1.3 Summary of Symmetry Operations, Symmetry Elements, and Point Groups.

Rotation axis. A rotation by 360°/n that brings a three-dimensional body into an equivalent configuration comprises a $\hat{C}_n$ symmetry operation. If this operation is performed a second time, the product $\hat{C}_n\hat{C}_n$ equals a rotation by 2(360°/n), which may be written as $\hat{C}_n^2$. If n is even, n/2 is integral and the rotation reduces to $\hat{C}_{n/2}$. In general, a $\hat{C}_n^m$ operation is reduced by dividing m and n by their least common divisor (e.g., $\hat{C}_9^6 = \hat{C}_3^2$). Continued rotation by 360°/n generates the set of operations:

$$\hat{C}_n,\ \hat{C}_n^2,\ \hat{C}_n^3,\ \hat{C}_n^4,\ \cdots\ \hat{C}_n^n$$

where $\hat{C}_n^n$ = rotation by a full 360° = $\hat{E}$ the identity. Therefore $\hat{C}_n^{n+m} = \hat{C}_n^m$. Operations resulting from a C_n symmetry axis comprise a group that is isomorphic to the cyclic group of order n. If a molecule contains no other symmetry elements than C_n, this set constitutes the symmetry point group for that molecule and the group specified is denoted $\mathbf{C_n}$. When additional symmetry elements are present, $\mathbf{C_n}$ forms a proper subgroup of the complete symmetry point group. Molecules that possess only a $\mathbf{C_n}$ symmetry element are rare, an example being $Co(NH_2CH_2CH_2NH_2)_2Cl_2^+$, which possesses a sole C_2 symmetry element.
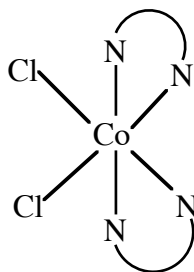
One special type of $\hat{C}_n$ operation exists only for linear molecules (e.g., HCl). Rotation by *any angle* around the internuclear axis defines a symmetry operation. This element is called C_∞ axis and an infinite number of operations $\hat{C}_\infty^\phi$ are associated with the element where ϕ denotes rotation in decimal degrees.

We already saw that molecules may contain more than one rotation axis. In BF_3, depicted below, a three-fold axis emerges from the plane of the paper intersecting the center of the

$$\begin{array}{ccc} F & & F \\ \diagdown & & \diagup \\ & B & \\ & | & \\ & F & \end{array}$$
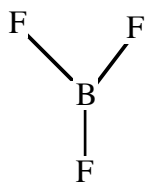
triangular projection. Three C_2 axes containing each B-F bond lie in the plane of the molecule perpendicular to the three-fold axis. The rotation axis of highest order (i.e., C_3) is called the principal axis of rotation. When the principal C_n axis has n even, then it contains a C_2 operation associated with this axis. Perpendicular C_2 axes and their associated operations must be denoted with prime and double prime superscripts.

Reflection planes. Mirror planes or planes of reflection are symmetry elements whose associated operation, reflection in the plane, inverts the projection of an object normal to the mirror plane. That is, reflection in the xy plane carries out the transformation (x,y,z) ⊘ $(x,y,-z)$. Mirror planes are denoted by the symbol σ and given the subscripts v, d, and h according to the following prescription. Planes of reflection that are perpendicular to a principal rotation axis of even or odd order are named σ_h (e.g., the plane containing the B and 3F atoms in BF_3). Mirror planes that contain a principal rotation axis are called vertical planes and designated σ_v. For example, in BF_3 there are three σ_v planes, each of which contains the boron atom, fluorine atom, and is perpendicular to the molecular plane. Notice that for an odd n-fold axis there will be n σ_v mirror planes which are similar. That is if we have one σ_v plane, then by operation of C_n a total of n times, we generate n equivalent mirror planes. The n σ_v operations comprise a *conjugate class*. For even n the σ_v planes fall into two classes of $n/2$ σ_v and $n/2$ σ_d planes, as illustrated earlier in the chapter.

Rotoreflection axes or improper rotation axes. This new operation is best thought of as the stepwise product of a rotation, and reflection in a plane perpendicular to the rotation axis. We need to introduce it since a product such as $\hat{C}_6\hat{\sigma}_h$ is not equal to either a normal rotation or reflection. To satisfy group closure a new symmetry operation must be introduced. An

inversion operation is the simplest rotoreflection operation and is given the name $\hat{S}_2$ or $\hat{\imath}$. That $\hat{S}_2 = \hat{\imath}$ is immediately apparent because $\hat{\imath}\cdot(x,y,z) = (-x,-y,-z)$ and $\hat{C}_2(z)\hat{\sigma}(xy)\cdot(x,y,z) = \hat{C}_2(z)\cdot(x,y,-z) = (-x,-y,-z)$. Because $\hat{C}_n$ and $\hat{\sigma}_h$ commute we have $\hat{S}_n = \hat{C}_n\hat{\sigma}_h$ for the general rotoreflection operation. Since $\hat{\sigma}_h{}^n = \hat{E}$ for even m and for m odd $\hat{\sigma}_h{}^m = \hat{\sigma}_h$, *an S_n axis requires simultaneous independent existence of a $C_{n/2}$ rotation axis and an inversion center when n is even*. For example, an S_6 axis generates the operations for the point group $\mathbf{S_6}$. They are shown below.

$$\hat{S}_6,\ \hat{S}_6{}^2 = \hat{C}_3{}^2\hat{\sigma}_h{}^2 = \hat{C}_3{}^2,\ \hat{S}_6{}^3 = \hat{S}_2 = \hat{C}_2\hat{\sigma}_h = \hat{\imath},\ \hat{S}_6{}^4 = \hat{C}_3{}^2,\ \hat{S}_6{}^5 = \hat{C}_6{}^5\hat{\sigma}_h,\ \hat{S}_6{}^6 = \hat{E}.$$

An odd order rotoreflection axis requires independent existence of a C_n axis and a σ_h symmetry element. An S_7 axis generates the following operations.

$$\hat{S}_7,\ \hat{S}_7{}^2 = \hat{C}_7{}^2,\ \hat{S}_7{}^3,\ \hat{S}_7{}^4 = \hat{C}_7{}^4,\ \hat{S}_7{}^5,\ \hat{S}_7{}^6 = \hat{C}_7{}^6,\ \hat{S}_7{}^7 = \hat{C}_7{}^7\hat{\sigma}_h{}^7 = \hat{\sigma}_h,\ \hat{S}_7{}^8 = \hat{C}_7{}^8 =$$
$$\hat{C}_7,\ \hat{S}_7{}^9 = \hat{C}_7{}^2\hat{\sigma}_h,\ \hat{S}_7{}^{10} = \hat{C}_7{}^3,\ \hat{S}_7{}^{11} = \hat{C}_7{}^4\hat{\sigma}_h,\ \hat{S}_7{}^{12} = \hat{C}_7{}^5,\ \hat{S}_7{}^{13} = \hat{C}_7{}^6\hat{\sigma}_h,\ \hat{S}_7{}^{14} = \hat{E}$$

The S_7 axis generates a cyclic group of order fourteen and requires the independent existence of C_7 and σ_h. This group is denoted $\mathbf{C_{7h}}$ and not $\mathbf{S_7}$.

Conjugate Symmetry Elements and Operations. In the symmetry group of BF_3 the sequence of operations $\hat{C}_3{}'^{-1}\hat{\sigma}_v\hat{C}_3$ means to rotate by 120 ° perform $\hat{\sigma}_v$, then rotate back 120°. This sequence of operations is equivalent to reflection in a plane rotated 120° from the initial one, as shown below. The similarity transformation $(\hat{C}_3{}^2)^{-1}\hat{\sigma}_v\hat{C}_3{}^2$ generates an operation, which is the third vertical mirror plane. The three equivalent σ_v symmetry operations belong to the same conjugate class. Symmetry equivalent symmetry operations (i.e., *operations belonging to symmetry elements that are interchanged by symmetry operations of the group) belong to the same conjugate class*. In BF_3 all the operations associated with the equivalent C_2 elements belong to the same class. This may be verified by the similarity transformations $\hat{C}_3{}^{-1}\hat{C}_2\hat{C}_3$ and $(\hat{C}_3{}^2)^{-1}\hat{C}_2\hat{C}_3{}^2$ operating on any of the three C_2 axis.
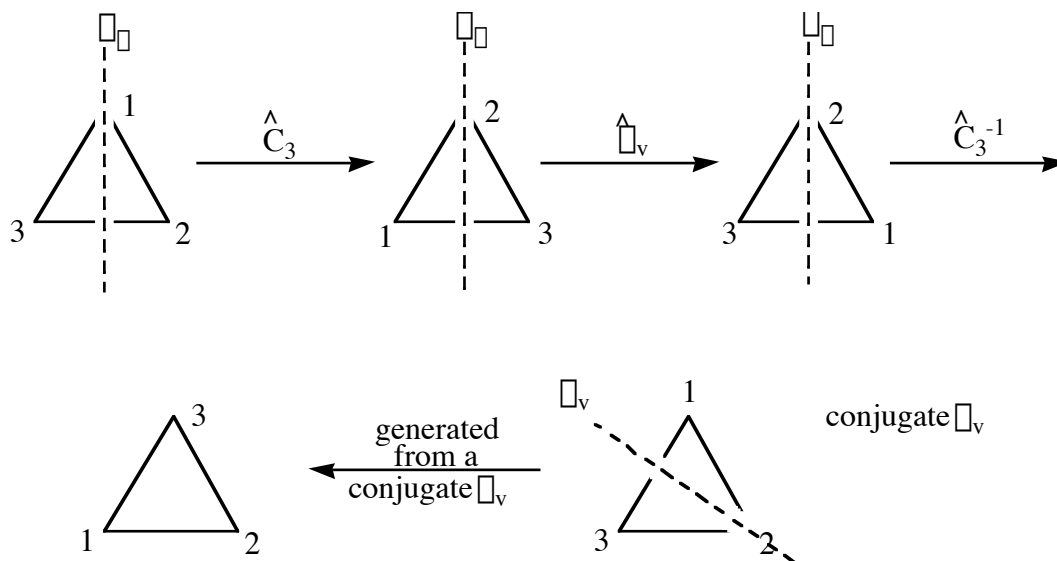
When the principal axis is of even order two types of vertical reflection planes σ_v and σ_d are possible. Consider the planar ion $PtCl_4^{2-}$, which contains one four-fold axis normal to the molecular plane and four perpendicular C_2 axis as shown. Clearly the pair of axis labeled $C_2{'}$
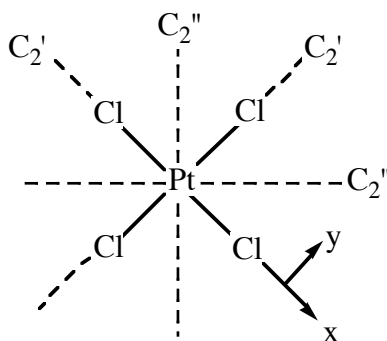

are equivalent, as are the pair of axis $C_2"$ since the four-fold rotation interchanges elements among the pairs; however, the $C_2{'}$ and $C_2"$ axis are not equivalent. There is no operation that will interchange these elements. Primes designate C_2 axes perpendicular to an even principal axis. The $\hat{C}_4{}^2$ operation associated with the four-fold axis is called $\hat{C}_2$. You might be surprised to find that a C_4 axis and one perpendicular $C_2{'}$ axis generate the remaining three "primed" two-fold axes. Action of $\hat{C}_4$ on one $C_2{'}$ axis generates the other $C_2{'}$ axis. With the application of $\hat{C}_4$ or $\hat{C}_2$ no new axes are generated; however, consider the product of operators $\hat{C}_4\hat{C}_2{'}$ acting on the point (x,y,z). Take one $C_2{'}$ axis to lie along the x axis and choose C_4 coincident with the z

axis. The operation $\hat{C}_2'$ on the general point (x,y,z) produces a new point at $(x,-y,-z)$. The $\hat{C}_4$ operation does not change z and rotates the molecule in the x,y plane. So $\hat{C}_4 (x,y,z)$ Ø
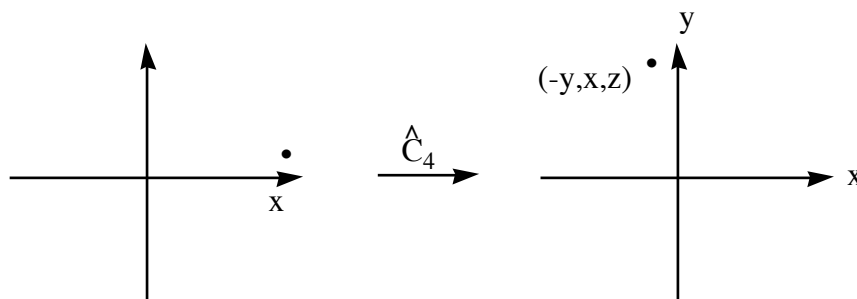

$(-y,x,z)$ and the product $\hat{C}_4\hat{C}_2'(x,y,z) = \hat{C}_4(x,-y,-z) = (y,x,-z)$ is equivalent to rotation around the C_2'' axis bisecting the xy quadrant of the coordinate system because $\hat{C}_2'' (x,y,z) \neq (y,x,-z)$.
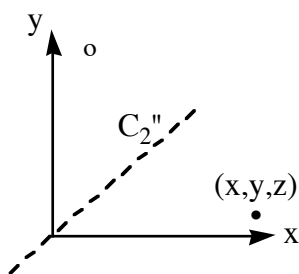
This proves that the combination of a $\hat{C}_2'$ operation with $\hat{C}_4$ generates the $\hat{C}_2''$ operation, and that the two C_2' belong to the same conjugate class. You may prove that the two $\hat{C}_2''$ comprise a second class.

There are likewise two classes of vertical reflection planes. The two planes containing the C_4 axis and one C_2' axis are called σ_v. Those mirror planes containing the C_2'' axis are denoted σ_d. This illustrates an interesting consequence of a vertical reflection plane. Consider the effect of $\hat{\sigma}_v$ or $\hat{\sigma}_d$ on rotation around the principal axis. The effect of $\hat{\sigma}_v$ is to change the sense of

$C_n^{\ m}$ $\qquad$ $C_n^{\ -m}$
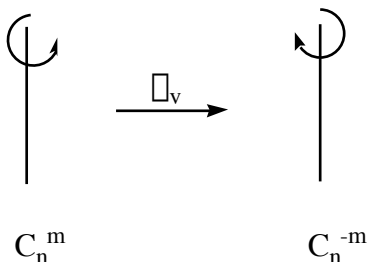
rotation from counterclockwise to clockwise. This means that rotation by 360°/n and -360°/n are equivalent. In other words a rotation $\hat{C}_n^m$ and its inverse $\hat{C}_n^{-m}$ belong to the same conjugate class when a mirror plane contains the rotation axis. For example, the operations of a C_7 axis fall into the classes (C_7, C_7^6); (C_7^2, C_7^5); (C_7^3, C_7^4) and for a C_6 axis the classes are (C_6, C_6^5); (C_3, C_3^2); (C_2) when a σ_v or σ_d mirror plane also exists.

Molecular symmetry groups. When you search for molecular symmetry elements, look for rotations, reflections and rotoreflection elements, which interchange equivalent atoms in a molecule and leave others untouched. The short hand notation for the various point groups uses abbreviations, which often specify the key symmetry elements present. The complete set of symmetry operations of a molecule defines a group, since they satisfy all the necessary mathematical conditions. When confronted with a molecule whose symmetry group must be determined, the following approach can be used.

Special symmetry groups usually are self-evident. The group $\mathbf{D_{\infty h}}$ is the point group of homonuclear diatomic molecules and other linear molecules that possess a σ_h plane (e.g., CO_2). For linear molecules an infinite number of σ_v planes always exist. The symbol D in a group name always means that there are n-two-fold axes perpendicular to the n-fold principal axis. The presence of σ_h and σ_v planes in a molecule always requires the presence of $n \perp C'_2$ axes, since one can show that $\hat{\sigma}_h \hat{\sigma}_v = \hat{C}'_2$; however, the converse is not true. Therefore, there are an infinite number of C_2 axes perpendicular to the C_∞ axis of the molecule. The C_∞ axis and σ_h generate an infinite number of S_∞^ϕ operations; one is $\hat{S}_2 = \hat{\imath}$.

If a linear molecule does not contain a σ_h plane, e.g., HCl or OCS, then it belongs to the $\mathbf{C_{\infty v}}$ point group. This point group contains a C_∞ axis and an infinite number of σ_v planes. Clearly $\mathbf{C_{\infty v}}$ is a proper subgroup of $\mathbf{D_{\infty h}}$.

A free atom belongs to the symmetry group $\mathbf{K_h}$, which is the group of symmetry operations of a sphere. We shall not be concerned with this point group; however, a

consequence of spherical symmetry is the requirement that the angular wavefunctions of atoms behave like spherical harmonics.
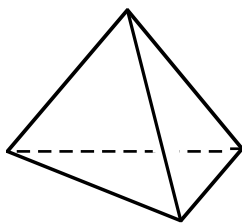
There are seven special symmetry groups, which contain multiple high order (C_n, n > 3) axes. These are the only possibilities for 3-dimensional objects. The groups may be derived from

octahedron   **tetrahedron**   **cube**
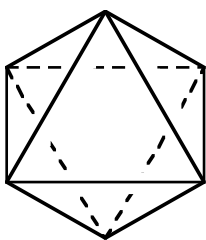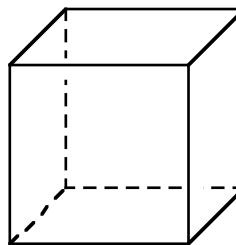
O_h T_d O_h
$3\,C_4$ $4\,C_3$ $3\,C_4$
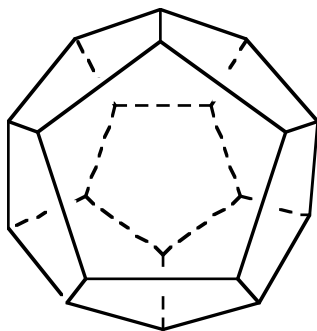
dodecahedron   **icosahedron**
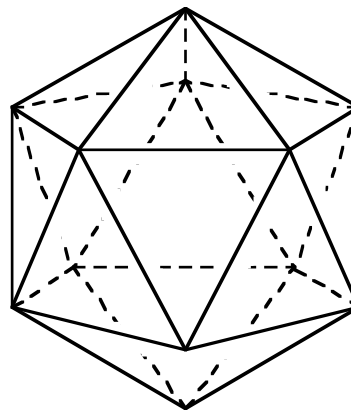
I_h I_h
$12\,C_5$ **axes** $12\,C_5$ **axes**

Figure 1.16. The Five Platonic Solids and Their Point Groups, with The High Order C $_n$ Axes Listed.

the symmetry operations of the five Platonic solids (octahedron, tetrahedron, cube, icosahedron, dodecahedron). Platonic solids are solids, shown in figure 1.16, whose edges and verticies are all equivalent and whose faces are all some regular polygon. The symmetry operations of the tetrahedron comprise the group T_d. The cube and octahedron possess equivalent elements and their operations define the O_h group.

The pentagonal dodecahedron and icosahedron likewise define I_h. We will restrict our discussion to the O_h group and its subgroups, O, T_d, T_h, and T, since I_h and its subgroup I are encountered less frequently. The collection of groups {O, T_d, T_h, and T} are often referred to as cubic groups. The symmetry elements belonging to an octahedron are: three C_4 axes that pass through opposite verticies of the octahedron; four C_3 axes that pass through opposite triangular faces of the octahedron; six C_2 axes that bisect opposite edges of the octaedron; four S_6 axes coincident with the C_3 axes; three S_4 axes coincident with the C_4 axes; an inversion center or S_2 axis coincident with C_4; three σ_h which are perpendicular to one C_4 axis and contain two others. Therefore, a single plane defined as σ_h, also can be thought of as σ_v with respect to the other C_4 axis. Similarly, there are six planes called σ_d, which are also σ_v planes containing a C_3 axis. Subgroups of O_h are generated by removing the following symmetry elements:

O = lacks i, S_4, S_6, σ_h and σ_d and is called the pure rotation subgroup of O_h.

T_d = this group lacks C_4, i and σ_h and is the group of tetrahedral molecules, e.g., CH_4.

T_h = this uncommon group is derived from T_d by removing S_4 and σ_d elements.

T = the pure rotation subgroup of T_d contains only C_3 and C_2 axes.

If a molecule belongs to none of these special groups, then focus on the highest order rotation axis. Those rare molecules that possess only one n-fold rotation axis and no other symmetry elements belong to the C_n symmetry group, which is cyclic. If only a rotation axis exists and no mirror planes or other elements are obvious, a last check should be made for an S_n axis of order higher than the obvious rotation axis. When a higher order S_n axis can be found,

then the $\mathbf{S_n}$ groups (n = even) are obtained. Naturally n must be even since $\hat{S}_n{}^n = \hat{\sigma}_h$ when n is odd and both C_n and σ_h exist independently. These groups (n = odd) are conventionally designated $\mathbf{C_{nh}}$. Also, when n = 2, the $\mathbf{S_2}$ group (remember $S_2 = i$) is conventionally called $\mathbf{C_i}$.

If we add to a $\mathbf{C_n}$ group $n\sigma_v$ (n odd) or $n/2\sigma_v$ and $n/2\sigma_d$ (n even) mirror planes, but no other rotation axes, then the $\mathbf{C_{nv}}$ groups are generated. If to the elements of $\mathbf{C_n}$ we add a horizontal mirror plane, then we generate the $\mathbf{C_{nh}}$ groups. The product of $\hat{C}_n$ and $\hat{\sigma}_h$ also generate an S_n symmetry element and its associated operations.

When additional n-two-fold axes perpendicular to C_n are present, but no mirror planes, then the $\mathbf{D_n}$ groups are generated. Addition of a σ_h plane to the rotation symmetry elements of a $\mathbf{D_n}$ group generates the $\mathbf{D_{nh}}$ groups. Similar to the $\mathbf{C_{nh}}$ groups an S_n symmetry axis is also produced (if n is even an inversion center will be present). The product $\hat{C}_2\hat{\sigma}_h$ (where C_2 is associated with n $\perp C_2$ axes in the $\mathbf{D_{nh}}$ group) generates vertical mirror planes so that the $\mathbf{D_{nh}}$ group also contains $n\sigma_v$ planes (n odd) or $n/2\sigma_v$ and $n/2\sigma_d$ planes (n even). If in addition to the elements of a $\mathbf{D_n}$ group an S_{2n} axis is present, then the $\mathbf{D_{nd}}$ groups are obtained. The product $\hat{S}_n\hat{C}_2$ (C_2 belongs to a C_2 axis perpendicular to the n-fold axis) yields the operation $\hat{\sigma}_d$ so that an additional n dihedral mirror planes are required.

If a molecule contains as the only symmetry element a mirror plane, then the group is called $\mathbf{C_s}$. Finally, if no symmetry elements, other than E, exist, then the molecular symmetry group is the trivial one called $\mathbf{C_1}$. Table I.1 summarizes the groups we just discussed and their associated elements. It provides a useful reminder of all the necessary elements when assigning symmetry point groups.

Table 1.1 Common Point Groups and Their Symmetry Elements

Point Group		Symmetry Elements Present
C_1		E
C_s		E, σ_h
C_i		E, i
C_n		E, C_n
D_n	n = odd	E, C_n, $n \perp C_2$
D_n	n = even	E, C_n, $n/2 \perp C_2'$, $n/2 \perp C_2''$
C_{nv}	n = odd	E, C_n, $n\sigma_v$
C_{nv}	n = even	E, C_n, $n/2\sigma_v$, $n/2\sigma_d$
C_{nh}	n = odd	E, C_n, σ_h, S_n
C_{nh}	n = even	E, C_n, σ_h, S_n, i
D_{nh}	n = odd	E, C_n, σ_h, $n \perp C_2$, S_n, $n\sigma_v$
D_{nh}	n = even	E, C_n, σ_h, $n/2 \perp C_2'$, $n/2 \perp C_2''$, S_n, $n/2\sigma_v$, $n/2\sigma_d$, i
D_{nd}	n = odd	E, C_n, $n \perp C_2$, i, S_{2n}, $n\sigma_d$
D_{nd}	n = even	E, C_n, nC_2', S_{2n}, $n\sigma_d$
S_n	n = even only	E, S_n, $C_{n/2}$ and i if $n/2$ odd
T		E, $4C_3$, $3C_2$
T_h		E, $4C_3$, $3C_2$, $4S_{2n}$, i, $3\sigma_h$
T_d		E, $4C_3$, $3C_2$, $3S_4$, $6\sigma_d$
O		E, $3C_4$, $4C_3$, $6C_2$
O_h		E, $3C_4$, $4C_3$, $6C_2$, $4S_6$, $3S_4$, i, $3\sigma_h$, $6\sigma_d$
I		E, $6C_5$, $10C_3$, $15C_2$
I_h		E, $6C_5$, $10C_3$, $15C_2$, i, $6S_{10}$, $10S_6$, 15σ
K_h		E, infinite numbers of all symmetry elements

1.4 Site Symmetry of Molecules and Ions in Solids

Most of the elements, as well as most inorganic compounds, exist as solids. The ideas about symmetry point groups can be applied to molecules or ions in crystal lattices in the context of site symmetry and pseudosymmetry. A crystal results from the periodic repetition of a specific arrangement of atoms through space. For a regular infinite array of objects the act of translation in space can be a valid symmetry operation, in addition to those described previously. Consider the infinite one-dimensional lattice

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Translation to the right or left by an integral multiple of the lattice spacing yields an indistinguishable physical configuration. This operation is important in considering atomic arrays in crystals. Seven three dimensional boxes (or parallelpipeds) used to summarize three-dimensional packing are given in Table I.2. Each box can be classified by the lengths of its three edges a, b, and c, which are assigned using the convention for a right-handed coordinate system.

Table I.2: The Seven Crystal Systems

System	*Conditions on Cell Parameters*	*Lattice Symmetry*
triclinic	$a \neq b \neq c; \alpha \neq \beta \neq \gamma$	C_i or $\bar{1}$
monoclinic	$a \neq b \neq c; \alpha = \gamma = 90°, \beta > 90°$	C_{2h} or 2/m
orthorhombic	$a \neq b \neq c; \alpha = \beta = \gamma = 90°$	D_{2h} or mmm
tetragonal	$a = b \neq c; \alpha = \beta = \gamma = 90°$	D_{4h} or 4/mmm
trigonal (rhombohedral setting)[*]	$a = b = c; \alpha = \beta = \gamma \neq 90°$	D_{3d} or $\bar{3}$ m
hexagonal	$a = b = c; \alpha = \beta = 90°; \gamma = 120°$	D_{6h} or 6/mmm
cubic	$a = b = c; \alpha = \beta = \gamma = 90°$	O_h or m3m

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[*]A hexagonal setting is also possible.

The angles between the vectors are defined as α = between b and c, β = between a and c and γ = between a and b. These unit cells summarize the fundamental packing patterns possible in

solids. The rightmost column in this table lists the symmetry point group of the crystal system in conventional (Schoenflies) notation, along with the Hermann-Maugin equivalent used by crystallographers and solid state chemists. In the latter notation C_n rotation axes are denoted by n, mirror planes by m and σ_h mirror planes are denoted n/m. An inversion center is specified by a bar above the principal rotation axis. In a formal approach to space groups the addition of centered lattices and the possible subsymmetries within each unit cell would be developed to yield the 230 space groups. For an excellent discussion of these considerations we recommend the text by Stout and Jensen listed in the references for this chapter. Extensive tabulations for the symmetry elements of each space group can be found in the reference work, *International Tables for X-ray Crystallography*, available in most libraries. The discussion here will be limited to the relation between the lattice symmetry for the solid and the point group symmetry of an individual ion or molecule in the unit cell.

It is important to recognize that for molecules in crystals *there is not necessarily a correlation between molecular symmetry and the symmetry of the unit cell*. Highly symmetrical molecules may crystallize in low symmetry unit cells and molecules of low symmetry may crystallize in unit cells of high symmetry. Atoms, molecules, or ions in a crystal may occupy two types of positions in a unit cell. The first is called a general position, which exists for all unit cells. There is no crystal symmetry associated with a general position. When a high symmetry molecule, e.g., an octahedral metal complex, occupies a general position then it rigorously possesses no symmetry because the environment of the crystal about it is asymmetric. The asymmetry of the local environment distorts the site symmetry to $\mathbf{C_1}$ or $\mathbf{1}$; however, an octahedral pseudosymmetry remains. The low symmetry crystal environment can often be detected spectroscopically from a splitting of degenerate E or T energy levels. Perturbation of a molecule's symmetry in the crystal from its isolated symmetry, as in the gas phase, may be great or small. The magnitude of the perturbation depends on the strength of interactions between the molecule and its environment. In a molecular crystal, where the forces will primarily be Van der Waals in nature, the deviation from the idealized gas phase molecular symmetry will be small.

In ionic crystal, where strong electrostatic forces are present, the distortion of the idealized symmetry is expected to be greater.

The other kind of position in a unit cell is called a special position. These special positions generally have unit cell (x, y, z) coordinates of 0, 1/2, 1/4, or 1/3 and are listed for each space group in the *International Tables for X-ray Crystallography*. When a molecule or ion occupies a special position then it possesses a rigorous site symmetry, which is determined by the crystal environment. Several different site symmetries are possible in a unit cell, the highest being the maximum symmetry of the cell. Thus cubic unit cells may have special positions of O_h symmetry, which an octahedral molecule could occupy. If an octahedral molecule occupies such a position, then the symmetry is rigorously O_h and splitting of degenerate energy levels by a low symmetry crystal environment does not occur. Coupling between molecules in the unit cell may, however, give exciton splittings, as noted later.

A simple example illustrates the essential points. Consider the case of triclinic crystals. Two space groups are possible. One, denoted $P\bar{1}$, has the maximum symmetry indicated in Table I.2. The other P1, a subgroup of $P\bar{1}$, has no symmetry. In P1 every position in the unit cell has a crystal environment with complete asymmetry. There is generally only one molecule (more rigorously 1 asymmetric unit since a pair or *e.g.*, a hydrogen bonded cluster of molecules can sometimes form a packing unit) per unit cell in this space group. In $P\bar{1}$, which possesses an inversion center at the origin of the unit cell, an arbitrary point or general position (x, y, z) is transformed to (-x, -y, -z) by the inversion operation. Thus, there must be two molecules (asymmetric units) per unit cell if they occupy a general position. It is possible for molecules that contain an inversion center to occupy the special position (0. 0, 0). Then there need be only one asymmetric unit per cell, with the added condition that it possess rigorous inversion symmetry. Similar conditions hold for higher symmetry space groups, but the basic concept resembles that illustrated above.

Another concern, beyond that of the site symmetry in a crystal, is the possibility of coupling between asymmetric units in a crystal. In ionic solids the forces that interconnect all

the asymmetric units in a cell makes it imperative that these couplings be considered if one wants to understand vibrations in the solid state. Even molecular crystals can exhibit unusual splittings from such phenomena. One example occurs for coupling between excited states in crystals and this is often referred to as exciton coupling. For example, the excited states θ_1 and θ_2 of two asymmetric units in $P\bar{1}$ could interact to yield composite sum and difference net states ($\theta_1 + \theta_2$ and $\theta_1 - \theta_2$). In this way a single excited state of the isolated molecule gives rise to two crystal states of different energy. The student with a serious interest in solid-state spectroscopy will need to delve into this in more detail. For most readers this section serves as a caveat should they attempt to interpret spectra of solids.

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1.6 Problems

1) Determine which of the following are groups. For those, that are not groups, specify the missing conditions.

   a) The set of all positive integers with group multiplication defined as normal addition.

   b) The set of all integers (± and 0) with group multiplication defined as normal addition.

   c) The set of all integers (± and 0) with group multiplication defined as normal multiplication.

2) Prove that all groups of prime order are isomorphic to the cyclic group of that order.

3) Give the point group to which the following molecules belong.

   a) MnO_4^{2-} c) WF_6

   b) $Rh_6(CO)_{16}$ d) Mo_6Cl_{12} (8 face capping, 4 terminal Cl)

   e) methane   f) cubane

   g) benzene   h) $Mn_2(CO)_{10}$

   i) $Re_2Cl_8^{2-}$ j) $OsCl_4N^-$

   k) H_2S l)
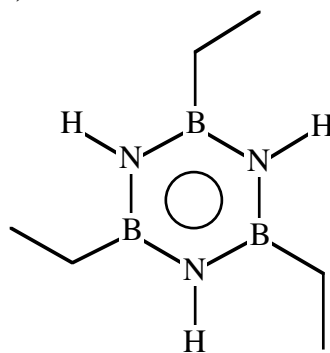
(planar conformation ignore H on carbons)

   m) $Co(en)_3^{3+}$ n) cis-$MoCl_2(CO)_4$

   o) $trans$-$MoCl_2(CO)_4$ p) fac-$Mo(CO)_3(PPh_3)_3$ (coordination symmetry only,

   i.e., ignore Ph groups)

   q) mer-$Mo(CO)_3(PPh_3)_3$ r) Al_2Cl_6

   s) $BrCl_2F$ t) CO_2

u) S_8 (cyclic crown structure)   v) PPh_3 (with propeller conformation of phenyl rings)

w) HOCl   x) cyclo-$(BCl)_4(NCH_3)_4$

y) $Ce(NO_3)_6^{2-}$ (the coordination environment of Ce is icosahedral-each nitrate is bound in a

   planar bidentate fashion such that trans NO_3^- groups are eclipsed).

z) PF_5

4)   Consider the 2-dimensional packing of regular polygons of three-fold through eight-fold symmetry. Which ones can form a close-packed planar network with no overlapping or gaps in the plane?

5)   Based on work in 4 what are the allowed rotational symmetry axes in unit cells of 3-dimensional crystalline solids?

6)   Consider the $\hat{S}_2$ operation around the z axis. Show that its effect on the vector (x, y, z) is the same as the inversion operation.

Key to Problems

1) a) Not group - identity element missing and inverse missing.

   b) Yes

   c) Not group - inverse elements missing.

2) Proof: Consider how one generates a group of prime order. Lagrange's theorem tells us the elements of a group must be an integral divisor of the order of the group. If n = prime then the elements are of order n. Since the # of elements = n, then one element a, and its powers generate the group

$$a, a^2, \cdots, a^n$$

   This is just the cyclic group of order n. Q.E.D.

3) a) $\mathbf{T_d}$; b) $\mathbf{T_d}$; c) $\mathbf{O_h}$; d) $\mathbf{O_h}$; e) $\mathbf{T_d}$; f) $\mathbf{O_h}$; g) $\mathbf{D_{6h}}$; h) $\mathbf{D_{4d}}$; i) $\mathbf{D_{4h}}$; j) $\mathbf{C_{4v}}$; k) $\mathbf{C_{2v}}$; l) $\mathbf{C_{3h}}$; m) $\mathbf{D_3}$; n) $\mathbf{C_{2v}}$; o) $\mathbf{D_{4h}}$; p) $\mathbf{C_{3v}}$; q) $\mathbf{C_{2v}}$; r) $\mathbf{D_{2h}}$; s) $\mathbf{C_1}$; t) $\mathbf{D_{\infty h}}$; u) $\mathbf{D_{4d}}$; v) $\mathbf{C_3}$; w) $\mathbf{C_s}$; x) $\mathbf{S_4}$; y) $\mathbf{T_h}$; z) $\mathbf{D_{3h}}$

4) It is possible to pack triangles, squares, and hexagons in a close packed 2-dimensional array but not pentagons: See figure on following page.

5) $C_2, C_3, C_4,$ and C_6; note: the C_4 requires the possibility of $\hat{C}_4^2 = \hat{C}_2$.