

SYMMETRY OPERATIONS

*All that will come when it will; but we, meanwhile,
Have much to do. Leave the future to itself.*

Sophocles, "Antigone"

One of the most noticeable things about molecules is their "symmetry," just as in looking at people one notices that the left side is (approximately) the mirror image of the right side. (Try it with your hands and a mirror.) Similarly, crystals have a fundamental symmetry in that they are formed from a "unit cell" repeated throughout space, much as identical bricks repeated in three dimensions form a wall. A closer look also reveals symmetries within this "unit cell" similar to those in an isolated molecule. The terms "symmetry" and "unit cell" will be defined shortly. This paragraph is intended only to point out that they are not new concepts and are used intuitively by all of us. Even though the concepts are simple and intuitive they are extremely important. In fact, the idea that a crystal is made up of a unit cell repeated throughout space forms the foundation of the modern theory of solids. For this reason the first three chapters of this book are devoted to a discussion and amplification of these ideas. However, as mentioned in the preface, one also may start this book with Chapter 6, where there is a very brief overview of the important concepts needed in the rest of the text. Nevertheless, when the first three chapters are studied in detail, the result will be a good background in crystal structures and their symmetries. The reader will find this basic to all studies in solid state science.

In this chapter, the point group operations for molecules are discussed first. Next, the important symmetry operations for crystals are introduced which, along with the point group operations, include translation, glide operations, and screw operations. Then, given any molecule, we show how the point group, and a symbol for the point group, can be determined. This symbol alone describes all the symmetry operations possessed by the molecule. A similar procedure is used to determine the point group of a crystal. In fact, in Chapter 5 it is shown how the point group of the crystal determines the physical behavior of crystals in different directions (the anisotropy).

Warning: There are many new concepts and a considerable amount of new language introduced in this chapter. Neither the concepts nor the language are difficult, but it is important to understand them as they will be used often in the future.

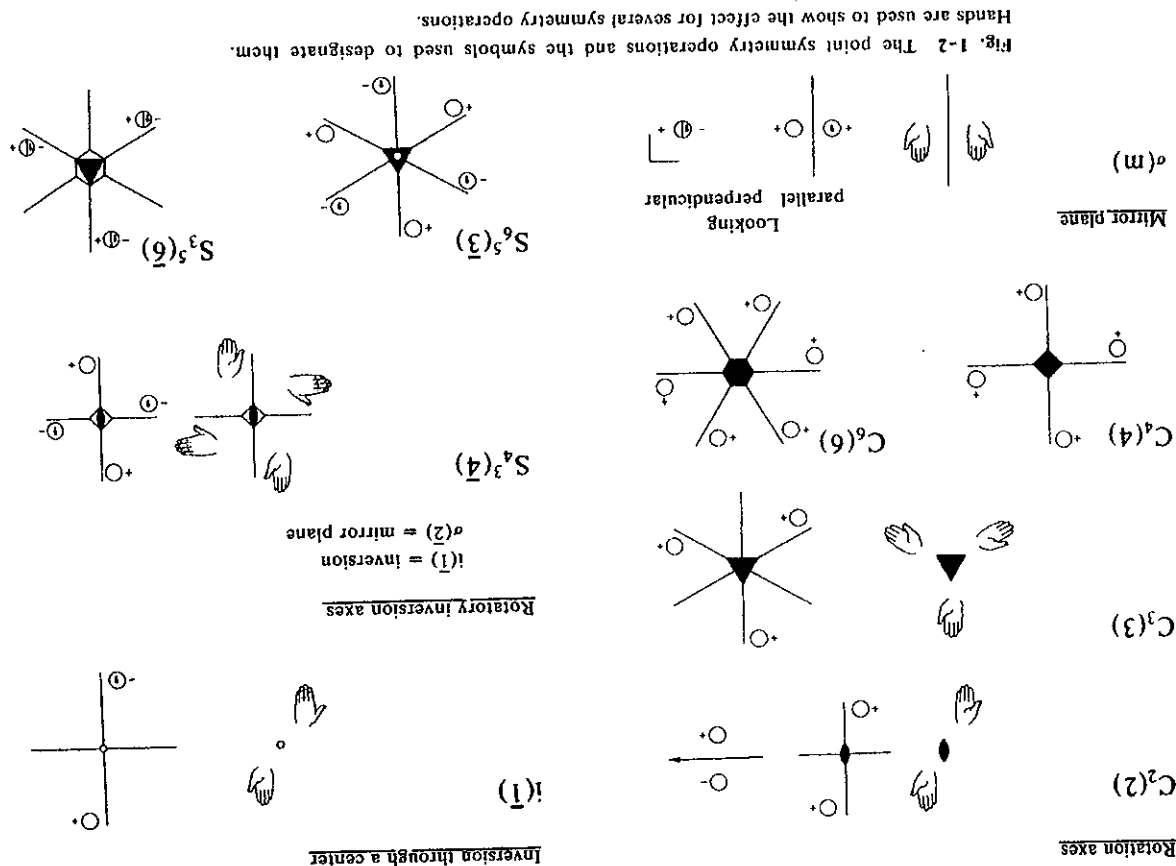


Fig. 1-2 The point symmetry operations and the symbols used to designate them.

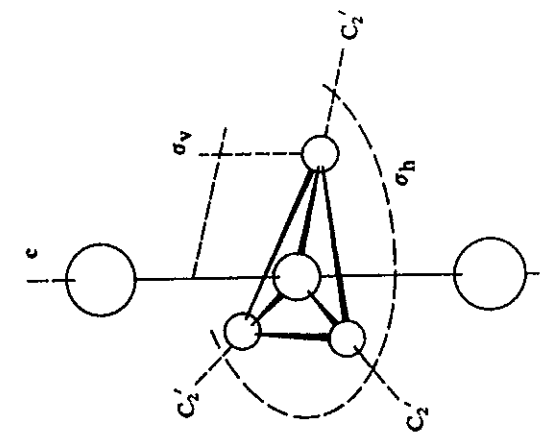


Fig. 1-1 A diagram of a PF_3Cl_2 molecule showing some of the symmetry operations. Naturally, an operation that takes a F atom into a Cl atom cannot be a symmetry operation, so it might be helpful to label the atoms.

1-2 Point Symmetry Operations

A point symmetry operation is a symmetry operation carried out with respect to a fixed point in space, that is, the point does not move during the operation. For example, the P-atom in Fig. 1-1 would be such a point for the operations just discussed. In order to discuss point symmetry operations it is useful to define a principal axis.

1-2a Principal axis The axis of highest symmetry of a molecule or crystal is called the principal axis or c-axis or z-axis. In Fig. 1-1 the Cl-P-Cl axis is the principal axis because there are more symmetry operations about this axis than any other. Axial molecules or crystals will always have a principal axis. For example, a fourfold axis (rotations by 0° , 90° , 180° , and 270° is higher than a twofold axis (rotations by 0° and 180°). However, this concept is not always appropriate since there are many molecules and crystals for which no one axis has higher rotation symmetry than any of the others. For these cases there is no principal axis. (For example, an orthorhombic crystal may have three twofold axes; in CH_4 or other high symmetry molecules there is no principal axis.)

1-1 A Symmetry Operation

A symmetry operation for a molecule or crystal is an operation that interchanges the positions of the various atoms in such a way that the molecule or crystal appears exactly as before the operation. (The molecule or crystal is said to be in an *equivalent position*.) Furthermore, such an operation, when repeatedly applied, must also produce an equivalent position. Symmetry operations are sometimes called **covering operations**.

As an example, consider the PF_3Cl_2 molecule shown in Fig. 1-1. Twelve symmetry operations can be found. Some of the easier ones to see are: three rotations by 180° about each of the P-F axes, labeled C_2' in the figure; similarly, three mirror planes, each plane containing the Cl atoms, the P atom, and a different F atom, one of which is labeled σ_v in the figure; and rotations by 120° and 240° about the c-axis. One very important symmetry operation is the **identity operation**, which leaves the molecule unchanged. This is possessed by all objects.

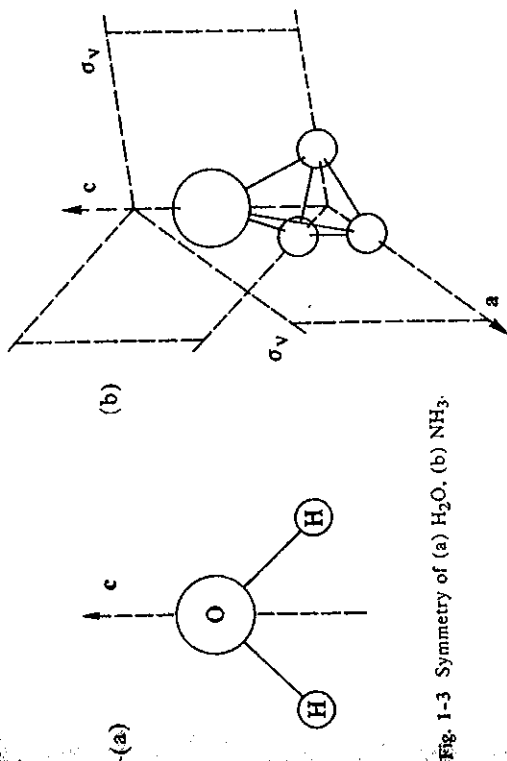
In general, many different types of symmetry operations are used, such as the interchange of electrons, time reversal, and the interchange of quarks in particle physics. However, in the following chapters we shall consider only the spatial interchange of atoms. In the next section these types of symmetry operations are examined systematically and in many of the latter chapters the symmetry is used implicitly if not explicitly.

1-2b Point symmetry operations Table 1-1 summarizes the meaning of the point symmetry operations using the Schoenflies notation. Figure 1-2 (page 2) shows diagrams of the effects of these symmetry operations, repeated to bring the object back to the starting position. Also shown are the diagrammatic symbols, such as the triangle, diamond, and hexagon, that are used to denote the symmetry operations. The notation is simple. The circles with +, -, and commas are convenient ways to represent any *general object* such as a collection of atoms. Hands are also used for the simpler operations because they are a convenient general object. The + and - signs signify a general object either above or below the plane of the paper. A circle with a comma in it is the **enantiomeric** or mirror image of a circle without a comma. The left and right hands are the enantiomeric images of each other. Mirror planes and centers of inversion will produce enantiomeric images of molecules. A split circle means one circle is above the plane and one below. These symbols, which are used particularly in space group diagrams, conveniently show the meanings of the point symmetry operations listed in Table 1-1. **Warning:** A circle with a "+" next to it does not mean a circle is above the plane of the paper. It means a general arbitrarily shaped object is above the paper. Hands are ideal to use but they tend to clutter the diagrams.

Although the Schoenflies notation is used by most solid state chemists and physicists, crystallographers always use the International

Table 1-1 Symmetry operations.

- E Identity** – The molecule or crystal is not rotated at all (or rotated by 2π about any axis). All objects possess this symmetry operation. Taking r as a vector from the origin to any point. $Er \rightarrow r$.
- i Inversion** – The molecule is inverted through some origin, which is called the center of inversion. (An equilateral triangle and a five-pointed star do not have i as a symmetry operation, but a square and six-pointed star do.) The operation is $i(x, y, z) \rightarrow (-x, -y, -z)$.
- C_n Rotation** – Sometimes called a **proper rotation**. A rotation of the molecule by $360^\circ/n$ or $2\pi/n$ about an axis, in the sense of a right-hand screw by convention. If the axis is not the principal axis (i.e. c-axis or z-axis), often, but not always, there will be a prime or other superscript: C_n' or C_n^x where C_n^x means a C_n operation about the x-axis. This is different from a numerical superscript, for example C_2^2 means apply C_2 two times, that is, C_3^2 is the same as a rotation by 240° . (PF_3Cl_2 in Fig. 1-1 has C_3 , C_3^2 and three C_2 's.) For example, taking the z-axis as the principal axis, $C_4(x, y, z) \rightarrow (y, -x, z)$, and $C_2^x(x, y, z) \rightarrow (x, -y, -z)$.
- σ Reflection** – Reflection of the molecule in a plane. The particular plane of reflection will sometimes be specified by a subscript. Reflection in a plane means the transfer of all of the points to the other side of the plane an equal distance along perpendiculars to the plane. For example, for a reflection across the x-plane, which contains the yz-axis, $\sigma(x, y, z) \rightarrow (-x, y, z)$.
- σ_h Reflection in the horizontal plane** – The plane of reflection is perpendicular to the principal axis and contains the origin. (PF_3Cl_2 has one σ_h .)
- σ_v Reflection in a vertical plane** – The plane contains the principal axis. (PF_3Cl_2 has three σ_v through the z-axis.)
- σ_d Reflection in a diagonal plane** – Like σ_v , this plane also contains the principal axis but bisects the angle between the twofold axes perpendicular to the principal axis.
- S_n Improper rotation** – A rotation by $2\pi/n$ followed by a reflection in a horizontal plane. For example, $S_n = \sigma_h C_n$. Again $S_n^m \equiv (S_n)^m \equiv (\sigma_h C_n)^m$. (This is a subtle operation so please note: $S_2 = i$; $S_3^2 S_3 \neq E$ rather $S_3^3 = \sigma_h$ and $S_3^6 = E$; try it. An object with S_n symmetry need not have σ_h and C_n as symmetry operations. Methane CH_4 is one such example.) $S_4(x, y, z) \rightarrow (y, -x, -z)$.

Fig. 1-3 Symmetry of (a) H_2O . (b) NH_3 .

(or Hermann-Mauguin) notation. The correspondence of the symbols E , $\bar{1}$, n , and m to the Schoenflies symbols is

$$1 \equiv E, \quad \bar{1} \equiv i, \quad n \equiv C_n, \quad m \equiv \sigma, \quad \bar{n} \equiv iC_n \quad (1-1)$$

The use of the rotatory inversion axis, \bar{n} , where a rotation is followed by an inversion rather than a reflection as in the Schoenflies approach, sometimes makes going from one notation to another a bit of a nuisance, as can be seen in Fig. 1-2. Nevertheless, it is necessary, for a solid state scientist at least, not to be intimidated by the International notation. Thus, for pedagogical purposes we will follow an unusual convention. *When not inconvenient, we will write the symmetry operation symbols (and later point group and space group symbols) in the Schoenflies notation immediately followed, in parentheses, by the International symbol.* This is done in Fig. 1-2. Problem 2 helps us to understand how to go between these two notations and to see why $\bar{6} = S_3^5$ and $\bar{3} = S_6^5$. Don't be intimidated!

1-2c Inverse of symmetry operations Note that the inverse of every symmetry operation must also be a symmetry operation. The inverse of a symmetry operation A is a symmetry operation B such that the application of A followed by B will return the molecule or crystal to a position identical (not just equivalent) to the starting position, that is, $BA = E$. Note the convention in the order of writing B to the left of A . Several symmetry operations, such as $E(1)$, $i(\bar{1})$, and $\sigma(m)$ are their own inverses. Other situations are more complicated, that is, $\sigma_h C_3 = E$ or $S_3^5 S_3 = E$; the latter must be tried to be believed. In

Symmetry Operation

$$\begin{array}{l} C_n^m \\ S_n^m \\ S_n^m \end{array}$$

Inverse

$$\begin{array}{l} C_n^{n-m} \\ S_n^{n-m} \\ S_n^{2n-m} \end{array} \quad \begin{array}{l} m, n \text{ even} \\ m, n \text{ odd} \\ m, n \text{ odd} \end{array}$$

$S_n^m = C_n^m$ for n odd and m even.

1-2d Examples We give several examples of the symmetry operations of molecules shown in Figs. 1-1 and 1-3.

Example 1. PF_3Cl_2 has E , C_3 and C_3^2 about the principal axis. There are three σ_v containing the principal axis. Three C_2 are perpendicular to the principal axis as is a σ_h -plane. Then there are S_3 and S_3^5 . The 12 operations would usually be written as E , C_3 , C_3^2 , $3C_2$, $3\sigma_v$, σ_h , S_3 , S_3^5 .

Example 2. The four symmetry operations of H_2O are E , C_2 , $2\sigma_v$. Both planes contain the c -axis and one contains the molecule.

Example 3. NH_3 has E , C_3 , C_3^2 , $3\sigma_v$. Note that in PF_3Cl_2 there is one point that must be considered as the origin for these point symmetry operations, while for H_2O and NH_3 any point along the principal axis can be considered the origin.

1-2e Stereographic projection A stereographic projection is a very useful way to visualize the effects of point symmetry operations. It is usually constructed by assuming that a unit sphere surrounds the object. A point in the $+z$ hemisphere is projected onto the xy -plane by determining the intersection, with that plane, of the line connecting the point to the south pole of the sphere. If the point is in the $-z$ hemisphere the north pole is used. We observe the projections by looking down the $+z$ -axis. The points in the $+z$ or $-z$ hemisphere are respectively labeled by a circle (o) or a dot (\bullet) on the xy -plane. It is important to realize that general points, also called general equivalent positions (perhaps best called arbitrary points), are pictured in the stereographic projection. That is, the points must not be on a symmetry plane, line, or point. Several examples should clarify this sometimes confusing subject. Refer to Fig. 1-4.

Example a. H_2O has four symmetry operations E , C_2 , and $2\sigma_v$. Start with a circle at position 1 and apply $E(1)$, naturally resulting in the same circle at position 1; apply $C_2(2)$ to the starting circle at 1, resulting in 2; apply $\sigma_v(m)$ to the starting circle 1, resulting in 3; apply the other $\sigma_v(m)$ to the starting circle at 1, resulting in 4. Note that the order of application of the symmetry operations and the starting position are irrelevant. Also note the convention that thick lines representing the $2\sigma_v$ and the symbol for C_2 in the center, as in Fig. 1-2. Since stereograms are for general points there always are as many points as there are symmetry operations.

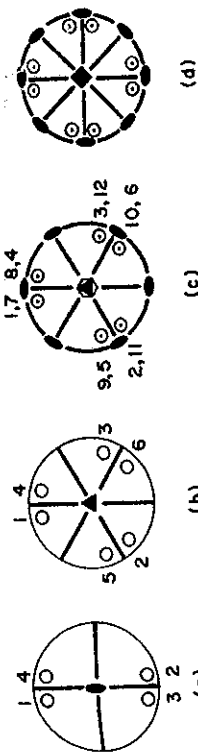


Fig. 1-4 Stereograms for some of the examples.

Example b. The molecule NH_3 has E , C_3 , C_3^2 , $3\sigma_v$. $E(1)$ applied to 1 gives 1; $C_3(3)$ applied to 1 gives 2; $C_3^2(3^2)$ applied to 1 gives 3; and each of the $3\sigma_v$ applied to 1, 2, and 3, respectively, gives 4, 5, and 6. Again notice the thick lines in the figure for the $3\sigma_v$ and the symbol in the center for C_3 .

Example c. PF_3Cl_2 has E , C_3 , C_3^2 , $3C_2$, $3\sigma_v$, σ_h , S_3 , S_3^5 . The results are labeled in the same order as the symmetry operations where the first entry refers to the circle and the second to the dot. Notice that the thick lines again represent the $3\sigma_v$ and the line for the large circle, which represents σ_h , is also thick. The symbol in the center refers to $S_3(\overline{6}^5)$, while the $3C_2$ in the plane of the paper, the xy -plane, are also shown.

Example d. The stereogram for an object with the following symmetry operations is given: E , C_4 , C_2 , C_4^3 , $2C_2'$, $2C_2''$, i , S_4 , S_4^3 , σ_h , $2\sigma_v$, $2\sigma_d$. (C_2' is in the σ_v plane and C_2'' is in the σ_d plane.) Note the thick lines for the $2\sigma_d$ as well as $2\sigma_v$ and the symbols for the four twofold axes in the xy -plane. The line for the large circle also is thick, representing σ_h .

Warning: The notations in Fig. 1-2 and 1-4 are different. In Fig. 1-2 an object below the plane of the paper is a circle with a $-$ sign, while in Fig. 1-4 it is a dot. Commas are used in Fig. 1-2, while no such comparable symbol appears in Fig. 1-4. The notation of circles with \pm signs and commas in Fig. 1-2 is used for space groups while the circle and dots in Fig. 1-4 are used for point groups. Although it may be confusing at first, this is common usage and we shall go along with this notation.

1-3 The Point Groups of a Molecule

Now we can write down all the symmetry operations for any molecule. Further, given all the symmetry operations, its stereogram may be drawn. We might ask if there is some shorthand notation so that this information can be passed succinctly to others. The answer is yes, and we now discuss how to determine the point group of a mole-