
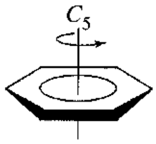
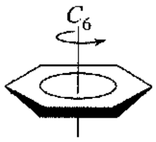
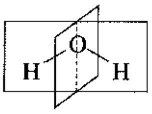
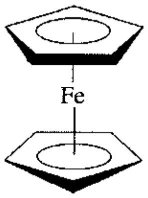
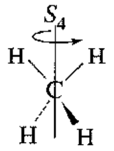
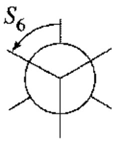
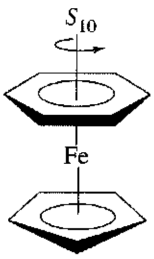


FIGURE 4-6 Improper Rotation or Rotation-Reflection.

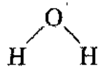
TABLE 4-1
Summary Table of Symmetry Elements and Operations

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

EXAMPLES

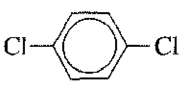
Find all the symmetry elements in the following molecules; consider only the atoms when assigning symmetry. Lone pairs influence shapes, but molecular symmetry is based on the geometry of the atoms.

H_2O

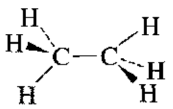


H_2O has two planes of symmetry, one in the plane of the molecule and one perpendicular to the molecular plane, as shown in Table 4-1. It also has a C_2 axis collinear with the intersection of the mirror planes. H_2O has no inversion center.

p-Dichlorobenzene This molecule has three mirror planes: the molecular plane; a plane perpendicular to the molecule, passing through both chlorines; and a plane perpendicular to the first two, bisecting the molecule between the chlorines. It also has three C_2 axes, one perpendicular to the molecular plane (see Table 4-1) and two within the plane: one passing through both chlorines and one perpendicular to the axis passing through the chlorines. Finally, *p*-dichlorobenzene has an inversion center.



Ethane (staggered conformation) Ethane has three mirror planes, each containing the C—C bond axis and passing through two hydrogens on opposite ends of the molecule. It has a C_3 axis collinear with the carbon-carbon bond and three C_2 axes bisecting the angles between the mirror planes. (Use of a model is especially helpful for viewing the C_2 axes). Ethane also has a center of inversion and an S_6 axis collinear with the C_3 axis (see Table 4-1).



EXERCISE 4-1

Using diagrams as necessary, show that $S_2 \equiv i$ and $S_1 \equiv \sigma$.

EXERCISE 4-2

Find all the symmetry elements in the following molecules:

NH_3 Cyclohexane (boat conformation) Cyclohexane (chair conformation) XeF_2

4-2 POINT GROUPS

Each molecule has a set of symmetry operations that describes the molecule's overall symmetry. This set of symmetry operations is called the **point group** of the molecule. **Group theory**, the mathematical treatment of the properties of groups, can be used to determine the molecular orbitals, vibrations, and other properties of the molecule. With only a few exceptions, the rules for assigning a molecule to a point group are simple and straightforward. We need only to follow these steps in sequence until a final classification of the molecule is made. A diagram of these steps is shown in Figure 4-7.

1. Determine whether the molecule belongs to one of the cases of very low symmetry (C_1, C_s, C_i) or high symmetry (T_d, O_h, $C_{\infty v}$, $D_{\infty h}$, or I_h) described in Tables 4-2 and 4-3.
2. For all remaining molecules, find the rotation axis with the highest *n*, the highest order C_n axis for the molecule.
3. Does the molecule have any C_2 axes perpendicular to the C_n axis? If it does, there will be *n* of such C_2 axes, and the molecule is in the *D* set of groups. If not, it is in the *C* or *S* set.
4. Does the molecule have a mirror plane (σ_h) perpendicular to the C_n axis? If so, it is classified as C_{nh} or D_{nh}. If not, continue with Step 5.
5. Does the molecule have any mirror planes that contain the C_n axis (σ_v or σ_d)? If so, it is classified as C_{nv} or D_{nd}. If not, but it is in the *D* set, it is classified as D_n. If the molecule is in the *C* or *S* set, continue with Step 6.

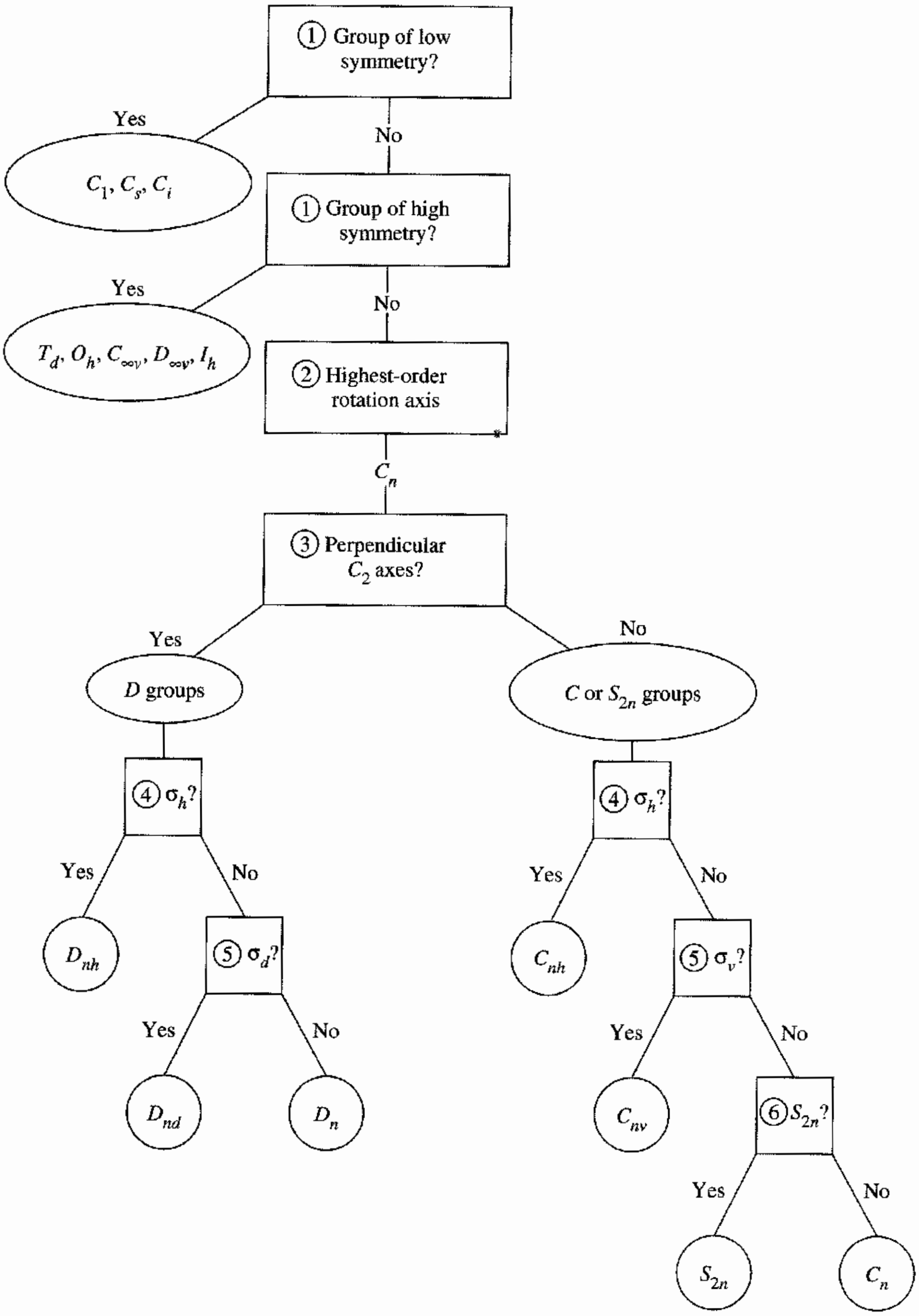


FIGURE 4-7 Diagram of the Point Group Assignment Method.

6. Is there an S_{2n} axis collinear with the C_n axis? If so, it is classified as S_{2n}. If not, the molecule is classified as C_n.

Each step is illustrated in the following text by assigning the molecules in Figure 4-8 to their point groups. The low- and high-symmetry cases are treated differently because of their special nature. Molecules that are not in one of these low- or high-symmetry point groups can be assigned to a point group by following Steps 2 through 6.

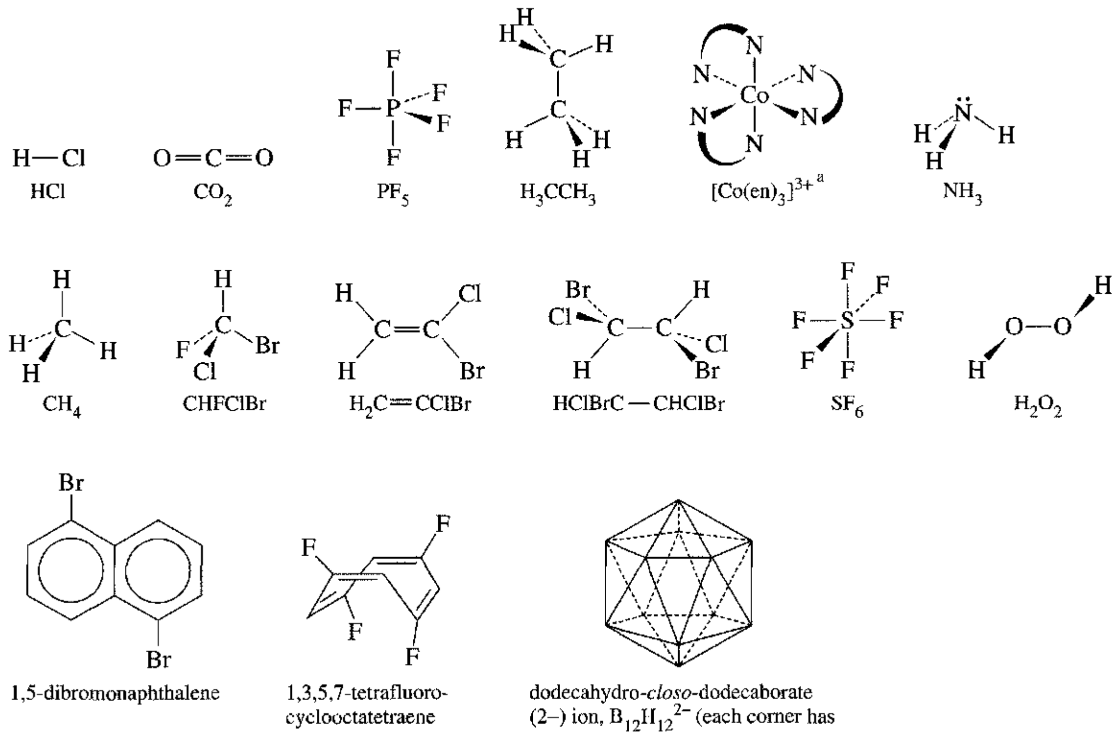


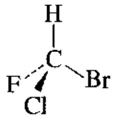
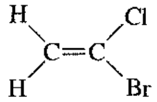
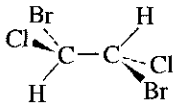
FIGURE 4-8 Molecules to be Assigned to Point Groups.
[a] en = ethylenediamine = $NH_2CH_2CH_2NH_2$, represented by N⌒N.

4-2-1 GROUPS OF LOW AND HIGH SYMMETRY

1. Determine whether the molecule belongs to one of the special cases of low or high symmetry.

First, inspection of the molecule will determine if it fits one of the low-symmetry cases. These groups have few or no symmetry operations and are described in Table 4-2.

TABLE 4-2
Groups of Low Symmetry

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

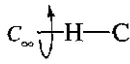
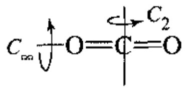
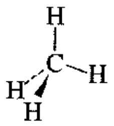
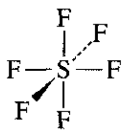
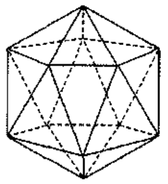
Low symmetry

CHFClBr has no symmetry other than the identity operation and has C_1 symmetry, $H_2C{=}CClBr$ has only one mirror plane and C_s symmetry, and HClBrC—CHClBr in the conformation shown has only a center of inversion and C_i symmetry.

High symmetry

Molecules with many symmetry operations may fit one of the high-symmetry cases of linear, tetrahedral, octahedral, or icosahedral symmetry with the characteristics described in Table 4-3. Molecules with very high symmetry are of two types, linear and polyhedral. Linear molecules having a center of inversion have $D_{\infty h}$ symmetry; those lacking an inversion center have $C_{\infty v}$ symmetry. The highly symmetric point groups T_d, O_h, and I_h are described in Table 4-3. It is helpful to note the C_n axes of these molecules. Molecules with T_d symmetry have only C_3 and C_2 axes; those with O_h symmetry have C_4 axes in addition to C_3 and C_2; and I_h molecules have C_5, C_3, and C_2 axes.

TABLE 4-3
Groups of High Symmetry

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

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

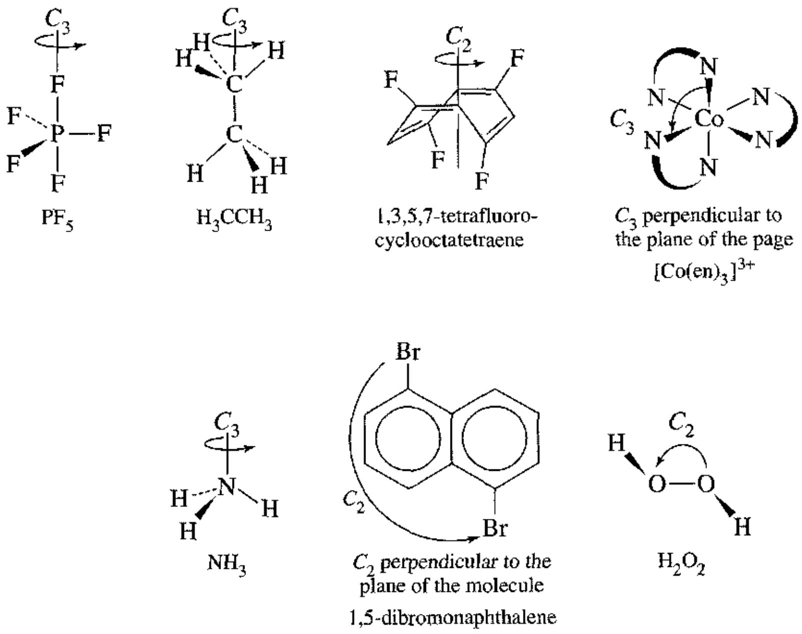
HCl has $C_{\infty v}$ symmetry, CO_2 has $D_{\infty h}$ symmetry, CH_4 has tetrahedral (T_d) symmetry, SF_6 has octahedral (O_h) symmetry, and $B_{12}H_{12}^{2-}$ has icosahedral (I_h) symmetry

There are now seven molecules left to be assigned to point groups out of the original 15.

4-2-2 OTHER GROUPS

2. Find the rotation axis with the highest n, the highest order C_n axis for the molecule. This is the principal axis of the molecule.

The rotation axes for the examples are shown in Figure 4-9. If they are all equivalent, any one can be chosen as the principal axis.



PF_5

H_3CCH_3

1,3,5,7-tetrafluoro-cyclooctatetraene

C_3 perpendicular to the plane of the page

$[Co(en)_3]^{3+}$

NH_3

C_2 perpendicular to the plane of the molecule

1,5-dibromonaphthalene

H_2O_2

FIGURE 4-9 Rotation Axes.

3. Does the molecule have any C_2 axes perpendicular to the C_n axis?

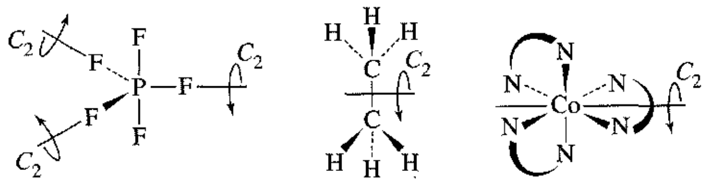
The C_2 axes are shown in Figure 4-10.

NH_3 No

1,5-dibromonaphthalene No

H_2O_2 No

1,3,5,7-tetrafluorocylooctatetraene No



PF_5 Yes

H_3CCH_3 Yes

$[Co(en)_3]^{3+}$ Yes

FIGURE 4-10 Perpendicular C_2 Axes.

Yes *D Groups*	**No** *C or S Groups*
PF_5, H_3CCH_3, $[Co(en)_3]^{3+}$	NH_3, 1,5-dibromonaphthalene, H_2O_2, 1,3,5,7-tetrafluorocyclooctatetraene
Molecules with C_2 axes perpendicular to the principal axis are in one of the groups designated by the letter D; there are n C_2 axes.	Molecules with no perpendicular C_2 axes are in one of the groups designated by the letters C or S.

No final assignments of point groups have been made, but the molecules have now been divided into two major categories, the D set and the C or S set.

4. Does the molecule have a mirror plane (σ_h horizontal plane) perpendicular to the C_n axis?

The horizontal mirror planes are shown in Figure 4-11.

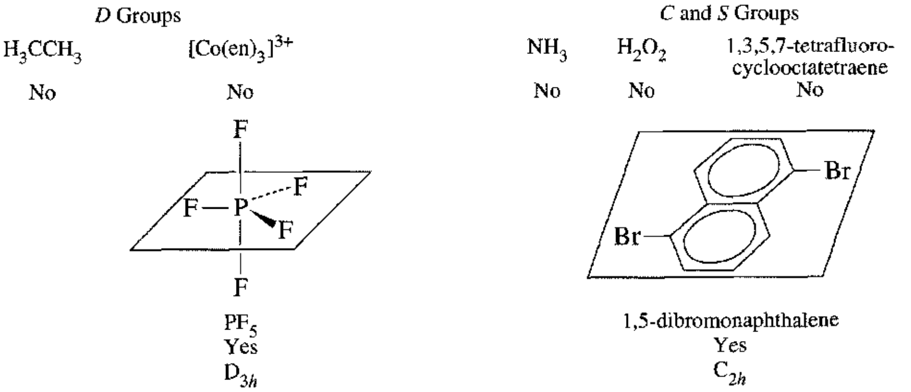


FIGURE 4-11 Horizontal Mirror Planes.

D Groups	*C and S Groups*
Yes $\boxed{D_{nh}}$	**Yes** $\boxed{C_{nh}}$
PF_5 is D_{3h}	1,5-dibromonaphthalene is C_{2h}

These molecules are now assigned to point groups and need not be considered further. Both have horizontal mirror planes.

No D_n *or* D_{nd}	**No** C_n, C_{nv}, *or* S_{2n}
H_3CCH_3, $[Co(en)_3]^{3+}$	NH_3, H_2O_2, 1,3,5,7-tetrafluorocyclooctatetraene

None of these have horizontal mirror planes; they must be carried further in the process.

5. Does the molecule have any mirror planes that contain the C_n axis?

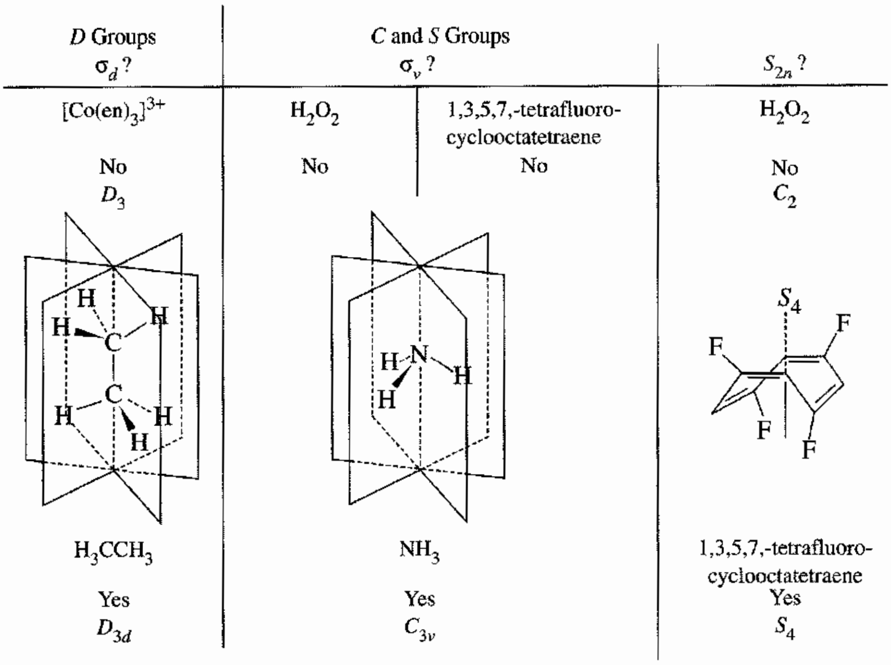


FIGURE 4-12 Vertical or Dihedral Mirror Planes or S_{2n} Axes.

These mirror planes are shown in Figure 4-12.

D Groups	*C and S Groups*
Yes $\boxed{D_{nd}}$	**Yes** $\boxed{C_{nv}}$
H_3CCH_3 (staggered) is D_{3d}	NH_3 is C_{3v}

These molecules have mirror planes containing the major C_n axis, but no horizontal mirror planes, and are assigned to the corresponding point groups. There will be *n* of these planes.

No $\boxed{D_n}$	**No** C_n or S_{2n}
$[Co(en)_3]^{3+}$ is D_3	H_2O_2, 1,3,5,7-tetrafluorocyclooctatetraene

These molecules are in the simpler rotation groups D_n, C_n, and S_{2n} because they do not have any mirror planes. D_n and C_n point groups have *only* C_n axes. S_{2n} point groups have C_n and S_{2n} axes and may have an inversion center.

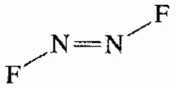
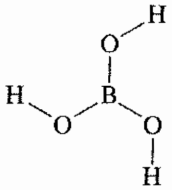
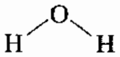
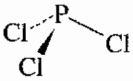
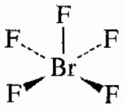
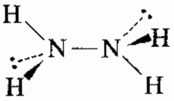
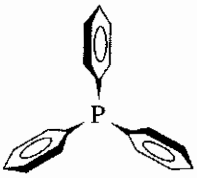
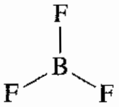
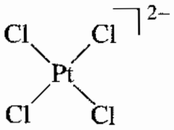
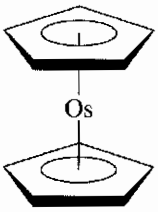
6. Is there an S_{2n} axis collinear with the C_n axis?

D Groups	*C and S Groups*
Any molecules in this category that have S_{2n} axes have already been assigned to groups. There are no additional groups to be considered here.	**Yes** $\boxed{S_{2n}}$ 1,3,5,7-tetrafluorocyclooctatetraene is S_4 **No** $\boxed{C_n}$ H_2O_2 is C_2

We have only one example in our list that falls into the S_{2n} groups, as seen in Figure 4-12.

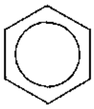
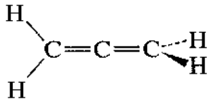
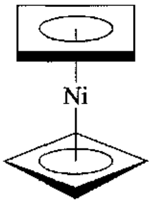
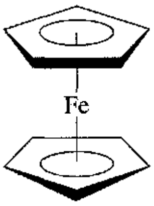
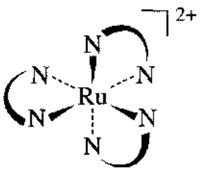
A branching diagram that summarizes this method of assigning point groups was given in Figure 4-7 and more examples are given in Table 4-4.

TABLE 4-4
Further Examples of *C* and *D* Point Groups

General Label	*Point Group and Example*		
C_{nh}	C_{2h}	difluorodiazene	
	C_{3h}	$B(OH)_3$, planar	
C_{nv}	C_{2v}	H_2O	
	C_{3v}	PCl_3	
	C_{4v}	BrF_5 (square pyramid)	
	$C_{\infty v}$	HF, CO, HCN	H—F C≡O H—C≡N
C_n	C_2	N_2H_4, which has a *gauche* conformation	
	C_3	$P(C_6H_5)_3$, which is like a three-bladed propeller distorted out of the planar shape by a lone pair on the P	
D_{nh}	D_{3h}	BF_3	
	D_{4h}	$PtCl_4^{2-}$	
	D_{5h}	$Os(C_5H_5)_2$ (eclipsed)	

Continued

TABLE 4-4—cont'd
Further Examples of *C* and *D* Point Groups

General Label	*Point Group and Example*		
	D_{6h}	benzene	
	$D_{\infty h}$	F_2, N_2, acetylene (C_2H_2)	F—F N≡N H—C≡C—H
D_{nd}	D_{2d}	$H_2C{=}C{=}CH_2$, allene	
	D_{4d}	Ni(cyclobutadiene)$_2$ (staggered)	
	D_{5d}	Fe(C_5H_5)$_2$ (staggered)	
D_n	D_3	$[Ru(NH_2CH_2CH_2NH_2)_3]^{2+}$ (treating the $NH_2CH_2CH_2NH_2$ group as a planar ring)	

EXAMPLES

Determine the point groups of the following molecules and ions from Figures 3-13 and 3-16:

XeF_4
1. XeF_4 is not in the groups of low or high symmetry.
2. Its highest order rotation axis is C_4.
3. It has four C_2 axes perpendicular to the C_4 axis and is therefore in the *D* set of groups.
4. It has a horizontal plane perpendicular to the C_4 axis. Therefore its point group is D_{4h}.

SF_4
1. It is not in the groups of high or low symmetry.
2. Its highest order (and only) rotation axis is a C_2 axis passing through the lone pair.
3. The ion has no other C_2 axes and is therefore in the *C* or *S* set.
4. It has no mirror plane perpendicular to the C_2.
5. It has two mirror planes containing the C_2 axis. Therefore, the point group is C_{2v}.

IOF_3
1. The molecule has no symmetry (other than *E*). Its point group is C_1.

EXERCISE 4-3

Use the procedure described above to verify the point groups of the molecules in Table 4-4.

C versus *D* point group classifications

All molecules having these classifications must have a C_n axis. If more than one C_n axis is found, the highest order axis (largest value of n) is used as the reference axis. In general, it is useful to orient this axis vertically.

	D Classifications	*C Classifications*
General Case: Look for C_n axes perpendicular to the highest order C_n axis.	nC_2 axes $\perp$ C_n axis	No C_2 axes $\perp$ C_n axis
Subcategories:		
If a horizontal plane of symmetry exists:	D_{nh}	C_{nh}
If n vertical planes exist:	D_{nd}	C_{nv}
If no planes of symmetry exist:	D_n	C_n

Notes:

1. Vertical planes contain the highest order C_n axis. In the D_{nd} case, the planes are designated *dihedral* because they are between the C_2 axes—thus, the subscript *d*.
2. Simply having a C_n axis does not guarantee that a molecule will be in a *D* or *C* category; don't forget that the high-symmetry T_d, O_h, and I_h point groups and related groups have a large number of C_n axes.
3. When in doubt, you can always check the character tables (Appendix C) for a complete list of symmetry elements for any point group.

Groups related to I_h, O_h, and T_d groups

The high-symmetry point groups I_h, O_h, and T_d are well known in chemistry and are represented by such classic molecules as C_{60}, SF_6, and CH_4. For each of these point groups, there is also a purely rotational subgroup (I, O, and T, respectively) in which the only symmetry operations other than the identity operation are proper axes of rotation. The symmetry operations for these point groups are in Table 4-5.

We are not yet finished with high-symmetry point groups. One more group, T_h, remains. The T_h point group is derived by adding a center of inversion to the T point group; adding i generates the additional symmetry operations S_6, S_6^5, and σ_h.

TABLE 4-5
Symmetry Operations for High-Symmetry Point Groups and Their Rotational Subgroups

Point Group	*Symmetry Operations*									
I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ
I	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2\ (\equiv C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2\ (\equiv C_4^2)$					
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$					
T	E	$\overbrace{4C_3\ 4C_3^2}$	$3C_2$							
T_h	E	$4C_3 4C_3^2$	$3C_2$			i	$4S_6$	$4S_6^5$	$3\sigma_h$	

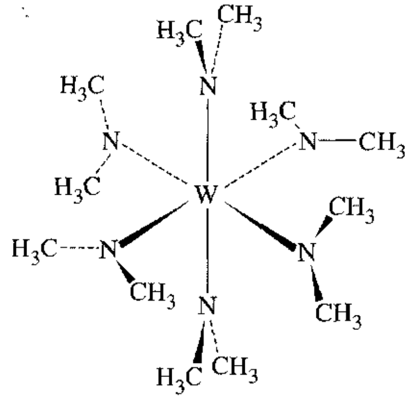


FIGURE 4-13 $W[N(CH_3)_2]_6$, a Molecule with T_h Symmetry.

T_h symmetry is rare but is known for a few molecules. The compound shown in Figure 4-13 is an example. *I*, *O*, and *T* symmetry are rarely if ever encountered in chemistry.

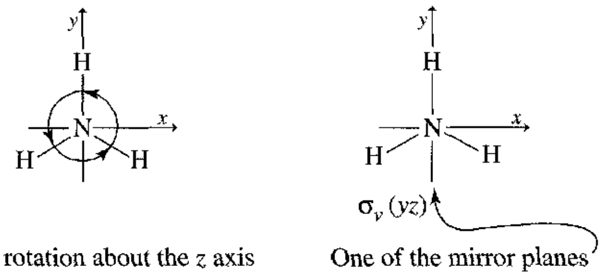
That's all there is to it! It takes a fair amount of practice, preferably using molecular models, to learn the point groups well, but once you know them, they can be extremely useful. Several practical applications of point groups appear later in this chapter, and additional applications are included in later chapters.

4-3 PROPERTIES AND REPRESENTATIONS OF GROUPS

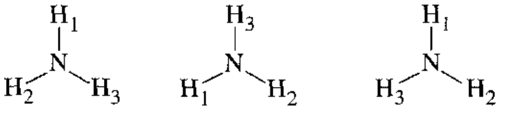
All mathematical groups (of which point groups are special types) must have certain properties. These properties are listed and illustrated in Table 4-6, using the symmetry operations of NH_3 in Figure 4-14 as an example.

4-3-1 MATRICES

Important information about the symmetry aspects of point groups is summarized in character tables, described later in this chapter. To understand the construction and use of character tables, we first need to consider the properties of matrices, which are the basis for the tables.[2]



C_3 rotation about the z axis One of the mirror planes



NH_3 after E NH_3 after C_3 NH_3 after $\sigma_v\,(yz)$

FIGURE 4-14 Symmetry Operations for Ammonia. (Top view) NH_3 is of point group C_{3v}, with the symmetry operations E, C_3, C_3^2, σ_v, σ_v', σ_v'', usually written as E, $2C_3$, and $3\sigma_v$ (note that $C_3^3 \equiv E$).

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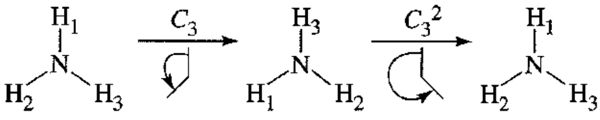
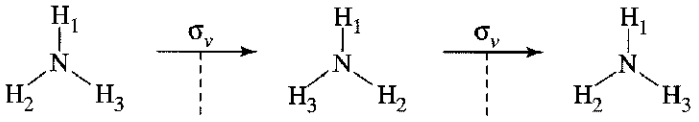
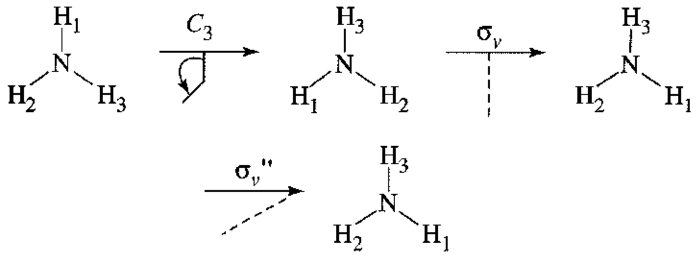
[2] More details on matrices and their manipulation are available in Appendix 1 of F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed., John Wiley & Sons, New York, 1990, and in linear algebra and finite mathematics textbooks.

TABLE 4-6
Properties of a Group

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

By **matrix** we mean an ordered array of numbers, such as

$$\begin{bmatrix} 3 & 2 \\ 7 & 1 \end{bmatrix} \quad \text{or} \quad [2 \quad 0 \quad 1 \quad 3 \quad 5]$$

To multiply matrices, it is first required that the number of vertical columns of the first matrix be equal to the number of horizontal rows of the second matrix. To find the product, sum, term by term, the products of each *row* of the first matrix by each *column* of the second (each term in a row must be multiplied by its corresponding term in the appropriate column of the second matrix). Place the resulting sum in the product matrix with the row determined by the row of the first matrix and the column determined by the column of the second matrix:

$$C_{ij} = \Sigma A_{ik} \times B_{kj}$$

Here C_{ij} = product matrix, with i rows and j columns
A_{ik} = initial matrix, with i rows and k columns
B_{kj} = initial matrix, with k rows and j columns

EXAMPLES

$$\begin{array}{cc} & k \\ i & \begin{bmatrix} 1 & 5 \\ 2 & 6 \end{bmatrix} \end{array} \times \begin{array}{cc} j & \\ \begin{bmatrix} 7 & 3 \\ 4 & 8 \end{bmatrix} & k \end{array} = \begin{array}{cc} j & \\ \begin{bmatrix} (1)(7) + (5)(4) & (1)(3) + (5)(8) \\ (2)(7) + (6)(4) & (2)(3) + (6)(8) \end{bmatrix} & i \end{array} = \begin{array}{cc} j & \\ \begin{bmatrix} 27 & 43 \\ 38 & 54 \end{bmatrix} & i \end{array}$$

This example has 2 rows and 2 columns in each initial matrix, so it has 2 rows and 2 columns in the product matrix; $i = j = k = 2$.

$$\begin{array}{cc} & k \\ i & \begin{bmatrix} 1 & 2 & 3 \end{bmatrix} \end{array} \begin{array}{cc} j & \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & k \end{array} =$$

$$\begin{array}{cc} j & \\ \begin{bmatrix} (1)(1) + (2)(0) + (3)(0) & (1)(0) + (2)(-1) + (3)(0) & (1)(0) + (2)(0) + (3)(1) \end{bmatrix} & i \end{array} = \begin{array}{cc} j & \\ \begin{bmatrix} 1 & -2 & 3 \end{bmatrix} & i \end{array}$$

Here, $i = 1, j = 3$, and $k = 3$, so the product matrix has 1 row (i) and 3 columns (j).

$$\begin{array}{cc} & k \\ i & \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{array} \begin{array}{cc} j & \\ \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} & k \end{array} = \begin{array}{cc} j & \\ \begin{bmatrix} (1)(1) + (0)(2) + (0)(3) \\ (0)(1) + (-1)(2) + (0)(3) \\ (0)(1) + (0)(2) + (1)(3) \end{bmatrix} & i \end{array} = \begin{array}{cc} j & \\ \begin{bmatrix} 1 \\ -2 \\ 3 \end{bmatrix} & i \end{array}$$

Here $i = 3, j = 1$, and $k = 3$, so the product matrix has 3 rows (i) and 1 column (j).

EXERCISE 4-4

Do the following multiplications:

a. $\begin{bmatrix} 5 & 1 & 3 \\ 4 & 2 & 2 \\ 1 & 2 & 3 \end{bmatrix} \times \begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 3 \\ 5 & 4 & 3 \end{bmatrix}$

b. $\begin{bmatrix} 1 & -1 & -2 \\ 0 & 1 & -1 \\ 1 & 0 & 0 \end{bmatrix} \times \begin{bmatrix} 2 \\ 1 \\ 3 \end{bmatrix}$

c. $\begin{bmatrix} 1 & 2 & 3 \end{bmatrix} \times \begin{bmatrix} 1 & -1 & -2 \\ 2 & 1 & -1 \\ 3 & 2 & 1 \end{bmatrix}$

4-3-2 REPRESENTATIONS OF POINT GROUPS

Symmetry operations: Matrix representations

Consider the effects of the symmetry operations of the C_{2v} point group on the set of x, y, and z coordinates. [The set of p orbitals (p_x, p_y, p_z) behaves the same way, so this is a useful exercise.] The water molecule is an example of a molecule having C_{2v} symmetry. It has a C_2 axis through the oxygen and in the plane of the molecule, no perpendicular C_2 axes, and no horizontal mirror plane, but it does have two vertical mirror planes,

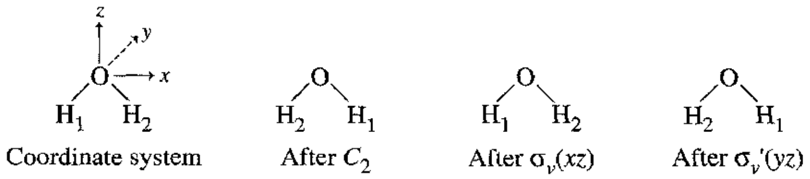


FIGURE 4-15 Symmetry Operations of the Water Molecule.

as shown in Table 4-1 and Figure 4-15. The z axis is usually chosen as the axis of highest rotational symmetry; for H_2O, this is the *only* rotational axis. The other axes are arbitrary. We will use the xz plane as the plane of the molecule.[3] This set of axes is chosen to obey the right-hand rule (the thumb and first two fingers of the right hand, held perpendicular to each other, are labeled x, y, and z, respectively).

Each symmetry operation may be expressed as a **transformation matrix** as follows:

$$[\text{New coordinates}] = [\text{transformation matrix}][\text{old coordinates}]$$

As examples, consider how transformation matrices can be used to represent the symmetry operations of the C_{2v} point group:

C_2: Rotate a point having coordinates (x, y, z) about the $C_2(z)$ axis. The new coordinates are given by

$$\begin{aligned} x' &= \text{new } x = -x \\ y' &= \text{new } y = -y \\ z' &= \text{new } z = z \end{aligned} \qquad \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{transformation matrix for } C_2$$

In matrix notation,

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

$$\begin{bmatrix} \text{New} \\ \text{coordinates} \end{bmatrix} = \begin{bmatrix} \text{transformation} \\ \text{matrix} \end{bmatrix} \begin{bmatrix} \text{old} \\ \text{coordinates} \end{bmatrix} = \begin{bmatrix} \text{new coordinates} \\ \text{in terms of old} \end{bmatrix}$$

$\sigma_v(xz)$: Reflect a point with coordinates (x, y, z) through the xz plane.

$$\begin{aligned} x' &= \text{new } x = x \\ y' &= \text{new } y = -y \\ z' &= \text{new } z = z \end{aligned} \qquad \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{transformation matrix for } \sigma_v(xz)$$

The matrix equation is

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

---

[3] Some sources use yz as the plane of the molecule. The assignment of B_1 and B_2 in Section 4-3-3 is reversed with this choice.

The transformation matrices for the four symmetry operations of the group are

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

EXERCISE 4-5

Verify the transformation matrices for the E and $\sigma_v{}'(yz)$ operations of the C_{2v} point group.

This set of matrices satisfies the properties of a mathematical **group**. We call this a **matrix representation** of the C_{2v} point group. This representation is a set of matrices, each corresponding to an operation in the group; these matrices combine in the same way as the operations themselves. For example, multiplying two of the matrices is equivalent to carrying out the two corresponding operations and results in a matrix that corresponds to the resulting operation (the operations are carried out right to left, so $C_2 \times \sigma_v$ means σ_v followed by C_2):

$$C_2 \times \sigma_v(xz) = \begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix} = \begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix} = \sigma_v{}'(yz)$$

The matrices of the matrix representation of the C_{2v} group also describe the operations of the group shown in Figure 4-15. The C_2 and $\sigma_v{}'(yz)$ operations interchange H_1 and H_2, whereas E and $\sigma_v(xz)$ leave them unchanged.

Characters

The **character**, defined only for a square matrix, is the trace of the matrix, or the sum of the numbers on the diagonal from upper left to lower right. For the C_{2v} point group, the following characters are obtained from the preceding matrices:

E	C_2	$\sigma_v(xz)$	$\sigma_v{}'(yz)$
3	−1	1	1

We can say that this set of characters also forms a **representation**. It is an alternate shorthand version of the matrix representation. Whether in matrix or character format, this representation is called a **reducible representation**, a combination of more fundamental **irreducible representations** as described in the next section. Reducible representations are frequently designated with a capital gamma (Γ).

Reducible and irreducible representations

Each transformation matrix in the C_{2v} set above is "block diagonalized"; that is, it can be broken down into smaller matrices along the diagonal, with all other matrix elements equal to zero:

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

All the nonzero elements become 1×1 matrices along the principal diagonal.

When matrices are block diagonalized in this way, the x, y, and z coordinates are also block diagonalized. As a result, the x, y, and z coordinates are independent of each other. The matrix elements in the 1,1 positions (numbered as row, column) describe the results of the symmetry operations on the x coordinate, those in the 2,2 positions describe the results of the operations on the y coordinate, and those in the 3,3 positions describe the results of the operations on the z coordinate. The four matrix elements for x form a representation of the group, those for y form a second representation, and those for z form a third representation, all shown in the following table:

Irreducible representations of the C_{2v} point group, which add to make up the reducible representation Γ

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

Each row is an irreducible representation (it cannot be simplified further), and the characters of these three irreducible representations added together under each operation (column) make up the characters of the reducible representation Γ, just as the combination of all the matrices for the x, y, and z coordinates makes up the matrices of the reducible representation. For example, the sum of the three characters for x, y, and z under the C_2 operation is -1, the character for Γ under this same operation.

The set of 3 × 3 matrices obtained for H_2O is called a reducible representation, because it is the sum of irreducible representations (the block diagonalized 1 × 1 matrices), which cannot be reduced to smaller component parts. The set of characters of these matrices also forms the reducible representation Γ, for the same reason.

4-3-3 CHARACTER TABLES

Three of the representations for C_{2v}, labeled A_1, B_1, and B_2 below, have been determined so far. The fourth, called A_2, can be found by using the properties of a group described in Table 4-7. A complete set of irreducible representations for a point group is called the **character table** for that group. The character table for each point group is unique; character tables for the common point groups are included in Appendix C.

The complete character table for C_{2v} with the irreducible representations in the order commonly used, is

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

The labels used with character tables are as follows:

x, y, z	transformations of the x, y, z coordinates or combinations thereof
R_x, R_y, R_z	rotation about the x, y, and z axes
R	any symmetry operation [such as C_2 or $\sigma_v(xz)$]
χ	character of an operation
i and j	designation of different representations (such as A_1 or A_2)
h	order of the group (the total number of symmetry operations in the group)

The labels in the left column used to designate the representations will be described later in this section. Other useful terms are defined in Table 4-7.

TABLE 4-7

Properties of Characters of Irreducible Representations in Point Groups

Property	*Example: C_{2v}*
1. The total number of symmetry operations in the group is called the **order (h)**. To determine the order of a group, simply total the number of symmetry operations as listed in the top row of the character table.	Order = 4 [4 symmetry operations: E, C_2, $\sigma_v(xz)$, and $\sigma_v'(yz)$].
2. Symmetry operations are arranged in **classes**. All operations in a class have identical characters for their transformation matrices and are grouped in the same column in character tables.	Each symmetry operation is in a separate class; therefore, there are 4 columns in the character table.
3. The number of irreducible representations equals the number of classes. This means that character tables have the same number of rows and columns (they are square).	Because there are 4 classes, there must also be 4 irreducible representations—and there are.
4. The sum of the squares of the **dimensions** (characters under E) of each of the irreducible representations equals the order of the group. $h = \sum_i [\chi_i(E)]^2$	$1^2 + 1^2 + 1^2 + 1^2 = 4 = h$, the order of the group.
5. For any irreducible representation, the sum of the squares of the characters multiplied by the number of operations in the class (see Table 4-8 for an example), equals the order of the group. $h = \sum_R [\chi_i(R)]^2$	For A_2, $1^2 + 1^2 + (-1)^2 + (-1)^2 = 4 = h$. Each operation is its own class in this group.
6. Irreducible representations are **orthogonal** to each other. The sum of the products of the characters (multiplied together for each class) for any pair of irreducible representations is 0. $\sum_R \chi_i(R)\chi_j(R) = 0$, when $i \neq j$ Taking any pair of irreducible representations, multiplying together the characters for each class and multiplying by the number of operations in the class (see Table 4-8 for an example), and adding the products gives zero.	B_1 and B_2 are orthogonal: $(1)(1)+(-1)(-1)+(1)(-1)+(-1)(1)=0$ $E \quad C_2 \quad \sigma_v(xz) \quad \sigma_v'(yz)$ Each operation is its own class in this group.
7. **A totally symmetric representation** is included in all groups, with characters of 1 for all operations.	C_{2v} has A_1, which has all characters = 1.

The A_2 representation of the C_{2v} group can now be explained. The character table has four columns; it has four classes of symmetry operations (Property 2 in Table 4-7). It must therefore have four irreducible representations (Property 3). The sum of the products of the characters of any two representations must equal zero (orthogonality, Property 6). Therefore, a product of A_1 and the unknown representation must have 1 for two of the characters and -1 for the other two. The character for the identity operation of this new representation must be 1 [$\chi(E) = 1$] in order to have the sum of the squares of these characters equal 4 (required by Property 4). Because no two representations can be the same, A_2 must then have $\chi(E) = \chi(C_2) = 1$, and $\chi(\sigma_{xz}) = \chi(\sigma_{yz}) = -1$. This representation is also orthogonal to B_1 and B_2, as required.

Another example: C_{3v}(NH$_3$)

Full descriptions of the matrices for the operations in this group will not be given, but the characters can be found by using the properties of a group. Consider the C_3 rotation shown in Figure 4-16. Rotation of 120° results in new x' and y' as shown, which can be described in terms of the vector sums of x and y by using trigonometric functions:

$$x' = x\cos\frac{2\pi}{3} - y\sin\frac{2\pi}{3} = -\frac{1}{2}x - \frac{\sqrt{3}}{2}y$$

$$y' = x\sin\frac{2\pi}{3} + y\cos\frac{2\pi}{3} = \frac{\sqrt{3}}{2}x - \frac{1}{2}y$$

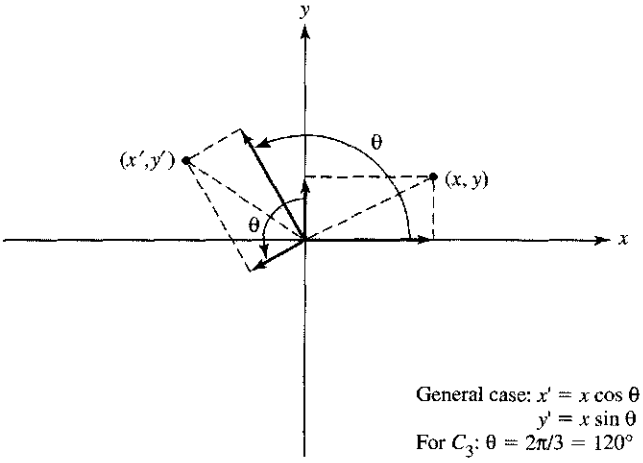
The transformation matrices for the symmetry operations shown are as follows:

$$E: \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3: \begin{bmatrix} \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} & 0 \\ \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{v(xz)}: \begin{bmatrix} 1 & 0 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

In the C_{3v} point group, $\chi(C_3^2) = \chi(C_3)$, which means that they are in the same class and described as $2C_3$ in the character table. In addition, the three reflections have identical characters and are in the same class, described as $3\sigma_v$.

The transformation matrices for C_3 and C_3^2 cannot be block diagonalized into 1×1 matrices because the C_3 matrix has off-diagonal entries; however, the matrices can be block diagonalized into 2×2 and 1×1 matrices, with all other matrix elements equal to zero:

$$E: \begin{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & 0 \end{matrix} & [1] \end{bmatrix} \quad C_3: \begin{bmatrix} \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & 0 \end{matrix} & [1] \end{bmatrix} \quad \sigma_{v(xz)}: \begin{bmatrix} \begin{bmatrix} 1 & 0 \\ -1 & 0 \end{bmatrix} & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & 0 \end{matrix} & [1] \end{bmatrix}$$



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

FIGURE 4-16 Effect of Rotation on Coordinates of a Point.

The C_3 matrix must be blocked this way because the (x, y) combination is needed for the new x' and y'; the other matrices must follow the same pattern for consistency across the representation. In this case, x and y are not independent of each other.

The characters of the matrices are the sums of the numbers on the principal diagonal (from upper left to lower right). The set of 2×2 matrices has the characters corresponding to the E representation in the following character table; the set of 1×1 matrices matches the A_1 representation. The third irreducible representation, A_2, can be found by using the defining properties of a mathematical group, as in the C_{2v} example above. Table 4-8 gives the properties of the characters for the C_{3v} point group.

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

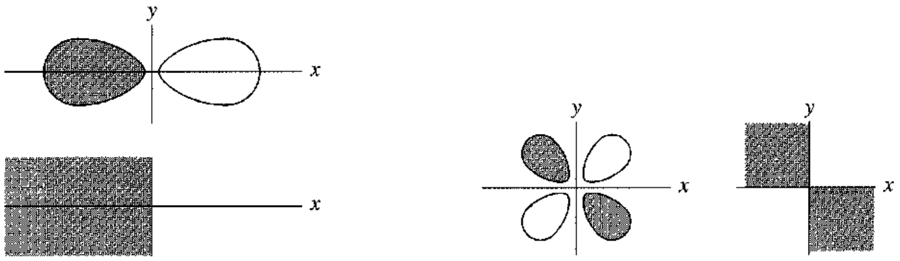
TABLE 4-8
Properties of the Characters for the C_{3v} Point Group

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

Additional features of character tables

1. When operations such as C_3 are in the same class, the listing in a character table is $2C_3$, indicating that the results are the same whether rotation is in a clockwise or counterclockwise direction (or, alternately, that C_3 and C_3^2 give the same result). In either case, this is equivalent to two columns in the table being shown as one. Similar notation is used for multiple reflections.

2. When necessary, the C_2 axes perpendicular to the principal axis (in a D group) are designated with primes; a single prime indicates that the axis passes through several atoms of the molecule, whereas a double prime indicates that it passes between the atoms.
3. When the mirror plane is perpendicular to the principal axis, or horizontal, the reflection is called σ_h. Other planes are labeled σ_v or σ_d; see the character tables in Appendix C.
4. The expressions listed to the right of the characters indicate the symmetry of mathematical functions of the coordinates x, y, and z and of rotation about the axes (R_x, R_y, R_z). These can be used to find the orbitals that match the representation. For example, x with positive and negative directions matches the p_x orbital with positive and negative lobes in the quadrants in the xy plane, and the product xy with alternating signs on the quadrants matches lobes of the d_{xy} orbital, as in Figure 4-17. In all cases, the totally symmetric s orbital matches the first representation in the group, one of the A set. The rotational functions are used to describe the rotational motions of the molecule. Rotation and other motions of the water molecule are discussed in Section 4-4-2.



p_x orbitals have the same symmetry as x (positive in half the quadrants, negative in the other half).

d_{xy} orbitals have the same symmetry as the function xy (sign of the function in the four quadrants).

FIGURE 4-17 Orbitals and Representations.

In the C_{3v} example described previously the x and y coordinates appeared together in the E irreducible representation. The notation for this is to group them as (x, y) in this section of the table. This means that x and y together have the same symmetry properties as the E irreducible representation. Consequently, the p_x and p_y orbitals together have the same symmetry as the E irreducible representation in this point group.

5. Matching the symmetry operations of a molecule with those listed in the top row of the character table will confirm any point group assignment.
6. Irreducible representations are assigned labels according to the following rules, in which symmetric means a character of 1 and antisymmetric a character of -1 (see the character tables in Appendix C for examples).

   a. Letters are assigned according to the dimension of the irreducible representation (the character for the identity operation).

Dimension	*Symmetry Label*	
1	A	if the representation is symmetric to the principal rotation operation $(\chi(C_n) = 1)$.
	B	if it is antisymmetric $(\chi(C_n) = -1)$.
2	E	
3	T	

b. Subscript 1 designates a representation symmetric to a C_2 rotation perpendicular to the principal axis, and subscript 2 designates a representation antisymmetric to the C_2. If there are no perpendicular C_2 axes, 1 designates a representation symmetric to a vertical plane, and 2 designates a representation antisymmetric to a vertical plane.

c. Subscript g (gerade) designates symmetric to inversion, and subscript u (ungerade) designates antisymmetric to inversion.

d. Single primes are symmetric to σ_h and double primes are antisymmetric to σ_h when a distinction between representations is needed (C_{3h}, C_{5h}, D_{3h}, D_{5h}).

4-4 EXAMPLES AND APPLICATIONS OF SYMMETRY

4-4-1 CHIRALITY

Many molecules are not superimposable on their mirror image. Such molecules, labeled **chiral** or **dissymmetric**, may have important chemical properties as a consequence of this nonsuperimposability. An example of a chiral organic molecule is CBrClFI, and many examples of chiral objects can also be found on the macroscopic scale, as in Figure 4-18.

Chiral objects are termed dissymmetric. This term does not imply that these objects necessarily have *no* symmetry. For example, the propellers shown in Figure 4-18 each have a C_3 axis, yet they are nonsuperimposable (if both were spun in a clockwise direction, they would move an airplane in opposite directions!). In general, we can say that a molecule or some other object is chiral if it has no symmetry operations (other than E) or if it has *only proper rotation axes.*

EXERCISE 4-6

Which point groups are possible for chiral molecules? (Hint: Refer as necessary to the character tables in Appendix C.)

Air blowing past the stationary propellers in Figure 4-18 will be rotated in either a clockwise or counterclockwise direction. By the same token, plane-polarized light will be rotated on passing through chiral molecules (Figure 4-19); clockwise rotation is designated **dextrorotatory**, and counterclockwise rotation **levorotatory**. The ability of chiral molecules to rotate plane-polarized light is termed **optical activity** and may be measured experimentally.

Many coordination compounds are chiral and thus exhibit optical activity if they can be resolved into the two isomers. One of these is $[Ru(NH_2CH_2CH_2NH_2)_3]^{2+}$, with

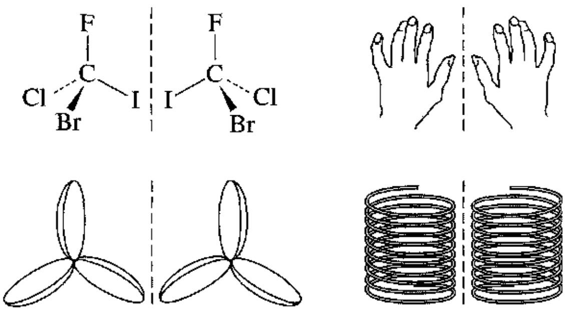


FIGURE 4-18 A Chiral Molecule and Other Chiral Objects.

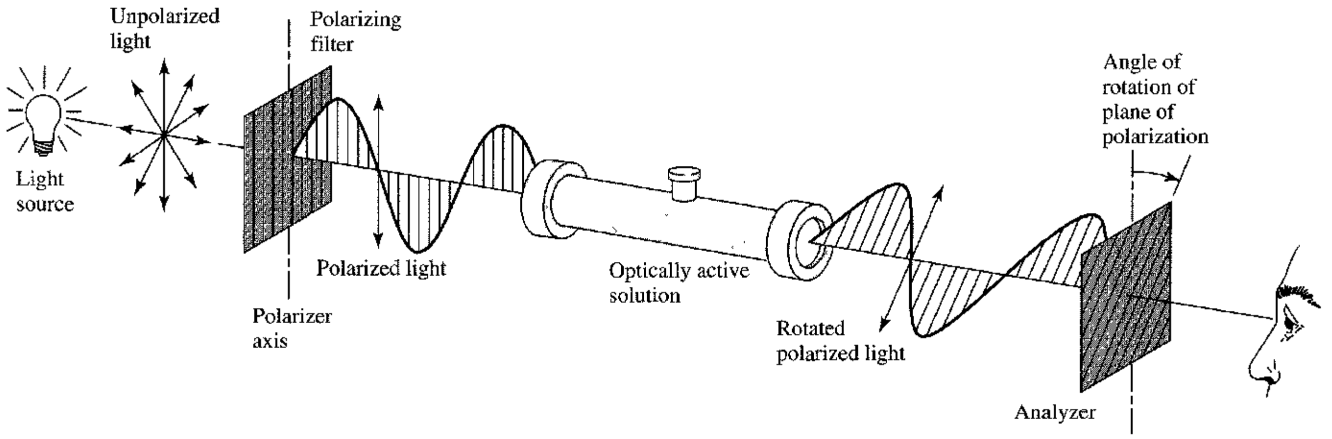


FIGURE 4-19 Rotation of Plane-Polarized Light.

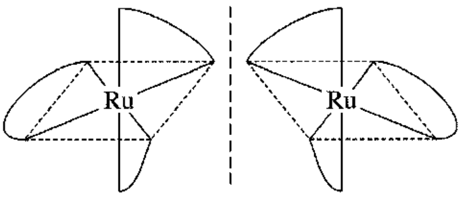


FIGURE 4-20 Chiral Isomers of $[Ru(NH_2CH_2CH_2NH_2)_3]^{2+}$.

D_3 symmetry (Figure 4-20). Mirror images of this molecule look much like left- and right-handed three-bladed propellers. Further examples will be discussed in Chapter 9.

4-4-2 MOLECULAR VIBRATIONS

Symmetry can be helpful in determining the modes of vibration of molecules. Vibrational modes of water and the stretching modes of CO in carbonyl complexes are examples that can be treated quite simply, as described in the following pages. Other molecules can be studied using the same methods.

Water (C_{2v} symmetry)

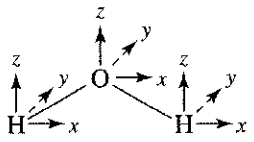


FIGURE 4-21 A Set of Axes for the Water Molecule.

Because the study of vibrations is the study of motion of the individual atoms in a molecule, we must first attach a set of x, y, and z coordinates to each atom. For convenience, we assign the z axes parallel to the C_2 axis of the molecule, the x axes in the plane of the molecule, and the y axes perpendicular to the plane (Figure 4-21). Each atom can move in all three directions, so a total of nine transformations (motion of each atom in the x, y, and z directions) must be considered. For N atoms in a molecule, there are $3N$ total motions, known as **degrees of freedom**. Degrees of freedom for different geometries are summarized in Table 4-9. Because water has three atoms, there must be nine different motions.

We will use transformation matrices to determine the symmetry of all nine motions and then assign them to translation, rotation, and vibration. Fortunately, it is only necessary to determine the characters of the transformation matrices, not the individual matrix elements.

In this case, the initial axes make a column matrix with nine elements, and each transformation matrix is 9×9. A nonzero entry appears along the diagonal of the matrix only for an atom that does not change position. If the atom changes position during the symmetry operation, a 0 is entered. If the atom remains in its original location and

TABLE 4-9
Degrees of Freedom

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

the vector direction is unchanged, a 1 is entered. If the atom remains but the vector direction is reversed, a -1 is entered. (Because all the operations change vector directions by 0° or 180° in the C_{2v} point group, these are the only possibilities.) When all nine vectors are summed, the character of the reducible representation Γ is obtained. The full 9×9 matrix for C_2 is shown as an example; note that only the diagonal entries are used in finding the character.

$$\begin{array}{r} \mathrm{O}\left\{\vphantom{\begin{matrix}x'\\y'\\z'\end{matrix}}\right. \\ \mathrm{H}_a\left\{\vphantom{\begin{matrix}x'\\y'\\z'\end{matrix}}\right. \\ \mathrm{H}_b\left\{\vphantom{\begin{matrix}x'\\y'\\z'\end{matrix}}\right. \end{array} \begin{bmatrix} x' \\ y' \\ z' \\ x' \\ y' \\ z' \\ x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \\ x \\ y \\ z \\ x \\ y \\ z \end{bmatrix} \begin{array}{l} \left.\vphantom{\begin{matrix}x\\y\\z\end{matrix}}\right\}\mathrm{O} \\ \left.\vphantom{\begin{matrix}x\\y\\z\end{matrix}}\right\}\mathrm{H}_a \\ \left.\vphantom{\begin{matrix}x\\y\\z\end{matrix}}\right\}\mathrm{H}_b \end{array}$$

The H_a and H_b entries are not on the principal diagonal because H_a and H_b exchange with each other in a C_2 rotation, and $x'(H_a) = -x(H_b)$, $y'(H_a) = -y(H_b)$, and $z'(H_a) = z(H_b)$. Only the oxygen atom contributes to the character for this operation, for a total of -1.

The other entries for Γ can also be found without writing out the matrices, as follows:

E:	All nine vectors are unchanged in the identity operation, so the character is 9.
C_2:	The hydrogen atoms change position in a C_2 rotation, so all their vectors have zero contribution to the character. The oxygen atom vectors in the x and y directions are reversed, each contributing -1, and in the z direction they remain the same, contributing 1, for a total of -1. [The sum of the principal diagonal $= \chi(C_2) = (-1) + (-1) + (1) = -1$.]
$\sigma_v(xz)$:	Reflection in the plane of the molecule changes the direction of all the y vectors and leaves the x and z vectors unchanged, for a total of $3 - 3 + 3 = 3$.
$\sigma_v'(yz)$:	Finally, reflection perpendicular to the plane of the molecule changes the position of the hydrogens so their contribution is zero; the x vector on the oxygen changes direction and the y and z vectors are unchanged, for a total of 1.

Because all nine direction vectors are included in this representation, it represents all the motions of the molecule, three translations, three rotations, and (by difference) three vibrations. The characters of the reducible representation Γ are shown as the last row below the irreducible representations in the C_{2v} character table.

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

Reducing representations to irreducible representations

The next step is to separate this representation into its component irreducible representations. This requires another property of groups. The number of times that any irreducible representation appears in a reducible representation is equal to the sum of the products of the characters of the reducible and irreducible representations taken one operation at a time, divided by the order of the group. This may be expressed in equation form, with the sum taken over all symmetry operations of the group.[4]

$$\begin{pmatrix}\text{Number of irreducible}\\ \text{representations of}\\ \text{a given type}\end{pmatrix} = \frac{1}{\text{order}}\sum_R\left[\begin{pmatrix}\text{number}\\ \text{of operations}\\ \text{in the class}\end{pmatrix}\times\begin{pmatrix}\text{character of}\\ \text{reducible}\\ \text{representation}\end{pmatrix}\times\begin{pmatrix}\text{character of}\\ \text{irreducible}\\ \text{representation}\end{pmatrix}\right]$$

In the water example, the order of C_{2v} is 4, with one operation in each class $(E, C_2, \sigma_v, \sigma_v')$. The results are then

$$n_{A_1} = \frac{1}{4}[(9)(1) + (-1)(1) + (3)(1) + (1)(1)] = 3$$

$$n_{A_2} = \frac{1}{4}[(9)(1) + (-1)(1) + (3)(-1) + (1)(-1)] = 1$$

$$n_{B_1} = \frac{1}{4}[(9)(1) + (-1)(-1) + (3)(1) + (1)(-1)] = 3$$

$$n_{B_2} = \frac{1}{4}[(9)(1) + (-1)(-1) + (3)(-1) + (1)(1)] = 2$$

The reducible representation for all motions of the water molecule is therefore reduced to $3A_1 + A_2 + 3B_1 + 2B_2$.

Examination of the columns on the far right in the character table shows that translation along the x, y, and z directions is $A_1 + B_1 + B_2$ (translation is motion along the x, y, and z directions, so it transforms in the same way as the three axes) and that rotation in the three directions (R_x, R_y, R_z) is $A_2 + B_1 + B_2$. Subtracting these from the total above leaves $2A_1 + B_1$, the three vibrational modes, as shown in Table 4-10. The number of vibrational modes equals $3N - 6$, as described earlier. Two of the modes are totally symmetric (A_1) and do not change the symmetry of the molecule, but one is antisymmetric to C_2 rotation and to reflection perpendicular to the plane of the molecule (B_1). These modes are illustrated as symmetric stretch, symmetric bend, and antisymmetric stretch in Table 4-11.

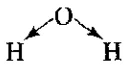
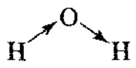
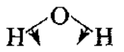
---

[4] This procedure should yield an integer for the number of irreducible representations of each type; obtaining a fraction in this step indicates a calculation error.

TABLE 4-10
Symmetry of Molecular Motions of Water

All Motions	*Translation* (x, y, z)	*Rotation* (R_x, R_y, R_z)	*Vibration (Remaining Modes)*
$3A_1$	A_1		$2A_1$
A_2		A_2	
$3B_1$	B_1	B_1	B_1
$2B_2$	B_2	B_2	

TABLE 4-11
The Vibrational Modes of Water

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

A molecular vibration is infrared active (has an infrared absorption) only if it results in a change in the dipole moment of the molecule. The three vibrations of water can be analyzed this way to determine their infrared behavior. In fact, the oxygen atom also moves. Its motion is opposite that of the hydrogens and is very small, because its mass is so much larger than that of the hydrogen atoms. The center of mass of the molecule does not move in vibrations.

Group theory can give us the same information (and can account for the more complicated cases as well; in fact, group theory in principle can account for *all* vibrational modes of a molecule). In group theory terms, a vibrational mode is active in the infrared *if it corresponds to an irreducible representation that has the same symmetry (or transforms) as the Cartesian coordinates x, y, or z,* because a vibrational motion that shifts the center of charge of the molecule in any of the *x*, *y*, or *z* directions results in a change in dipole moment. Otherwise, the vibrational mode is not infrared active.

EXAMPLES

Reduce the following representations to their irreducible representations in the point group indicated (refer to the character tables in Appendix C):

C_{2h}	E	C_2	i	σ_h
Γ	4	0	2	2

Solution:

$$n_{A_g} = \frac{1}{4}[(4)(1) + (0)(1) + (2)(1) + (2)(1)] = 2$$

$$n_{B_g} = \frac{1}{4}[(4)(1) + (0)(-1) + (2)(1) + (2)(-1)] = 1$$

$$n_{A_u} = \frac{1}{4}[(4)(1) + (0)(1) + (2)(-1) + (2)(-1)] = 0$$

$$n_{B_u} = \frac{1}{4}[(4)(1) + (0)(-1) + (2)(-1) + (2)(1)] = 1$$

Therefore, $\Gamma = 2A_g + B_g + B_u$.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	6	3	−2

Solution:

$$n_{A_1} = \frac{1}{6}[(6)(1) + (2)(3)(1) + (3)(-2)(1)] = 1$$

$$n_{A_2} = \frac{1}{6}[(6)(1) + (2)(3)(1) + (3)(-2)(-1)] = 3$$

$$n_E = \frac{1}{6}[(6)(2) + (2)(3)(-1) + (3)(-2)(0)] = 1$$

Therefore, $\Gamma = A_1 + 3A_2 + E$.

Be sure to include the number of symmetry operations in a class (column) of the character table. This means that the second term in the C_{3v} calculation must be multiplied by 2 ($2C_3$; there are two operations in this class), and the third term must be multiplied by 3, as shown.

EXERCISE 4-7

Reduce the following representations to their irreducible representations in the point groups indicated:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_1	4	1	0	0	2

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_2	4	0	0	2	0

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_3	7	−1	−1	−1	−1

EXERCISE 4-8

Analysis of the x, y, and z coordinates of each atom in NH_3 gives the following representation:

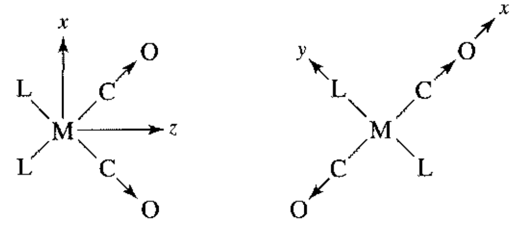
C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	12	0	2

a. Reduce Γ to its irreducible representations.

b. Classify the irreducible representations into translational, rotational, and vibrational modes.

c. Show that the total number of degrees of freedom = $3N$.

d. Which vibrational modes are infrared active?



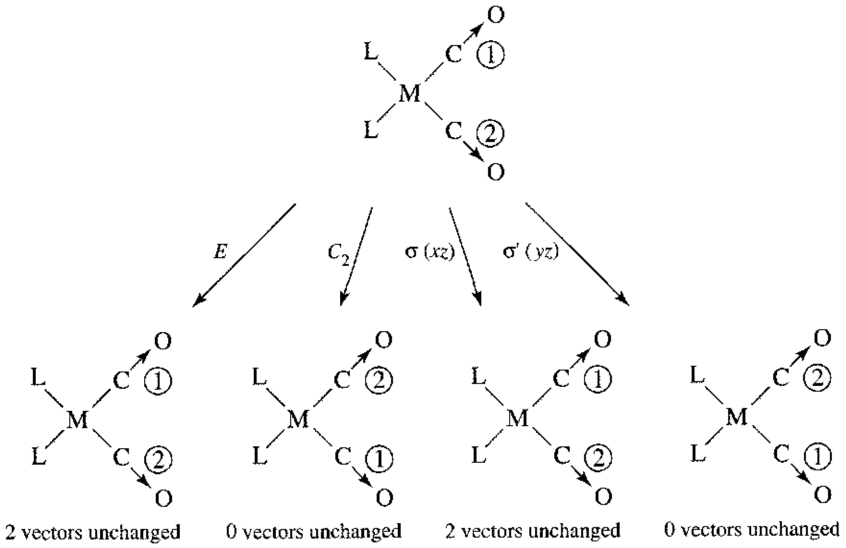
Cis-dicarbonyl complex *Trans*-dicarbonyl complex

FIGURE 4-22 Carbonyl Stretching Vibrations of *cis*- and *trans*-Dicarbonyl Square Planar Complexes.

Selected vibrational modes

It is often useful to consider a particular type of vibrational mode for a compound. For example, useful information often can be obtained from the C—O stretching bands in infrared spectra of metal complexes containing CO (carbonyl) ligands. The following example of *cis*- and *trans*-dicarbonyl square planar complexes shows the procedure. For these complexes,[5] a simple IR spectrum can distinguish whether a sample is *cis*- or *trans*-$ML_2(CO)_2$; the number of C—O stretching bands is determined by the geometry of the complex (Figure 4-22).

***cis*-$ML_2(CO)_2$, point group C_{2v}.** The principal axis (C_2) is the z axis, with the xz plane assigned as the plane of the molecule. Possible C—O stretching motions are shown by arrows in Figure 4-23; either an increase or decrease in the C—O distance is possible. These vectors are used to create the reducible representation below using the symmetry operations of the C_{2v} point group. A C—O bond will transform with a character of 1 *if it remains unchanged* by the symmetry operations, and with a character of 0 *if it is changed.* These operations and their characters are shown in Figure 4-23. Both



	E	C_2	$\sigma(xz)$	$\sigma'(yz)$
Γ	2	0	2	0

FIGURE 4-23 Symmetry Operations and Characters for *cis*-$ML_2(CO)_2$.

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[5] M represents any metal and L any ligand other than CO in these formulas.

stretches are unchanged in the identity operation and in the reflection through the plane of the molecule, so each contributes 1 to the character, for a total of 2 for each operation. Both vectors move to new locations on rotation or reflection perpendicular to the plane of the molecule, so these two characters are 0.

The reducible representation Γ reduces to $A_1 + B_1$:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ	2	0	2	0		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_1	1	−1	1	−1	x, R_y	xz

A_1 is an appropriate irreducible representation for an IR-active band, because it transforms as (has the symmetry of) the Cartesian coordinate z. Furthermore, the vibrational mode corresponding to B_1 should be IR active, because it transforms as the Cartesian coordinate x.

In summary:

There are two vibrational modes for C—O stretching, one having A_1 symmetry and one B_1 symmetry. Both modes are IR active, and we therefore expect to see two C—O stretches in the IR. This assumes that the C—O stretches are not sufficiently similar in energy to overlap in the infrared spectrum.

***trans*-$ML_2(CO)_2$, point group D_{2h}.** The principal axis, C_2, is again chosen as the z axis, which this time makes the plane of the molecule the xy plane. Using the symmetry operation of the D_{2h} point group, we obtain a reducible representation for C—O stretches that reduces to $A_g + B_{3u}$:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
Γ	2	0	0	2	0	2	2	0	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

The vibrational mode of A_g symmetry is not IR active, because it does not have the same symmetry as a Cartesian coordinate x, y, or z (this is the IR-inactive symmetric stretch). The mode of symmetry B_{3u}, on the other hand, is IR active, because it has the same symmetry as x.

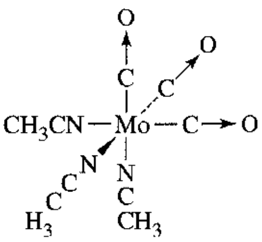
In summary:

There are two vibrational modes for C—O stretching, one having the same symmetry as A_g, and one the same symmetry as B_{3u}. The A_g mode is IR inactive (does not have the symmetry of x, y, or z); the B_{3u} mode is IR active (has the symmetry of x). We therefore expect to see one C—O stretch in the IR.

It is therefore possible to distinguish *cis*- and *trans*-$ML_2(CO)_2$ by taking an IR spectrum. If one C—O stretching band appears, the molecule is *trans*; if two bands appear, the molecule is *cis*. A significant distinction can be made by a very simple measurement.

EXAMPLE

Determine the number of IR-active CO stretching modes for *fac*-$Mo(CO)_3(NCCH_3)_3$, as shown in the diagram.



This molecule has C_{3v} symmetry. The operations to be considered are E, C_3, and σ_v. E leaves the three bond vectors unchanged, giving a character of 3. C_3 moves all three vectors, giving a character of 0. Each σ_v plane passed through one of the CO groups, leaving it unchanged, while interchanging the other two. The resulting character is 1.

The representation to be reduced, therefore, is

E	$2C_3$	$3\sigma_v$
3	0	1

This reduces to $A_1 + E$. A_1 has the same symmetry as the Cartesian coordinate z and is therefore IR active. E has the same symmetry as the x and y coordinates together and is also IR active. It represents a degenerate pair of vibrations, which appear as one absorption band.

EXERCISE 4-9

Determine the number of IR-active C—O stretching modes for $Mn(CO)_5Cl$.

GENERAL REFERENCES

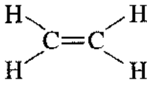
There are several helpful books on this subject. Good examples are F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed., John Wiley & Sons, New York, 1990; S. F. A. Kettle, *Symmetry and Structure (Readable Group Theory for Chemists)*, 2nd ed., John Wiley & Sons, New York, 1995; and I. Hargittai and M. Hargittai, *Symmetry Through the Eyes of a Chemist*, 2nd ed., Plenum Press, New York, 1995. The latter two also provide information on space groups used in solid state symmetry, and all give relatively gentle introductions to the mathematics of the subject.

PROBLEMS

4-1 Determine the point groups for

- **a.** Ethane (staggered conformation)
- **b.** Ethane (eclipsed conformation)
- **c.** Chloroethane (staggered conformation)
- **d.** 1,2-Dichloroethane (staggered *anti* conformation)

4-2 Determine the point groups for

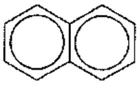
- **a.** Ethylene 
$H_2C{=}CH_2$
- **b.** Chloroethylene
- **c.** The possible isomers of dichloroethylene

4-3 Determine the point groups for

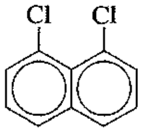
- **a.** Acetylene
- **b.** $H{-}C{\equiv}C{-}F$
- **c.** $H{-}C{\equiv}C{-}CH_3$
- **d.** $H{-}C{\equiv}C{-}CH_2Cl$
- **e.** $H{-}C{\equiv}C{-}Ph$ (Ph = phenyl)

4-4 Determine the point groups for

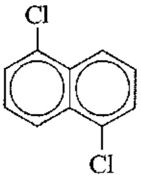
a. Naphthalene



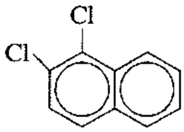
b. 1,8-Dichloronaphthalene



c. 1,5-Dichloronaphthalene

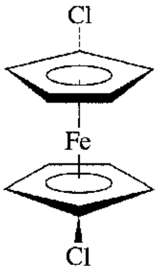


d. 1,2-Dichloronaphthalene

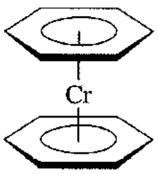


4-5 Determine the point groups for

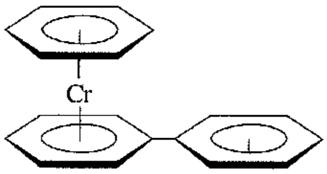
a. 1,1′-Dichloroferrocene



b. Dibenzenechromium (eclipsed conformation)

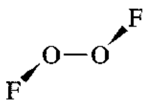


c.



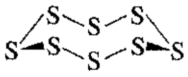
d. H_3O^+

e. O_2F_2

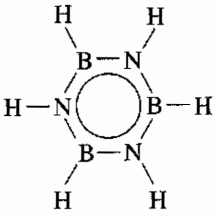


f. Formaldehyde, H_2CO

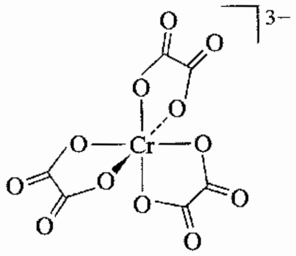
g. S_8 (puckered ring)



h. Borazine (planar)



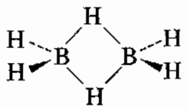
i. $[Cr(C_2O_4)_3]^{3-}$



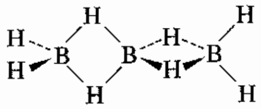
j. A tennis ball (ignoring the label, but including the pattern on the surface)

4-6 Determine the point group for

- **a.** Cyclohexane (chair conformation)
- **b.** Tetrachloroallene $Cl_2C{=}C{=}CCl_2$
- **c.** SO_4^{2-}
- **d.** A snowflake
- **e.** Diborane



- **f.** The possible isomers of tribromobenzene
- **g.** A tetrahedron inscribed in a cube (alternate corners of the cube are also corners of the tetrahedron).
- **h.** B_3H_8



4-7 Determine the point group for

- **a.** A sheet of typing paper
- **b.** An Erlenmeyer flask (no label)
- **c.** A screw
- **d.** The number 96
- **e.** Five examples of objects from everyday life; select items from five different point groups.
- **f.** A pair of eyeglasses (assuming lenses of equal strength)
- **g.** A five-pointed star
- **h.** A fork (assuming no decoration)
- **i.** Captain Ahab, who lost a leg to Moby Dick
- **j.** A metal washer

4-8 Determine the point groups of the molecules in the following end-of-chapter problems from Chapter 3:

- **a.** Problem 3-12
- **b.** Problem 3-16

4-9 Determine the point groups of the molecules and ions in

- **a.** Figure 3-8
- **b.** Figure 3-15

4-10 Determine the point groups of the following atomic orbitals, including the signs on the orbital lobes:

- **a.** p_x
- **b.** d_{xy}
- **c.** $d_{x^2-y^2}$
- **d.** d_{z^2}

4-11 Show that a cube has the same symmetry elements as an octahedron.

4-12 For *trans*-1,2-dichloroethylene, of C_{2h} symmetry,

a. List all the symmetry operations for this molecule.

b. Write a set of transformation matrices that describe the effect of each symmetry operation in the C_{2h} group on a set of coordinates x, y, z for a point. (Your answer should consist of four 3×3 transformation matrices.)

c. Using the terms along the diagonal, obtain as many irreducible representations as possible from the transformation matrices. (You should be able to obtain three irreducible representations in this way, but two will be duplicates.) You may check your results using the C_{2h} character table.

d. Using the C_{2h} character table, verify that the irreducible representations are mutually orthogonal.

4-13 Ethylene is a molecule of D_{2h} symmetry.

a. List all the symmetry operations of ethylene.

b. Write a transformation matrix for each symmetry operation that describes the effect of that operation on the coordinates of a point x, y, z.

c. Using the characters of your transformation matrices, obtain a reducible representation.

d. Using the diagonal elements of your matrices, obtain three of the D_{2h} irreducible representations.

e. Show that your irreducible representations are mutually orthogonal.

4-14 Using the D_{2d} character table,

a. Determine the order of the group.

b. Verify that the E irreducible representation is orthogonal to each of the other irreducible representations.

c. For each of the irreducible representations, verify that the sum of the squares of the characters equals the order of the group.

d. Reduce the following representations to their component irreducible representations:

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_1	6	0	2	2	2
Γ_2	6	4	6	2	0

4-15 Reduce the following representations to irreducible representations:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	6	3	2
Γ_2	5	−1	−1

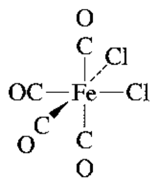
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

4-16 For D_{4h} symmetry show, using sketches, that d_{xy} orbitals have B_{2g} symmetry and that $d_{x^2-y^2}$ orbitals have B_{1g} symmetry. (Hint: you may find it useful to select a molecule that has D_{4h} symmetry as a reference for the operations of the D_{4h} point group.)

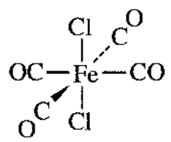
4-17 Which items in Problems 5, 6, and 7 are chiral? List three items *not* from this chapter that are chiral.

4-18 For the following molecules, determine the number of IR-active C—O stretching vibrations:

a.

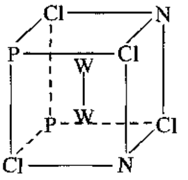


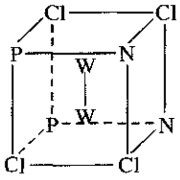
b.

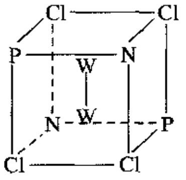


4-19 Using the x, y, and z coordinates for each atom in SF_6, determine the reducible representation, reduce it, classify the irreducible representations into translational, rotational, and vibrational modes, and decide which vibrational modes are infrared active.

4-20 Three isomers of $W_2Cl_4(NHEt)_2(PMe_3)_2$ have been reported. These isomers have the core structures shown below. Determine the point group of each (Reference: F. A. Cotton, E. V. Dikarev, and W.-Y. Wong, *Inorg. Chem.*, **1997**, *36*, 2670.)

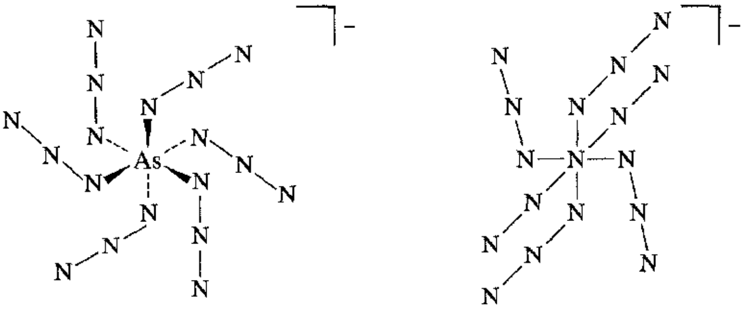

I


II


III

4-21 There is considerable evidence for the existence of protonated methane, CH_5^+. Calculations have indicated that the lowest energy form of this ion has C_s symmetry. Sketch a reasonable structure for this structure. The structure is unusual, with a type of bonding only mentioned briefly in previous chapters. (Reference: G. A. Olah and G. Rasul, *Acc. Chem. Res.*, **1997**, *30*, 245.)

4-22 The hexaazidoarsenate(V) ion, $[As(N_3)_6]^-$, has been reported as the first structurally characterized binary arsenic (V) azide species. Two views of its structure are shown below. A view with three As—N bonds pointing up and three pointing down (alternating) is shown in (a); a view down one of the N—As—N axes is shown in (b). What is its point group? (Reference: T. M. Klapötke, H. Nöth, T. Schütt, and M. Warchhold, *Angew Chem., Int. Ed.*, **2000**, *39*, 2108.)


(a) (b)

4-23 Derivatives of methane can be obtained by replacing one or more hydrogen atoms with other atoms, such as F, Cl, or Br. Suppose you had a supply of methane and the necessary chemicals and equipment to make derivatives of methane containing all possible combinations of the elements H, F, Cl, and Br. What would be the point groups of the molecules you could make? You should find 35 possible molecules, but they can be arranged into five sets for assignment of point groups.

4-24 Determine the point groups of the following molecules:

a. F_3SCCF_3, with a triple S≡C bond