J. Am. Chem. Soc. **1980**, *102*, 4615–4622

Classification of Molecular Symmetry by Framework Groups

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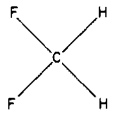
Abstract: The concept of a *framework group* is introduced to specify the full symmetry properties of a molecular structure. This specifies not only the geometrical symmetry operations of the point group but also the location of the nuclei with respect to symmetric subspaces such as central points, rotation axes, and reflection planes. A notation for framework groups is proposed. An algorithm is given for generation of all framework groups possible for a molecule of given composition. Full tabulation is given for small molecules.

Introduction

The description of molecular symmetry in terms of the point group of the nuclear framework is commonplace.[1,2] However, the symmetry information about a molecule provided in this way is frequently incomplete. One particular point group may correspond to several distinguishable nuclear arrangements which behave quite differently when the symmetry operations of the group are applied. Consider, for example, planar (**1**) and perpendicular (**2**) structures for difluoromethane, each having symmetrical (isosceles triangle) CF_2 and CH_2 groups with a common axis. Both of these structures belong to the point group C_{2v} (with a twofold rotation axis C_2 and two reflection planes σ_v, and σ_v'), but they differ in the way in which the hydrogen and fluorine nuclei are arranged in the planes. As a consequence, the nuclei behave differently under the reflection operations. For example, if σ_v is the CF_2 plane, reflection in σ_v leaves all nuclei unmoved in **1** but interchanges the two hydrogen nuclei in **2**. These differences would be reflected in various physical measurements. In **1**, there are two distinct H–F distances whereas in **2**, all such distances are equal. This would lead, for example, to different electron diffraction patterns. **1** and **2** would also have different types of nuclear magnetic resonance spectra since **1** has two distinguishable H–F spin-coupling constants (cis and trans) whereas **2** has only one. Structures such as **1** and **2** would also have different numbers of vibrations of a given symmetry type. Herzberg has published extensive tables of possible vibrational symmetries for most point groups.[1] It is clearly desirable to distinguish all cases such as 1 and 2 in a systematic theory of molecular symmetry.



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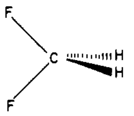

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The reason for these limitations of current group-theoretical classification is that point group specification is an unduly coarse method of conveying symmetry information. The point groups specify the symmetry properties of a general body of finite extension and apply to all types of bodies including those with a continuous distribution of matter. If the body consists of only a finite number of particles, further classification becomes possible. Such a body may be called a *framework* and its set of symmetry elements then constitutes a *framework group.* Complete specification of these symmetry elements would include the geometrical transformation (rotation, reflection, etc.) *and* information about the way particles are permuted by the operation. Structures **1** and **2** above would then belong to the same point group but to different framework groups. The first objective of this paper is to develop this concept and to provide a convenient notation for complete specification of the symmetry properties of any molecular structure.

A second objective is the systematic enumeration of all distinguishable framework groups for a molecule of given composition. Although all possibilities are easily written down by inspection for the smallest molecules, an orderly description is desirable for larger systems where many structures may have to be considered. We shall develop an algorithm for such enumeration in the general case and give explicit tabulations for molecules containing up to six atoms.

General Notation for Nuclear Framework Symmetry

Before proceeding to a precise definition of a framework group, we shall develop a notation for molecular symmetry which conveys more information than the point group itself. (We shall use the Schonflies notation for point groups throughout this paper with boldface italic type, e.g. C_{2v}, for the groups themselves.) As mentioned in the introduction, a full description of molecular symmetry also requires specification of nuclear positions relative to the symmetry elements of the point group.

For this purpose, we note that all nuclear framework structures (except those with completely asymmetric structures belonging to the point group C_1) are associated with some of the following features: (i) a unique central point which will be denoted by the symbol O, (ii) one or more rotation axes denoted by C_n where n is the order of the rotation, and (iii) one or more reflection planes denoted by σ. It is useful to divide the full three-dimensional space up into a number of subspaces on the basis of these features. The subspace consisting of a central point by itself will be denoted by O. Such points occur as centers of inversion, intersection of two rotational axes, or intersection of a rotation axis with a reflection or rotation–reflection plane. Next, a linear subspace C_n is defined as all points on the axis of the rotation operation C_n except for a central point O, should such exist. A planar subspace σ is similarly defined as all points in the plane of the reflection operation σ other than a center O or points on any rotational axis. These spaces may all be described as *symmetric subspaces* of the full three-dimensional space. Finally, the remaining part of the full space, external to all of the symmetric subspaces, will be denoted by the symbol X. It should be emphasized that these subspaces do not overlap so that every point in the full space belongs to one and only one subspace.

We begin the discussion of molecular symmetry by cataloging the symmetric subspaces for all of the point groups. These are listed in the first two columns of Table I. It should be noted that this is not the same as a listing of the symmetry operations of the group although the notation is chosen so that the correspondence is as close as possible. In the discussion of this table, it is convenient to treat first the point groups without rotational axes of an order greater than 2 ($n \leq 2$). At the beginning, C_s has just one reflection plane σ, so that the full space is spanned by the subspaces σ and X. C_i has just one center of inversion O, so that

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[1] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, 1945.

[2] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1997 (1955).

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Table I. Symmetric Subspaces and k values

group	subspaces	k values
C_1	X	1
C_s	σ, X	1, 2
C_i	O, X	1, 2
C_n	C_n, X	1, n
C_{2v}	$C_2, \sigma_v, \sigma_v', X$	1, 2, 2, 4
C_{nv} (n odd)	$C_n, n\sigma_v, X$	1, n, 2n
C_{nv} (n even, >2)	$C_n, {}^1/_2 n\sigma_v, {}^1/_2 n\sigma_d, X$	1, n, n, 2n
C_{nh}	O, C_n, σ_h, X	1, 2, n, 2n
S_{2n}	O, C_n, X	1, 2, 2n
D_n (n odd)	O, C_n, nC_2, X	1, 2, n, 2n
D_n (n even)	$O, C_n, {}^1/_2 nC_2', {}^1/_2 nC_2'', X$	1, 2, n, n, 2n
D_{nd}	$O, C_n, nC_2', n\sigma_d, X$	1, 2, 2n, 2n, 4n
D_{2h}	$O, C_2, C_2', C_2'', \sigma, \sigma', \sigma'', X$	1, 2, 2, 2, 4, 4, 4, 8
D_{nh} (n odd)	$O, C_n, nC_2, \sigma_h, n\sigma_v, X$	1, 2, n, 2n, 2n, 4n
D_{nh} (n even, >2)	$O, C_n, {}^1/_2 nC_2', {}^1/_2 nC_2'', \sigma_h, {}^1/_2 n\sigma_v, {}^1/_2 n\sigma_d, X$	1, 2, n, n, 2n, 2n, 2n, 4n
T	$O, 4C_3, 3C_2, X$	1, 4, 6, 12
T_d	$O, 4C_3, 3C_2, 6\sigma_d, X$	1, 4, 6, 12, 24
T_h	$O, 4C_3, 3C_2, 3\sigma_h, X$	1, 8, 6, 12, 24
O	$O, 3C_4, 4C_3, 6C_2, X$	1, 6, 8, 12, 24
O_h	$O, 3C_4, 4C_3, 6C_2, 6\sigma_d, 3\sigma_h, X$	1, 6, 8, 12, 24, 24, 48
I	$O, 6C_5, 10C_3, 15C_2, X$	1, 12, 20, 30, 60
I_h	$O, 6C_5, 10C_3, 15C_2, 15\sigma, X$	1, 12, 20, 30, 60, 120
$C_{\infty v}$	$C_\infty, \infty\sigma_v$	1, ∞
$D_{\infty h}$	$O, C_\infty, \infty C_2, \infty\sigma_v$	1, 2, ∞, ∞

the subspaces are O and X. Similarly C_2 has one twofold rotation axis C_2, with subspaces C_2 and X. The next point group C_{2v} has two perpendicular reflection planes σ_v and σ_v' intersecting in an axis C_2[4]. This leads to the four subspaces C_2, σ_v, σ_v', and X. C_{2h} has a reflection plane σ_h perpendicular to a twofold axis C_2, the intersection being a center of inversion O. Thus, there are four subspaces O, C_2, σ_h, and X. The next point group is S_4 (S_{2n} with $n = 2$). This also has a single twofold rotation axis (although it is also a fourfold rotation–reflection axis). The intersection of this twofold axis and the rotation–reflection plane gives a unique central point O which is *not* a center of inversion. There are just three subspaces, O, C_2, and X. Note that the plane of the rotation–reflection operation is not used in defining a subspace as it is not a genuine reflection plane. The next group is D_2 (D_n with $n = 2$). This has three mutually perpendicular twofold rotation axes, denoted by C_2, C_2', C_2'', which meet in a central point O, also not a center of inversion. Since there are no reflection planes, there are five subspaces O, C_2, C_2', C_2'', and X. The point group D_{2d} (D_{nd} with $n = 2$) has the symmetry elements of D_2 plus two reflection operations involving planes σ_d which contain the axis C_2 but bisect the angle between the other two axes. For this point group, these other two twofold axes are denoted by $2C'_2$ (rather than C_2', C_2'') because they are *equivalent*, that is convertible into each other by symmetry operations of the group. The reflection planes are also equivalent and written as $2\sigma_d$. Thus, the subspaces are O, C_2, $2C_2'$, $2\sigma_d$, and X. After this comes the group D_{2h}, which has three perpendicular reflection planes, each perpendicular to one of the twofold axes. We take the pairs (C_2,σ), (C_2',σ'), and (C_2'',σ'') to be perpendicular.[3] The corresponding set of subspaces is O, C_2, C_2', C_2'', σ, σ', σ'', and X.

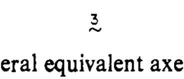
We next consider the higher uniaxial and dihedral groups C_n, C_{nv}, C_{nh}, S_{2n}, D_n, D_{nd}, and D_{nh} for $n > 2$. For some of these, the subspaces are different for odd and even values of n. If n is odd, the point group C_{nv} has n equivalent reflection planes σ_v. For even n, on the other hand, C_{nv} has two sets of ${}^1/_2 n$ equivalent reflection planes σ_v and σ_d. For C_n, C_{nh}, and S_{2n} the subspaces are similar to those already noted for $n = 2$. For D_n, odd and even n again have to be distinguished. For all n, there is one n-fold rotation axis C_n and n twofold axes perpendicular to C_n. If n is odd, the latter are all equivalent, but for even n, they split into two separate sets ${}^1/_2 nC_2'$ and ${}^1/_2 nC_2''$. (Note these are denoted by C_2 and C_2' in ref 1 and 2. We shall use C_2' and C_2'' to allow a common notation for all D_n with even n.) For the group D_{nd}, all the twofold axes are equivalent ($n > 2$) as are all the reflection planes. Finally D_{nh} has different properties for odd and even n in a manner similar to C_{nv} and D_n. For all these groups, the subspaces are easily tabulated in the same way as for groups with $n \leq 2$.

The next entries in Table I are the polyhedral groups T, T_d, T_h, O, O_h, I, and I_h. The tetrahedral group T has four threefold axes and three twofold axes, all meeting at a central point. In addition, T_d has six reflection planes σ_d, each containing two threefold axes. T_h has three reflection planes σ_h, each containing two threefold axes. The octahedral group O has three fourfold axes, four threefold axes, and six twofold axes. O_h also has six reflection planes σ each containing two threefold axes, and three reflection planes σ_h, each containing two fourfold axes. The icosahedral group I has six fivefold axes, ten threefold axes, and fifteen twofold axes. In addition, I_h has fifteen reflection planes σ. Again, the subspaces are as indicated in the second column.

To complete the first two columns of Table I, we add the groups $C_{\infty v}$ and $D_{\infty h}$ corresponding to linear molecules. For $C_{\infty v}$, all planes σ_v containing the ∞-fold rotation axis C_∞ are included. For the group $D_{\infty h}$, there is also an inversion center O, an infinite number of twofold axes perpendicular to C_∞ and a reflection plane σ_h. The latter two spaces coincide and are not distinguished. For these groups, there is no residual space X.

We can now specify a full notation for molecular symmetry. In addition to the point group, we list the symmetry subspaces from Table I. To this list, we add the symbol X at the end to denote the remaining asymmetric part of the full three-dimensional space. We enclose these subspaces in brackets following the point group symbol. The group C_{2v}, for example, is then listed as $C_{2v}[C_2,\sigma_v,\sigma_v',X]$. Individual nuclei in a molecule with this symmetry are now assigned to the subspace which contains them. They may be listed in parentheses following the subspace symbol. Thus structure **1** for difluoromethane has symmetry $C_{2v}[C_2(\mathrm{C}),\sigma_v(\mathrm{F_2H_2}),\sigma_v',X]$ while the perpendicular form **2** is specified by $C_{2v}[C_2(\mathrm{C}),\sigma_v(\mathrm{F_2}),\sigma_v'(\mathrm{H_2}),X]$. Note that we have followed the convention[3] of assigning the symbol σ_v to the molecular plane in **1**.

The notation can be shortened by omitting those subspaces to which no nuclei are assigned. **1** and **2** are then represented by $C_{2v}[C_2(\mathrm{C}),\sigma_v(\mathrm{F_2H_2})]$ and $C_{2v}[C_2(\mathrm{C}),\sigma_v(\mathrm{F_2}),\sigma_v'(\mathrm{H_2})]$, respectively. An example with nuclei in asymmetric positions is ethylene oxide (**3**), for which the symmetry notation is $C_{2v}[C_2(\mathrm{O}),\sigma_v(\mathrm{C_2}),X(\mathrm{H_4})]$.



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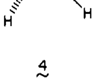
For molecules with several equivalent axes or planes, we list only the set of nuclei in one of the equivalent subspaces. For example, the symmetries of ammonia (**4**) and cyclopropane (**5**) are denoted



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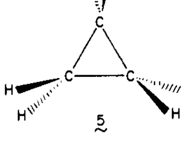

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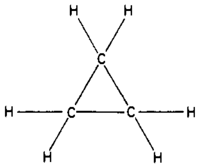
(3) To avoid ambiguity it is desirable to relate the notation to that discussed by Herzberg and Mulliken (HM) in ref 1 and 2. We shall not specify cartesian axes for any group. For C_{2v}, the symbol σ_v is used for $\sigma_v(yz)$ of HM and corresponds to the plane of planar C_{2v} molecules. For D_{2h}, we take C_2, C_2', and O_2'' to correspond to $C_2(x)$, $C_2(y)$, and $C_2(z)$ of HM and σ, σ', and σ'' to correspond to $\sigma(yz)$, $\sigma(zx)$, and $\sigma(xy)$ of HM, respectively. σ is then the molecular plane of planar D_{2h} molecules.

Table II. $(i_1 \ldots i_s)$ Sets for i = 1, 2, and 3

group	s	i		
		1	2	3
C_1	1	(1)	(2)	(3)
C_s	2	(10)	(01)(20)	(11)(30)
C_i	2	(10)	(01)	(11)
C_2	2	(10)	(01)(20)	(11)(30)
C_{2v}	4	(1000)	(0010)(0100)(2000)	(1010)(1100)(3000)
C_{2h}	4	(1000)	(0010)(0100)	(1010)(1100)
S_4	3	(100)	(010)	(110)
D_2	5	(10000)	(00010)(00100)(01000)	(10010)(10100)(11000)
D_{2d}	5	(10000)	(01000)	(11000)
D_{2h}	8	(10000000)	(00010000)(00100000)(01000000)	(10010000)(10100000)(11000000)
C_3	2	(10)	(20)	(01)(30)
C_{3v}	3	(100)	(200)	(010)(300)
C_{3h}	4	(1000)	(0100)	(0010)(1100)
S_6	3	(100)	(010)	(110)
D_3	4	(1000)	(0100)	(0010)(1100)
D_{3d}	5	(10000)	(01000)	(11000)
D_{3h}	6	(100000)	(010000)	(001000)(110000)
T	4	(1000)		
T_d	5	(10000)		
$C_{\infty v}$	3	(10)	(20)	(30)
$D_{\infty h}$	5	(10000)	(01000)	(11000)

by $C_{3v}[C_3(\mathrm{N}),3\sigma_v(\mathrm{H})]$ and $D_{3h}[3C_2(\mathrm{C}),3\sigma_v(\mathrm{H}_2)]$, respectively. The symbols $3\sigma_v(\mathrm{H}_2)$ are to be interpreted as "three equivalent σ_v subspaces each containing two hydrogen nuclei". Alternative D_{3h} structures for C_3H_6 such as the planar forms **6** and **7** would



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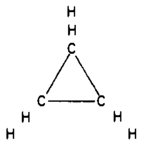

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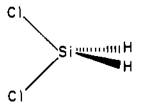
be denoted by $D_{3h}[3C_2(\mathrm{C}),\sigma_h(\mathrm{H}_6)]$ and $D_{3h}[3C_2(\mathrm{CH}_2)]$, respectively.

Framework Groups

Suppose that we are dealing with a nuclear framework A_iB_j..., containing i nuclei of type A, j nuclei of type B, ... The symmetry properties of the molecule do not depend on the actual nature of the nuclei A, B, ... but only on the numbers i, j, ... present of different types. For example, difluoromethane (**2**) and dichlorosilane (**8**) have exactly the same framework symmetry



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properties. Both belong to the general composition AB_2C_2 and both have symmetries which may be described by $C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{B}_2),\sigma_v'(\mathrm{C}_2)]$.

Framework groups are now introduced to describe the full symmetry properties of a framework with a given composition A_iB_j..., specified by the set of integers i, j, ... Molecules with different sets i, j, ... will belong to different framework groups. Since all frameworks can be treated as general bodies, each framework group represents a subclassification of a point group. The elements of a framework group are specified in two parts: (a) as geometrical operations (rotations, reflections, etc.) and (b) as consequent permutations of nuclei of the same type. The classification beyond that of the point group arises because of b.

The permutations that the nuclei undergo upon application of the geometrical symmetry operations depend precisely on the subspaces to which they are assigned. We may, therefore, identify the framework group by the notation introduced in the previous section. Thus, $C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{B}_2),\sigma_v'(\mathrm{C}_2)]$ becomes the label of the framework group to which **2** and **8** belong. The elements of this group are as follows: (1) the identify E, leaving all nuclei unchanged, (2) the twofold rotation C_2, permuting both pairs B_2 and C_2, (3) the reflection σ_v, permuting the pair C_2, and (4) the reflection σ_v', permuting the pair B_2. The planar structure **1**, on the other hand, belongs to the framework group $C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{B}_2\mathrm{C}_2)]$, the elements of which are as follows: (1) the identity E, leaving all nuclei unchanged, (2) the twofold rotation C_2, permuting both pairs B_2 and C_2, (3) the reflection σ_v, leaving all nuclei unchanged, and (4) the reflection σ_v', permuting both pairs B_2 and C_2.

Both of these framework groups are clearly isomorphic with the point group C_{2v} since the elements combine in the same multiplicative way. However, since they differ in the permutational part of the element specification, the two groups are distinguished. Two structures will be said to belong to the same framework group only if all elements are identical apart from simple relabeling such as interchanges of the symbols B and C or σ_v and σ_v' in the example given.

Nuclear Arrangements of One Species for All Point Groups

As a preliminary to the generation of full lists of framework groups, we shall consider the problem of finding all ways in which i nuclei of species A can be incorporated into a molecule for which the full point group is specified. In any symmetrical molecule, each nucleus of type A belongs to a set of k (≥ 1) equivalent A nuclei which are permuted in some manner by the various symmetry operations of the point group. The value of k depends on the location of the nuclei within the molecule (at a central point, on a rotation axis, in a reflection plane, or in an asymmetric position). For example, in a molecule with C_s symmetry (one reflection plane σ), nuclei may lie in σ as unique atoms (k = 1) or in asymmetric positions as pairs related by reflection in σ (k = 2). In other words, all nuclei in the symmetric subspace σ have k = 1 while all others in the residual asymmetric space X have k = 2. This information is listed in the final column of Table I.

Corresponding series of k values are listed for all the point groups in Table I, ordered in the same way as the subspaces in the preceding column. In all cases, the final entry applies to the residual asymmetric space X and is equal to the order of the point group. All of the k values listed in Table I follow directly from application of the symmetry operations. This may be illustrated by the point group D_{3h}. If a nucleus is at the center O, it is unmoved by all operations of the group so that k = 1. If one nucleus lies on the threefold axis above the center, there must be another symmetrically below because of the σ_h reflection operation. Hence the C_3 subspace has k = 2. If a nucleus is on one of the twofold axes (but not at the center), there must be nuclei at similar

Table III. A_i Framework Groups

point group	$(i_1 \ldots i_8)$	framework group	descriptn
		A_2 Molecules	
$D_{\infty h}$	(0100)	$D_{\infty h}[C_\infty(\mathrm{A}_2)]$	
		A_3 Molecules	
C_s	(30)	$C_s[\sigma(\mathrm{A}_3)]$	
C_{2v}	(1010)	$C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{A}_2)]$	isoceles triangle
D_{3h}	(001000)	$D_{3h}[3C_2(\mathrm{A})]$	equilateral triangle
$C_{\infty v}$	(30)	$C_{\infty v}[C_\infty(\mathrm{A}_3)]$	linear
$D_{\infty h}$	(1100)	$D_{\infty h}[O(\mathrm{A}),C_\infty(\mathrm{A}_2)]$	symmetric linear
		A_4 Molecules	
C_1	(4)	$C_1[X(\mathrm{A}_4)]$	
C_s	(21)	$C_s[\sigma(\mathrm{A}_2),X(\mathrm{A}_2)]$	nonplanar
	(40)	$C_s[\sigma(\mathrm{A}_4)]$	planar
C_2	(02)	$C_2[X(\mathrm{A}_4)]$	
C_{2v}	(0020)	$C_{2v}[\sigma_v(\mathrm{A}_4)]$	planar
	(0110)	$C_{2v}[\sigma_v(\mathrm{A}_2),\sigma_v'(\mathrm{A}_2)]$	nonplanar
	(2010)	$C_{2v}[C_2(\mathrm{A}_2),\sigma_v(\mathrm{A}_2)]$	planar
C_{2h}	(0020)	$C_{2h}[\sigma_h(\mathrm{A}_4)]$	parallelogram
D_2	(00001)	$D_2[X(\mathrm{A}_4)]$	twisted rectangle
D_{2d}	(00010)	$D_{2d}[2\sigma_d(\mathrm{A}_2)]$	
D_{2h}	(00000010)	$D_{2h}[\sigma(\mathrm{A}_4)]$	rectangle
	(00110000)	$D_{2h}[C_2(\mathrm{A}_2),C_2'(\mathrm{A}_2)]$	rhombus
C_{3v}	(110)	$C_{3v}[C_3(\mathrm{A}),3\sigma_v(\mathrm{A})]$	trigonal pyramid
D_{3h}	(101000)	$D_{3h}[O(\mathrm{A}),3C_2(\mathrm{A})]$	trigonal planar + center
D_{4h}	(00010000)	$D_{4h}[2C_2(\mathrm{A}_2)]$	square planar
T_d	(01000)	$T_d[4C_3(\mathrm{A})]$	regular tetrahedron
$C_{\infty v}$	(40)	$C_{\infty v}[C_\infty(\mathrm{A}_4)]$	linear
$D_{\infty h}$	(0200)	$D_{\infty h}[C_\infty(\mathrm{A}_4)]$	symmetric linear
		A_5 Molecules	
C_1	(5)	$C_1[X(\mathrm{A}_5)]$	
C_s	(12)	$C_s[\sigma(\mathrm{A}),X(\mathrm{A}_4)]$	
	(31)	$C_s[\sigma(\mathrm{A}_3),X(\mathrm{A}_2)]$	
	(50)	$C_s[\sigma(\mathrm{A}_5)]$	planar
C_2	(12)	$C_2[C_2(\mathrm{A}),X(\mathrm{A}_4)]$	
C_{2v}	(1001)	$C_{2v}[C_2(\mathrm{A}),X(\mathrm{A}_4)]$	rectangular pyramid
	(1020)	$C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{A}_4)]$	planar
	(1110)	$C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{A}_2),\sigma_v'(\mathrm{A}_2)]$	nonplanar
	(3010)	$C_{2v}[C_2(\mathrm{A}_3),\sigma_v(\mathrm{A}_2)]$	planar
C_{2h}	(1020)	$C_{2h}[O(\mathrm{A}),\sigma_h(\mathrm{A}_4)]$	parallelogram + center
D_2	(10001)	$D_2[O(\mathrm{A}),X(\mathrm{A}_4)]$	twisted rectangle + center
D_{2d}	(10010)	$D_{2d}[O(\mathrm{A}),2\sigma_d(\mathrm{A}_2)]$	
D_{2h}	(10000010)	$D_{2h}[O(\mathrm{A}),\sigma(\mathrm{A}_4)]$	rectangle + center
	(10110000)	$D_{2h}[O(\mathrm{A}),C_2(\mathrm{A}_2),C_2'(\mathrm{A}_2)]$	rhombus + center
C_{3v}	(210)	$C_{3v}[C_3(\mathrm{A}_2),3\sigma_v(\mathrm{A})]$	
D_{3h}	(011000)	$D_{3h}[C_3(\mathrm{A}_2),3C_2(\mathrm{A})]$	trigonal bipyramid
C_{4v}	(1010)	$C_{4v}[C_4(\mathrm{A}),2\sigma_v(\mathrm{A}_2)]$	square pyramid
D_{4h}	(10010000)	$D_{4h}[O(\mathrm{A}),2C_2(\mathrm{A}_2)]$	square + center
D_{5h}	(001000)	$D_{5h}[5C_2(\mathrm{A})]$	regular pentagon
T_d	(11000)	$T_d[O(\mathrm{A}),4C_3(\mathrm{A})]$	tetrahedron + center
$C_{\infty v}$	(50)	$C_{\infty v}[C_\infty(\mathrm{A}_5)]$	linear
$D_{\infty h}$	(1200)	$D_{\infty h}[O(\mathrm{A}),C_\infty(\mathrm{A}_4)]$	symmetric linear
		A_6 Molecules	
C_1	(6)	$C_1[X(\mathrm{A}_6)]$	
C_s	(03)	$C_s[X(\mathrm{A}_6)]$	
	(22)	$C_s[\sigma(\mathrm{A}_2),X(\mathrm{A}_4)]$	
	(41)	$C_s[\sigma(\mathrm{A}_4),X(\mathrm{A}_2)]$	
	(60)	$C_s[\sigma(\mathrm{A}_6)]$	planar
C_i	(03)	$C_i[X(\mathrm{A}_6)]$	
C_2	(03)	$C_2[X(\mathrm{A}_6)]$	
	(22)	$C_2[C_2(\mathrm{A}_2),X(\mathrm{A}_4)]$	
C_{2v}	(0011)	$C_{2v}[\sigma(\mathrm{A}_2),X(\mathrm{A}_4)]$	
	(0030)	$C_{2v}[\sigma_v(\mathrm{A}_6)]$	
	(0120)	$C_{2v}[\sigma_v(\mathrm{A}_4),\sigma_v'(\mathrm{A}_2)]$	
	(2001)	$C_{2v}[C_2(\mathrm{A}_2),X(\mathrm{A}_4)]$	
	(2020)	$C_{2v}[C_2(\mathrm{A}_2),\sigma_v(\mathrm{A}_4)]$	planar
	(2110)	$C_{2v}[C_2(\mathrm{A}_2),\sigma_v(\mathrm{A}_2),\sigma_v'(\mathrm{A}_2)]$	
	(4010)	$C_{2v}[C_2(\mathrm{A}_4),\sigma_v(\mathrm{A}_2)]$	planar
C_{2h}	(0011)	$C_{2h}[\sigma_h(\mathrm{A}_2),X(\mathrm{A}_4)]$	
	(0030)	$C_{2h}[\sigma_h(\mathrm{A}_6)]$	planar
	(0120)	$C_{2h}[C_2(\mathrm{A}_2),\sigma_h(\mathrm{A}_4)]$	
D_2	(00011)	$D_2[C_2(\mathrm{A}_2),X(\mathrm{A}_4)]$	
D_{2d}	(01010)	$D_{2d}[C_2(\mathrm{A}_2),2\sigma_d(\mathrm{A}_2)]$	
D_{2h}	(00010010)	$D_{2h}[C_2(\mathrm{A}_2),\sigma(\mathrm{A}_4)]$	rectangular bipyramid
	(00010100)	$D_{2h}[C_2'(\mathrm{A}_2),\sigma(\mathrm{A}_4)]$	planar
	(00120000)	$D_{2h}[C_2(\mathrm{A}_4),C_2'(\mathrm{A}_2)]$	

Table III. (*continued*)

point group	$(i_1 \ldots i_8)$	framework group	descriptn
	(01110000)	$D_{2h}[C_2(A_2),C_2'(A_2),C_2''(A_2)]$	
C_3	(02)	$C_3[X(A_6)]$	
C_{3v}	(020)	$C_{3v}[3\sigma_v(A_2)]$	
	(310)	$C_{3v}[C_3(A_3),3\sigma_v(A)]$	
C_{3h}	(0020)	$C_{3h}[\sigma_h(A_6)]$	
D_3	(0001)	$D_3[X(A_6)]$	twisted trigonal prism
D_{3d}	(00010)	$D_{3d}[3\sigma_d(A_2)]$	trigonal antiprism
D_{3h}	(000010)	$D_{3h}[3\sigma_v(A_2)]$	trigonal prism
	(000100)	$D_{3h}[\sigma_h(A_6)]$	
	(002000)	$D_{3h}[3C_2(A_2)]$	
	(111000)	$D_{3h}[O(A),C_3(A_2),3C_2(A)]$	trigonal bipyramid + center
C_{4v}	(2010)	$C_{4v}[C_4(A_2),2\sigma_v(A_2)]$	
D_{4h}	(01010000)	$D_{4h}[C_4(A_2),2C_2(A_2)]$	square bipyramid
C_{5v}	(110)	$C_{5v}[C_5(A),5\sigma_v(A)]$	pentagonal pyramid
D_{5h}	(101000)	$D_{5h}[O(A),5C_2(A)]$	regular pentagon + center
D_{6h}	(00010000)	$D_{6h}[3C_2(A_2)]$	regular hexagon
O_h	(010000)	$O_h[3C_4(A_2)]$	regular octahedron
$C_{\infty v}$	(60)	$C_{\infty v}[C_\infty(A_6)]$	linear
$D_{\infty h}$	(0300)	$D_{\infty h}[C_\infty(A_6)]$	symmetric linear

positions on the other twofold axes (by application of the threefold rotations). Hence, $k = 3$. If there are atoms in the σ_h plane not on twofold axes, then $k = 6$ by application of threefold rotations and σ_v reflections. In the σ_v reflection planes away from rotation axes, the value of k is also 6 by virtue of threefold rotation and σ_h reflection. Finally, if there is an atom in a completely asymmetric position, the full set must contain 12 equivalent atoms by application of all the group operations. Similar arguments are easily applied to all other finite point groups. The groups $\boldsymbol{C}_{\infty v}$ and $\boldsymbol{D}_{\infty h}$ can be handled in a similar manner, the principal difference being that $k = \infty$ for all points off the axis.

We now return to the general problem of enumerating all possible arrangements of i nuclei of species A if the point group G is prescribed. If the possible k values for G (from Table I) are $k_1, k_2, ..., k_s$, then we must list all sets of integers, $i_1, i_2, ..., i_s$ (≥ 0) such that

$$\Sigma = i \qquad (1)$$

where

$$\Sigma = i_1k_1 + i_2k_2 + ... + i_sk_s \qquad (2)$$

If the point group has a central point O, the value of i_1 is restricted to zero or one since two nuclei cannot occupy the same point in space. There are no other restrictions apart from the requirement (1).

All possible $(i_1i_2...i_s)$ sets satisfying (1) may be enumerated sequentially by the following procedure. Begin testing with $i_1 = i_2 = ... = i_s = 0$ and increment i_s by one until the Σ becomes equal to or greater than i. If equality is found, the $(i_1i_2...i_s)$ set is placed in the list of solutions of (1). Next increment i_{s-1} by one and repeat the increments of i_s from zero as before. After all solutions with $i_1 = i_2 = ... = i_{s-2} = 0$ have been found in this way, increment i_{s-2} by one and repeat the increments of i_{s-1} and i_s in the same way. At each stage, if an equality is found for (1), the $(i_1i_2...i_s)$ set is added sequentially to the list. The process terminates when i_1 is incremented to i.

As an example, consider the point group C_s with $i = 3$. The k values are $k_1 = 1$ and $k_2 = 2$ (Table I). The (i_1i_2) sets are tested in the order beginning (00), (01), and (02) giving Σ values of 0, 2, and 4 from (2). Σ is now greater than i so the search proceeds with (10) and (11). (11) leads to $\Sigma = 3$, so this is the first solution. Next (20) and (21) are tried giving $\Sigma = 2$ and 4 again leading to $\Sigma > i$. Finally (30) gives $\Sigma = 3$ leading to a second and final solution. The ordered set of solutions is therefore (11) and (30).

A partial list of the $(i_1...i_s)$ sets for $i = 1$, 2, and 3 is given in Table II. Fuller tables are easily written down or generated by computer program. It is worth noting at this point that no solutions of (1) exist for some i and some point groups. For example, there are no solutions for $i = 2$ or 3 with the tetrahedral groups $\boldsymbol{T}$ or $\boldsymbol{T}_d$. This implies that no molecule with 2 or 3 atoms of any species can have a structure belonging to either of these point groups.

Enumeration of Framework Groups for Elemental Molecules A_i

We now turn to the main problem of enumerating all possible framework groups for a molecule of given composition, beginning with systems A_i containing only i nuclei of one type. This will be accomplished by considering all point groups in turn and then enumerating the structures for each. This requires a prescribed sequential order for the point groups. We shall begin with $\boldsymbol{C}_1$, $\boldsymbol{C}_s$, and $\boldsymbol{C}_i$ and then proceed through $\boldsymbol{C}_n$, $\boldsymbol{C}_{nv}$, $\boldsymbol{C}_{nh}$, $\boldsymbol{S}_{2n}$, $\boldsymbol{D}_n$, $\boldsymbol{D}_{nd}$, $\boldsymbol{D}_{nh}$ first for $n = 2$, then for $n = 3$, and so forth. This may be terminated at $n = i$, since the molecule A_i cannot have a rotation axis of order higher than i unless it is linear. Next we proceed through the polyhedral groups $\boldsymbol{T}$, $\boldsymbol{T}_d$, $\boldsymbol{T}_h$, $\boldsymbol{O}$, $\boldsymbol{O}_h$, $\boldsymbol{I}$, and $\boldsymbol{I}_h$ and finally consider the groups $\boldsymbol{C}_{\infty v}$ and $\boldsymbol{D}_{\infty h}$ appropriate to linear molecules.

Within a particular point group G, we can consider all possible arrangements of i nuclei (of type A) in terms of the integer sets $(i_1...i_s)$ obtained in the previous section. This gives an ordered list of structures $G(i_1...i_s)$. However, this list is too large and some of the entries have to be eliminated to get a final list of molecular symmetries for the point group G. There are two reasons for this, leading to two elimination rules.

In the first place, we note that each arrangement of A nuclei $(i_1...i_s)$ does not *by itself* establish that G is the point group appropriate to the molecule. The $(i_1...i_s)$ arrangements rather identify ways in which the A nuclei can be incorporated into a larger molecule with point group G. By themselves, the A nuclei may correspond to a structure with higher symmetry than G. Under these circumstances, the structure $G(i_1...i_s)$ is eliminated from the list. This is the first elimination rule.

The second reason for eliminating structures is that two may differ only by insignificant redefinition of symmetry elements. In the group $\boldsymbol{C}_{2v}$, for example, there are two reflection planes σ_v and σ_v'. Structures which differ only by redefining the plane σ_v as σ_v' and *vice versa* clearly have indistinguishable molecular symmetries. Consequently, the second rule is that any entry $G(i_1...i_s)$ is eliminated from the list if it is indistinguishable in the above sense from an earlier entry.

The generation of the list of framework groups may be illustrated by the simplest nontrivial case, triatomic molecules A_3. We begin with the group $\boldsymbol{C}_1$ ($s = 1$, $k_1 = 1$) for which the only $(i_1...i_s)$ set is (3), corresponding to three A nuclei in general positions. However, these nuclei must lie in a plane, so this structure actually has the higher symmetry $\boldsymbol{C}_s$. Thus $\boldsymbol{C}_1(3)$ is eliminated as a possible symmetry for the A_3 molecule by the first rule. Turning to the next group $\boldsymbol{C}_s$, possible $(i_1...i_s)$ sets are (11) or (30). $\boldsymbol{C}_s(11)$ would have one nucleus in σ and one pair related by reflection. Such a structure by itself is an isosceles triangle and clearly has $\boldsymbol{C}_{2v}$

Table IV. A_iB_j Framework Groups

point group	$(i_1 \ldots i_g)(j_1 \ldots j_g)$	framework group	descriptn
		AB Molecules	
$C_{\infty v}$	(10)(10)	$C_{\infty v}[C_{\infty}(\mathrm{AB})]$	linear
		$\mathrm{AB_2}$ Molecules	
C_s	(10)(20)	$C_s[\sigma(\mathrm{AB_2})]$	
C_{2v}	(1000)(0010)	$C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{B_2})]$	isosceles triangle
$C_{\infty v}$	(10)(20)	$C_{\infty v}[C_{\infty}(\mathrm{AB_2})]$	linear
$D_{\infty h}$	(1000)(0100)	$D_{\infty h}[O(\mathrm{A}),C_{\infty}(\mathrm{B_2})]$	symmetric linear
		$\mathrm{AB_3}$ Molecules	
C_1	(10)(3)	$C_1[X(\mathrm{AB_3})]$	
C_s	(10)(11)	$C_s[\sigma(\mathrm{AB}),X(\mathrm{B_2})]$	nonplanar
	(10)(30)	$C_s[\sigma(\mathrm{AB_3})]$	planar
C_{2v}	(1000)(1010)	$C_{2v}[C_2(\mathrm{AB}),\sigma_v(\mathrm{B_2})]$	planar
C_{3v}	(100)(010)	$C_{3v}[C_3(\mathrm{A}),3\sigma_v(\mathrm{B})]$	trigonal pyramid
D_{3h}	(100000)(001000)	$D_{3h}[O(\mathrm{A}),3C_2(\mathrm{B})]$	trigonal planar
$C_{\infty v}$	(10)(30)	$C_{\infty v}[C_{\infty}(\mathrm{AB_3})]$	linear
		$\mathrm{AB_4}$ Molecules	
C_1	(1)(4)	$C_1[X(\mathrm{AB_4})]$	
C_s	(10)(02)	$C_s[\sigma(\mathrm{A}),X(\mathrm{B_4})]$	
	(10)(21)	$C_s[\sigma(\mathrm{AB_2}),X(\mathrm{B_2})]$	
	(10)(40)	$C_s[\sigma(\mathrm{AB_4})]$	planar
C_2	(10)(02)	$C_2[C_2(\mathrm{A}),X(\mathrm{B_4})]$	
C_{2v}	(1000)(0001)	$C_{2v}[C_2(\mathrm{A}),X(\mathrm{B_4})]$	rectangular pyramid
	(1000)(0020)	$C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{B_4})]$	planar
	(1000)(0110)	$C_{2v}[C_2(\mathrm{A}),\sigma_v(\mathrm{B_2}),\sigma_v'(\mathrm{B_2})]$	nonplanar
	(1000)(1010)	$C_{2v}[C_2(\mathrm{AB_2}),\sigma_v(\mathrm{B_2})]$	planar
C_{2h}	(1000)(0020)	$C_{2h}[O(\mathrm{A}),\sigma_h(\mathrm{B_4})]$	parallelogram + center
D_2	(10000)(00001)	$D_2[O(\mathrm{A}),X(\mathrm{B_4})]$	
D_{2d}	(10000)(00010)	$D_{2d}[O(\mathrm{A}),2\sigma_d(\mathrm{B_2})]$	
D_{2h}	(10000000)(00000010)	$D_{2h}[O(\mathrm{A}),\sigma(\mathrm{B_4})]$	rectangle + center
	(10000000)(00110000)	$D_{2h}[O(\mathrm{A}),C_2(\mathrm{B_2}),C_2'(\mathrm{B_2})]$	rhombus + center
C_{3v}	(100)(110)	$C_{3v}[C_3(\mathrm{AB}),3\sigma_v(\mathrm{B})]$	
C_{4v}	(1000)(0010)	$C_{4v}[C_4(\mathrm{A}),2\sigma_v(\mathrm{B_2})]$	square pyramid
D_{4h}	(10000000)(00010000)	$D_{4h}[O(\mathrm{A}),2C_2(\mathrm{B_2})]$	square + center
T_d	(10000)(01000)	$T_d[O(\mathrm{A}),4C_3(\mathrm{B})]$	tetrahedron + center
$C_{\infty v}$	(10)(40)	$C_{\infty v}[C_{\infty}(\mathrm{AB_4})]$	linear
$D_{\infty h}$	(1000)(0200)	$D_{\infty h}[O(\mathrm{A}),C_{\infty}(\mathrm{B_4})]$	symmetric linear
		$\mathrm{AB_5}$ Molecules	
C_1	(1)(5)	$C_1[X(\mathrm{AB_5})]$	
C_s	(10)(12)	$C_s[\sigma(\mathrm{AB}),X(\mathrm{B_4})]$	
	(10)(31)	$C_s[\sigma(\mathrm{AB_3}),X(\mathrm{B_2})]$	
	(10)(50)	$C_s[\sigma(\mathrm{AB_5})]$	planar
C_2	(10)(12)	$C_2[C_2(\mathrm{AB}),X(\mathrm{B_4})]$	
C_{2v}	(1000)(1001)	$C_{2v}[C_2(\mathrm{AB}),X(\mathrm{B_4})]$	
	(1000)(1020)	$C_{2v}[C_2(\mathrm{AB}),\sigma_v(\mathrm{B_4})]$	planar
	(1000)(1110)	$C_{2v}[C_2(\mathrm{AB}),\sigma_v(\mathrm{B_2}),\sigma_v'(\mathrm{B_2})]$	
	(1000)(3010)	$C_{2v}[C_2(\mathrm{AB_3}),\sigma_v(\mathrm{B_2})]$	planar
C_{3v}	(100)(210)	$C_{3v}[C_3(\mathrm{AB_2}),3\sigma_v(\mathrm{B})]$	
D_{3h}	(100000)(011000)	$D_{3h}[O(\mathrm{A}),C_3(\mathrm{B_2}),3\sigma_v(\mathrm{B})]$	trigonal bipyramid + center
C_{4v}	(1000)(1010)	$C_{4v}[C_4(\mathrm{AB}),2\sigma_v(\mathrm{B_2})]$	
C_{5v}	(100)(010)	$C_{5v}[C_5(\mathrm{A}),5\sigma_v(\mathrm{B})]$	pentagonal pyramid
D_{5h}	(100000)(001000)	$D_{5h}[O(\mathrm{A}),5C_2(\mathrm{B})]$	regular pentagon + center
$C_{\infty v}$	(10)(50)	$C_{\infty v}[C_{\infty}(\mathrm{AB_5})]$	linear
		$\mathrm{A_2B_2}$ Molecules	
C_1	(2)(2)	$C_1[X(\mathrm{A_2B_2})]$	
C_s	(01)(20)	$C_s[\sigma(\mathrm{B_2}),X(\mathrm{A_2})]$	nonplanar
	(20)(20)	$C_s[\sigma(\mathrm{A_2B_2})]$	planar
C_2	(01)(01)	$C_2[X(\mathrm{A_2B_2})]$	
C_{2v}	(0010)(0010)	$C_{2v}[\sigma_v(\mathrm{A_2B_2})]$	planar
	(0010)(0100)	$C_{2v}[\sigma_v(\mathrm{A_2}),\sigma_v'(\mathrm{B_2})]$	nonplanar
	(0010)(2000)	$C_{2v}[C_2(\mathrm{B_2}),\sigma_v(\mathrm{A_2})]$	planar
C_{2h}	(0010)(0010)	$C_{2h}[\sigma_h(\mathrm{A_2B_2})]$	parallelogram
D_{2h}	(00010000)(00100000)	$D_{2h}[C_2(\mathrm{A_2}),C_2'(\mathrm{B_2})]$	rhombus
$C_{\infty v}$	(20)(20)	$C_{\infty v}[C_{\infty}(\mathrm{A_2B_2})]$	linear
$D_{\infty h}$	(0100)(0100)	$D_{\infty h}[C_{\infty}(\mathrm{A_2B_2})]$	symmetric linear
		$\mathrm{A_2B_3}$ Molecules	
C_1	(20)(3)	$C_1[X(\mathrm{A_2B_3})]$	
C_s	(01)(11)	$C_s[\sigma(\mathrm{B}),X(\mathrm{A_2B_2})]$	
	(01)(30)	$C_s[\sigma(\mathrm{B_3}),X(\mathrm{A_2})]$	
	(20)(11)	$C_s[\sigma(\mathrm{A_2B}),X(\mathrm{B_2})]$	
	(20)(30)	$C_s[\sigma(\mathrm{A_2B_3})]$	planar
C_2	(01)(11)	$C_2[C_2(\mathrm{B}),X(\mathrm{A_2B_2})]$	
C_{2v}	(0010)(1010)	$C_{2v}[C_2(\mathrm{B}),\sigma_v(\mathrm{A_2B_2})]$	planar
	(0010)(1100)	$C_{2v}[C_2(\mathrm{B}),\sigma_v(\mathrm{A_2}),\sigma_v'(\mathrm{B_2})]$	

Table IV. (*continued*)

point group	$(i_1 \ldots i_8)(j_1 \ldots j_8)$	framework group	descriptn
	(0010)(3000)	$C_{2v}[C_2(B_3),\sigma_v(A_2)]$	planar
	(2000)(1010)	$C_{2v}[C_2(A_2B),\sigma_v(B_2)]$	planar
C_{2h}	(0010)(1010)	$C_{2h}[O(B),\sigma_h(A_2B_2)]$	parallelogram + center
D_{2h}	(00010000)(10100000)	$D_{2h}[O(B),C_2(A_2),C_2'(B_2)]$	rhombus + center
C_{3v}	(200)(010)	$C_{3v}[C_3(A_2),3\sigma_v(B)]$	
D_{3h}	(010000)(001000)	$D_{3h}[C_3(A_2),3C_2(B)]$	trigonal bipyramid
$C_{\infty v}$	(20)(30)	$C_{\infty v}[C_\infty(A_2B_3)]$	linear
$D_{\infty h}$	(0100)(1100)	$D_{\infty h}[O(B),C_\infty(A_2B_2)]$	symmetric linear

Table V. $A_iB_jC_k$ and $A_iB_jC_kD_l$ Framework Groups

point group	framework group	descriptn
	ABC Molecules	
C_s	$C_s[\sigma(ABC)]$	
$C_{\infty v}$	$C_{\infty v}[C_\infty(ABC)]$	
	ABC_2 Molecules	
C_1	$C_1[X(ABC_2)]$	
C_s	$C_s[\sigma(AB),X(C_2)]$	nonplanar
	$C_s[\sigma(ABC_2)]$	planar
C_{2v}	$C_{2v}[C_2(AB),\sigma_v(C_2)]$	planar
$C_{\infty v}$	$C_\infty(ABC_2)]$	linear
	ABC_3 Molecules	
C_1	$C_1[X(ABC_3)]$	
C_s	$C_s[\sigma(ABC),X(C_2)]$	
	$C_3[\sigma(ABC_3)]$	planar
C_{2v}	$C_{2v}[C_2(ABC),\sigma_v(C_2)]$	planar
C_{3v}	$C_{3v}[C_3(AB),3\sigma_v(C)]$	
$C_{\infty v}$	$C_{\infty v}[C_\infty(ABC_3)]$	linear
	AB_2C_2 Molecules	
C_1	$C_1[X(AB_2C_2)]$	
C_s	$C_s[\sigma(A),X(B_2C_2)]$	
	$C_s[\sigma(AB_2),X(C_2)]$	
	$C_s[\sigma(AB_2C_2)]$	planar
C_2	$C_2[C_2(A),X(B_2C_2)]$	
C_{2v}	$C_{2v}[C_2(A),\sigma_v(B_2C_2)]$	planar
	$C_{2v}[C_2(A),\sigma_v(B_2),\sigma_v'(C_2)]$	
	$C_{2v}[C_2(AB_2),\sigma_v(C_2)]$	planar
C_{2h}	$C_{2h}[O(A),\sigma_h(B_2C_2)]$	parallelogram + center
D_{2h}	$D_{2h}[O(A),C_2(B_2),C_2'(C_2)]$	rhombus + center
$C_{\infty v}$	$C_{\infty v}[C_\infty(AB_2C_2)]$	linear
$D_{\infty h}$	$D_{\infty h}[O(A),C_\infty(B_2C_2)]$	symmetric linear
	ABCD Molecules	
C_1	$C_1[X(ABCD)]$	
C_s	$C_s[\sigma(ABCD)]$	
$C_{\infty v}$	$C_{\infty v}[C_\infty(ABCD)]$	linear
	$ABCD_2$ Molecules	
C_1	$C_1[X(ABCD_2)]$	
C_s	$C_s[\sigma(ABC),X(D_2)]$	
	$C_s[\sigma(ABCD_2)]$	planar
C_{2v}	$C_{2v}[C_2(ABC),\sigma_v(D_2)]$	planar
$C_{\infty v}$	$C_{\infty v}[C_\infty(ABCD_2)]$	linear

symmetry. $C_s(11)$ is, therefore, also eliminated by the first rule. $C_{\infty s}(30)$ is the general asymmetric structure with the three nuclei defining the reflection plane σ. This possibility is retained and is the first entry in the list of A_3 framework groups. For the group C_i the only possibility is $C_i(11)$. This would be a symmetric linear molecule with the higher symmetry $D_{\infty h}$ so the group C_i is eliminated. For the group C_2, the structures $C_2(11)$ and $C_2(30)$ are eliminated by the first rule as they correspond to the higher symmetries C_{2v} and $C_{\infty v}$, respectively. Hence the group C_2 is not possible for A_3 molecules. For the group C_{2v}, the possibilities are $C_{2v}(1010)$, $C_{2v}(1100)$, and $C_{2v}(3000)$. The first two of these are indistinguishable since they differ only by interchange of σ_v and σ_v'. $C_{2v}(1100)$ is therefore eliminated by the second rule. Proceeding systematically through the point groups, all subsequent entries are eliminated by the first rule until $D_{3h}(001000)$ which corresponds to an equilateral triangle. Finally, the linear structures corresponding to $C_{\infty v}$ and $D_{\infty h}$ are possible.

This information about the five possible framework groups of A_3 molecules is summarized in Table III, which also includes the fuller explicit notation introduced in the General Notation for Nuclear Framework Symmetry. It should be noted that in translating from the $(i_1...i_s)$ notation to the full notation, σ_v' is replaced by σ_v for the C_{2v} structure to be consistent with convention.[3] Table III also gives the corresponding framework groups of A_4, A_5, and A_6 molecules. Here it should be noted that some of the point groups can be associated with more than one possible framework group. For example, an A_4 molecule can have D_{2h} symmetry either as a rectangle or as a rhombus.

Enumeration of Framework Groups for Compound Molecules A_iB_j...

The possible framework groups for a compound molecule A_iB_j... can be enumerated in a similar manner. For each point group G, there will be a set of $(i_1, i_2, ..., i_s)$ satisfying (1), a set of $(j_1, j_2, ...)$ satisfying

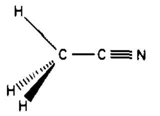
$$j_1k_1 + j_2k_2 + ... = j \qquad (3)$$

and so forth. All combinations of these sets will give a full set of nuclear arrangements which may be denoted by $G(i_1...)_A(j_1...)_B$.... The suffixes A, B, ... may be dropped without ambiguity. The full set may be ordered by passing through the individual $(i_1...)$ and $(j_1...)$ sets starting from the right. For example, an A_2B_3 molecule belonging to the point group C_s has (Table II) possible ordered i sets of (01) and (20) and j sets of (11) and (30). These would be combined in the order (01)(11), (01)(30), (20)(11), and (20)(30).

The ordered full set of nuclear arrangements has to be reduced by using rules similar to those given in the previous section. In the first place, each structure has to be examined to see whether it has higher symmetry than the point group G under consideration. Here the whole molecule must be considered and not the nuclear subsets A_i, B_j, ... For example, A_3B_3 molecules may have the symmetry $C_3(01)(01)$ although A_3 by itself with $C_3(01)$ has higher symmetry (D_{3h}). The second rule is that structures which differ from a previous one only by renaming symmetry subspaces (e.g., $\sigma_v \leftrightarrow \sigma_v'$) or by interchanging the symbols of nuclei present in equal numbers (e.g., $AB_2C_2 \leftrightarrow AC_2B_2$) are eliminated. A third rule that must be added is that the total number of nuclei assigned to a central point O cannot exceed one. This leads to further elimination of structures. The resulting lists of framework groups for all compound molecules containing up to five atoms and some with six are given in Tables IV and V.

Further Modification of Notation

The notation proposed in the General Notation for Nuclear Framework Symmetry specifies completely the framework group of the molecule, i.e., the point group, its symmetry operations, and the consequent permutations of like nuclei. One further feature which can be designated without an undue increase in complexity is the sequential order of particles assigned to the linear subspaces (points on rotation axes apart from the center of symmetry). This is not strictly symmetry information but may be simply described by writing each nucleus in a linear subspace separately in the order in which they are encountered passing along the line. For example, the molecules methyl cyanide (**9**) and methyl isocyanide (**10**) both belong to the AB_2C_3 framework group $C_{3v}[C_3(AB_2),3\sigma_v(C)]$, but their structures may be denoted separately by $C_{3v}[C_3(CCN),3\sigma_v(H)]$ and $C_{3v}[C_3(CNC),3\sigma_v(H)]$, respectively. Of course, this notation still does not specify anything about the position of the group of three equivalent hydrogen atoms.



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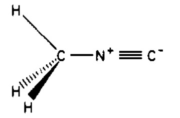
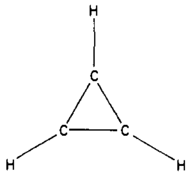
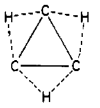


10

If the framework group has a center of symmetry, the latter may be replaced by a dot to relate its position to that of other nuclei in the linear subspaces. For example, the two D_{3h} structures **11** and **12** for C_3H_3 both belong to the A_3B_3 framework group



11



12

$D_{3h}[^3C_2(AB)]$ but may be distinguished as $D_{3h}[3C_2(.CH)]$ for **11** and $D_{3h}[^3C_2(C.H)]$ for **12**.

Conclusion

The principal purpose of this paper has been to propose a complete classification of the nuclear symmetries of molecules in terms of framework groups, together with an associated notation. The clearest advantages that would follow from adoption of such a scheme are provision of (1) a simple method of distinguishing molecular structures which belong to the same point group but really have different symmetry properties, (2) a classification of molecular structures by framework groups, such that all nuclear arrangements belonging to the same framework group have identical symmetry properties, and (3) an ordered enumeration of all possible framework groups for a molecule of given composition.

Acknowledgments. This work was supported by the National Science Foundation under Grant CHE-79-01061. It parallels unpublished work by Professor Kurt Mislow and collaborators at Princeton University. I am indebted to Professor Mislow for some valuable correspondence. I also wish to thank Dr. D. J. DeFrees for valuable suggestions about the manuscript.

Interpretation of Temperature-Dependent ESR Spectra of Peroxy Polyethylene Radicals in Urea-Polyethylene Complex

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Abstract: Temperature-dependent ESR spectra of peroxy polyethylene radicals in urea-polyethylene complexes are successfully simulated by the modified Bloch equations in terms of g anisotropy averaging of *one* radical. The motional model that averages the **g** tensor corresponds to 180° rotational jumps of the O-O fragment around the C-O bond. An activation energy of 16.6 kJ/mol is derived for this motion. A comparison of peroxy with nitroxide spin probes in polyethylene shows that the peroxy probe is more sensitive to the particular motional model that controls the dynamics.

Introduction

Formation of peroxy radicals by high-energy irradiation of polymers in the presence of oxygen has been extensively studied by electron spin resonance (ESR).[1] In most cases the spectra show g anisotropy, and the interpretation of the results is facilitated by the usually constant principal values of the **g** tensor for peroxy-polymer radicals. These values are typically 2.038 (g_1), 2.008 (g_2), and 2.002 (g_3) at low temperatures. The highest principal value is along the oxygen-oxygen bond. In many instances it has been found that the principal values of the **g** tensor vary with temperature and molecular motions are usually invoked to account for these changes.

Peroxy radicals in γ-irradiated polyethylene are less stable than in other polymers[2] and are also less stable than the alkyl or allyl radicals formed exclusively in the absence of oxygen. By a combination of favorable microwave power saturation properties and temperature, however, the temperature dependence of ESR spectra of peroxy radicals in polyethylene[3] (PE) and in urea-polyethylene complexes[4] (UPEC) has recently been published. Results for UPEC are shown in Figure 1. Basically it is seen that the lowest principal value of the **g** tensor, g_3, remains constant and at the highest temperature g_2 and g_1 are averaged. At intermediate temperatures it is hard to interpret the spectra visually. Similar results are obtained in PE. In both cases[3,4] the ESR spectra were interpreted as a superposition of two chemically identical radicals, A and B, both being peroxy polyethylene radicals, trapped however at different locations and with different motional freedom. Rotation about the polymer chain axis was assumed, parallel to the direction of g_3. In radicals of type B the motion around the chain axis is postulated to be more rapid than for radicals of type A and therefore more effective in averaging g_2 and g_1. In order to simulate the spectra, a different ratio of A/B at each temperature was assumed and this ratio changed significantly, between 0.12 and 1.5 in PE and between 0.085 and 1.0 in UPEC.

We have recently reported a study of g anisotropy from the triphenylmethyl peroxy radical in γ-irradiated triphenylacetic acid as a function of temperature.[5] In the limits of low and high temperatures, the spectra are relatively easy to interpret by assuming respectively rhombic and axial **g** tensors. In the intermediate temperature range the spectrum is very complex, containing extra features over the entire range of g values. These experimental spectra were simulated successfully by the formalism of the modified Bloch equations, assuming 120° jumps of the O-O group around the C-O bond. This model is quite reasonable if we remember that the C-O bond has a threefold axis of symmetry for the three phenyl groups in the molecule. This method has also been applied to a mobile peroxide $(CO_2-O_2)^-$ on a MgO surface.[6] We have stressed the important fact that extra lines in a g an-

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