27
1-26-77
25 to NTIS

MASTER

ORNL/TM-5666

The Use of Group Theory in the Interpretation of Infrared and Raman Spectra

E. Silberman
H. W. Morgan

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy $4.00; Microfiche $3.00

ORNL/TM-5666

Contract No. W-7405-eng-26

Physics Division

THE USE OF GROUP THEORY IN THE INTERPRETATION OF INFRARED AND RAMAN SPECTRA

E. Silberman
H. W. Morgan

Date Published: January 1977

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

CONTENTS

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ABSTRACT

Application of the mathematical theory of groups to the symmetry of molecules is a powerful method which permits the prediction, classification, and qualitative description of many molecular properties. In the particular case of vibrational molecular spectroscopy, applications of group theory lead to simple methods for the prediction of the number of bands to be found in the infrared and Raman spectra, their shape and polarization, and the qualitative description of the normal modes with which they are associated. This report contains the tables necessary for the application of group theory to vibrational spectroscopy and instructions on how to use them for molecular gases, liquids, and solutions. A brief introduction to the concepts, definitions, nomenclature, and formulae is also included.

THE USE OF GROUP THEORY IN THE INTERPRETATION OF INFRARED AND RAMAN SPECTRA

1. INTRODUCTION

Application of the mathematical theory of groups to the symmetry of molecules is a powerful method which permits the prediction, classification, and qualitative description of many molecular properties. Most of this information would be unobtainable from first principles because of the difficulties in solving the complicated equations, and, in most cases, very long calculations would be necessary in order to obtain equivalent information by other methods.

In the particular case of vibrational molecular spectroscopy, applications of group theory lead to simple methods for the prediction of the number of bands to be found in the infrared and Raman spectra, their shape and polarization, and the qualitative description of the normal modes with which they are associated.

This summary will include the tables necessary for the application of group theory to vibrational spectroscopy and instructions on how to use them for molecular gases, liquids, and solutions. A brief introduction to the concepts, definitions, nomenclature, and formulae will be presented, but no theoretical justification of the methods will be given. More complete descriptions of the theory underlying such methods, as well as their extensions to molecular solids and polymers, can be found, at different levels of difficulty, in the annotated bibliography included at the end of this section.

2. THE POINT GROUPS

The movement of a molecule from one position to another that is indistinguishable from the original one (because every atom has been replaced by another of the same kind or has not moved at all) is called a symmetry operation. Each symmetry operation has to be carried out with respect to a geometrical entity (point, line, or plane) which is called a symmetry element. There are a limited number of possible symmetry operations; they are listed in Table 1, together with their usual symbols and associated symmetry elements. The identity, a trivial symmetry which all molecules have, has been included because it has to be taken into account in the calculations that follow. The axis of symmetry of the highest order (if it exists) is called "principal axis," and it is customarily considered to be vertical; if a coordinate system is used, the principal axis should coincide with the z axis.

Table 1. Symmetry operations

Symbol	Operation	Description
I	Identity	Rotation by 360°
C_p	p-Fold rotation	Rotation by angle $2\pi/p$
σ	Reflection	Reflection by a plane
S_p	Rotation-reflection	Rotation by angle $2\pi/p$ followed by reflection
i	Inversion	"Reflection" of each point through the origin, or center of mass

A molecule may have one or more symmetry elements. Not all combinations of symmetry elements are possible; on the other hand, the presence of certain pairs of symmetry elements implies the existence of certain others. Each set of compatible symmetry operations is called a "point group" because (1) no symmetry operation can move the point coincident with the center of mass (which is unique and cannot, therefore, be shifted to an "equivalent" position), and (2) each set must satisfy the conditions to constitute a mathematical "group."

Because very few known molecules have symmetry axes of order greater than six (except ∞), the number of point groups of practical interest is limited. Table 2 lists those groups and gives typical examples of molecules that have the corresponding symmetry in their equilibrium configuration. Some point groups for which examples are not known are listed because of the possibility of having to deal with molecules that belong to them in a perturbed configuration (as may happen in liquids) or in excited states.

Table 2. The symmetry elements of the point groups of interest to molecular spectroscopy

Point group[a]	Symmetry elements[b,c]		Examples
C_1	E		CHFClBr, $CH_3 \cdot CHO$
C_2	C_2		H_2O_2 (nonplanar)
C_3	C_3		
C_4	C_4	C_2''(c. C_4)[d]	
C_6	C_6	C_2''(c. C_6), C_3(c. C_6)	
C_i ($\equiv S_2$)	i		*trans*-ClBrHC·CHBrCl
S_4	S_4	C_2''(c. S_4)	
S_6	S_6	C_3(c. S_6), i	
C_s ($\equiv C_{1v}$ $\equiv C_{1h}$)	σ		NOCl (nonlinear), NH_2D, C_2H_5Cl
C_{2v}	C_2, σ_v	σ_v'(p. σ_v)[e]	H_2O, H_2CCl_2, chlorobenzene
C_{3v}	C_3, $3\sigma_v$		NH_3, $HCCl_3$, $OPCl_3$
C_{4v}	C_4, $2\sigma_v$	$2\sigma_v'$(p. σ_v), C_2''(c. C_4)	IF_5, $Fe(CO)_5$
C_{6v}	C_6, $3\sigma_v$	$3\sigma_v'$(b. σ_v),[f] C_2''(c. C_6), C_3(c. C_6)	
$C_{\infty v}$	C_∞, $\infty\sigma_v$	Any C_p(c. C_∞)	HCl, HCN, HCCCl
C_{2h}	C_2, σ_h	i	*trans*-ClHC=CHCl, C_3O_2
C_{3h}	C_3, σ_h	S_3(c. C_3)	H_3BO_3, $C^+(NH_2)_3$
C_{4h}	C_4, σ_h	C_2''(c. C_4), S_4(c. C_4), i	
C_{6h}	C_6, σ_h	C_2''(c. C_6), C_3(c. C_6), S_6(c. C_6), S_3(c. C_6), i	

Table 2 (continued)

Point group[a]	Symmetry elements[b,c]		Examples
$D_2 \equiv V$	C_2, C'_2(p. C_2)	C''_2(p. $C_2C'_2$)	
D_3	C_3, $3C_2$(p. C_3)		
D_4	C_4, $2C_2$(p. C_4, m.p.)[g]	$2C'_2$(b. C'_2), C''_2(c. C_4)	
D_6	C_6, $3C_2$(p. C_6)	$3C'_2$(b. C_2), C''_2(c. C_6), C_3(c. C_6)	
D_{2d} ($\equiv V_d$)	C_2, $2C'_2$(p. C_2, m.p.), $2\sigma_d$(t. C_2)[h]	S_4(c. C_2)	B_2Cl_4, $H_2C_3H_2$, N_4S_4
D_{3d}	C_3, $3C_2$(p. C_3), $3\sigma_d$	S_6(c. C_3), i	C_2H_6, C_6H_{12} (cyclohexane), $(SiH_3)_2O$
D_{4d}	C_4, $4C_2$(p. C_4), $4\sigma_d$	C''_2(c. C_4), S_8(c. C_4)	S_8
D_{2h} ($\equiv V_h$)	C_2, C'_2(p. C_2), σ(t. $C'_2C''_2$)	C''_2(p. $C_2C'_2$), σ'(t. $C_2C'_2$), σ''(t. $C_2C''_2$), i	C_2H_4, *p*-dichlorobenzene, naphtalene
D_{3h}	C_3, $3C_2$(p. C_3), σ_h	S_3(c. C_3), $3\sigma_v$	BF_3, 1,3,5-$C_6H_3Cl_3$
D_{4h}	C_4, $2C_2$(p. C_4), $2C'_2$(p. C_4), σ_h	C''_2(c. C_4), S_4(c. C_4), $2\sigma_v$, $2\sigma_d$, i	C_4H_8, $PtCl_4{}^{2-}$
D_{5h}	C_5, $5C_2$(p. C_5), σ_h	S_5(c. C_5), $5\sigma_v$	Cyclopentane (plane and symmetric), ferrocene eclipsed)
D_{6h}	C_6, $3C_2$(p. C_6), $3C'_2$(p. C_6), σ_h	C''_2(c. C_6), C_3(c. C_6), S_3(c. C_6), S_6(c. C_6), $3\sigma_v$, $3\sigma_d$	C_6H_6 (benzene)

Table 2 (continued)

Point group[a]	Symmetry elements[b,c]		Examples
$D_{\infty h}$	C_∞, ∞C_2(p. C_∞), σ_h	Any C_p(c. C_∞), any S_p(c. C_∞), $\infty\sigma_v$, i	O_2, CO_2, C_2H_2
T	$4C_3$, $3C_2$(m.p., b. C_3's)		
T_d	$4C_3$, $3C_2$(m.p., b. C_3's), $3S_4$(c. C_2), $6\sigma_d$(t. C_3's)		CH_4, BF_4^-, NH_4^+, SO_4^{2-}
T_h	$4C_3$, $3C_2$(m.p.), i	3σ(t. C_2's), $4S_6$(c. C_3's)	
O	$3C_4$(m.p.), $4C_3$	$3C_2''$(c. C_4), $6C_2$	
O_h	$3C_4$(m.p.), $4C_3$(cube diagonals), i	$3C_2$(c. C_4), $6C_2$(t. centers opposite cube edges), $3S_4$(c. C_4), $4S_6$(c. C_3), $3\sigma_h$(p. C_4), $6\sigma_d$(t. opposite cube edges)	SF_6, $PtCl_6^{2-}$, UF_6

[a] In the C_{2v}, C_{4v}, and C_{6v} groups, σ_v should (if possible) pass through more atoms than σ_v' (which is sometimes labeled σ_d in C_{4v} and C_{6v}); if the rule is not applicable, σ_v should intersect more bonds than σ_v'. Similar rules should be used to label C_2, C_2', and C_2'' in groups D_2 and D_{2h}, and C_2 and C_2' in groups D_4, D_6, D_{2d}, D_{4h}, and D_{6h}.

[b] The element E (identity), which is contained in every point group, has been omitted.

[c] Axes and planes preceded by a number are equivalent (can be transformed one into the other by another symmetry operation).

[d] c. = coincident with.

[e] p. = perpendicular to.

[f] b. = bisecting.

[g] m.p. = mutually perpendicular.

[h] t. = through.

A few remarks may facilitate the use of Table 2:

1. The first column gives the name of the group in the Schoenflies notation habitually used by molecular spectroscopists; the corresponding notation in the Hermann and Mauguin system used in crystallography, and more recently in solid state spectroscopy, can be found in most of the tables given in the bibliography. Although it is not necessary to memorize the symbols and symmetry elements of the point groups, it can be useful to notice that: (a) the groups C_p and S_p contain essentially only the corresponding axis, the special cases being C_1 (which really does not have any symmetry) and C_i (which has only a center of symmetry equivalent to the operation S_2); (b) the groups C_{pv} and C_{ph} are generated by adding a σ_v or σ_h plane to the groups C_p, the special case being C_s, whose plane of symmetry can equally well be considered horizontal or vertical, justifying the equivalent names C_{1v} and C_{1h}; (c) the dihedral groups D_p are generated by adding a C_2 perpendicular to the principal axis of a group C_p; the operations with both axes generate new C_2's perpendicular to the C_p; (d) the addition of vertical planes σ_d bisecting adjacent C_2's of each D_p group gives origin to the D_{pd} groups; (e) the addition of a horizontal plane σ_h to each D_p group gives origin to the D_{ph} groups; and (f) all the above mentioned groups are called axial point groups and can be characterized as not having more than one (if any) axis of order three or higher. Groups that have more than one three-fold or four-fold axis are called cubic point groups, and only two of them are likely to be found in free molecules — T_d, which has the symmetry of a regular tetrahedron, and O_h, of which the cube and the regular octahedron are the typical examples. The cubic groups T, T_h, and O have been included because of their usefulness in the study of the spectra of many crystals.

2. The symmetry elements that constitute each point group have been separated into two columns to facilitate the search when trying to assign symmetry to a molecule. The first column lists the minimum set that characterizes the group and, in most cases, justifies its symbol. The second column contains symmetry elements that are a consequence of the presence of the former ones. All the elements are equally important

for the deduction of the molecular properties derived from the molecular symmetry.

3. The table contains the 32 "crystallographic" point groups from which the 230 crystal space groups can be derived by addition of new elements of symmetry (translations, screw axes, glide planes). The reader must be reminded that the methods for the interpretation of crystal spectra are more complicated than the methods applicable only to isolated molecules that will be described. A first approximation to the spectra of molecular crystals can be obtained, however, by treating each molecule or ion in the crystal as isolated, but with its own symmetry reduced to the symmetry of the crystal at the "site" where the molecule or ion is located.

3. GROUPS, REPRESENTATIONS, CHARACTER TABLES, AND THE REDUCTION FORMULA

A set of elements *A*, *B*, *C*, ... that can be combined in pairs according to a certain rule is said to constitute a group if (1) each binary combination yields an element of the set, (2) the associative law holds for the combination of more than two elements, (3) the set contains an identity element (its combination with all the other elements leaves them unchanged), and (4) each element has an inverse in the set (their combination yields the identity). The combination is usually called "product" although it does not need to be a product in the ordinary algebraic sense and, in general, will not be commutative. It may be useful to tabulate all the binary products in a "multiplication table."

The elements of a group may have any degree of complexity or abstractness, and the operations necessary to obtain their products may be very complicated. Usually it is possible to establish a correspondence between each element of a group and a number or a matrix belonging to another group in such a way that the multiplication tables of both groups are "parallel." The group of numbers or matrices is called a representation of the original group and its dimension is equal to the order of the square matrices that constitute it (the dimension is 1 if its elements are numbers). Many properties of a group can be found by operating with their representations, which may vary in number and dimensions. Frequently, mathematical operations may be performed that will factorize the matrices of a high-order representation into matrices of lower orders, which constitute representations of lower dimensions. When that process is carried out in such a way that the lower order matrices cannot be further factorized, it is said that the higher order reducible representation has been reduced to its irreducible representations. It can be proven that there are only a limited number of irreducible representations of any group; they can, therefore, be found and tabulated. For many applications of group theory it is enough to know the character (sum of diagonal elements) of the representations, a fact which explains the interest in the availability of tables of characters of the irreducible representations of the point groups.

The reduction of a reducible representation to its irreducible components may be a complicated process, but there is a simple reduction formula which gives the number of times each irreducible representation will appear when the reduction process is completed. If the g elements of a group have characters χ_i ($i = 1, 2, 3, \ldots, g$) in some reducible representation and characters χ_i^γ ($i = 1, 2, 3, \ldots, g$) in the irreducible representation q, the reduction of the former will contain the latter N^γ times, with

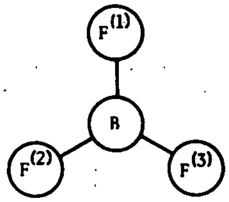
$$N^\gamma = \frac{1}{g} \sum_{i=1}^{g} \chi_i^\gamma \chi_i \, .$$

4. THE CHARACTER TABLES OF THE POINT GROUPS

The symmetry operations of the point can be described by the equations that relate the coordinates of each atom before and after each operation. The coefficients of these equations may be arranged in matrices that represent the symmetry operations. The dimension of these reducible representations will depend on the choice of a coordinate system. If cartesian coordinates are used, each atom will require three coordinates, and a molecule with N atoms will yield a representation of dimension 3N; use of internal coordinates (distances between atoms, angles between bonds, etc.) may yield representations of dimension 3N - 6 (3N - 5 for linear molecules). All these representations can be factorized into the irreducible representations whose characters are given in Table 3, together with some additional information that will be necessary for the applications to molecular spectroscopy.

To explain Table 3, we will use a typical example. Let us reproduce part of the character table for the point group D_{3h}, to which the planar molecule BF_3 belongs.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_1''	1	1	1	-1	-1	-1
A_2'	1	1	-1	1	1	-1
A_2''	1	1	-1	-1	-1	1
E'	2	-1	0	2	-1	0
E''	2	-1	0	-2	1	0



BF_3 molecule

In addition to the Schoenflies symbol of the group, the first line contains all the symmetry operations that constitute it. The number 2 in $2C_3$ indicates that the group includes, in fact, the two C_3 operations C_3^1 and C_3^2 (rotations of 120° and 240° around the C_3 axis); but because both operations have the same characters in all the representations, it is unnecessary to repeat the column. The number 3 in $3C_2$ indicates, similarly, that there are three binary axes [through $BF^{(1)}$, $BF^{(2)}$, and $BF^{(3)}$ in BF_3], each one contributing an identical column to the table. There is one reflection through a horizontal plane (the plane of the molecule, which is perpendicular to the principal axis C_3), to improper rotations S_3^1 and S_3^2 around the axis S_3 (coincident with C_3), and three reflections through the vertical planes (which contain C_3 and each one of the C_2's). Addition of the trivial symmetry E completes the 12 elements of D_{3h}.

Each one of the following lines of the table contains the characters of one of the irreducible representations of the group, preceded by its

Table 3. Character tables of point groups

The C_p groups

C_1	E		
A	1	R; T	α

C_2	E	C_2		
A	1	1	T_z; R_z	α_{xx}, α_{yy}, α_{zz}, α_{xy}
B	1	-1	T_x, T_y; R_x, R_y	α_{yz}, α_{zx}

C_3	E	C_3	C_3^2		$\varepsilon = e^{\frac{2\pi i}{3}}$
A	1	1	1	T_z; R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
E	1	ε	ε^*	(T_x, T_y); (R_x, R_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$, $(\alpha_{yz}, \alpha_{zx})$
	1	ε^*	ε		

C_4	E	C_4	C_2''	C_4^3		
A	1	1	1	1	T_z; R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
B	1	-1	1	-1		$\alpha_{xx} - \alpha_{yy}$, α_{xy}
E	1	i	-1	$-i$	(T_x, T_y); (R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$
	1	$-i$	-1	i		

C_6	E	C_6	C_3	C_2''	C_3^2	C_6^5		$\varepsilon = e^{\frac{2\pi i}{6}}$
A	1	1	1	1	1	1	T_z; R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
B	1	-1	1	-1	1	-1		
E_1	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*	(T_x, T_y); (R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$
	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε		
E_2	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		

The S_p groups

C_i	E	i		
A_g	1	1	R	α
A_u	1	-1	T	

S_4	E	S_4	C_2''	S_4^3		
A	1	1	1	1	R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
B	1	-1	1	-1	T_z	$\alpha_{xx} - \alpha_{yy}$, α_{xy}
E	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}i\\-i\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\left.\begin{matrix}-i\\i\end{matrix}\right\}$	(T_x, T_y); (R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$

S_6	E	C_3	C_3^2	i	S_6^5	S_6		$S_6 = C_3 \times i \quad \varepsilon = e^{\frac{2\pi i}{3}}$
A_g	1	1	1	1	1	1	R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
E_g	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\varepsilon\\\varepsilon^*\end{matrix}$	$\begin{matrix}\varepsilon^*\\\varepsilon\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\varepsilon\\\varepsilon^*\end{matrix}$	$\left.\begin{matrix}\varepsilon^*\\\varepsilon\end{matrix}\right\}$	(R_x, R_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$; $(\alpha_{yz}, \alpha_{zx})$
A_u	1	1	1	-1	-1	-1	T_z	
E_u	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\varepsilon\\\varepsilon^*\end{matrix}$	$\begin{matrix}\varepsilon^*\\\varepsilon\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\varepsilon\\-\varepsilon^*\end{matrix}$	$\left.\begin{matrix}-\varepsilon^*\\-\varepsilon\end{matrix}\right\}$	(T_x, T_y)	

The C_{pv} groups

C_s	E	σ		
A'	1	1	T_x, T_y; R_z	α_{xx}, α_{yy}, α_{zz}, α_{xy}
A''	1	-1	T_z; R_x, R_y	α_{yz}, α_{zx}

C_{2v}	E	C_2	$\sigma_v(zx)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	T_z	α_{xx}, α_{yy}, α_{zz}
A_2	1	1	-1	-1	R_z	α_{xy}
B_1	1	-1	1	-1	T_x; R_y	α_{zx}
B_2	1	-1	-1	1	T_y; R_x	α_{yz}

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	T_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
A_2	1	1	-1	R_z	
E	2	-1	0	(T_x,T_y); (R_x,R_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$; $(\alpha_{yz}, \alpha_{zx})$

C_{4v}	E	$2C_4$	C_2''	$2\sigma_v$	$2\sigma_v'$		
A_1	1	1	1	1	1	T_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$\alpha_{xx} - \alpha_{yy}$
B_2	1	-1	1	-1	1		α_{xy}
E	2	0	-2	0	0	(T_x,T_y); (R_x,R_y)	$(\alpha_{yz}, \alpha_{zx})$

C_{6v}	E	$2C_6$	$2C_3$	C_2''	$3\sigma_v$	$3\sigma_v'$		
A_1	1	1	1	1	1	1	T_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
A_2	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	(T_x,T_y); (R_x,R_y)	$(\alpha_{yz}, \alpha_{zx})$
E_2	2	-1	-1	2	0	0		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$

$C_{\infty v}$	E	$2C_\infty^\phi$	. . .	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	. . .	1	T_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
$A_2 \equiv \Sigma^-$	1	1	. . .	-1	R_z	
$E_1 \equiv \Pi$	2	$2 \cos \phi$	. . .	0	(T_x,T_y); (R_x,R_y)	$(\alpha_{yz}, \alpha_{zx})$
$E_2 \equiv \Delta$	2	$2 \cos 2\phi$	. . .	0		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
$E_3 \equiv \Phi$	2	$2 \cos 3\phi$	. . .	0		
...	...	...	...	...		

The C_{ph} groups

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	α_{xx}, α_{yy}, α_{zz}, α_{xy}
B_g	1	-1	1	-1	R_x, R_y	α_{yz}, α_{zx}
A_u	1	1	-1	-1	T_z	
B_u	1	-1	-1	1	T_x, T_y	

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5		$\varepsilon = e^{\frac{2\pi i}{3}}$
A'	1	1	1	1	1	1	R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
E'	1	ε	ε^*	1	ε	ε^*	(T_x, T_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
	1	ε	ε	1	ε^*	ε		
A''	1	1	1	-1	-1	-1	T_z	
E''	1	ε	ε^*	-1	$-\varepsilon$	$-\varepsilon^*$	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$
	1	ε^*	ε	-1	$-\varepsilon^*$	$-\varepsilon$		

C_{4h}	E	C_4	C_2''	C_4^3	i	S_4^3	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
B_g	1	-1	1	-1	1	-1	1	-1		$\alpha_{xx} - \alpha_{yy}$, α_{xy}
E_g	1	i	-1	$-i$	1	i	-1	$-i$	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$
	1	$-i$	-1	i	1	$-i$	-1	i		
A_u	1	1	1	1	-1	-1	-1	-1	T_z	
B_u	1	-1	1	-1	-1	1	-1	1		
E_u	1	i	-1	$-i$	-1	$-i$	1	i	(T_x, T_y)	
	1	$-i$	-1	i	-1	i	1	$-i$		

C_{6h}	E	C_6	C_3	C_2''	C_3^2	C_6^5	i	S_3^5	S_6^5	σ_h	S_6	S_3		$\varepsilon = e^{\frac{2\pi i}{6}}$
A_g	1	1	1	1	1	1	1	1	1	1	1	1	R_z	$\alpha_{xx} + \alpha_{yy}$, α_{zz}
B_g	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
E_{1g}	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$
	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε		
E_{2g}	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		
A_u	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	T_z	
B_u	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
E_{1u}	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*	-1	$-\varepsilon$	ε^*	1	ε	$-\varepsilon^*$	(T_x, T_y)	
	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε	-1	$-\varepsilon^*$	ε	1	ε^*	$-\varepsilon$		
E_{2u}	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	-1	ε^*	ε	-1	ε^*	ε		
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	-1	ε	ε^*	-1	ε	ε^*		

The D_p groups

$D_2 \equiv V$	E	$C_2(z)$	$C_2'(y)$	$C_2''(x)$		
A	1	1	1	1		$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
B_1	1	1	-1	-1	T_z, R_z	α_{xy}
B_2	1	-1	1	-1	T_y, R_y	α_{zx}
B_3	1	-1	-1	1	T_x, R_x	α_{yz}

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A_2	1	1	-1	$T_z; R_z$	
E	2	-1	0	$(T_x, T_y); (R_x, R_y)$	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy}); (\alpha_{yz}, \alpha_{zx})$

D_4	E	$2C_4$	$C_4^2 = C_2''$	$2C_2$	$2C_2'$		
A_1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A_2	1	1	1	-1	-1	T_z, R_z	
B_1	1	-1	1	1	-1		$\alpha_{xx} - \alpha_{yy}$
B_2	1	-1	1	-1	1		α_{xy}
E	2	0	-2	0	0	$(T_x, T_y); (R_x, R_y)$	$(\alpha_{yz}, \alpha_{zx})$

D_6	E	$2C_6$	$2C_3$	C_2''	$3C_2$	$3C_2'$		
A_1	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A_2	1	1	1	1	-1	-1	$T_z; R_z$	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	$(T_x, T_y); (R_x, R_y)$	$(\alpha_{yz}, \alpha_{zx})$
E_2	2	-1	-1	2	0	0		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$

The D_{pd} groups

$D_{2d} = V_d$	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}$, α_{zz}
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$\alpha_{xx} - \alpha_{yy}$
B_2	1	-1	1	-1	1	T_z	α_{xy}
E	2	0	-2	0	0	(T_x, T_y); (R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}$, α_{zz}
A_{2g}	1	1	-1	1	1	-1	R_z	
E_g	2	-1	0	2	-1	0	(R_x, R_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$, $(\alpha_{yz}, \alpha_{zx})$
A_{1u}	1	1	1	-1	-1	-1		
A_{2u}	1	1	-1	-1	-1	1	T_z	
E_u	2	-1	0	-2	1	0	(T_x, T_y)	

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2''	$4C_2$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}$, α_{zz}
A_2	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1	-1	1	T_z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(T_x, T_y)	
E_2	2	0	-2	0	2	0	0		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$

The D_{ph} groups

$D_{2h} \equiv V_h$	E	$C_2(z)$	$C_2'(y)$	$C_2''(x)$	i	$\sigma(xy)$	$\sigma''(zx)$	$\sigma'(yz)$		
A_g	1	1	1	1	1	1	1	1		α_{xx}, α_{yy}, α_{zz}
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	α_{xy}
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	α_{zx}
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	α_{yz}
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	T_z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	T_y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	T_x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(T_x, T_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	T_z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$

D_{4h}	E	$2C_4$	C_2''	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$\alpha_{xx} - \alpha_{yy}$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		α_{xy}
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	$(\alpha_{yz}, \alpha_{xy})$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	T_z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(T_x, T_y)	

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A_2'	1	1	1	-1	1	1	1	-1	R_z	
E_1'	2	2 cos 72°	2 cos 144°	0	2	2 cos 72°	2 cos 144°	0	(T_x, T_y)	
E_2'	2	2 cos 144°	2 cos 72°	0	2	2 cos 144°	2 cos 72°	0		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
A_1''	1	1	1	1	-1	-1	-1	-1		
A_2''	1	1	1	-1	-1	-1	-1	1	T_z	
E_1''	2	2 cos 72°	2 cos 144°	0	-2	-2 cos 72°	-2 cos 144°	0	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$
E_2''	2	2 cos 144°	2 cos 72°	0	-2	-2 cos 144°	-2 cos 72°	0		

D_{6h}	E	$2C_6$	$2C_3$	C_2''	$3C_2$	$3C_2'$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	T_z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	-2	0	0	(T_x, T_y)	
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

$D_{\infty h}$	E	$2C_\infty^{\phi}$	...	$\infty\sigma_v$	i	$2S_\infty^{\phi}$	...	∞C_2		
Σ_g^+	1	1	...	1	1	1	...	1		$\alpha_{xx}+\alpha_{yy}, \alpha_{zz}$
Σ_g^-	1	1	...	-1	1	1	...	-1	R_z	
Π_g	2	$2 \cos \phi$	...	0	2	$-2 \cos \phi$	...	0	(R_x, R_y)	$(\alpha_{yz}, \alpha_{zx})$
Δ_g	2	$2 \cos 2\phi$	...	0	2	$2 \cos 2\phi$	...	0		$(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$
...	...	...	...	...	...	...	...	...		
Σ_u^+	1	1	...	1	-1	-1	...	-1	T_z	
Σ_u^-	1	1	...	-1	-1	-1	...	1		
Π_u	2	$2 \cos \phi$	...	0	-2	$2 \cos \phi$	...	0	(T_x, T_y)	
Δ_u	2	$2 \cos 2\phi$	...	0	-2	$-2 \cos 2\phi$	...	0		
...	...	...	...	...	...	...	...	...		

The Cubic groups

T	E	$4C_3$	$4C_3^2$	$3C_2$		$\varepsilon = e^{\frac{2\pi i}{3}}$
A	1	1	1	1		$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
E	1	ε	ε^*	1		$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$
	1	ε^*	ε	1		
F	3	0	0	-1	(T), (R)	$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$
F_1	3	0	-1	1	-1	(R)	
F_2	3	0	-1	-1	1	(T)	$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$

T_h	E	$4C_3$	$4C_3^2$	$3C_2$	i	$4S_6$	$4S_6^2$	$3\sigma_h$		$\varepsilon = e^{\frac{2\pi i}{3}}$
A_g	1	1	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
E_g	1	ε	ε^*	1	1	ε	ε^*	1		$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz},$ $\alpha_{xx} - \alpha_{yy})$
	1	ε^*	ε	1	1	ε^*	ε	1		
F_g	3	0	0	-1	3	0	0	-1	(R_x, R_y, R_z)	$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$
A_u	1	1	1	1	-1	-1	-1	-1		
E_u	1	ε	ε^*	1	-1	$-\varepsilon$	$-\varepsilon^*$	-1		
	1	ε^*	ε	1	-1	$-\varepsilon^*$	$-\varepsilon$	-1		
F_u	3	0	0	-1	-3	0	0	1	(T_x, T_y, T_z)	

O	E	$8C_3$	$3C_2''$	$6C_4$	$6C_2$		
A_1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$
F_1	3	0	-1	1	-1	(R); (T)	
F_2	3	0	-1	-1	1		$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$

O_h	E	$8C_3$	$3C_2''$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
E_g	2	-1	2	0	0	2	-1	2	0	0		$(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy})$
F_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	(R_x, R_y, R_z)	$(\alpha_{xy}, \alpha_{yz}, \alpha_{zx})$
F_{2g}	3	0	-1	-1	1	3	0	-1	-1	1		
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		
E_u	2	-1	2	0	0	-2	1	-2	0	0		
F_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	(T_x, T_y, T_z)	
F_{2u}	3	0	-1	-1	1	-3	0	1	1	-1		

conventional symbol. This symbol gives some information about the characteristics of the representation, according to the following convention:

- A one-dimensional representation will be recognized to be "symmetric" or "asymmetric" with respect to a symmetry operation when the corresponding character is +1 or -1 respectively. For two- and three-dimensional representations the characters may be ±2 and ±3 respectively.
- *A* or *B*: one-dimensional representations which are symmetric or antisymmetric, respectively, with respect to rotations about the principal axis C_p.
- *E*: two-dimensional representations.
- *F*: three-dimensional representations (sometimes designated *T*).
- 1 or 2: subscripts attached to *A*'s and *B*'s to designate representations that are symmetric or antisymmetric, respectively, with respect to rotations about a C_2 perpendicular to the principal axis. If such a C_2 does not exist, it is replaced by a σ_v.
- *g* or *u*: subscripts attached to all letters in groups with a center of symmetry to indicate representations that are respectively symmetric or antisymmetric with respect to the inversion through the center.
- Primes or double primes: superscripts attached to all letters, when appropriate, to designate a representation that is symmetric or antisymmetric, respectively, with respect to reflection through a σ_h.
- Σ^+ or Σ^-: one-dimensional representations for the groups of linear molecules that are respectively symmetric or antisymmetric with respect to reflection through a σ_v.
- Π, Δ, Φ, etc.: two-dimensional representations for the groups of linear molecules.

The physical meaning of the symmetric or antisymmetric behavior of the representations will become clearer after the explanation of their use in vibrational spectroscopy.

The right side of the character tables contains information about the symmetry of the components of molecular translations (T), rotations (R), and polarizabilities (α). This information is given through their assignment to the different representations and will be used in the prediction of vibrational spectra. The symbol T is an abbreviation for the set T_x, T_y, T_z; the R replaces R_x, R_y, R_z and means α_{xx}, α_{yy}, α_{zz}, α_{xy}, α_{yz}, α_{zx}. Degenerate components are enclosed in parentheses.

5. GROUP THEORY AND MOLECULAR VIBRATIONS

Up to this point we have mentioned only the symmetry of molecules in their equilibrium configuration. But it can be proven that the displacements of the atoms during molecular vibrations are constrained to specific patterns determined by the molecular symmetry. This fact results in a close relationship between the normal vibrations and the irreducible representations of the point group. This relationship is the basis for the application of the group theory to vibrational spectroscopy. The most important consequences of this application are: (1) The normal modes of vibration can be classified according to the irreducible representation to which they "belong." (2) This classification provides some description of the normal modes because the character table indicates if they are symmetric or antisymmetric with respect to some symmetry operations; in this application, "symmetric" means that the operation performed on the vibrating molecule will keep the vectors representing the atomic displacements unchanged, while "antisymmetric" means that the same vectors will change to the opposite direction. (3) The degeneracy of the normal modes is given by the dimensions of their representations. (4) The normal modes belonging to the same representation as any component of a translation are infrared active. (5) In the gas phase of symmetric top molecules, the vibrations in the same representation as T_z are "parallel" and should show the typical PQR structure. (6) The normal modes belonging to the same representation as any component of the polarizability are Raman active; only the vibrations belonging to the completely symmetric representation (all characters equal to 1) can originate polarized bands.

6. THE PREDICTION OF THE FUNDAMENTAL VIBRATIONAL BANDS

In this section we will describe step by step a procedure for the calculation of the number and polarization of the fundamental bands that should appear in the infrared and Raman spectra of a molecule of known configuration.

Step 1: Assignment of the molecule to a point group

By working on a model or a good drawing of the molecule, one can locate all the symmetry elements. There are no systematic procedures to perform this step, but experience shows that a short practice period will provide the necessary skills. It may be useful to look first for a proper axis of rotation of the highest order. If none exists the molecule can only belong to C_s, C_i, or C_1, and the search for a plane or center of symmetry will decide among them. If one or more C_p's exist, select the one of the highest order and determine in Table 2 the groups that contain it. The left half of the list of symmetric elements can be used as a guide to select which elements to look for next to reduce the possible choices. This procedure should continue until only one group is left and a careful check has been done to verify that no element belonging to a higher symmetry group is present.

Step 2: Calculation of the characters of a reducible representation

Once all the symmetry elements have been located and the point group has been determined, the characters of each symmetry operation in a reducible representation of dimension 3N - 6 can be calculated according to the following rules:

- For each operation E or C_p: Count the number of atoms that are not shifted when the symmetry operation is performed. Subtract 2. Multiply by the appropriate factor in Table 4.
- For each operation i, S, or σ: Count the number of atoms that are not shifted when the symmetry operation is performed. Multiply by the appropriate factor in Table 4.

Table 4. Contribution to character per unshifted atom

Operation i	χ_i	Operation i	χ_i
E	3	σ	1
C_2	-1	i	-3
C_3^1, C_3^2	0	S_3^1, S_3^2	-2
C_4^1, C_4^3	1	S_4^1, S_4^2	-1
C_5^1, C_5^4	1.618	S_5^1, S_5^4	-0.302
C_5^2, C_5^3	-0.618	S_5^2, S_5^3	-2.618
C_6^1, C_6^2	2	S_6^1, S_6^2	0

Step 3: Calculation of the number of fundamental vibrations belonging to each representation (symmetry species)

In molecular spectroscopy, the irreducible representations of the point groups are often referred to as "symmetry types" or "symmetry species," and the reduction formula is slightly modified to account explicitly for the fact that the columns of the character table may contain more than one symmetry operation.

The number of fundamental vibrations of symmetry type γ is given by:

$$N^{\gamma} = \frac{1}{g} \sum_{i=1}^{c} n_i \chi_i \chi_i^{\gamma} ,$$

where

n_i = number of operations in the ith column of the character table,

c = number of columns in the character table (equal to number of representations),

$g = \sum_{i=1}^{c} n_i$ = total number of operations in the point group,

χ_i = character of the reducible representation of the operations of column i (determined in step 2),

χ_i^γ = character of the γ irreducible representation of the operations of column i.

In some groups there are imaginary or complex characters, but they always appear as conjugate pairs in two one-dimensional representations which are the components of a degenerate mode E. When the reduction formula is applied, the real sum of both complex characters has to be used as the character for the species E. Notice that

$$i + (-i) = 0 \quad \text{and} \quad e^{2\pi i/n} + e^{-2\pi i/n} = 2 \cos \frac{2\pi}{n} .$$

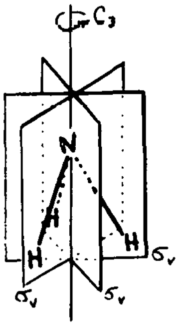
Step 4: Determination of the number of fundamental bands in the infrared and Raman spectra

- Infrared spectra: will include all the fundamental modes with the same symmetry as T_x, T_y, and/or T_z. The vibrations in the same species as (T_x,T_y) or (T_x,T_y,T_z) will be double or triple degenerate respectively.
- Raman spectra: will include all the fundamental modes with the same symmetry as any component of α. The vibrations in the same species as α_{xx}, α_{yy}, α_{zz} will be polarized (totally in the cubic groups, partially in the rest). The vibrations in the same species as α_{xy}, α_{yz}, and/or α_{zx} will be depolarized.

7. EXAMPLES

7.1 AMMONIA (NH_3)

Step 1



As a pyramid with the N at the cusp and the three H at the corners of an equilateral triangular base, ammonia shows $1C_3$ (through the N, perpendicular to the base) and $3\sigma_v$

(through the C_3 and each NH bond). Inspection of Table 2 gives immediately a point group C_{3v}.

Step 2

Atoms unshifted per symmetry operation:

$$u_E = 4\ , \qquad u_{C_3} = 1 \text{ (the N)}\ , \qquad u_{\sigma_v} = 2 \text{ (the N, one H)}\ ,$$

$$\chi_E = (4 - 2)\cdot 3 = 6\ , \quad \chi_{C_3} = (1 - 2)\cdot 0 = 0\ , \quad \chi_{\sigma_v} = 2\cdot 1 = 2\ .$$

Step 3

From the character table for the group C_{3v}:

$$n_E = 1\ , \quad n_{C_3} = 2\ , \quad n_{\sigma_v} = 3\ ,$$

$$c = 3\ , \qquad g = 1 + 2 + 3 = 6\ ,$$

$$N^A = \frac{1}{6}\,[1\cdot 6\cdot 1 + 2\cdot 0\cdot 1 + 3\cdot 2\cdot 1] = 2\ ,$$

$$N^A = \frac{1}{6}\,[1\cdot 6\cdot 1 + 2\cdot 0\cdot 1 + 3\cdot 2\cdot (-1)] = 0\ ,$$

$$N^E = \frac{1}{6}\,[1\cdot 6\cdot 2 + 2\cdot 0\cdot (-1) + 3\cdot 2\cdot 0] = 2\ .$$

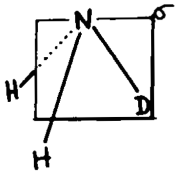
Ammonia has, therefore, two nondegenerate vibrations of species A_1 and two doubly degenerate vibrations of species E. This result is usually represented by

$$\Gamma = 2A_1 + 2E\ .$$

Step 4

The character table shows that (1) all bands being infrared and Raman active, each spectrum should show four bands; (2) in the Raman, the A_1 bands may be partially polarized and the E bands will be depolarized; and (3) in the infrared spectra of gaseous ammonia the A_1 bands are "parallel" and should show PQR structure.

7.2 MONODEUTERATED AMMONIA (NH_2D)



Step 1

There is only a σ (through ND and bisecting the two NH bonds). The point group is, therefore, C_s.

Step 2

$$u_E = 4 \,, \qquad u_\sigma = 2 \,,$$

$$\chi_E = (4 - 2)\cdot 3 = 6 \,, \qquad \chi_\sigma = 2\cdot 1 = 2 \,.$$

Step 3

$$n_E = 1 \,, \qquad n_\sigma = 1 \,,$$

$$c = 2 \,, \qquad g = 1 + 1 = 2 \,,$$

$$N^{A'} = \frac{1}{2}\,[1\cdot 6\cdot 1 + 1\cdot 2\cdot 1] = 4 \,,$$

$$N^{A''} = \frac{1}{2}\,[1\cdot 6\cdot 1 + 1\cdot 2\cdot(-1)] = 2 \,.$$

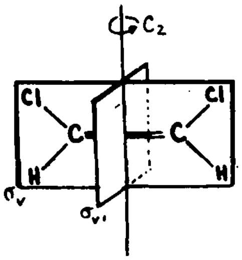
Monodeuterated ammonia has, therefore, six nondegenerate vibrations which can be represented by

$$\Gamma = 4A' + 2A'' \,.$$

Step 4

From the character table for the point group C_s: (1) All bands being infrared and Raman active, each spectrum should show six bands. (2) In the Raman, the A' bands may be partially polarized and the A'' bands will be depolarized. (3) No prediction about the shapes of the infrared bands of the gas can be made.

7.3 1,2-DICHLOROETHYLENE (*cis*) (*c*-ClHC·CClH)



Step 1

The plane of the molecule (σ) and the plane through the center of the C=C bond and perpendicular to it (σ') are planes of symmetry. The intersection of both planes is a C_2. There are no other symmetry elements (except the identity) and the molecule belongs, therefore, to the C_{2v} point group.

Step 2

$u_E = 6$, $\qquad u_{C_2} = 0$,

$\chi_E = (6 - 2)\cdot 3 = 12$, $\qquad \chi_{C_2} = (0 - 2)\cdot(-1) = 2$,

$u_{\sigma_v} = 6$, $\qquad u_{\sigma_{v'}} = 0$,

$\chi_{\sigma_v} = 6\cdot 1 = 6$, $\qquad \chi_{\sigma_{v'}} = 0\cdot 1 = 0$.

Step 3

$n_E = 1$, $\qquad n_{C_2} = 1$, $\qquad n_{\sigma_v} = 1$, $\qquad n_{\sigma_{v'}} = 1$,

$c = 4$, $\qquad g = 1 + 1 + 1 + 1 = 4$,

$$N^{A_1} = \frac{1}{4}\,[1\cdot 12\cdot 1 + 1\cdot 2\cdot 1 + 1\cdot 6\cdot 1 + 1\cdot 0\cdot 1] = 5\ ,$$

$$N^{A_2} = \frac{1}{4}\,[1\cdot 12\cdot 1 + 1\cdot 2\cdot 1 + 1\cdot 6\cdot (-1) + 1\cdot 0\cdot (-1)] = 2\ ,$$

$$N^{B_1} = \frac{1}{4}\,[1\cdot 12\cdot 1 + 1\cdot 2\cdot (-1) + 1\cdot 6\cdot 1 + 1\cdot 0\cdot (-1)] = 4\ ,$$

$$N^{B_2} = \frac{1}{4}\,[1\cdot 12\cdot 1 + 1\cdot 2\cdot (-1) + 1\cdot 6\cdot (-1) + 1\cdot 0\cdot 1] = 1\ .$$

Therefore

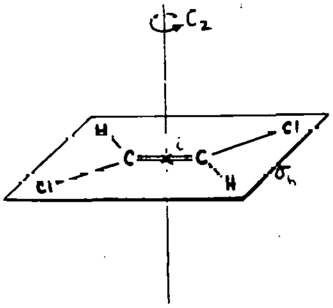
$$\Gamma = 5A_1 + 2A_2 + 4B_1 + B_2\ .$$

Step 4

From the character table of point group C_{2v}: (1) All bands are Raman active and only the A_2 bands are infrared inactive. There will be, therefore, $5A_1 + 4B_1 + 1B_2 = 10$ infrared bands and $5A_1 + 2A_2 + 4B_1 + 1B_2 = 12$ Raman bands (of which 10 should coincide with the infrared). (2) The $5A_1$ Raman bands may be polarized; the rest will be depolarized.

7.4 1,2-DICHLOROETHYLENE (*trans*) (*t*-ClHC·CClH)

Step 1



The plane of the molecule is the only plane of symmetry and there is a C_2 perpendicular to it in the center of the C=C bond. This center is also a center of symmetry. Table 2 shows that the point group is C_{2h}.

Step 2

$$u_E = 6 \,, \qquad u_{C_2} = 0 \,,$$

$$\chi_E = (6 - 2)\cdot 3 = 12 \,, \qquad \chi_{C_2} = (0 - 2)\cdot(-1) = 2 \,,$$

$$u_i = 0 \,, \qquad u_{\sigma_h} = 6 \,,$$

$$\chi_i = 0\cdot(-3) = 0 \,, \qquad \chi_{\sigma_h} = 6\cdot 1 = 6 \,.$$

Step 3

$$n_E = 6 \,, \qquad n_{C_2} = 1 \,, \qquad n_i = 1 \,, \qquad n_{\sigma_h} = 1 \,,$$

$$c = 4 \,, \qquad g = 1 + 1 + 1 + 1 = 4 \,,$$

$$N^{A_g} = \frac{1}{4}\,[1\cdot 12\cdot 1 + 1\cdot 2\cdot 1 + 1\cdot 0\cdot 1 + 1\cdot 6\cdot 1] = 5 \,,$$

$$N^{B_g} = \frac{1}{4}\,[1\cdot 12\cdot 1 + 1\cdot 2\cdot(-1) + 1\cdot 0\cdot 1 + 1\cdot 6\cdot(-1)] = 1 \,,$$

$$N^{A_u} = \frac{1}{4}\,[1\cdot 12\cdot 1 + 1\cdot 2\cdot 1 + 1\cdot 0\cdot(-1) + 1\cdot 6\cdot(-1)] = 2 \,,$$

$$N^{B_u} = \frac{1}{4}\,[1\cdot 12\cdot 1 + 1\cdot 2\cdot(-1) + 1\cdot 0\cdot(-1) + 1\cdot 6\cdot 1] = 4 \,.$$

Therefore

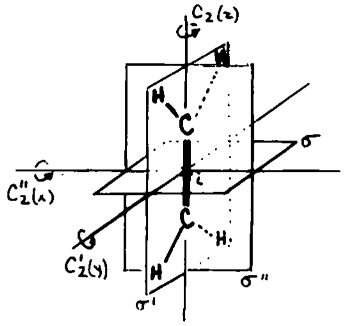
$$\Gamma = 5A_g + B_g + 2A_u + 4B_u \,.$$

Step 4

From the character table of the point group C_{2h}: (1) There will be $2A_u + 4B_u = 6$ infrared bands and $5A_g + 1B_g = 6$ Raman bands; there should not be any coinciding frequencies. (2) The $5A_g$ Raman bands may be partially polarized; the B_g will be depolarized.

7.5 ETHYLENE (C_2H_4)

Step 1



There are no C_3's or higher order axes, but it is easy to find three perpendicular C_2's passing through the center of the C=C bond — one coincident with the bond, one laying in the molecular plane, and the third perpendicular to the first two. Thus, the possible groups are reduced to D_2, D_{2d}, or D_{2h}. The existence of the three planes of symmetry determined by pairs of C_2 decides in favor of D_{2h}.

Step 2

$$u_E = 6\ , \quad u_{C_2} = 2\ , \quad u_{C'_2} = 0\ , \quad u_{C''_2} = 0\ ,$$

$$u_i = 0\ , \quad u_\sigma = 0\ , \quad u_{\sigma'} = 2\ , \quad u_{\sigma''} = 6\ ,$$

$$\chi_E = (6 - 2)\cdot 3 = 12\ , \qquad \chi_{C_2} = (2 - 2)\cdot(-1) = 0\ ,$$

$$\chi_{C'_2} = (0\cdot 2)\cdot(-1) = 2\ , \qquad \chi_{C''_2} = (0 - 2)\cdot(-1) = 2\ ,$$

$$\chi_i = 0\cdot(-3) = 0\ , \qquad \chi_\sigma = 0\cdot 1 = 0\ ,$$

$$\chi_{\sigma'} = 2\cdot 1 = 2\ , \qquad \chi_{\sigma''} = 6\cdot 1 = 6\ .$$

Step 3

$$n_E = 1\ , \quad n_{C_2} = 1\ , \quad n_{C'_2} = 1\ , \quad n_{C''_2} = 1\ ,$$

$$n_i = 1\ , \quad n_\sigma = 1\ , \quad n_{\sigma'} = 1\ , \quad n_{\sigma''} = 1\ ,$$

$$c = 8\ , \qquad g = 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 = 8\ ,$$

$$N^{A_g} = \frac{1}{8}\,[1\cdot 12\cdot 1 + 1\cdot 0\cdot 1 + 1\cdot 2\cdot 1 + 1\cdot 2\cdot 1 + 1\cdot 0\cdot 1$$

$$+ 1\cdot 0\cdot 1 + 1\cdot 2\cdot 1 + 1\cdot 6\cdot 1] = 3\ ,$$

$$\begin{aligned} N^{B_{1g}} = \frac{1}{8}\,[&1\cdot12\cdot1 + 1\cdot0\cdot1 + 1\cdot2\cdot(-1) + 1\cdot2\cdot(-1) + 1\cdot0\cdot1 \\ &+ 1\cdot0\cdot1 + 1\cdot2\cdot(-1) + 1\cdot6\cdot(-1)] = 0\ , \end{aligned}$$

$$\begin{aligned} N^{B_{2g}} = \frac{1}{8}\,[&1\cdot12\cdot1 + 1\cdot0\cdot(-1) + 1\cdot2\cdot1 + 1\cdot2\cdot(-1) + 1\cdot0\cdot1 \\ &+ 1\cdot0\cdot(-1) + 1\cdot2\cdot1 + 1\cdot6\cdot(-1)] = 1\ , \end{aligned}$$

$$\begin{aligned} N^{B_{3g}} = \frac{1}{8}\,[&1\cdot12\cdot1 + 1\cdot0\cdot(-1) + 1\cdot2\cdot(-1) + 1\cdot2\cdot1 + 1\cdot0\cdot1 \\ &+ 1\cdot0\cdot(-1) + 1\cdot2\cdot(-1) + 1\cdot6\cdot1] = 2\ , \end{aligned}$$

$$\begin{aligned} N^{A_{u}} = \frac{1}{8}\,[&1\cdot12\cdot1 + 1\cdot0\cdot1 + 1\cdot2\cdot1 + 1\cdot2\cdot1 + 1\cdot0\cdot(-1) + 1\cdot0\cdot(-1) \\ &+ 1\cdot2\cdot(-1) + 1\cdot6\cdot(-1)] = 1\ , \end{aligned}$$

$$\begin{aligned} N^{B_{1u}} = \frac{1}{8}\,[&1\cdot12\cdot1 + 1\cdot0\cdot1 + 1\cdot2\cdot(-1) + 1\cdot2\cdot(-1) + 1\cdot0\cdot(-1) \\ &+ 1\cdot0\cdot(-1) + 1\cdot2\cdot1 + 1\cdot6\cdot1] = 2\ , \end{aligned}$$

$$\begin{aligned} N^{B_{2u}} = \frac{1}{8}\,[&1\cdot12\cdot1 + 1\cdot0\cdot(-1) + 1\cdot2\cdot1 + 1\cdot2\cdot(-1) + 1\cdot0\cdot(-1) \\ &+ 1\cdot0\cdot1 + 1\cdot2\cdot(-1) + 1\cdot6\cdot1] = 2\ , \end{aligned}$$

$$\begin{aligned} N^{B_{3u}} = \frac{1}{8}\,[&1\cdot12\cdot1 + 1\cdot0\cdot(-1) + 1\cdot2\cdot(-1) + 1\cdot2\cdot1 + 1\cdot0\cdot(-1) \\ &+ 1\cdot0\cdot1 + 1\cdot2\cdot1 + 1\cdot6\cdot(-1)] = 1\ . \end{aligned}$$

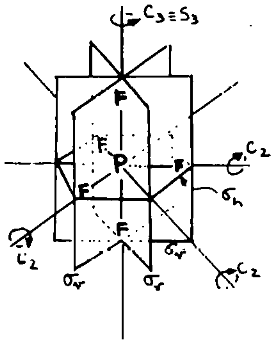
Therefore

$$\Gamma = 3A_g + B_{2g} + 2B_{3g} + A_u + 2B_{1u} + 2B_{2u} + B_{3u}\ .$$

Step 4

From the character table of the point group D_{2h}: (1) There will be $2B_{1u} + 2B_{2u} + 1B_{3u} = 5$ infrared bands and $3A_g + 1B_{2g} + 2B_{3g} = 6$ Raman bands; there should not be any coinciding frequencies. (2) The $3A_g$ bands may be polarized; the other three Raman bands will be depolarized.

7.6 PHOSPHORUS PENTAFLUORIDE (PF_5)



Step 1

There is an obvious C_3 through the axial fluorine atoms and each horizontal PF bond coincides with a C_2. The plane of the equatorial fluorine atoms is a plane of symmetry. These elements can be found in the D_{3h} group, which can be verified by finding the S_3 (coincident with C_3) and the $3\sigma_v$ (through C_3 and each C_2).

Step 2

$$u_E = 6\ , \qquad u_{C_3} = 3\ , \qquad u_{C_2} = 2\ ,$$

$$u_{\sigma_h} = 4\ , \qquad u_{S_3} = 1\ , \qquad u_{\sigma_v} = 4\ ,$$

$$\chi_E = (6 - 2)\cdot 3 = 12\ , \qquad \chi_{C_3} = (3 - 2)\cdot 0 = 0\ ,$$

$$\chi_{C_2} = (2 - 2)\cdot(-1) = 0\ , \qquad \chi_{\sigma_h} = 4\cdot 1 = 4\ ,$$

$$\chi_{S_3} = 1\cdot(-2) = -2\ , \qquad \chi_{\sigma_v} = 4\cdot 1 = 4\ .$$

Step 3

$$n_E = 1\ , \qquad n_{C_3} = 2\ , \qquad n_{C_2} = 3\ ,$$

$$n_{\sigma_h} = 1\ , \qquad n_{S_3} = 2\ , \qquad n_{\sigma_v} = 3\ ,$$

$$c = 6\ , \qquad g = 1 + 2 + 3 + 1 + 2 + 3 = 12\ ,$$

$$N^{A_1'} = \frac{1}{12}\,[1\cdot12\cdot1 + 2\cdot0\cdot1 + 3\cdot0\cdot1 + 1\cdot4\cdot1 + 2\cdot(-2)\cdot1 + 3\cdot4\cdot1] = 2\ ,$$

$$N^{A_2'} = \frac{1}{12}\,[1\cdot12\cdot1 + 2\cdot0\cdot1 + 3\cdot0\cdot(-1) + 1\cdot4\cdot1 + 2\cdot(-2)\cdot1 + 3\cdot4\cdot(-1)] = 0\ ,$$

$$N^{E'} = \frac{1}{12}\,[1\cdot12\cdot2 + 2\cdot0\cdot(-1) + 3\cdot0\cdot0 + 1\cdot4\cdot2 + 2\cdot(-2)\cdot(-1) + 3\cdot4\cdot0] = 3\ ,$$

$$N^{A_1''} = \frac{1}{12}\,[1\cdot12\cdot1 + 2\cdot0\cdot(-1) + 3\cdot0\cdot1 + 1\cdot4\cdot(-1) + 2\cdot(-2)\cdot(-1) + 3\cdot4\cdot(-1)] = 0\ ,$$

$$N^{A_2''} = \frac{1}{12}\,[1\cdot12\cdot1 + 2\cdot0\cdot1 + 3\cdot0\cdot(-1) + 1\cdot4\cdot(-1) + 2\cdot(-2)\cdot(-1) + 3\cdot4\cdot1] = 2\ ,$$

$$N^{E''} = \frac{1}{12}\,[1\cdot12\cdot2 + 2\cdot0\cdot(-1) + 3\cdot0\cdot0 + 1\cdot4\cdot(-2) + 2\cdot(-2)\cdot1 + 3\cdot4\cdot0] = 1\ .$$

Therefore

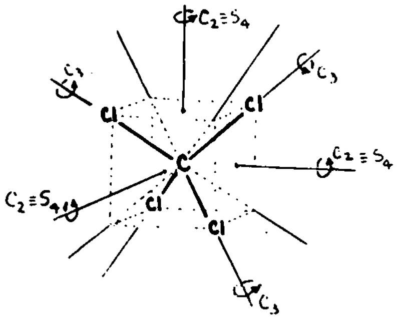
$$\Gamma = 2A_1' + 3E' + 2A_2'' + E''\ .$$

Step 4

From the character table of the point group D_{3h}: (1) There will be $3E' + 2A_2'' = 5$ infrared bands and $2A_1' + 3E' + 1E'' = 6$ Raman bands, the frequencies of the $3E'$ bands coinciding in both spectra. (2) The $2A_2''$ infrared bands of gaseous PF_5 should show PQR structure. (3) The $2A_1'$ Raman bands may be polarized; the other four Raman bands should be depolarized.

7.7 CARBON TETRACHLORIDE (CCl_4)

Step 1



Each CCl bond coincides with a C_3 axis and there are no C_4's. This description is only compatible with the groups T, T_d, and T_h. The fact that every pair of C_3's determines a plane of symmetry decides in favor of T_d. The existence of $3C_2$'s, bisecting pairs of C_4's, can be verified.

Step 2

$$u_E = 5\ , \qquad u_{C_3} = 2\ , \qquad u_{C_2} = 1\ , \qquad u_{S_4} = 1\ , \qquad u_{\sigma_d} = 3\ ,$$

$$\chi_E = (5-2)\cdot 3 = 9\ , \qquad \chi_{C_3} = (2-2)\cdot 0 = 0\ ,$$

$$\chi_{C_2} = (1-2)\cdot(-1) = 1\ , \qquad \chi_{S_4} = 1\cdot(-1) = -1\ ,$$

$$\chi_{\sigma_d} = 3\cdot 1 = 3\ .$$

Step 3

$$n_E = 1\ , \qquad n_{C_3} = 8\ , \qquad n_{C_2} = 3\ , \qquad n_{S_4} = 6\ , \qquad n_{\sigma_d} = 6\ ,$$

$$c = 5\ , \qquad g = 1 + 8 + 3 + 6 + 6 = 24\ ,$$

$$N^{A_1} = \frac{1}{24}\ [1\cdot 9\cdot 1 + 8\cdot 0\cdot 1 + 3\cdot 1\cdot 1 + 6\cdot(-1)\cdot 1 + 6\cdot 3\cdot 1] = 1\ ,$$

$$N^{A_2} = \frac{1}{24}\ [1\cdot 9\cdot 1 + 8\cdot 0\cdot 1 + 3\cdot 1\cdot 1 + 6\cdot(-1)\cdot(-1) + 6\cdot 3\cdot(-1)] = 0\ ,$$

$$N^{E} = \frac{1}{24}\,[1\cdot 9\cdot 2 + 8\cdot 0\cdot(-1) + 3\cdot 1\cdot 2 + 6\cdot(-1)\cdot 0 + 6\cdot 3\cdot 0] = 1\ ,$$

$$N^{F_1} = \frac{1}{24}\,[1\cdot 9\cdot 3 + 8\cdot 0\cdot 0 + 3\cdot 1\cdot(-1) + 6\cdot(-1)\cdot 1 + 6\cdot 3\cdot(-1)] = 0\ ,$$

$$N^{F_2} = \frac{1}{24}\,[1\cdot 9\cdot 3 + 8\cdot 0\cdot 0 + 3\cdot 1\cdot(-1) + 6\cdot(-1)\cdot(-1) + 6\cdot 3\cdot 1] = 2\ .$$

Therefore

$$\Gamma = A_1 + E + 2F_2\ .$$

Step 4

From the character table of the point group T_d: (1) All four bands should appear in the Raman spectra while only the $2F_2$ frequencies should show in the infrared. (2) The A_1 Raman band should be completely polarized, while the other three bands should be depolarized.

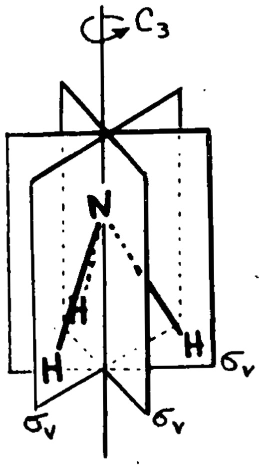


Fig. 1. Ammonia.

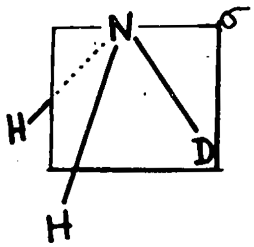


Fig. 2. Mono-deuterated ammonia.

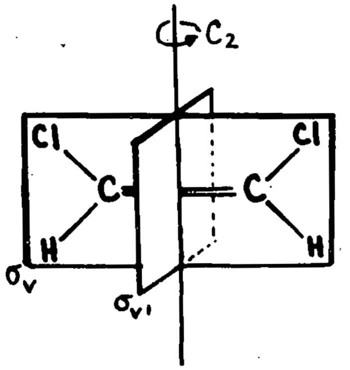


Fig. 3. *cis*-1,2-Dichloroethylene.

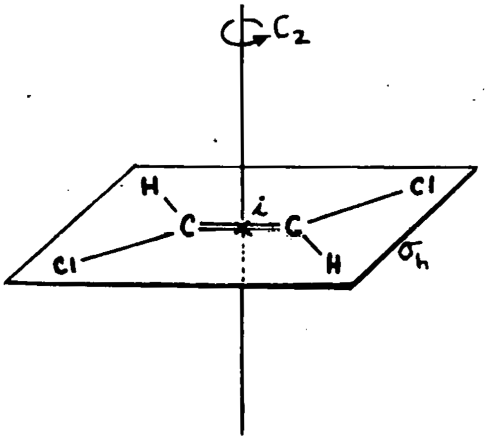


Fig. 4. *trans*-1,2-Dichloroethylene.

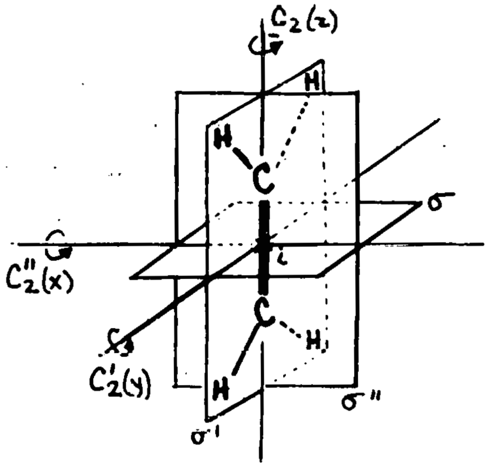


Fig. 5. Ethylene.

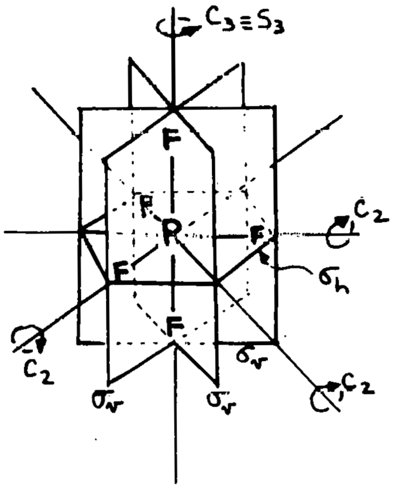


Fig. 6. Phosphorus pentafluoride.

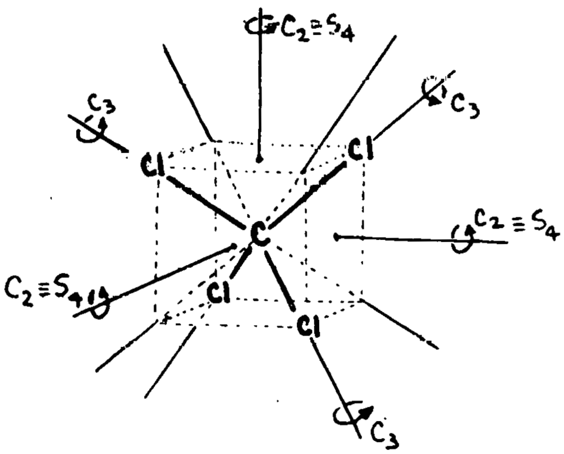


Fig. 7. Carbon tetrachloride.

BIBLIOGRAPHY

A. Two books with the main emphasis on group theory:

F. A. Cotton, *Chemical Applications of Group Theory,* Interscience Publishers (Division of John Wiley and Sons), 1963.
An elementary treatment of the basic theory and a clear description of its application to molecular vibrations, molecular orbitals and Ligand Field Theory.

J. R. Ferraro and J. S. Ziomek, *Introductory Group Theory (and its Application to Molecular Structure*), Plenum Press, 1969.
A practical guide for "scientists with only limited theoretical background." Includes detailed examples of calculations for several point groups.

B. Two classical references:

G. Herzberg, *Molecular Spectra and Molecular Structure. Vol. II: Infrared and Raman Spectra of Polyatomic Molecules,* D. Van Nostrand Company, 1945.
A comprehensive treatise with extensive data on most molecules studied until its publication. Group theory is not used explicitly, but tables are given for the determination of the symmetry and activity of fundamental, overtone, and combination bands.

E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations,* McGraw-Hill Book Company, 1955.
The undisputed principal reference for the theoretical treatment of molecular vibrations. Few practical examples, but a complete chapter is devoted to the detailed analysis of benzene.

C. Books on general molecular spectroscopy with at least one chapter on symmetry and group theory:

G. M. Barrow, *Introduction to Molecular Spectroscopy,* McGraw-Hill Book Company, 1962.

N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy,* Academic Press, 1964.

G. W. King, *Spectroscopy and Molecular Structure,* Holt, Rinehart and Winston Company, 1964.

K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* John Wiley and Sons, 1963.

D. Steele, *Theory of Vibrational Spectroscopy,* W. B. Saunders Company, 1971.

D. Two advanced books on group theory:

E. Wigner, *Group Theory,* Academic Press, 1959.

V. Heine, *Group Theory and Quantum Mechanics,* Pergamon Press, 1960.

INTERNAL DISTRIBUTION

1-65.	H. W. Morgan	69-70.	Laboratory Records
66-67.	Central Research Library	71.	Laboratory Records, ORNL R.C.
68.	Document Record Section	72.	ORNL Patent Office

EXTERNAL DISTRIBUTION

73.	Research and Technical Support Division, ERDA, Oak Ridge Operations, Oak Ridge, TN 37830
74-100.	Technical Information Center, Oak Ridge, TN 37830