

# Chapter I - Molecular Symmetry

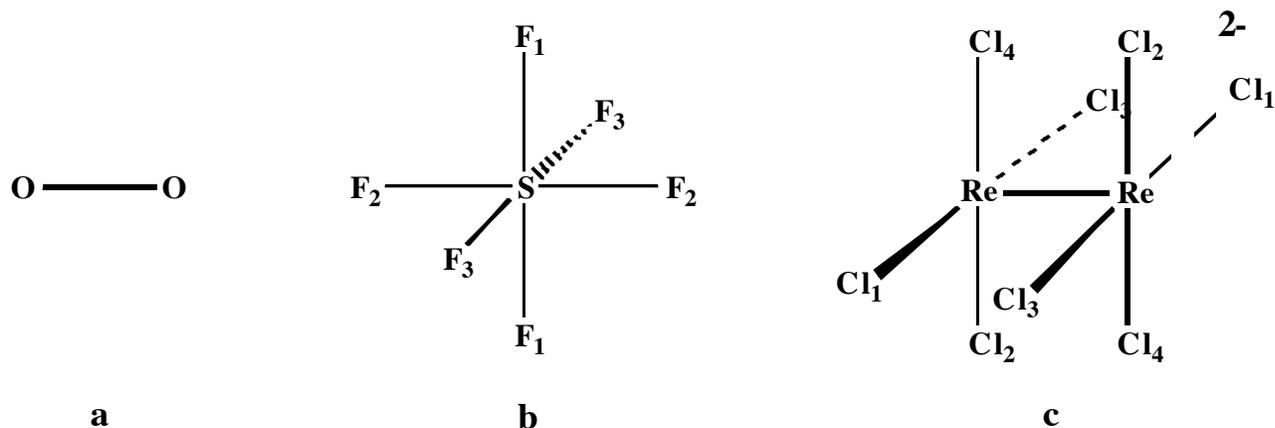
## 1.1 Symmetry Operations and Elements in Molecules

You probably remarked at one time or another, "that looks symmetrical." What does it mean when an object, such as a pyramid, painting, tree, or molecule has symmetry? This chapter explores the notion of symmetry quantitatively. This first requires the definition of symmetry operations and symmetry elements for a molecule.

*Symmetry Operation:* A transformation in three-dimensional space that preserves the size and shape of a molecule, and which brings it into an orientation in three dimensional space physically indistinguishable from the original one, is called a symmetry operation.

*Symmetry Element:* The geometrical plane, point, or axis associated with a particular symmetry operation or set of symmetry operations.

*Inversion Operation.* One of the simplest symmetry operations encountered is the inversion operation, whose element is a single point in space. This operation puts a premium on the ability to recognize the origin of the coordinate system where all symmetry elements intersect. Several examples of molecules that contain inversion centers appear in Figure 1.1.

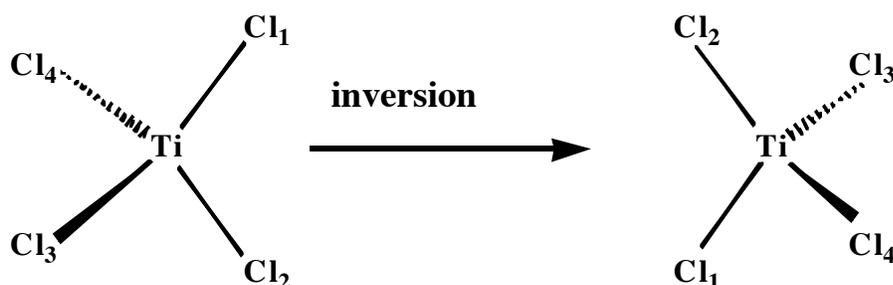


**Figure 1.1. Examples of molecules that contain an inversion center**  
a) dioxygen; b) sulfur hexafluoride; c) octachlorodirhenate(III) ion.

A center of inversion may be located at the center of an atom, such as on sulfur in SF<sub>6</sub>, or between a pair of inversion related atoms; for example, midway between the O-O bond in O<sub>2</sub> or the Re-Re bond in Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup>. The inversion operation, denoted *i*, derives its name because it takes an atom with coordinates (*x,y,z*) and transforms them to the inverted position (*-x,-y,-z*). The easiest way to perform this operation is to draw a line between an atom and the inversion center and then to continue this line an equal distance through the inversion center. For example in Figure 1.1 the

three pairs of F atoms in SF<sub>6</sub>, and the four pairs of Cl atoms related by the inversion operation have been denoted with subscripts 1, 2, 3, and 4.

You might remark, "Wait a minute! The 6 F in SF<sub>6</sub> and 8 Cl in Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> are all equivalent." That is correct, but the inversion operation only relates pairs of atoms, or the unique sulfur atom to itself. Additional symmetry operations that belong to these molecules need to be introduced before the complete picture emerges. Some molecules that look highly symmetrical lack an inversion center, as shown in Figure 1.2 for tetrahedral TiCl<sub>4</sub>. Application of the inversion operation centered at Ti produces an orientation distinguishable from the original one. The chlorine atoms in the drawing have been subscripted to illustrate where the inversion operation moves them.



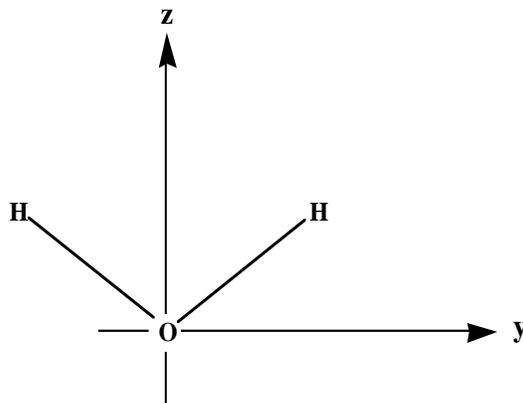
**Figure 1.2. Illustration of the lack of an inversion center in a tetrahedral molecule, such as TiCl<sub>4</sub>.**

Other examples of molecules that lack an inversion center include BF<sub>3</sub>, HCl, and trigonal bipyramidal Fe(CO)<sub>5</sub>.

*Reflection and Rotation Operations in the Water Molecule.* All possible symmetry elements in the water molecule can be described with the coordinate system defined in Figure 1.3. In this coordinate system, the molecule lies in the yz plane and the x axis emerges from the plane of the paper toward you. This book uses right-handed coordinate systems unless specified otherwise. A right-handed coordinate system is oriented such that the vector cross product  $\vec{x} \times \vec{y} = \vec{z}$ . The direction of  $\vec{z}$  is given by your thumb when curling the fingers of your right hand from the tip of vector  $\vec{x}$  toward  $\vec{y}$ .

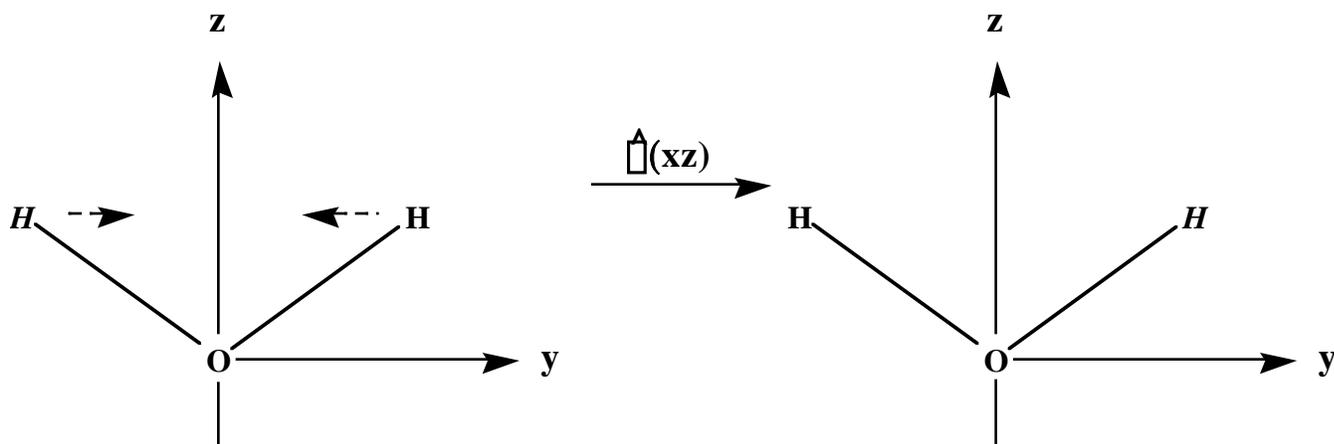
Reflection in the molecular yz plane of the water molecule leaves the atoms in identical positions. Therefore the reflection operation, denoted  $\hat{\sigma}(yz)$ , is a symmetry operation. A caret symbol ^ above operations distinguishes them from elements. The geometric yz plane represents the symmetry element associated with the operation  $\hat{\sigma}(yz)$ . An operation can be defined by its effect on a point (x,y,z) in space. A mirror plane operation reflects an object from one side of the plane to

the other. For the water molecule, with the specified coordinate system, the  $x$  axis lies perpendicular to the plane (Figure 1.3). Therefore, the effect of the operation is to invert the sign of the  $x$  coordinate and leave the  $y$  and  $z$  coordinates unchanged. In mathematical parlance,  $\hat{\sigma}(yz)(x,y,z) = (-x,y,z)$ . It is important to note that the choice of coordinate system is arbitrary. Convention is to always choose  $z$  to lie along the principal rotation axis. The origin may lie at the central atom or center of mass along  $z$ . The orientation of  $x$  and  $y$  are chosen for convenience, as will be apparent later.



**Figure 1.3. Water molecule with defined coordinate system.**

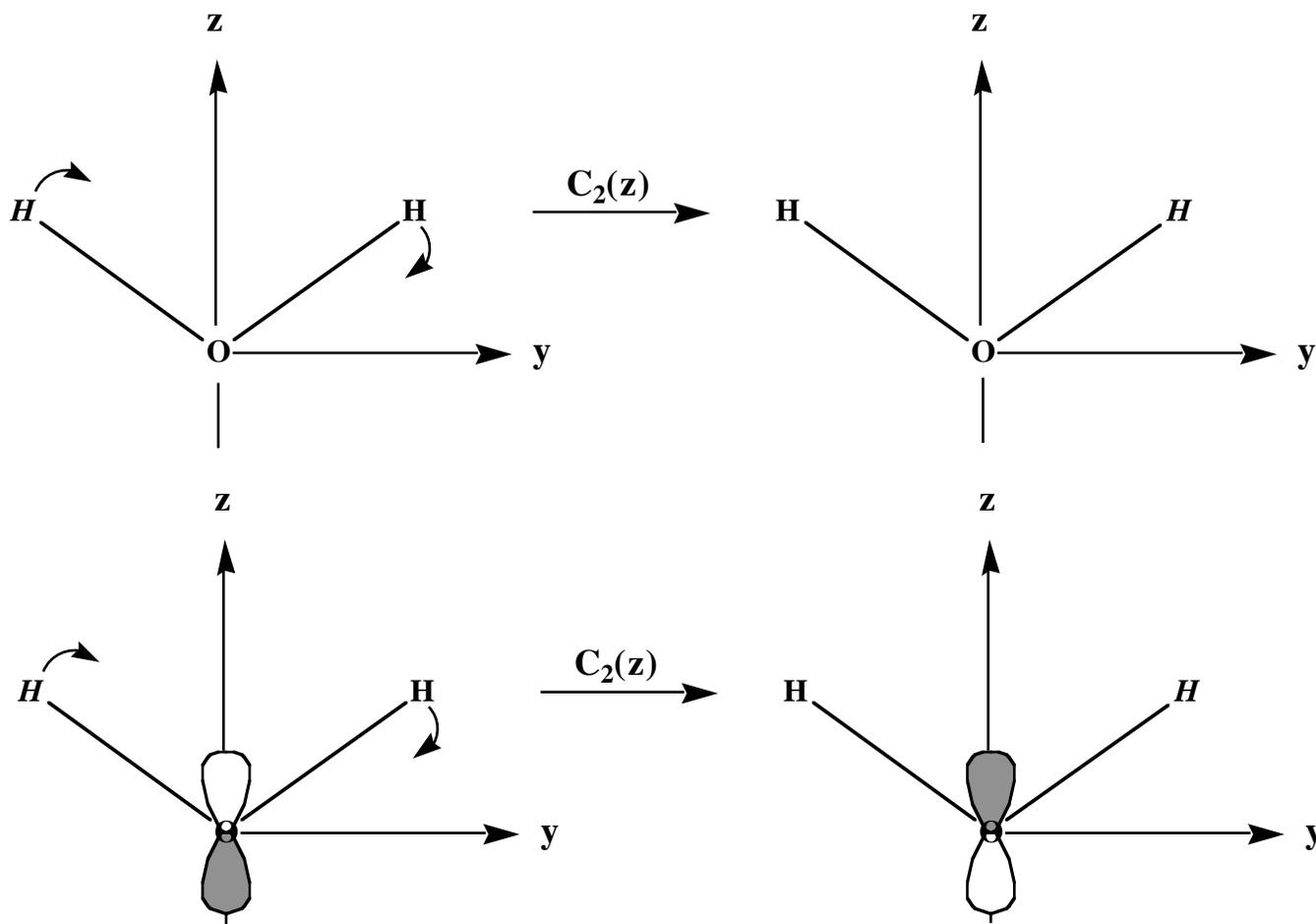
The molecular plane is not the only mirror plane in the water molecule! Consider the  $x$  plane perpendicular to the plane of the figure, which bisects the H-O-H bond angle. Reflection in this plane interchanges the two hydrogen atoms (Figure 1.4) but leaves oxygen at the origin.



**Figure 1.4. Reflection in the  $xz$  plane.**

Because the two hydrogen atoms are chemically identical, the configuration obtained after the

reflection operation cannot be distinguished from the original one. Therefore  $\hat{\sigma}(xz)$  is also a symmetry operation and the  $xz$  plane is a symmetry element. In the isotopically labeled system HDO, the  $\hat{\sigma}(xz)$  would not be a symmetry operation, but  $\hat{\sigma}(yz)$  would remain a symmetry operation.



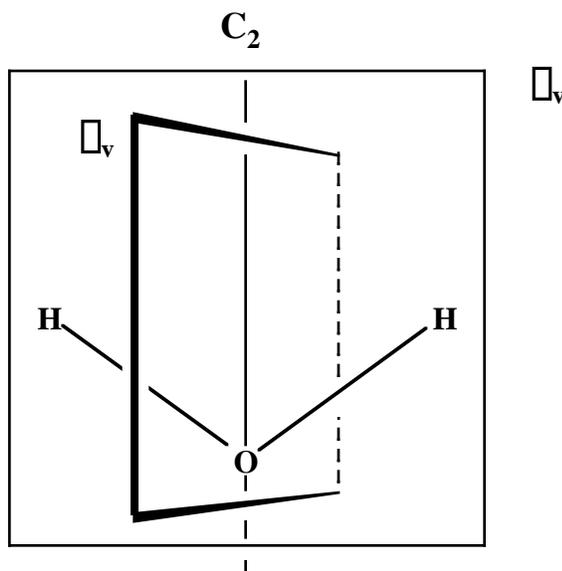
**Figure 1.5. Rotation in the  $xz$  plane.**

For  $H_2O$  another symmetry operation exists, rotation by  $180^\circ$  (either clockwise or counterclockwise) around the  $z$  axis (Figure 1.5), which is a symmetry operation denoted  $\hat{C}_2(z)$ . The associated symmetry element, the  $C_2$  axis, is the line along  $z$ . This operation, which interchanges the two equivalent hydrogen atoms, may seem to produce the same result as  $\hat{\sigma}(xz)$ ; however, a rotation operation differs fundamentally from a reflection operation.

Rotation around the  $z$  axis by  $180^\circ$  changes both the  $x$  and  $y$  coordinates  $(x, y, z) \rightarrow (-x, -y, z)$ , but reflection in  $\sigma(xz)$  only inverts the  $y$  coordinate normal to the plane. Because the  $x$  coordinates of the H atom nuclei are zero, the rotation operation appears to cause the same net effect as the

reflection; however, this is not true for the electron density distribution in the water molecule. The region of electron density around H that lies above the plane of the figure ( $x > 0$ ) remains above the plane of the figure when  $\hat{\sigma}(xz)$  is applied. The  $\hat{C}_2(z)$  operation moves the electron cloud for  $x > 0$  around a H atom to below the plane of the Figure ( $x < 0$ ) after rotation. A clearer indication of the difference between  $\hat{C}_2(z)$  and  $\hat{\sigma}(xz)$  is their effect on a  $p_x$  orbital of oxygen. Recall that a  $p_x$  orbital has a positive lobe for  $x > 0$  and a negative lobe for  $x < 0$ , as shown in the lower left part of Figure 1.5. The  $\hat{C}_2$  operation interchanges the positive and negative lobes of  $p_x$  (i.e.,  $p_x \rightarrow -p_x$ ), but  $\hat{\sigma}(xz)$  would leave the orbital unchanged ( $p_x \rightarrow p_x$ ). Thus, the difference between the  $\hat{C}_2(z)$  and  $\hat{\sigma}(xz)$  is physically meaningful for the three-dimensional water molecule. *It is important that the novice transform the idealized two-dimensional projections in this book for point atoms into three-dimensional reality with the aid of molecular models.*

The set  $\{\hat{C}_2(z), \hat{\sigma}(yz), \hat{\sigma}(xz)\}$  spans the entire collection of possible symmetry operations and associated symmetry elements for the water molecule. The  $C_2$  axis in water lies along the intersection of the two mirror planes. When mirror planes contain the principal rotation axis of a molecule they are denoted  $\sigma_v$  or  $\sigma_v^-$ . The complete set of symmetry elements for the water molecule can be represented as drawn in Figure 1.6.

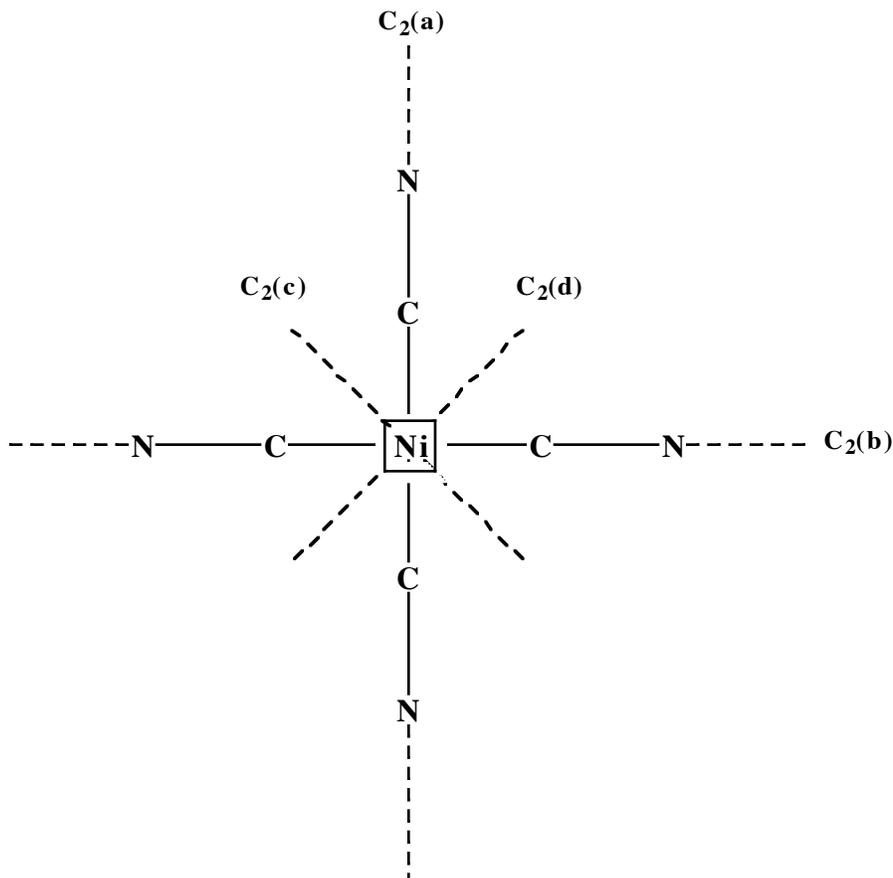


**Figure 1.6. Water molecule with associated symmetry elements.**

The choice of coordinate system in any problem is arbitrary, but usually it takes advantage of the inherent symmetry. For molecules, the conventional origin of the coordinate system lies at the center of mass. This point in space can be related to the symmetry elements present. *The symmetry*

operations of finite bodies in three-dimensional space leave at least one point of the body fixed. All symmetry elements intersect at this point. Before we consider symmetry operations in a systematic fashion let's examine a few more examples of molecular symmetry.

*Multiple Rotation Axes in Molecules.* The next degree of complexity in molecular symmetry hinges on the ability to recognize the presence of several rotation axes in molecules. While the absolute sense of a rotation (clockwise or counterclockwise) is as arbitrary as the choice of coordinate system, it is important to be consistent. *Positive rotations are assumed to be counterclockwise in this text.* For the general case of rotation in increments of  $\alpha$  degrees about a symmetry axis, the multiplicity of the  $C_n$  axis,  $n$ , is given by  $360^\circ/\alpha$ . For a square planar molecule, such as  $\text{Ni}(\text{CN})_4^{2-}$  in Figure 1.7, rotation in  $90^\circ$  increments ( $90^\circ$ ,  $180^\circ$ ,  $270^\circ$ , and  $360^\circ = 0^\circ$ ) about the  $z$  axis emerging from the plane of the paper constitutes the set of operations associated with the  $C_4$  symmetry axis.



**Figure 1.7. Rotation axes in square planar  $\text{Ni}(\text{CN})_4^{2-}$ .**

The  $z$  axis of the coordinate system is usually taken to lie along the highest symmetry rotation axis. The symmetry operations associated with the  $C_4$  axis are denoted  $\hat{C}_4^1$ ,  $\hat{C}_4^2$ ,  $\hat{C}_4^3$ , and  $\hat{C}_4^4$  for successive rotations by  $90^\circ$ ,  $180^\circ$ ,  $270^\circ$ , and  $360^\circ$ . Further rotation by  $90^\circ$  increments beyond  $360^\circ$

is equivalent to one of the preceding operations (e.g.,  $90^\circ = 360^\circ + 90^\circ = 470^\circ$ ); the periodicity of rotation around a circle always brings one back to the starting point at  $0^\circ$ . An important exception may occur for imaginary functions associated with odd-electron spin systems. A discussion of these complications occurs in Chapter 8. The operations of the  $C_4$  axis include the  $180^\circ$  and  $360^\circ$  rotations, which require the presence of a  $C_2$  axis. A simple way to recognize this is to reduce the exponent  $m$  and denominator  $n$  of a  $\hat{C}_n^m$  operation by division with their greatest common divisor, i.e.  $\hat{C}_4^2 = \hat{C}_2^1 = \hat{C}_2$ . Notice in this last example that the superscript 1 doesn't have to be written explicitly. *The highest symmetry axis in a molecule, such as  $C_4$  in the above example, is the principal rotation axis.* A  $C_4$  axis by necessity contains the operations of a coincident  $C_2$  axis.

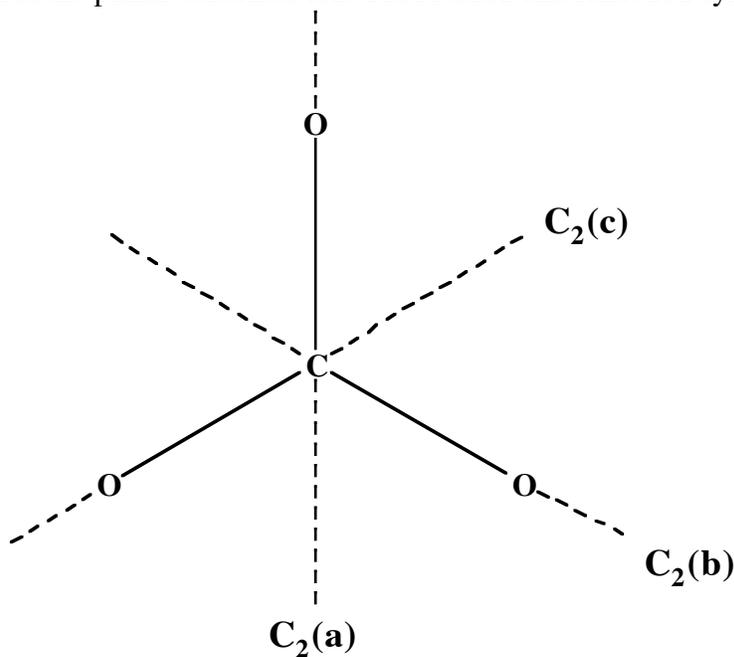
The  $0^\circ$  or  $360^\circ$  rotations, which do nothing, are given the special symbol  $\hat{E}$  for the identity operation. *All symmetry operations must give the identity operation when raised to some power. The minimum power necessary to generate the identity operation defines the order of an operation.* For example, reflection in a mirror plane an even number of times does nothing, and so  $\hat{\sigma}^2 = \hat{\sigma}^4 = \dots = \hat{E}$ . Applying the inversion operation an even number of times also generates the identity operation. Thus,  $\hat{C}_4$  is an operation of order four and  $\hat{\sigma}_h$  is an operation of order two, as is the inversion operation. The identity operation (order 1) acquires greater importance in the mathematics of symmetry groups.

For molecules that contain an obvious  $C_n$  axis, it is important to become adept at recognizing whether  $n$   $C_2$  axes lie in a plane perpendicular to the principal rotation axis. In the plane of the  $\text{Ni}(\text{CN})_4^{2-}$  ion of Figure 1.7, there are four  $C_2$  axes labeled  $C_2(a) - C_2(d)$ . One pair,  $C_2(a)$  and  $C_2(b)$  seem equivalent, since they pass through opposite cyanide ligands. The other pair,  $C_2(c)$  and  $C_2(d)$ , bisect the C-Ni-C angles. Rotation about any of these axes by  $180^\circ$  brings the molecule into a position that is indistinguishable from the original one. The concept of equivalent  $C_2$  axes, such as  $C_2(a)$  and  $C_2(b)$ , is an important one. *Sets of equivalent symmetry operations derived from equivalent symmetry elements form a class.* Thus,  $\hat{C}_2(a)$  and  $\hat{C}_2(b)$  belong to one class and  $\hat{C}_2(c)$  and  $\hat{C}_2(d)$  to another class. *A  $C_n$  axis will always contain either zero or  $n$  perpendicular  $C_2$  axes. For even  $n$  these axes, if present, often fall into two classes each containing  $n/2$  operations that are denoted  $\hat{C}_2'$  and  $\hat{C}_2''$ . For odd  $n$  all the  $n$   $\hat{C}_2'$  operations belong to the same class.*

The  $\text{Ni}(\text{CN})_4^{2-}$  ion contains several mirror planes that can be grouped into different classes. A unique mirror plane lies in the plane of the molecule. The important distinguishing feature is that the mirror plane lies perpendicular to the principal  $C_4$  rotation axis. *A mirror plane, which lies perpendicular to a principal rotation axis of the molecule, is denoted  $\sigma_h$ .* Next consider mirror planes that contain the principal rotation axis. The mirror plane  $\sigma_v(a)$  contains both the  $C_4$  axis and  $C_2(a)$  and emerges from the plane of the figure. This mirror plane interchanges the right and left halves of the molecule. This operation resembles  $\hat{\sigma}_v(b)$ , which contains the  $C_4$  axis and  $C_2(b)$ , and

which reflects the top and bottom halves of the molecule into one another. Both the  $\sigma_v(a)$  and  $\sigma_v(b)$  planes belong to the same class. The other pair of equivalent mirror planes contain the  $C_4$  axis, and either  $C_2(c)$  or  $C_2(d)$ . These planes, which bisect the C-Ni-C bond angles, are termed dihedral mirror planes,  $\sigma_d(a)$  and  $\sigma_d(b)$ . A  $C_n$  axis always contains either zero or  $n$  mirror planes. For even  $n$  these planes, if present, fall into two classes with each containing  $n/2$  operations that are denoted  $\sigma_v$  and  $\sigma_d$ . For odd  $n$  all the  $n \hat{\sigma}_v$  operations belong to the same class. The choice of which class is denoted  $\hat{\sigma}_v$  and which  $\hat{\sigma}_d$  is arbitrary, similar to the choice of coordinate system. This can lead to confusion if two people approach the same problem with different conventions. Before leaving the present example take note of the inversion center in  $\text{Ni}(\text{CN})_4^{2-}$ . The list of symmetry elements in this molecule includes a principal  $C_4$  axis, a  $\sigma_h$ ,  $2\sigma_d$ ,  $2\sigma_v$ ,  $2C_2'$ ,  $2C_2''$ , and  $\hat{i}$ .

Figure 1.8 illustrates the rotation axes present in a planar species that contains an odd order rotation axis, such as the planar carbonate ion. The rotation and reflection symmetry elements of

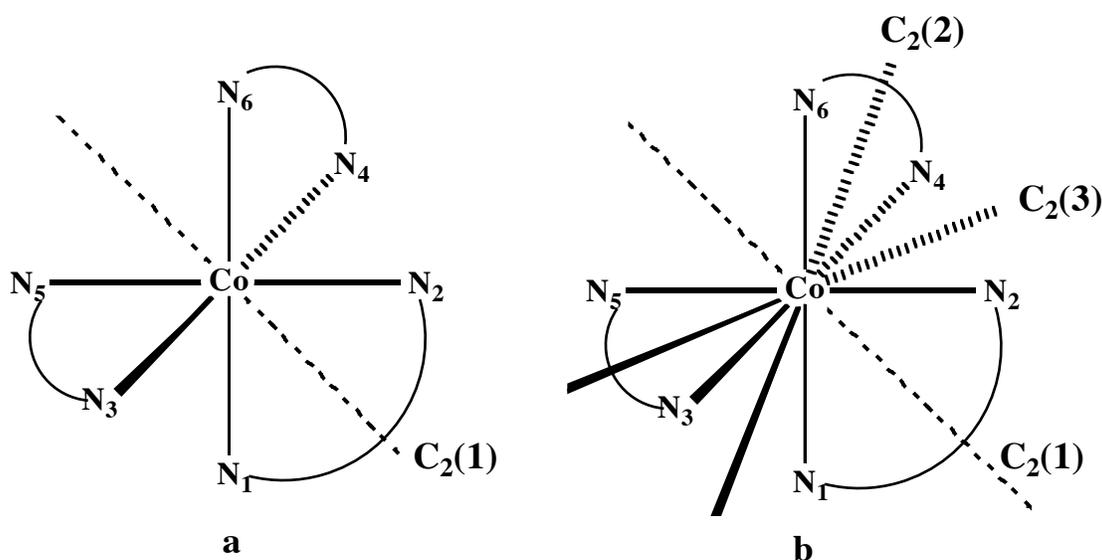


**Figure 1.8. Rotation axes in trigonal planar  $\text{CO}_3^{2-}$  as viewed down the  $C_3$  axis.**

this molecule are the  $C_3$  axis emerging from the plane of the drawing, a  $\sigma_h$ , 3  $C_2'$  axes perpendicular to the principal rotation axis (which belong to the same class) and 3 equivalent  $\sigma_v$  planes in the same class, which contain the  $C_3$  axis and one of the  $C_2$  axes. In planar molecules, the possibility of  $C_2$  axes perpendicular to the principal  $C_n$  axis were easy to recognize. For nonplanar molecules, the presence of perpendicular  $C_2$  axes may be difficult to visualize.

Consider an octahedral complex, which contains three bidentate ligands, such as  $\text{Co(en)}_3^{3+}$  [en = ethylenediamine] or  $\text{Ga(acac)}_3$  [acac = acetylacetonate]. *Frequently we will only be concerned with pseudosymmetry of a particular fragment in a large molecule or solid.* For example, if one wishes to describe the crystal field splitting of the d orbitals in  $\text{Co(en)}_3^{3+}$  then the symmetry of the coordination environment about the cobalt(III) ion is most important. For metal ions doped in solids (e.g.  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$  - the ruby laser) a useful approximation of their electronic environment is obtained by considering the symmetry of the first coordination sphere (frequently called the site symmetry of the ion).

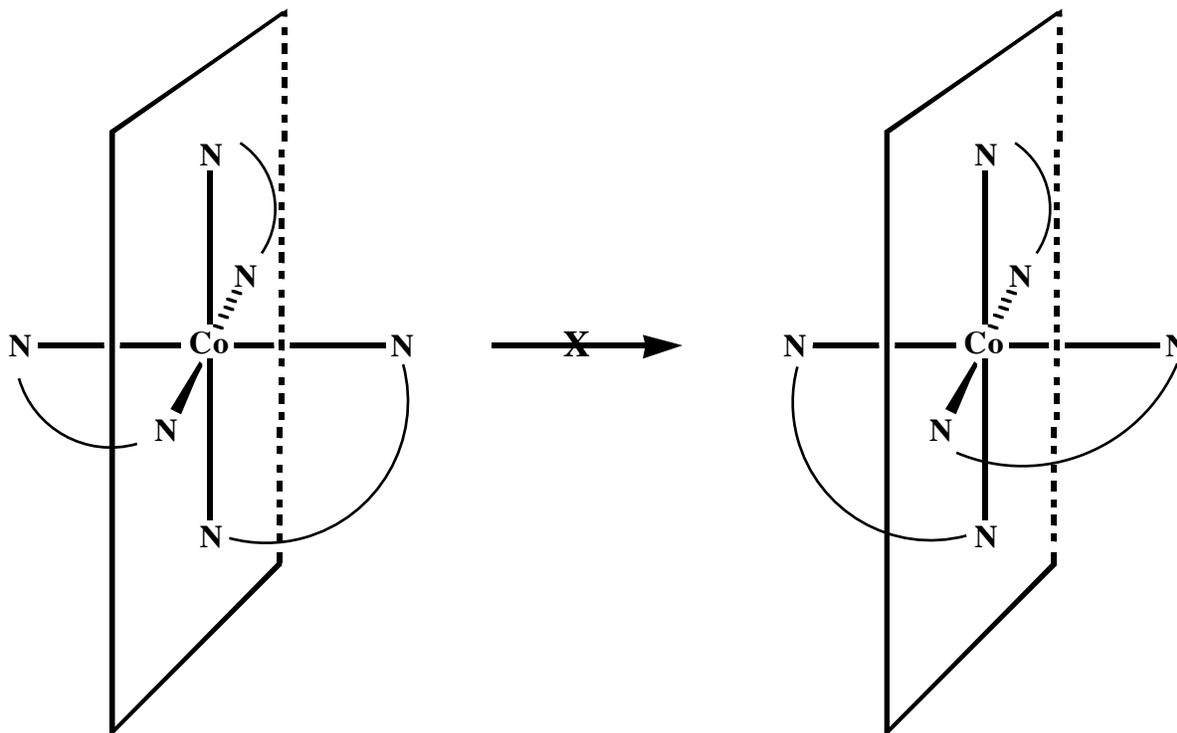
The effective symmetry about the metal ion in  $\text{Co(en)}_3^{3+}$  can be described by the simplified sketch of Figure 1.9. In this model a curved line represents the  $(\text{CH}_2)_2$  groups linking



**Figure 1.9. Rotation axes in  $\text{Co(en)}_3^{3+}$  a) shows one  $\text{C}_2$  axis and b) the two  $\text{C}_2$  axes perpendicular to the first.**

the two  $\text{NH}_2$  fragments. This model is reasonable because only the lone pair orbitals on the two nitrogens of ethylenediamine interact with cobalt. The hydrocarbon backbone linking the amine groups, as well as the hydrogen atoms bound to nitrogen, do not interact with the metal ion - at least to a first approximation. You might have wondered why we even bothered to add the lines linking pairs of N atoms in our model. Without them the pseudosymmetry about cobalt would conform to a perfect octahedron. One effect of the chelate ring that must be considered is the deviation of the N-Co-N angles from the ideal octahedral value of  $90^\circ$ , because of geometric constraints imposed by the  $\text{CH}_2$  linking groups. The lines joining the N atoms help represent the inequivalent angles (and therefore distances) between pairs of nitrogen atoms. Figure 1.9a depicts a  $\text{C}_2$  axis, whose associated operation interchanges  $\text{N}_1$  with  $\text{N}_2$ ,  $\text{N}_3$  with  $\text{N}_4$ , and  $\text{N}_5$  with  $\text{N}_6$ . With some three-dimensional thinking it is apparent that two other  $\text{C}_2$  axes lie perpendicular to the first one (Figure

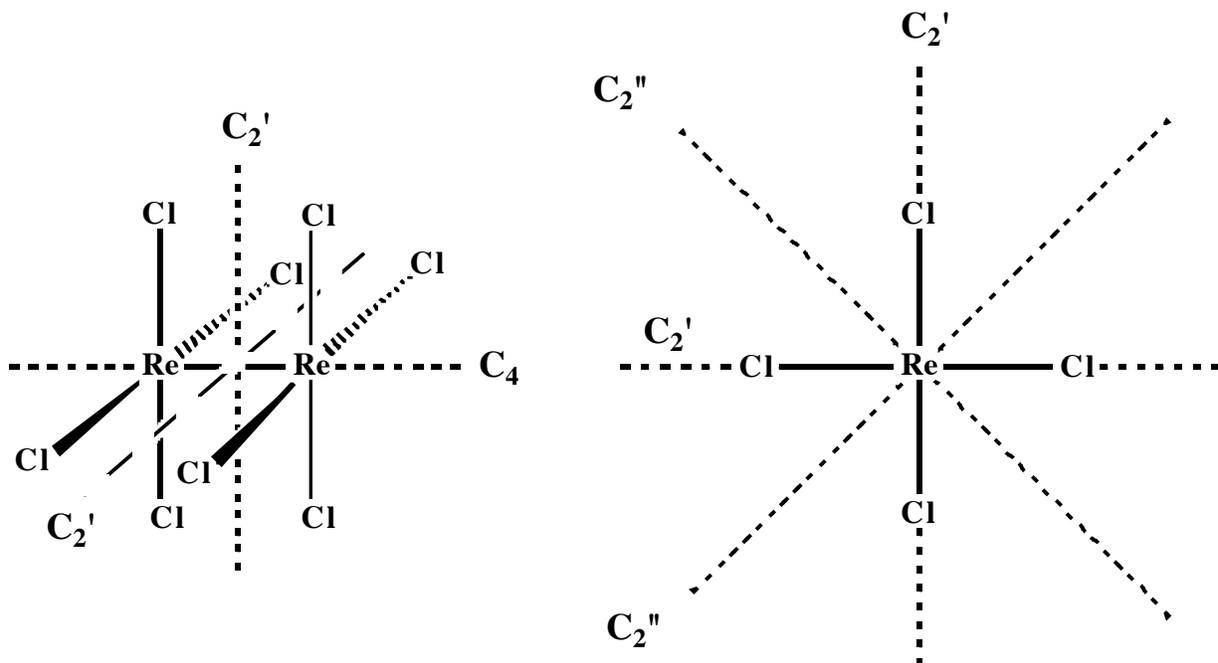
1.9b). The wise reader will examine a molecular model to better visualize this problem in three-dimensions. For nonplanar molecules, the use of models is essential for the novice.



**Figure 1.10. Illustration of the absence of reflection planes in  $\text{Co(en)}_3^{3+}$ .**

It should be apparent that the symmetry of  $\text{Co(en)}_3^{3+}$  resembles that of a 3-blade propeller. Those who are unaccustomed to geometric thinking can acquire this ability with the use of models. Careful inspection of Figure 1.9 and a molecular model shows that this structure possesses no mirror planes (nor an inversion center). For example, Figure 1.10 illustrates the absence of a possible mirror plane in a  $\text{CoN}_4$  plane because it brings the complex ion into an orientation different from the original one.

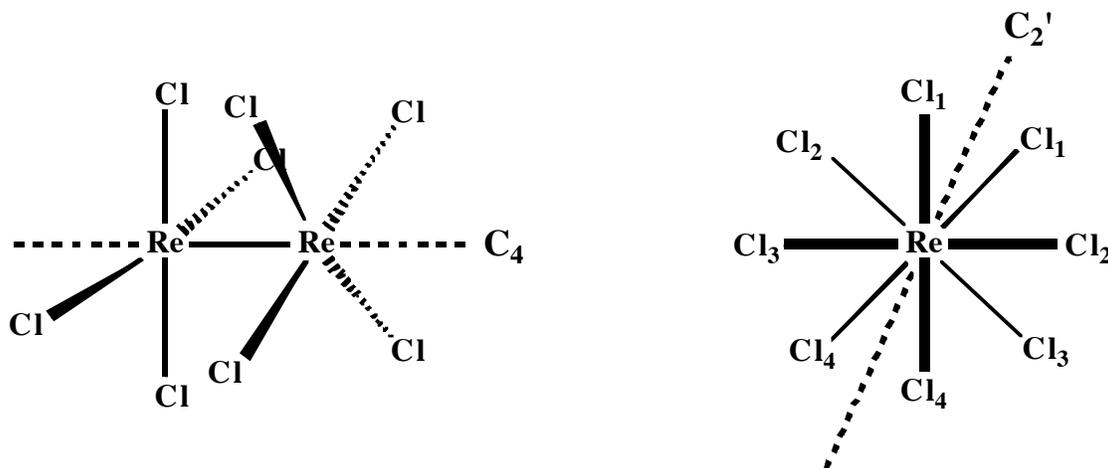
*Symmetry Aspects of Eclipsed vs. Staggered Conformations - Rotoreflexion Axes.* Consider the rotation axes present in molecules that can exist in eclipsed or staggered conformations. The  $\text{Re}_2\text{Cl}_8^{2-}$  ion adopts an eclipsed geometry in the ground state (Figure 1.11).



**Figure 1.11. Rotation axes in the eclipsed  $\text{Re}_2\text{Cl}_8^{2-}$  structure .**

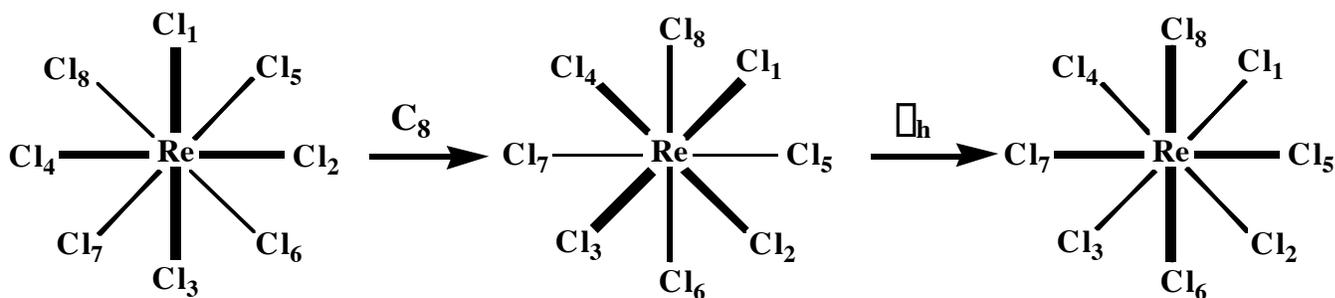
In addition to the principal  $C_4$  rotation axes, two  $C_2'$  axes lie perpendicular to the  $C_4$  axes. Also, in the plane of the two  $C_2'$  axes lie two  $C_2''$  axes, which are sketched in the right half of the figure. The  $C_2''$  axes may appear less obvious than the first two; however, *if there is one  $C_2$  axis perpendicular to a  $C_n$  axis then there must be  $n-1$  more to find.*

The rotation axes present in molecules that exist in a staggered conformation are subtle. Consider the  $\text{Re}_2\text{Cl}_8^{2-}$  ion in an excited-state staggered conformation, as shown in Figure 1.12. The presence of a  $C_2'$  axis perpendicular to the  $C_4$  axis, which passes through the midpoint of the Re-Re bond, is apparent in the end on projection shown in Figure 1.12. The subscripts on the Cl atoms indicate pairs of atoms interchanged by operation of the designated  $C_2'$  axis. There will be four such  $C_2'$  axes passing through the midpoint of the Re-Re bond. Their location is given by bisecting the  $\text{Cl}_{\text{back}}\text{-Re-Re-Cl}_{\text{front}}$  dihedral angles in the two-dimensional projection similar to that for the first such axis. Whenever one encounters a molecule with a staggering of atoms about an origin, then a careful search must proceed for  $C_2$  axes, which interchange atoms between the two staggered halves. These axes need not be oriented along bond directions as found for the  $C_2''$  axes in Figure 1.11 and the  $C_2'$  axes in Figure 1.12.



**Figure 1.12. Rotation axes in staggered  $\text{Re}_2\text{Cl}_8^{2-}$  - the drawing on the right is viewed end on down the Re-Re axis.**

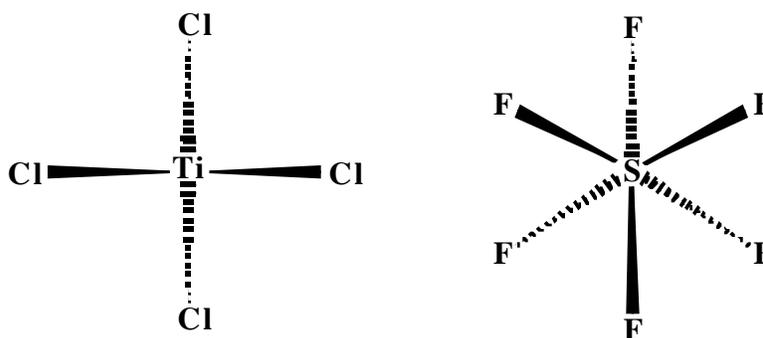
The eclipsed-staggered conformational problem also illustrates *a new kind of symmetry element, the rotoreflection or improper rotation axis, which is given the symbol  $\hat{S}_n$* . In the eclipsed conformation,  $\text{Re}_2\text{Cl}_8^{2-}$  possesses a  $\sigma_h$  plane, which interchanges the opposite equivalent halves of the molecule. In the staggered conformation no such plane exists. But if the molecule is rotated by  $45^\circ$ , and then subjected to a  $\sigma_h$  operation, then the opposite (staggered) halves are interchanged. This product, illustrated in Figure 1.13, amounts to multiplication of a rotation operation,  $\hat{C}_{360/45} = \hat{C}_8$ , and a reflection  $\hat{\sigma}_h$ , although neither the  $\hat{C}_8$  nor  $\hat{\sigma}_h$  operations exist independently! Therefore, the product  $\hat{C}_8\hat{\sigma}_h$  represents a new symmetry operation, denoted  $\hat{S}_8$ . *The  $\hat{S}_n^m$  operation, is generally defined as the product,  $\hat{C}_n^m\hat{\sigma}_h$ .*



**Figure 1.13. Improper rotation (rotoreflection)  $S_8$  symmetry operation in staggered  $\text{Re}_2\text{Cl}_8^{2-}$  viewed down the Re-Re axis.**

Although molecules, which adopt a staggered configuration, provide the most striking examples of  $S_n$  axes these symmetry operations are present in tetrahedral and octahedral molecules as well. Figure 1.14 shows tetrahedral  $\text{TiCl}_4$  viewed down one of its three  $S_4$  axes, and  $\text{SF}_6$  viewed

down one of its four  $S_6$  axes. Again the feature to recognize is the staggering of the front and back substituents.



**Figure 1.14. View down the coincident  $C_2$  and  $S_4$  axes of  $TiCl_4$  and down the  $C_3$  and  $S_6$  axes of  $SF_6$ .**

Independent existence of a  $C_n$  axis and  $\sigma_h$  clearly requires the presence of an  $S_n$  element according to the definition. Therefore the carbonate ion of Figure 1.8 possesses an  $S_3$  axis in addition to the symmetry elements described earlier. The simplest example of an  $\hat{S}_n$  operation is  $\hat{S}_2$ , which is given the special symbol  $\hat{i}$  to denote inversion. With a good physical sense for the symmetry operations possible in molecules, it is now appropriate to be systematic in the classification of symmetry properties of finite arrangements of atoms.

## 1.2 Symmetry Point Groups

Group theory is a mathematical formalism that can be used to classify a set of elements according to their "multiplication" properties. For the applications in this book, the "elements" will be the complete set of symmetry operations for a molecule. Given some set of elements  $\{\hat{\sigma}_1, \hat{\sigma}_2, \dots, \hat{\sigma}_n\}$  and a law for group "multiplication"  $\hat{\sigma}_i \cdot \hat{\sigma}_j$ , then  $\{\hat{\sigma}_1, \hat{\sigma}_2, \dots, \hat{\sigma}_n\}$  constitute an abstract group,  $G$ , of order  $n$  if:

- 1) The set is *closed under group multiplication*; i.e., if  $\hat{\sigma}_i$  and  $\hat{\sigma}_j$  belong to  $G$  then  $(\hat{\sigma}_i \cdot \hat{\sigma}_j) = \hat{\sigma}_k$  is also contained in  $G$ .
- 2) Group *multiplication is associative*; that is,  $\hat{\sigma}_i(\hat{\sigma}_j \hat{\sigma}_k) = (\hat{\sigma}_i \hat{\sigma}_j) \hat{\sigma}_k$ .
- 3) The *set contains an identity*, by convention ordered as the first element,  $\hat{\sigma}_1 = \hat{e}$  such that  $\hat{e} \hat{\sigma}_j = \hat{\sigma}_j \hat{e} = \hat{\sigma}_j$ .
- 4) If  $\hat{\sigma}_i$  is contained in set  $G$ , then there exists a  $\hat{\sigma}_k$  in  $G$  such that  $\hat{\sigma}_i \hat{\sigma}_k = \hat{\sigma}_k \hat{\sigma}_i = \hat{e}$ . The operation is called the *inverse* of  $\hat{\sigma}_i$  and denoted  $\hat{\sigma}_i^{-1} = \hat{\sigma}_k$ .

It is not necessary that group multiplication be commutative (i.e.,  $\hat{\sigma}_i \hat{\sigma}_j = \hat{\sigma}_j \hat{\sigma}_i$  need not hold); however, those *special groups for which multiplication does commute are called Abelian*. The

order of a group can be infinite, an example being the set of integers with group multiplication defined as addition. It is important to recognize that the process of "multiplication" is defined for the operators of a group and need not be restricted to normal scalar multiplication. The behavior of group elements with respect to "multiplication" can be defined in the form of a multiplication table shown below.

	$\hat{\Pi}_1$	$\hat{\Pi}_2$	...	$\hat{\Pi}_j$	$\hat{\Pi}_n$
$\hat{\Pi}_1$				.	
$\hat{\Pi}_2$				.	
$\hat{\Pi}_i$	.	.	.	$(\hat{\Pi}_i \hat{\Pi}_j)$	
$\hat{\Pi}_n$					

The element in the  $i$ 'th row and  $j$ 'th column equals  $\hat{\Pi}_i \hat{\Pi}_j$  (note the order  $\hat{\Pi}_i \hat{\Pi}_j$  and not  $\hat{\Pi}_j \hat{\Pi}_i$  is the convention adopted in this text). For example, consider the group of order three defined by the multiplication table below.

	$\hat{\Pi}_1$	$\hat{\Pi}_2$	$\hat{\Pi}_3$
$\hat{\Pi}_1$	$\hat{\Pi}_1$	$\hat{\Pi}_2$	$\hat{\Pi}_3$
$\hat{\Pi}_2$	$\hat{\Pi}_2$	$\hat{\Pi}_3$	$\hat{\Pi}_1$
$\hat{\Pi}_3$	$\hat{\Pi}_3$	$\hat{\Pi}_1$	$\hat{\Pi}_2$

You may verify that  $\{\hat{\Pi}_1, \hat{\Pi}_2, \hat{\Pi}_3\}$  constitute an Abelian group of order three. Commutativity is easily recognized by the symmetry of the multiplication table about the diagonal. By convention, the group identity is ordered as the first element  $\hat{\Pi}_1$  and given the special symbol  $\hat{e}$ . Therefore, the first row and first column in the table merely repeat the labeling. This redundancy can be omitted from in the abbreviated version of the multiplication table shown below.

$\hat{e}$	$\hat{\Pi}_2$	$\hat{\Pi}_3$
$\hat{\Pi}_2$	$\hat{\Pi}_3$	$\hat{e}$
$\hat{\Pi}_3$	$\hat{e}$	$\hat{\Pi}_2$

An example of Abelian groups that will be important in later applications is the set of cyclic groups. *The cyclic group of order  $n$  can be generated from the element,  $a$ , that satisfies the following conditions:*

- 1)  $\hat{a}^1 \neq \dots \neq \hat{a}^n$  uniqueness of the powers of  $a \leq n$  under a group multiplication.  
 2)  $\hat{a}^n = \hat{e}$ , the element  $a$  is of order  $n$ .

Given these properties, the set of elements  $\{\hat{a}, \hat{a}^2, \hat{a}^3, \dots, \hat{a}^n\}$  comprise an Abelian group of order  $n$ . Now systematically consider abstract groups of low order.

The trivial group of order 1 consists solely of the identity element  $\hat{e}$ . There is but a single group of order two.

$$\begin{array}{c|c} \hat{e} & \hat{a} \\ \hline \hat{a} & \hat{e} \end{array} = \begin{array}{c|c} \hat{e} & \hat{a} \\ \hline \hat{a} & \hat{a}^2 = \hat{e} \end{array}$$

There are no other possibilities, since that shown below does not satisfy closure.

$$\begin{array}{c|c} \hat{e} & \hat{a} \\ \hline \hat{a} & \hat{b} \end{array}$$

If a molecule possesses a mirror plane as its only symmetry element (*e.g.*  $\text{CH}_2\text{ClBr}$ ), then it is isomorphic to this group termed  $\text{C}_s$ . Other symmetry point groups that are isomorphic to the group of order two are defined by molecules that only contain a  $\text{C}_2$  axis (denoted  $\text{C}_2$ ) or molecules that only contain an inversion center (denoted  $\text{C}_i$ ). For order three, there is again only one group possible, the cyclic one shown below.

$$\begin{array}{c|cc} \hat{e} & \hat{a} & \hat{b} \\ \hline \hat{a} & \hat{b} & \hat{e} \\ \hat{b} & \hat{e} & \hat{a} \end{array}$$

If you have trouble seeing why this is cyclic, verify that in an abstract sense the above group multiplication table is equivalent to the following.

$$\hat{a}^3 = \begin{array}{c|cc} \hat{e} & \hat{a} & \hat{a}^2 \\ \hline \hat{a} & \hat{a}^2 & \hat{a}^3 \\ \hat{a}^2 & \hat{a}^3 & \hat{a} \end{array} \quad (\text{note } \hat{a}^2\hat{a}^2 = \hat{a}^3\hat{a} = \hat{e}\hat{a} = \hat{a} \text{ and we define } \hat{a}^2 \equiv \hat{b})$$

No matter how one chooses to represent the group of order three, although the symbols may differ, the structure of the group multiplication table (in other words, the abstract group) remains the same. *If two groups have the same structure, that is, if there is a one-to-one correspondence between elements of the group multiplication tables, then the groups are said to be isomorphic.* All groups of order 2 and 3 are isomorphic to the cyclic groups of order 2 and 3, respectively. Herein lies the great power of group theoretical methods. Once the behavior of the cyclic group of order 3 has been specified, then *because of isomorphism, the properties of all groups of order 3 are known.* Before defining these properties, consider groups of order 4. The cyclic group may be constructed

as in the preceding examples; however, there exists another group of order 4 distinct from the cyclic one, which has the multiplication table shown.

$\hat{e}$	$\hat{a}$	$\hat{b}$	$\hat{c}$
$\hat{a}$	$\hat{e}$	$\hat{c}$	$\hat{b}$
$\hat{b}$	$\hat{c}$	$\hat{e}$	$\hat{a}$
$\hat{c}$	$\hat{b}$	$\hat{a}$	$\hat{e}$

All groups of order 4 are isomorphic to one of these two groups. The latter group often is referred to as the Viergruppe (German for four-group) and given the symbol  $\mathbf{V}$ . Notice that both are Abelian.

The water molecule has a symmetry group isomorphic to the Viergruppe (Figure 1.3-1.6). The multiplication table can be partly constructed with the initial observation that all elements,  $\hat{C}_2$ ,  $\hat{\Gamma}_V(xz)$ , and  $\hat{\Gamma}_V(yz)$ , are of order two.

$\hat{e}$	$\hat{C}_2$	$\hat{\Gamma}_V(xz)$	$\hat{\Gamma}_V(yz)$
$\hat{C}_2$	$\hat{e}$		
$\hat{\Gamma}_V(xz)$		$\hat{e}$	
$\hat{\Gamma}_V(yz)$			$\hat{e}$

The operations on a point  $(x,y,z)$  in space can be used to compute the product operations.

$$\hat{C}_2 \begin{pmatrix} x \\ y \\ z \end{pmatrix} \longrightarrow \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

$$\hat{\Gamma}_V(xz) \begin{pmatrix} x \\ y \\ z \end{pmatrix} \longrightarrow \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

$$\hat{\Gamma}_V(yz) \begin{pmatrix} x \\ y \\ z \end{pmatrix} \longrightarrow \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

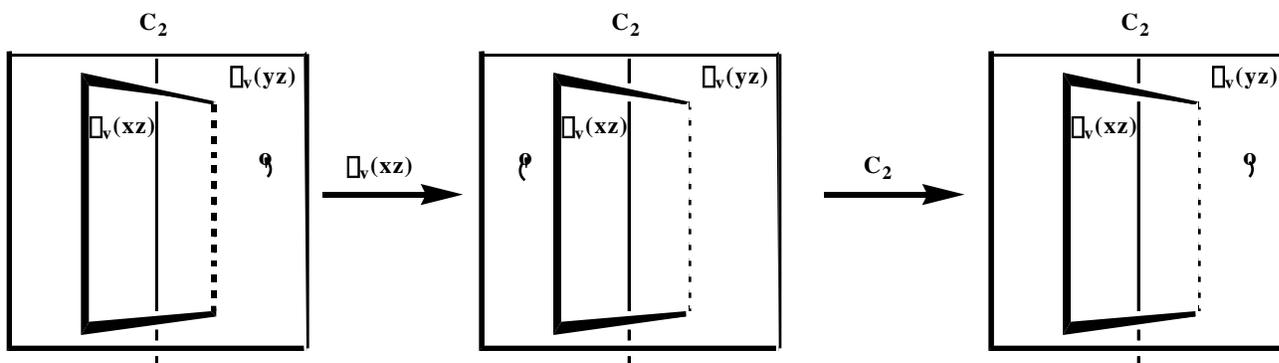
Therefore

$$\hat{C}_2 \hat{\Gamma}_V(xz) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \hat{C}_2 \begin{pmatrix} x \\ -y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix} = \hat{\Gamma}_V(yz) \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The overall effect is the same as  $\hat{\Gamma}_v(yz)$  and therefore  $\hat{C}_2\hat{\Gamma}_v(xz) = \hat{\Gamma}_v(yz)$ . It is very important to recognize that  $x,y,z$  are mere variables. The equation defining  $C_2$  means to invert the  $x$  and  $y$  coordinates. That is why in computing the product operation yields.

$$\hat{C}_2 \begin{pmatrix} x \\ -y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

An alternative method for determining product operations employs a visual approach. This employs an asymmetrical object, such as a comma, and how it moves under the various symmetry operations. It is important to use a comma, instead of a period, to distinguish right- and left-handed images involved in reflections. The sequence  $\hat{C}_2\hat{\Gamma}_v(xz)$  can be represented as shown in Figure 1.15. The solid comma represents a position above the plane of the page and a hollow one represents a position below the plane of the page. The commas in the left- and rightmost figures are related by reflection in the plane of the page.



**Figure 1.15.** The product  $C_2\hat{\Gamma}_v(xz) = \hat{\Gamma}_v(yz)$ , note that a solid comma represents above the  $yz$  plane and the hollow comma denotes below the  $yz$  plane.

This approach can be used to complete the multiplication table shown below:

$\hat{e}$	$\hat{C}_2$	$\hat{\Gamma}_v(xz)$	$\hat{\Gamma}_v(yz)$
$\hat{C}_2$	$\hat{e}$	$\hat{\Gamma}_v(yz)$	$\hat{\Gamma}_v(xz)$
$\hat{\Gamma}_v(xz)$	$\hat{\Gamma}_v(yz)$	$\hat{e}$	$\hat{C}_2$
$\hat{\Gamma}_v(yz)$	$\hat{\Gamma}_v(xz)$	$\hat{C}_2$	$\hat{e}$

This group, which contains  $\hat{C}_2$  and  $2\hat{\Gamma}_v$ , is denoted  $C_{2v}$ .

It is possible for a group to contain a group! *If the elements  $\{e, a, b, \dots\}$  contained in group  $G$  comprise a group under the same law of multiplication used in  $G$ , then the set is said to be a subgroup of  $G$ .* The group  $G$  and the identity  $e$  are trivial subgroups, and denoted improper subgroups of  $G$ . All other subgroups are called proper. For example, the cyclic group of order two is a proper subgroup of the Viereregruppe, as may be verified from the multiplication tables discussed earlier. In the  $C_{2v}$  group, there are three subgroups of order two that consist of the identity operation and either  $\hat{C}_2$ ,  $\hat{\sigma}_v(xz)$ , or  $\hat{\sigma}_v(yz)$ .

*Conjugate Classes and Equivalent Symmetry Operations.* Special relations may exist between different elements in a group. If the relation  $\square^{-1}a\square = b$  holds for  $a$ ,  $b$ , and  $\square$  as elements of a group  $G$ , then  $a$  and  $b$  are said to be related by a similarity transformation. Group elements related by a similarity transform are said to belong to the same class. Since every element in a group  $G$  has an inverse, then for any element  $\square$ :

$$\square^{-1}\square = \square\square^{-1} = e$$

Consider the product  $\square\square^{-1}a\square$ , where  $a$  also belongs to  $G$ . If the group is Abelian,  $\square\square^{-1}a\square = a\square\square^{-1}\square = ae = a$ , and every element occurs in a class by itself. In the Abelian group  $C_{2v}$  each operation (even  $\hat{\sigma}_v(xz)$  and  $\hat{\sigma}_v(yz)$ ) belongs to a different class. When the group is not Abelian  $\square a \neq a\square$  for all possible combinations of elements. In particular, assume that  $\square$  and  $a$  are two elements that do not commute. The product  $\square\square^{-1}a\square$  will equal some other element, say  $b$ , of  $G$ .

$$\square^{-1}a\square = b$$

*Element  $b$  is then said to be conjugate to element  $a$  of  $G$ . The above operation sometimes is called a similarity transformation of element  $a$ . Physically, the effect of the operation  $\square\square^{-1}a\square$  on a function  $f$  is to change  $f$  by operation  $\square$ , then by operation  $a$ , and then undo the change due to  $\square$ . Intuitively one expects that  $b$  must be an operation of a "similar nature" to  $a$ . In molecular symmetry groups, similar reflection, rotation, and improper rotation operations often can be segregated into classes of reflections, rotations, and improper rotations. It is useful to arrange the elements of a group into elements that are conjugate to each other. These *sets of equivalent group elements are called conjugate classes* and elements that belong to different classes commute.*

*Subgroups and Cosets.* An important observation owing to Lagrange is that *the order of a subgroup of a finite group is an integral divisor of the order of the group*. The proof runs as follows. Take the group  $G$  of order  $n$  and consider the restrictions on the subgroup  $H$  of order  $h$ . If  $H$  is a trivial subgroups, e.g.,  $G$  or  $e$ , then  $h$  is either  $n/1$  or  $n/n$  respectively. If  $H$  constitutes a proper subgroup, then consider an element  $i$  that is an element of  $G$  but not contained in  $H$ . Let the elements of  $H$  be denoted  $\{e, H_2, H_3, \dots, H_h\}$ . The collection of products  $\{i.e., iH_2, iH_3, \dots, iH_h\}$  is called the left coset of  $H$  and abbreviated as  $iH$ . The elements of  $iH$  cannot be elements of  $H$  since

$iH_k = H_j$  implies that  $iH_kH_k^{-1} = H_jH_k^{-1}$  or that  $i$  belongs to  $H$ . A similar rule defines the right coset  $Hi$ . If the set of elements  $eH + iH$  does not contain all the elements in  $G$ , then continue to choose some element  $j$  that belongs neither to  $H$  or to  $iH$ . At some point 'p'  $G$  can be expressed as a sum of left cosets of  $H$ .

$$G = eH + iH + jH + \cdots + pH$$

Therefore, the order  $n$  of  $G$  must be some integral multiple of the order  $h$  of subgroup  $H$ . The order of an element  $a$  is defined as that integral power for which  $a^q = e$  the identity element. A corollary of Lagrange's theorem is that *the order of an element in a group  $G$  of order  $n$  must be some integer divisor of  $n$* . This restriction on the elements is very helpful in constructing all possible groups of order  $n$ .

Thus, for a group of order 4 the order of symmetry elements can only be 4, 2, or 1. The cyclic group  $C_4$ , formed by the operations of a molecule with a single  $C_4$  axis, illustrates the case where the order of elements are four ( $\hat{C}_4^4 = \hat{e}$ ), two ( $(\hat{C}_4^2)^2 = \hat{C}_4^4 = \hat{e}$ ), and one ( $\hat{e}$ ). The  $C_{2v}$  group provides an example where the elements are only of order two ( $\hat{C}_2$  and  $2\hat{\sigma}_v$ ) and one ( $\hat{e}$ ).

Just as a similarity transformation could be applied to an operator, consider the action on a subgroup  $H$ .

$$\square^{-1}H\square = \{e, \square^{-1}H_2\square, \dots, \square^{-1}H_h\square\}$$

This set of elements also constitutes a subgroup of  $G$  since,

$$(\square^{-1}H_i\square)(\square^{-1}H_j\square) = (\square^{-1}H_iH_j\square)$$

and the closure requirement follows because  $H_iH_j$  also must be an element of  $H$ . Verification of the remaining group properties is left as an exercise. When  $\square^{-1}H\square = H$  then  $H$  contains elements in complete classes. It is called an invariant subgroup. For example, the identity and one  $\square_v$  from the point group  $C_{3v}$  is not an invariant subgroup, of  $C_{3v}$ , since it contains only one of the three  $\square_v$  elements.