4. SYMMETRY OF MOLECULES AND MOLECULAR VIBRATIONS

Introduction.

Symmetry: enormous help in the interpretation. Molecular symmetry → full use of group theory.

Symmetry is a common quality in science; most properties of elementary particles, atoms, and number of molecules are symmetric. Since symmetry is strictly defines relations between molecular spectra and molecular structures the present work focuses on the mathematical tools which are necessary to apply symmetry concepts to vibrational (infrared and Raman) spectroscopy.

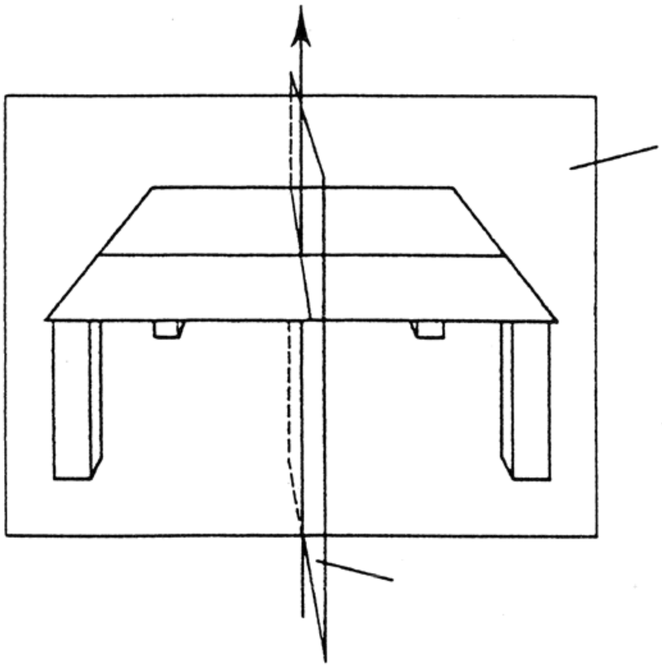
Point group analysis

Distribution of mol. vibrations among symmetry species.

Symmetry of molecule: the symmetry of nuclear arrangement in the equilibrium position. The symmetry of molecule determined by the collection of all symmetry options which send the equilibrium configuration into an equivalent configuration, simply by exchanging equivalent atoms using group theory:

- predict symmetry of vibrations
- without knowing Q;

Classification of molecules into point groups



The symmetry of the table

Symmetry Elements

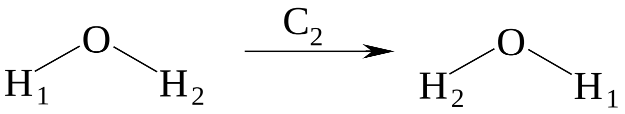
- In equilibrium configuration
- Geometrical operations → transformation → to the original configuration

1. Identity (E, I)

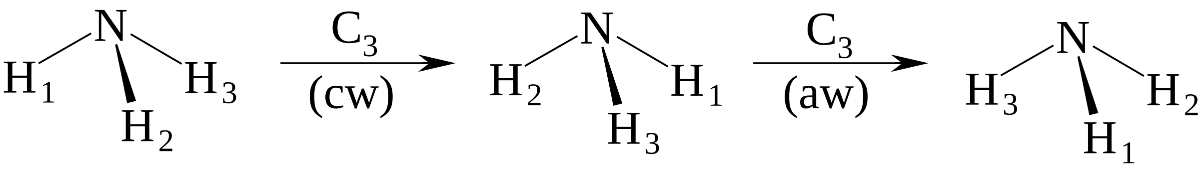
E – Einheit (G) } without change
I – Identical (E) } in orientation

2. Rotational Axes (C)

Clockwise, counterclockwise (anti-)



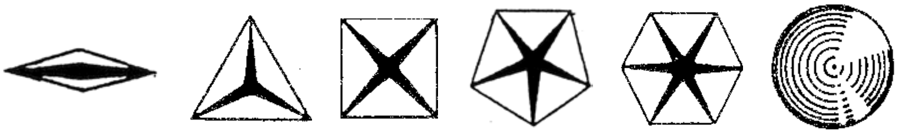
cw and aw are the same



cw and aw are not the same

$$\frac{2\pi}{n} = \frac{360^\circ}{n} \equiv C_n$$

180°	120°	90°	72°	60°	0°



n = 2	3	4	5	6	∞
C_2	C_3	C_4	C_5	C_6	C_∞

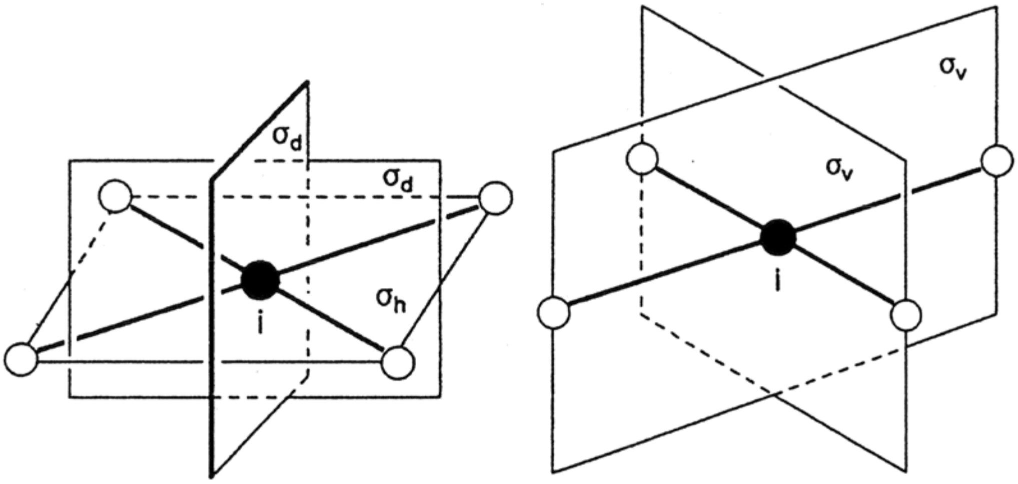
3. Planes of Symmetry (σ)

Two parts are mirror images of each other.

σ_v – “vertical”plane of symmetry (along the C_n axes)

σ_d – is bisecting the angle between two C_2 axes (“ diagonal”)

σ_h – “horizontal” when it is perpendicular to the main rotational axis.



Center of symmetry (i)

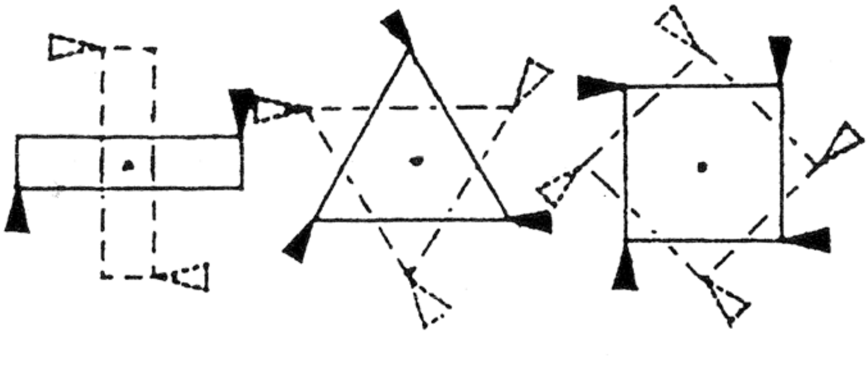
"Meeting point" of straight lines through equivalent atoms equidistant from point (i).

a) If "i" is situated on an atom, the total number of atoms in the molecule is **odd**. (e.g. octahedral molecules)

b) If "i" is not on an atom, the total number of atoms in the molecule is **even**. (e.g. C_2H_4, C_6H_6)

4.Rotation-Reflection Axes

Rotation 360°/n about an axis (C_n) and than reflected in a plane perpendicular to this axis.



S_4 S_6 S_8

(all S_i are perpendicular to the plane)

Summary:

Point Symmetry Elements and Symmetry Operations

Symmetry element	Symmetry operation
1. Identity (*E* or *I*)	Molecule unchanged
2. Axis of rotation (C_n)	Rotation about axis by $2\pi/n$
3. Center of symmetry or center of inversion (*i*)	Inversion of all atoms through center
4. Plane (σ)	Reflection in the plane
5. Rotation—reflection axis (S_n)	Rotation about axis by $2\pi/n$, followed by reflection in a plane perpendicular to the axis

Point Groups

A very elegant and easy method was developed by Adams and Newton for factor group analysis of crystals [1, 2]. A simple modification of the Bhagavantam-Venkatarayudu method [3] was used to calculate the contribution of each atom in a unit cell to a representation of the factor group. Results have been computed for all sites in all 230 space groups. By its nature the method also yields the results of equivalent analyses for 32 of the point groups of isolated molecules.

From 59 chemically important point groups of isolated molecules only 32 belong to 230 crystallographic point groups and can be treated by Adams-Newton method. These are the following symmetry species (in brackets are the representative crystallographic space groups): $\boldsymbol{C_1}$ *(1, P1)*,$\boldsymbol{C_S}$ *(6, Pm)*, $\boldsymbol{C_i} \equiv \boldsymbol{S_2}$ *(2, $P\bar{1}$)*, $\boldsymbol{C_2}$ *(3, P2)*, $\boldsymbol{C_3}$ *(143, P3)*, $\boldsymbol{C_4}$ *(75, P4)*, $\boldsymbol{C_6}$ *(168, P6)*, $\boldsymbol{D_2}$ *(16, P222)*, $\boldsymbol{D_3}$ *(149, P312)*, $\boldsymbol{D_4}$ *(89, P422)*, $\boldsymbol{D_6}$ *(177, P622)*, $\boldsymbol{C_{2v}}$ *(25, Pmm2)*, $\boldsymbol{C_{3v}}$ *(156, P3m1)*, $\boldsymbol{C_{4v}}$ *(99, P4mm)*, $\boldsymbol{C_{6v}}$ *(183, P6mm)*, $\boldsymbol{C_{2h}}$ *(10, P2/m)*, $\boldsymbol{C_{4h}}$ *(83, P4/m)*, $\boldsymbol{C_{6h}}$ *(175, P6/m)*, $\boldsymbol{D_{2h}}$ *(47, Pmmm)*, $\boldsymbol{D_{3h}}$ *(187, $P\bar{6}m2$)*, $\boldsymbol{D_{4h}}$ *(123, P4/mmm)*, $\boldsymbol{D_{6h}}$ *(191, P6/mmm)*, $\boldsymbol{D_{2d}}$ *(111, $P\bar{4}2m$)*, $\boldsymbol{D_{3d}}$ *(162, $P\bar{3}1m$)*, $\boldsymbol{S_4}$ *(81, $P\bar{4}$)*, $\boldsymbol{S_6}$ *(147, $P\bar{3}$)*, $\boldsymbol{T}$ *(195, P23)*, $\boldsymbol{T_d}$ *(215,*

$P\bar{4}3m$) , **T_h** *(200, Pm3)* , **O** *(207, P432)* and **O_h** *(221, Pm3m)* which had been summarized by M. Valli in 1995

The missing “extra” 27 molecular point groups are: **D_{4d} , C_5 , D_5, C_{5v}, C_{5h} , D_{5h} , D_{5d} , D_{6d} , C_7 , D_7, C_{7v}, C_{7h} , D_{7h} , D_{7d}, C_8 , D_8, C_{8v}, C_{8h} , D_{8h} , D_8, S_8 , I , I_h , $C_{\infty v}$, $D_{\infty h}$, SU_2** *and* **R_3.**

The classical point group analysis of molecules based on the reduction formula described in many text books and widely used in practice (see e.g. Ref. 5 and references therein) is rather complicated and easy to make errors. Therefore we present here the extension of the Adams-Newton method for calculation of a factor group representation for the above missing space groups, which will be very useful e.g. for point group analysis of complexes and derivatives of cyclopentadienyl rings exhibiting **C_5** rotational axes (**C_5**, **D_5**, ,**C_{5v}**, **C_{5h}**, **D_{5h}** ***and*** **D_{5d}** point groups). The use of these data will be illustrated by several examples of complex molecules which point group analysis are very complicated and time consuming by conventional methods.

References:

[1] D. M. ,Adams and D. C. Newton, *Tables for Factor Group An*alysis, Bcckman-RIIC Ltd, Sunley House, 4 Bedford Park, Croydon CR9 3LG, **1970.**

[2] D. M. ,Adams and D. C. Newton, *Tables for Factor-group Analysis of the Vibrational Spectra of Solids, J. Chem. Soc (A),* **1970**,2822-2827.

[3] S. Bhagavantam ,T. Venkatarayudu, *Theory of Groups and its Application to Physical Problems,* Academic Press, London,**1969.**

[4] M. Valli, *Vibrational Spectroscopy, Tables for Factor Group and Point Group Analysis*, Uppsala, **1995**

The set of all symmetry elements of a molecule can be made to form a mathematical system called a group.

Character tables for chemically important point groups

Nonaxial groups: **(*Binary groups*)**	C_1[a] C_s C_i
C_n groups: **(*Cyclic groups*)**	C_2 C_3 C_4 C_5[b] C_6 C_7 C_8
D_n groups: **(*Dihedral groups*)**	D_2 D_3 D_4 D_5 D_6 D_7 D_8
C_{nv} groups: **(*Cnical groups*)**	C_{2v} C_{3v} C_{4v} C_{5v} C_{6v} C_{7v} C_{8v}
C_{nh} groups	C_{2h} C_{3h} C_{4h} C_{5h} C_{6h} C_{7h} C_{8h}
D_{nh} group: ***(Prismatic groups)***	D_{2h} D_{3h} D_{4h} D_{5h} D_{6h} D_{7h} D_{8h}
D_{nd} groups: ***(Antiprizmatic groups)***	D_{2d} D_{3d} D_{4d} D_{5d} D_{6d} D_{7d} D_{8d}
S_n groups: ***(Rotation-Reflection groups)***	S_4 S_6 S_8
Cubic groups: ***(Terahedral/Cubic groups)***	T T_h T_d O O_h
Linear groups: ***(Cylindrical groups)***	$C_{\infty V}$ $D_{\infty V}$
Icosahedral groups[c]**:**	I Ih
Spherical groups:	SU_2 R_3

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[a] 32 molecular point groups existing among 230 crystallographic space groups and can be obtained in Adams-Newton tables (recently black color).

[b] 23 point groups marked in red (and italics letters) are not existing in crystal structures. Their so called VM sites and characters were developed by the authors.

[c] The very rare and unique icosahedral and spherical groups are not discussed (marked in blue and not bold letters).

Character Tables

The character table is used to classify molecular vibrations to the irreducible representation of the symmetry group.

Symbols of species

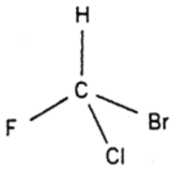
A	One-dimensional representations which are symmetric with respect to the rotation about the principal axis of rotation. $(C_n) = 1$.
B	One-dimensional representations which are antisymmetric with respect to the rotation about the principal axis of rotation. $(C_n) = 1$.
E	Two-dimensional representations. Occur in molecules having an axis higher than C_2.
F	Three-dimensional representations. Occur in molecules having more than two C_3 axes.

B_1, B_2 subscripts	Symmetric (1) or antisymmetric (2) with respect to a C_2 axis (or a vertical plane of symmetry) perpendicular to the principal axis.
A_g, A_u subscripts	Symmetric (g) or antisymmetric (u) with respect to a center of symmetry (*i*). g–gerade; u–ungerade
A’, A’’ primes	Symmetric(’) or antisymmetric (’’) with respect to σ.

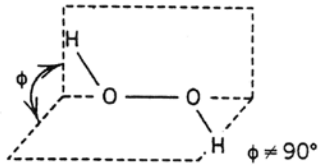
Linear molecules:

σ^+, Σ^+	Symmetric with respect to a plane of symmetry through the molecular axis.
σ^-, Σ^-	Antisymmetric with respect to a plane of symmetry through the molecular axis.
π, Δ, φ	Degenerate vibrations, with the degree of degeneracy increasing in this order.

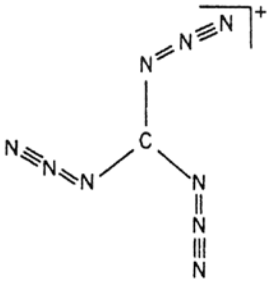
Examples for determination of point groups



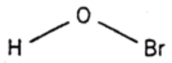
$CHFClBr$



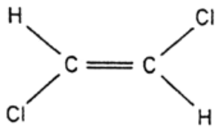
H_2O_2



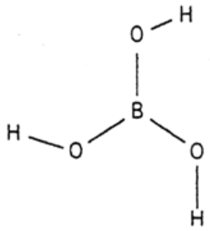
$C(N_3)_3^+$
(nonplanar)



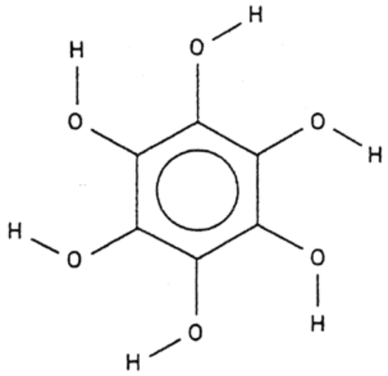
$HOBr$



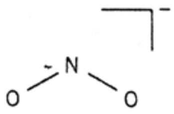
trans–$C_2H_2Cl_2$



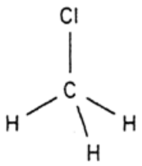
H_3BO_3
(planar)



$C_6(OH)_6$



NO_2^-



CH_3Cl

a.) H_2O

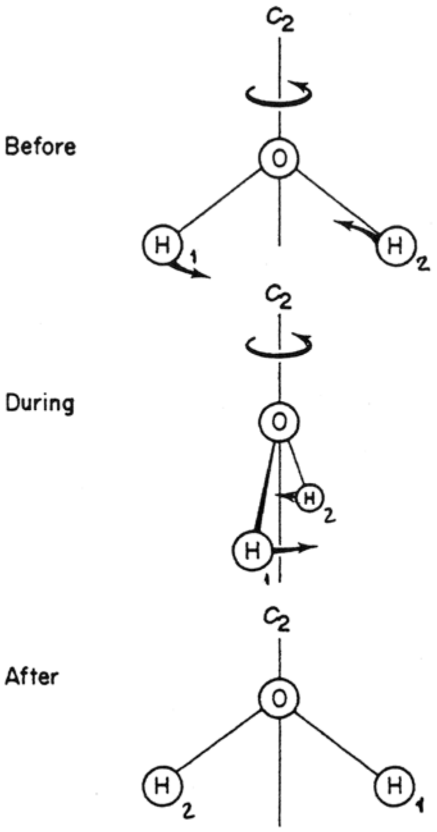
The conversion of the H_2O

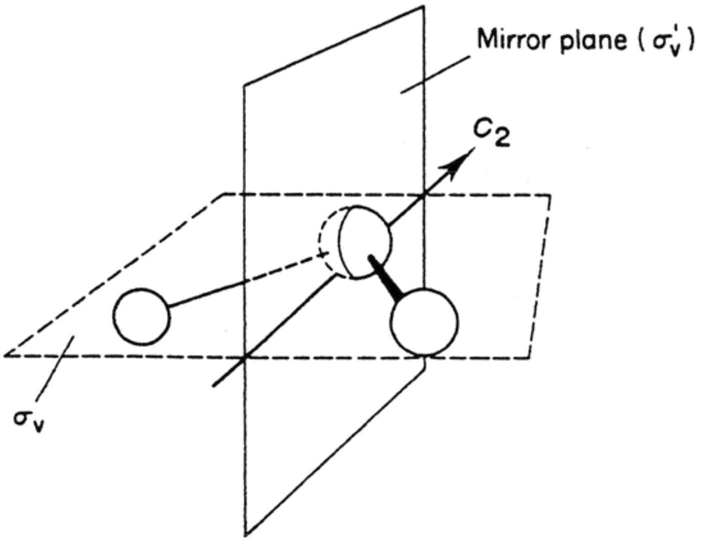
Rotation of 180°

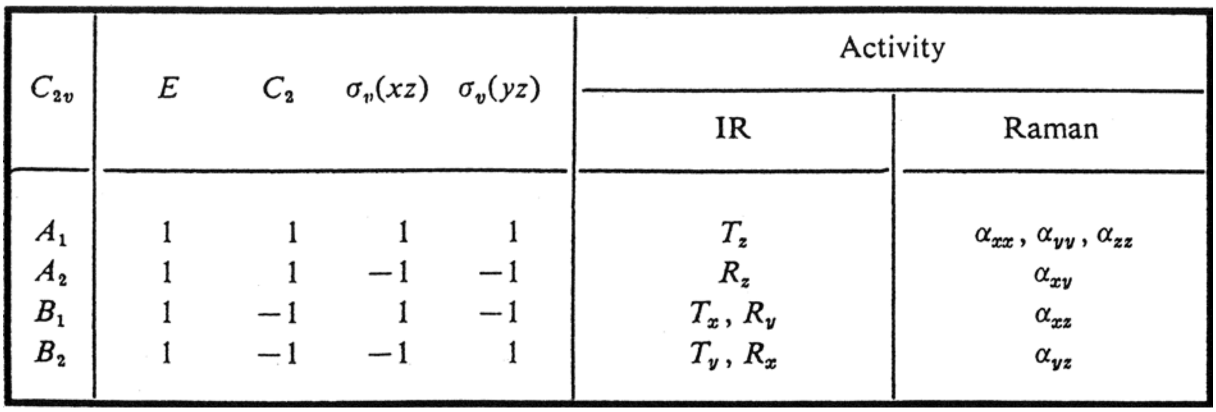
360°/n =180°

n = 2

$C_n \equiv C_2$

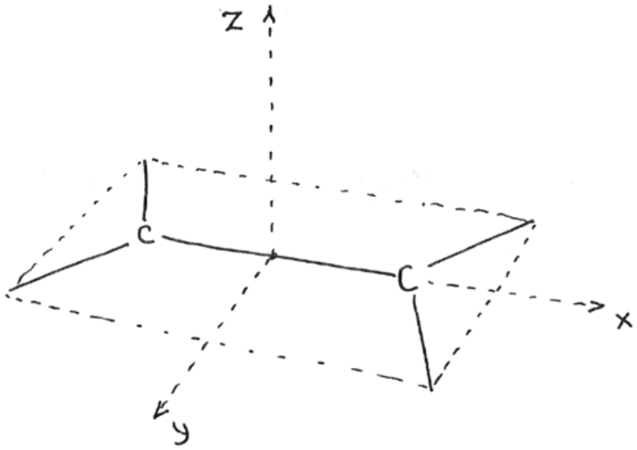


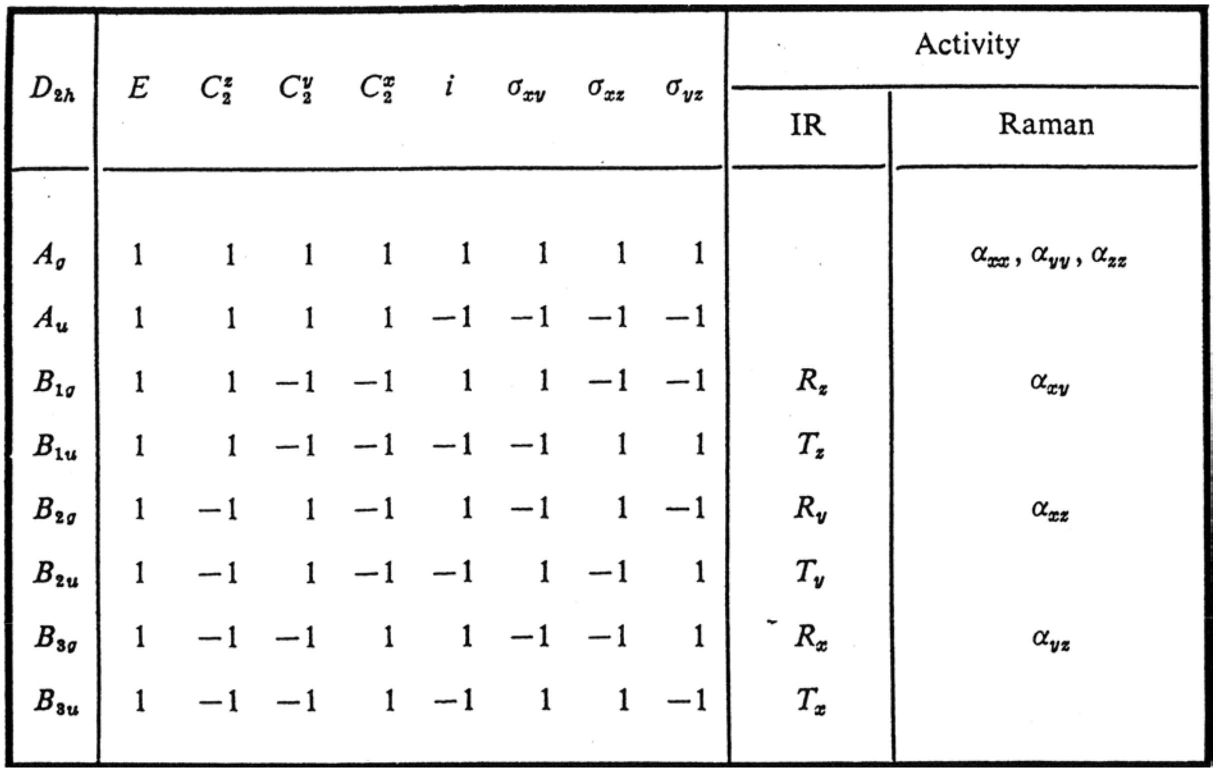




C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	Activity	
					IR	Raman
A_1	1	1	1	1	T_z	α_{xx}, α_{yy}, α_{zz}
A_2	1	1	-1	-1	R_z	α_{xy}
B_1	1	-1	1	-1	T_x, R_y	α_{xz}
B_2	1	-1	-1	1	T_y, R_x	α_{yz}

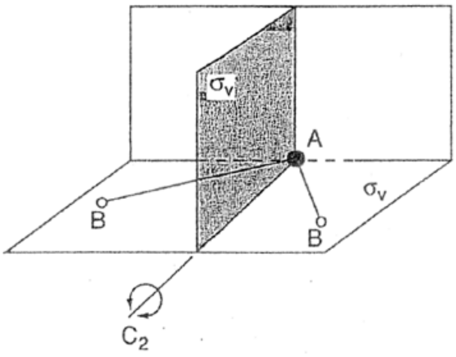
b.) Ethene (C_2H_4)



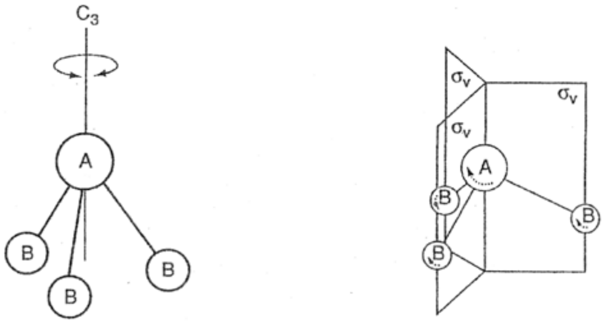


D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ_{xy}	σ_{xz}	σ_{yz}	Activity	
									IR	Raman
A_g	1	1	1	1	1	1	1	1		α_{xx}, α_{yy}, α_{zz}
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	α_{xy}
B_{1u}	1	1	-1	-1	-1	-1	1	1	T_z	
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	α_{xz}
B_{2u}	1	-1	1	-1	-1	1	-1	1	T_y	
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	α_{yz}
B_{3u}	1	-1	-1	1	-1	1	1	-1	T_x	

Symmetry elements of molecules.



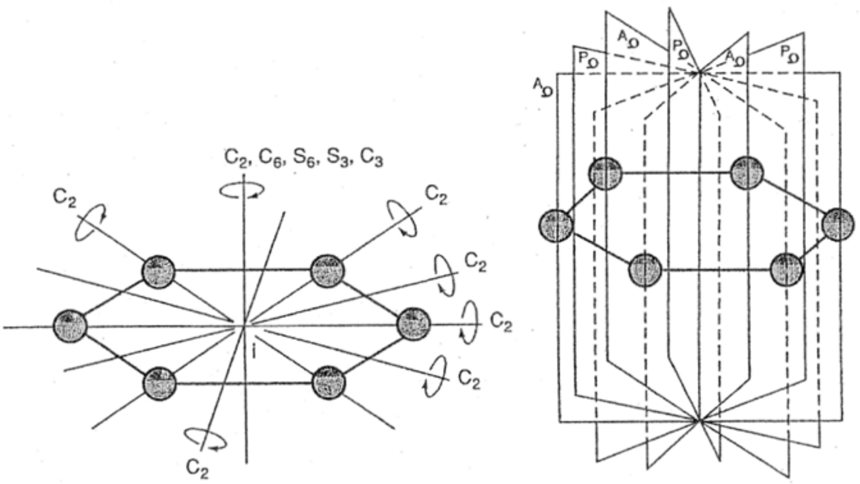
Symmetry elements for a bent AB_3 molecule.



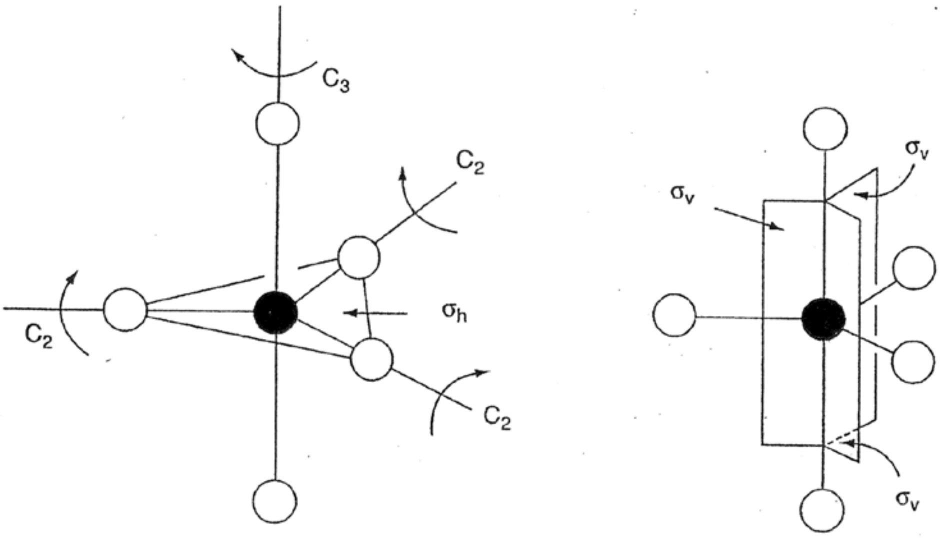
The C_3 symmetry element in pyramidal AB_3 molecule.
(a)

The σ_v symmetry element in pyramidal AB_3 molecule.
(b)

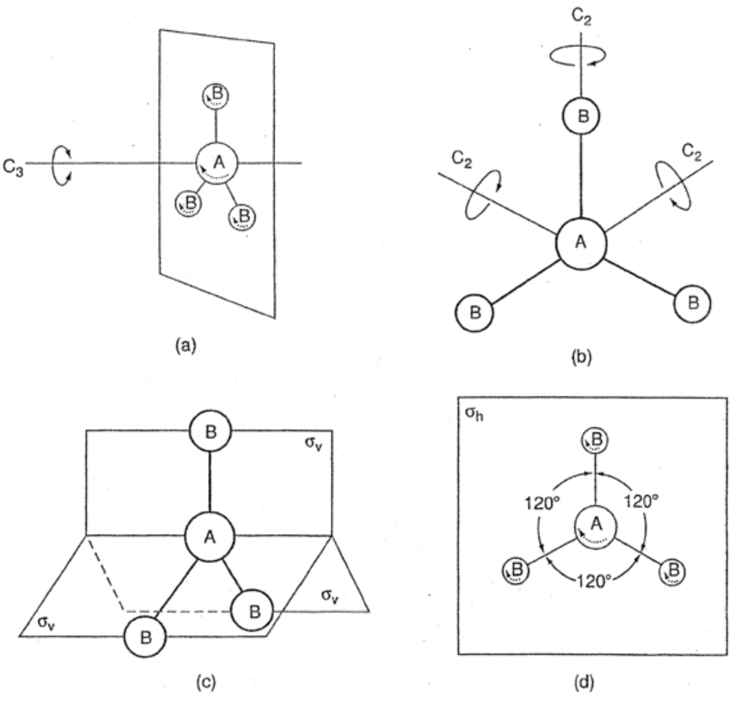
Symmetry elements for a pyramidal AB_3 molecule: (a) C_3 element; (b) σ_v element



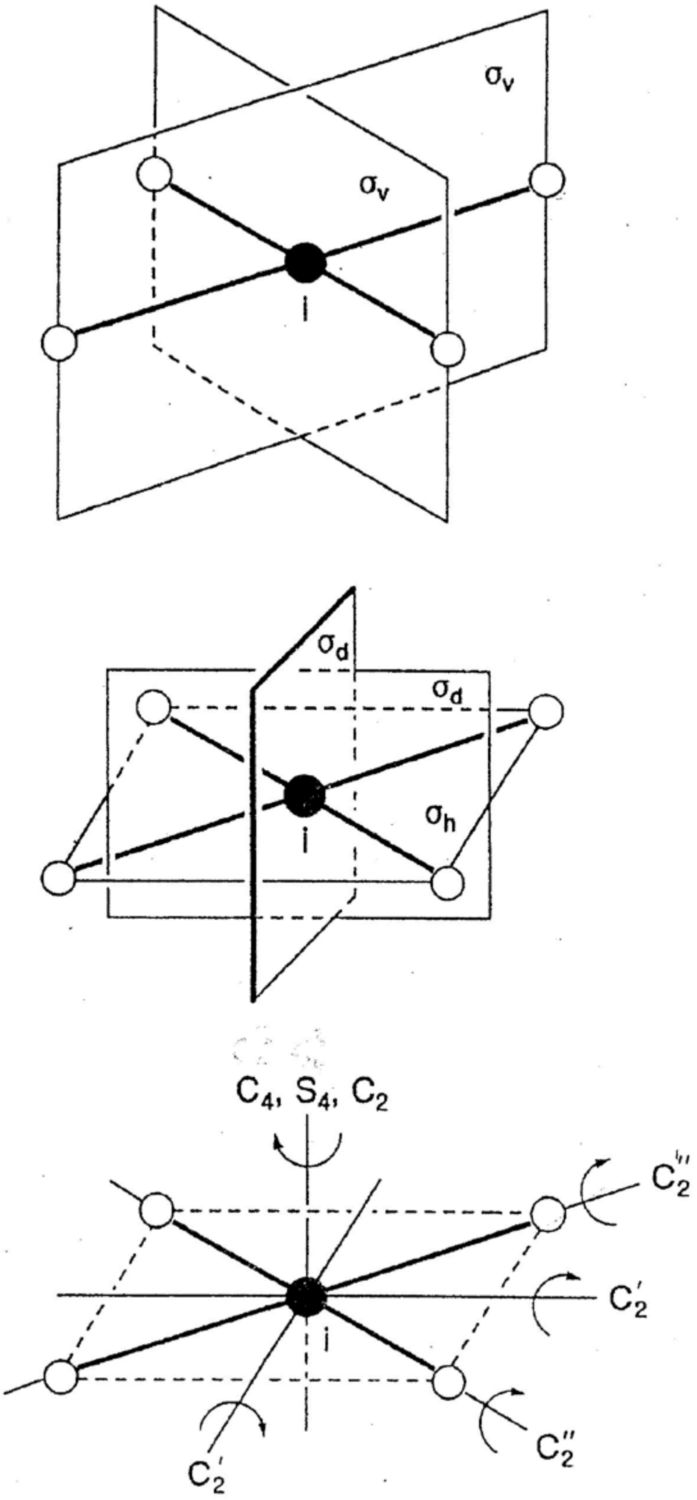
Symmetry elements for a planar hexagonal A_6B_6 molecule.



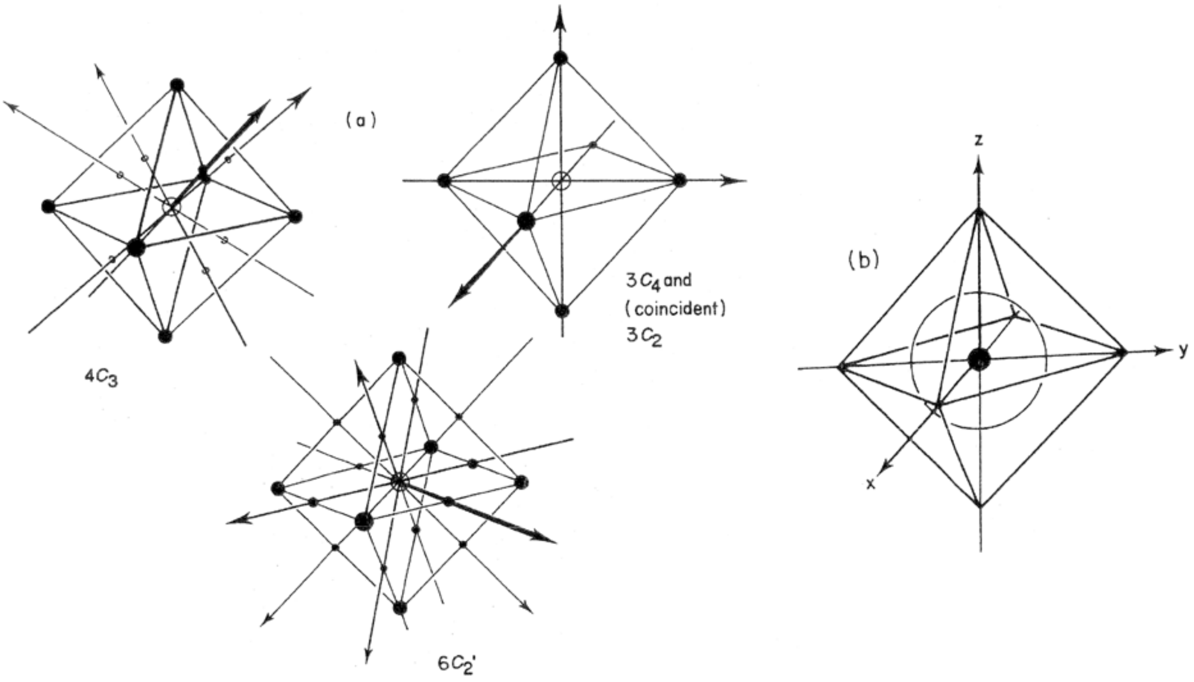
Symmetry elements for a trigonal bipyramidal AB_5 molecule.



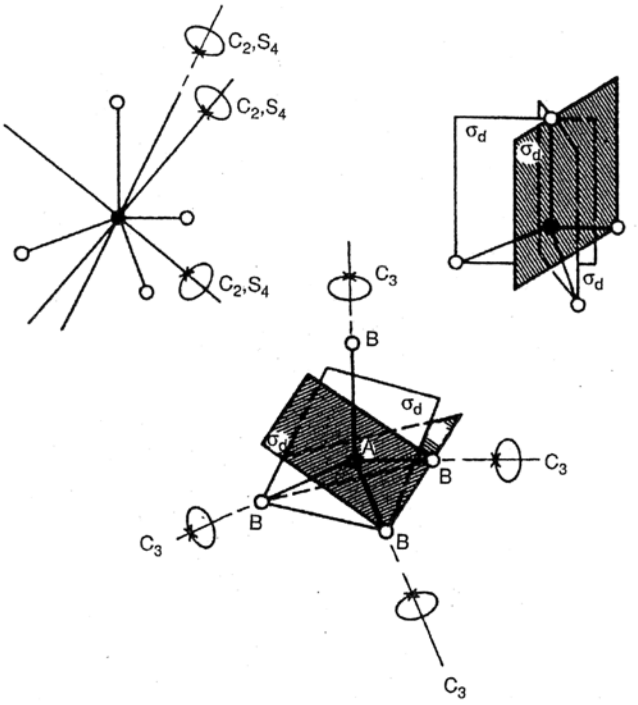
Symmetry elements for a planar AB_3 molecule: (a) C_3; (b) C_2; (c) σ_v and (d) σ_h.



Symmetry elements in D_{4h} point group.



(a) Rotational symmetry elements of an octahedron, divided between three diagrams of clarity.
(b) The conventional choice of coordinate axes for an octahedron.



Symmetry elements for tetrahedron.

4.1. Point group analysis of vibrations using Adams-Newton tables

IR

Factor group analysis Raman vibrations of crystals

Acoustic

A-N. Character tables:

– Vibrational freedom of each sets of equivalent atoms along symmetry species.

Equivalent atoms are occupying different

Wyckoff - sites

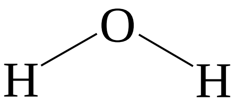
230 crystallographic point groups

32 molecular (general) point groups

C_5, S_5, C_{5n}, D_5, C_{5v}, and D_{5n}

Examples

Example(1): H_2O

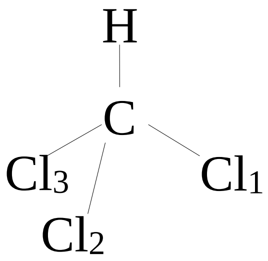


Point group: Space group:

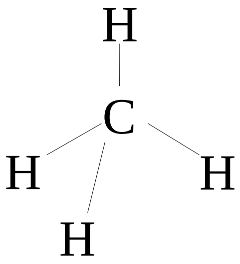
Table 1.

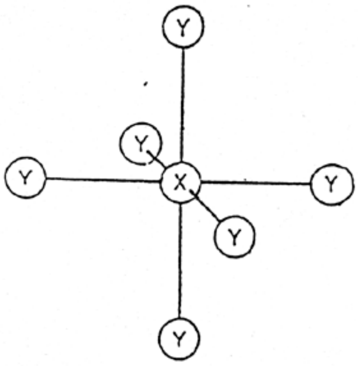
C_{2v} 25 C_{2v} A; C_S(2x) E; C_S(yz) G; C_1 I;

Example(2): Chloroform



Example(3): Methane

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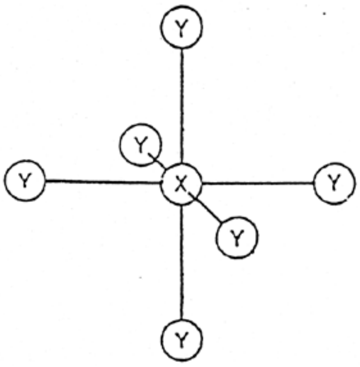
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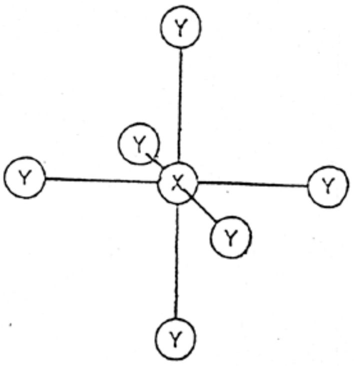
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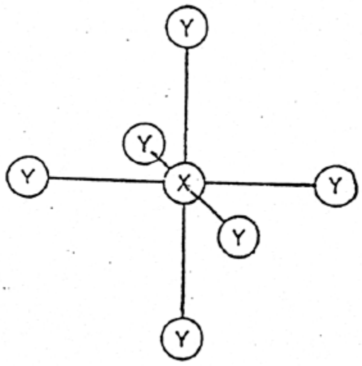
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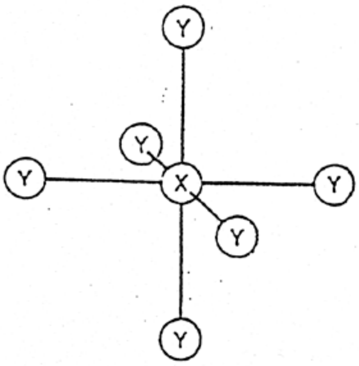
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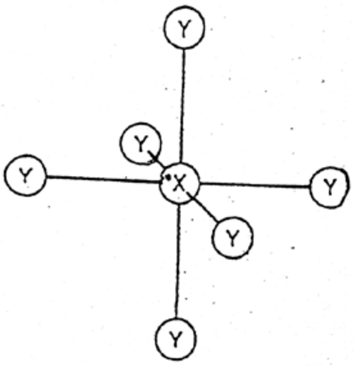
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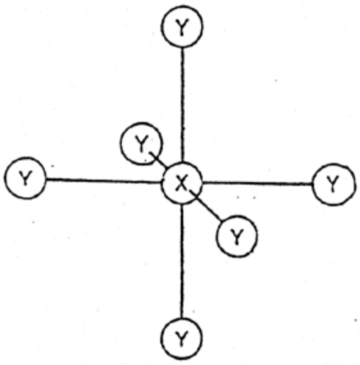
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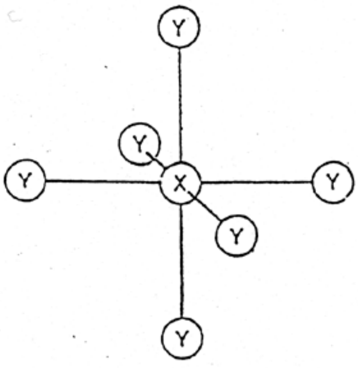
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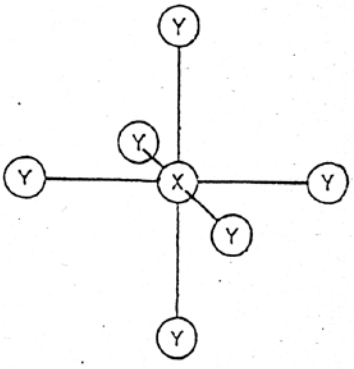
Y
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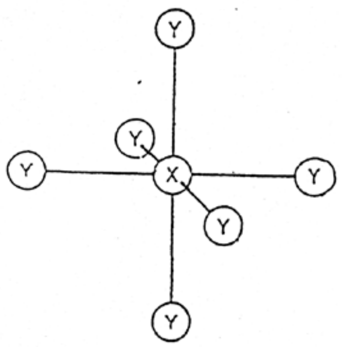
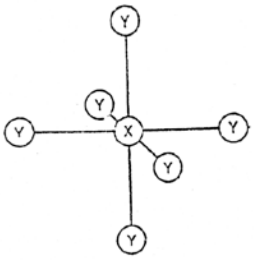
Example(4): XY6 Octahedral molecule



Examples(5): Octahedral-octahedrons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X
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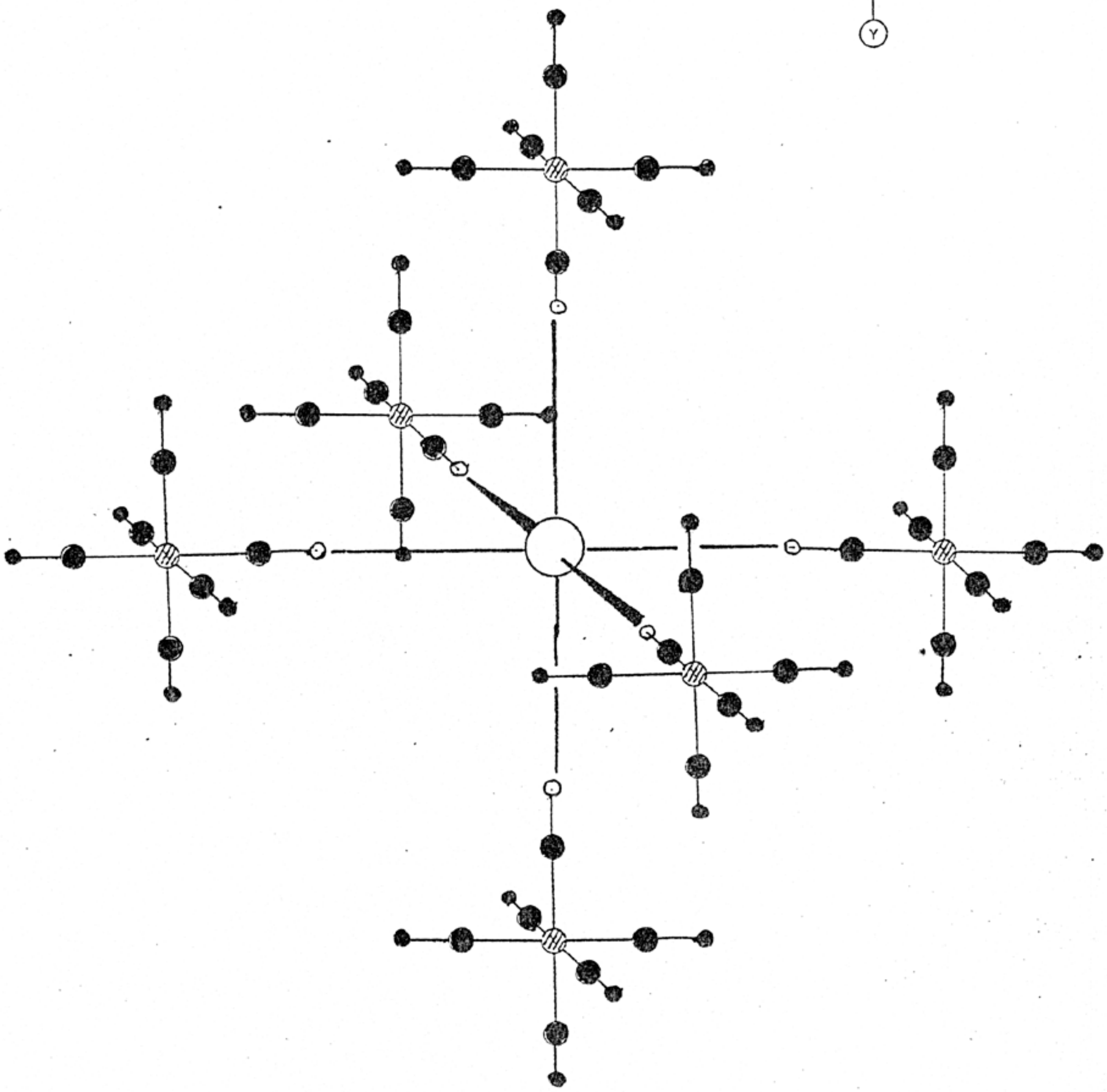
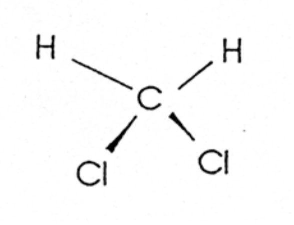
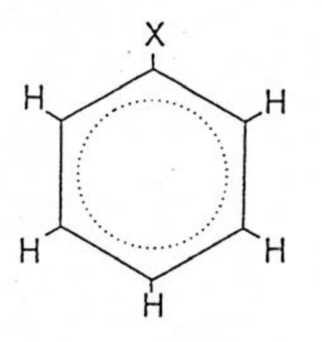
Y



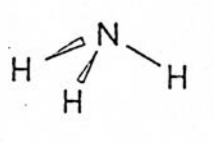
1. Dichloromethane



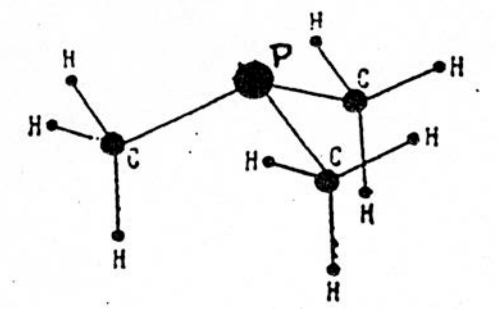
2. Monosubstituted benzene



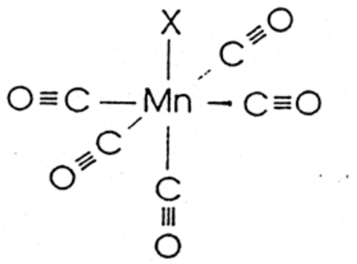
3. Ammonia



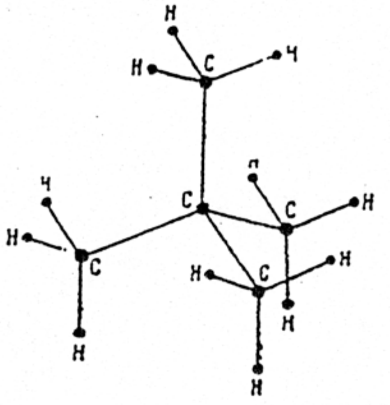
4. Trimethylphosphine



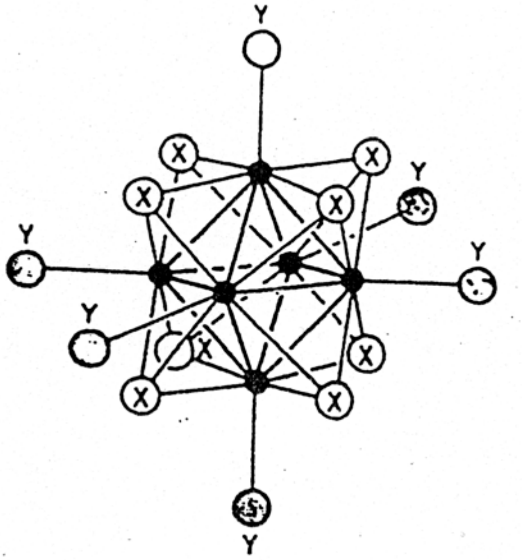
5. Metal-pentacarbonyls



6. Symmetric tetramethylmethane (T_d), $C(CH_3)_4$



7. Octahedral metal-cluster, like $[(Mo_6Cl_8)Cl_6]^{2-}$

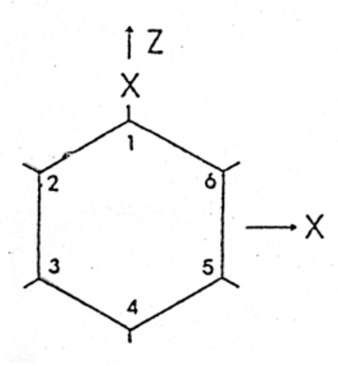


$(M_6X_8)Y_6^{2-}$

Examples for Point Group Analyses

1. Dichlormethane

2. Monosubstituted benzene



3. Ammonia

4. Trimethylphosphine

5. Metal-pentacarbonyls

6. Symmetric tetramethylmethane

7. Mo-cluster: $[(Mo_6Cl_8)Cl_6]^{2-}$

SHORT SUMMARY how to use Adams-Newton (A-N) tables for point group analysis of molecules

1.) Find the symmetry elements of the molecule and determine its point group (Lecture material p. 173-179).

2.) In Table 1 (page 3 A-N tables) find the number of crystallographic point groups with lists of possible sites and determine the Wyckoff- Sites (W-S) of all the atoms in the molecule. It should be obtained that in which symmetry elements are occupied by individual or identical sets of atoms.

Some regulations in obtaining W-S are:

a.) The "central" atom (C in CH_4, N in NH_3 or B in BF_3 etc.) is occupying the position involving all symmetry elements of the point group which is always refers to the **1A** W-S.

b.) The highest symmetry element should be selected for determination of W-S. For example in case of CH_4 the H atoms are sitting on C_3 axis and on σ_d symmetry planes (see p.173). Since symmetry axis is a "higher" symmetry elements than plane of symmetry it should be selected as W-S. In notation of Table 1 this refers to C_{3v} site (T_d= 215) which is identical to **4E** W-S (4 because we have 4 identical H atoms, see p. 181).

3.) From A-N character tables (starting from page 4) the characters for each W-S can be obtained for each atom or sets of identical atoms.

Each point group contains 4 tables.
a.) Its starts with the character tables of molecular point group than,
b.) Selection rules (we should ignore now),
c.) **W-S of the point group and their characters** (we should use this table).
d.) Characters for "Vector" (we will learn how to use them next time).

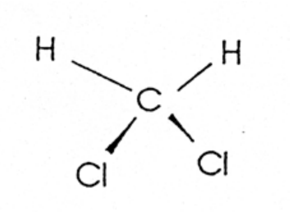
Put irreducible representations (species) in the head line of empty frame (p. 187-189) and put all the W-S in separate line and copy their characters in each line.

4.) By summarizing all the lines we came to the $\mathbf{N_{total}}$, which refers to 3N degree of freedom (N= number of atoms in the molecule).

5.) $\mathbf{N_{total}}$ contains 3 rotation (R_x, R_y and R_z) and 3 translation (T_x, T_y and T_z) degrees of freedom which are not internal vibrations. Find the distribution of R and T activity in symmetry species using the character tables of molecular point groups (first character table in each point group) and subtract their characters from $\mathbf{N_{total}}$ which will give $\mathbf{N_{vib}}$, e.g. 3N-6 vibrations.

6.) From the first character table of molecular point group determine the activity of of symmetry species.
A short recepy, how to operate:
a.) The first symmetry species (***A*** type species) is always Raman active and give polarized lines. It could be also IR active as well depending on molecular symmetry. This first ***A*** type species involves changing of diagonal terms of polarizability tensor (xx, yy and zz which short notations refer to α_{xx}, α_{yy} and α_{zz} diagonal tensor elements, respectively).
b.) The other Raman active species involving off diagonal polarizability tensor elements xy, xz and yz (α_{xy}, α_{xz} and α_{yz}, respectively) are depolarized.
c.) Species containing T_x, T_y and T_z translational vectors are IR active species. Componets of T correspond directly to the components of dipole moment vector.
d.) Species containing only R_x, R_y and R_z rotational modes or nothing (empty lines), they are inactive vibrations.

EXAMPLE: Dichloromethane (p.185, 187)



1.) Symmetry elements***:*** I, C_2, σ_{xz}, σ_{yz} = C_{2v} molecular point group = 25 crystallographic point group. Due to above sets of symmetry elements CH_2Cl_2 has C_{2v} point group.

2.) Determination of sites and Wyckoff Sites from Table1 page 3.

Atoms	Sites	Wyckoff Sites :
1C	C_{2v}	1A (the C atom is sitting on C_2 symmetry axis)
2H	C_s(yz)	2G (the 2H are in the σ_{yz} symmetry plane, which is the C_s(yz) site)
2Cl	C_s(xz)	2E (the 2Cl are in the σ_{xz} symmetry plane, which is the C_s(xz) site)

3.) Find A-N tables for No 25 group (page 10) and select the characters for 1A, 2G and 2E sites.

Atoms	Sites	Wyckoff Sites	A_1	A_2	B_1	B_2
1C	C_{2v}	1A	1	0	1	1
2H	C_s(yz)	2G	2	1	2	1
2Cl	C_s(xz)	2E	2	1	1	2

4.) Summarize the characters to get N(total):

Atoms	Sites	Wyckoff Sites	A_1	A_2	B_1	B_2
1C	C_{2v}	1A	1	0	1	1
2H	C_s(yz)	2G	2	1	2	1
2Cl	C_s(xz)	2E	2	1	1	2
N(total)			5	2	4	4

5.) From the molecular point group table find the three rotation R modes, which are in A_2, B_1 and B_2 species and put their characters in the table as: 0 1 1 1.
Similarly for the three translational T modes, which are in the A1, B1 and B2 species and put their characters in the table as: 1 0 1 1.
Substract R and T characters from N(total) to get **N(vibr)**

Atoms	Sites	Wyckoff Sites	A_1	A_2	B_1	B_2
1C	C_{2v}	1A	1	0	1	1
2H	C_s(yz)	2G	2	1	2	1
2Cl	C_s(xz)	2E	2	1	1	2
N(total)			5	2	4	4
R			0	1	1	1
T			1	0	1	1
N(vib)			**4**	**1**	**2**	**2**

6.) Determine the activity of **N(vib)** species from character table of molecular point group, which gives:

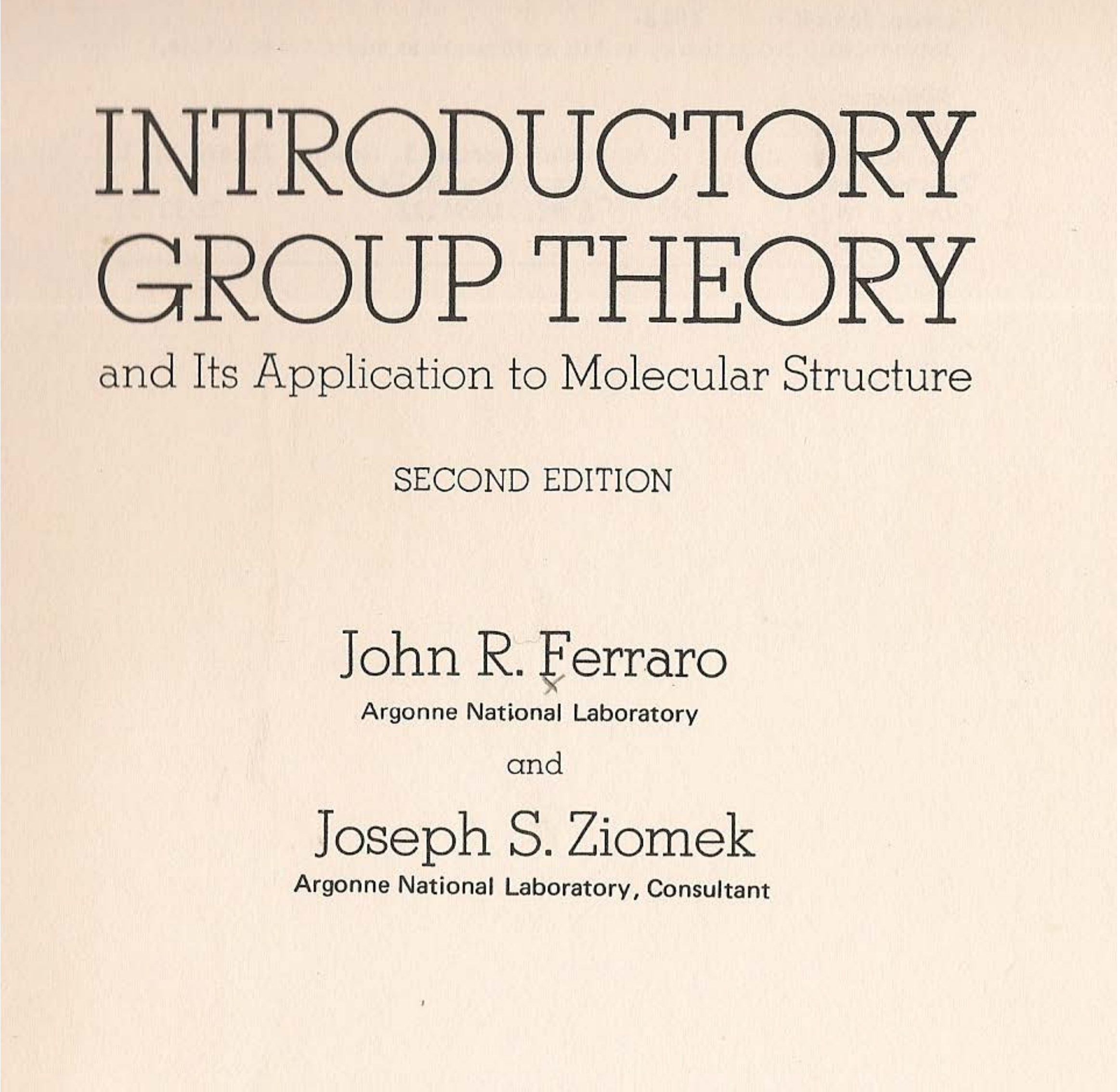
A_1: R,p and IR
A_2: R,dp and not IR active
B_1: R,dp and IR
B_2: R,dp and IR.

The symmetry species of **N(vib)** and their activities are the final results of point group analysis using A-N tables.

HOMEWORK

Please try to perform point group analysis for
Monosubstituted benzene (C_6H_5X),
Ammonia (NH_3),
Trimethyl phosphine ($P(CH_3)_3$),
Mg pentacarbonyl (Mg $(CO)_5X$ and
Symmetric tetramethyl methane ($C(CH_3)_4$).
See pictures and tables in pages 185-189.

Point group analysis generally used in the literature



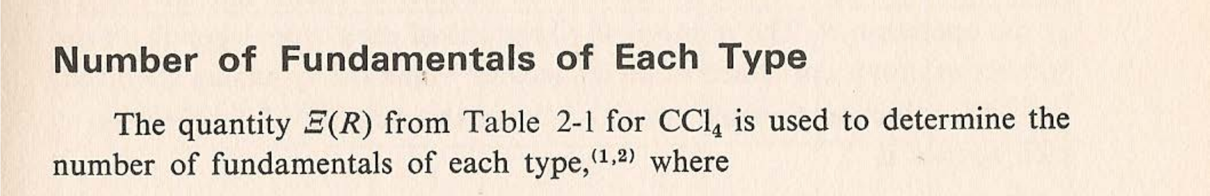
INTRODUCTORY GROUP THEORY

and Its Application to Molecular Structure

SECOND EDITION

John R. Ferraro
Argonne National Laboratory
and
Joseph S. Ziomek
Argonne National Laboratory, Consultant

Plenum Press, New York, London, 1975



Number of Fundamentals of Each Type

The quantity $\Xi(R)$ from Table 2-1 for CCl_4 is used to determine the number of fundamentals of each type,(1,2) where

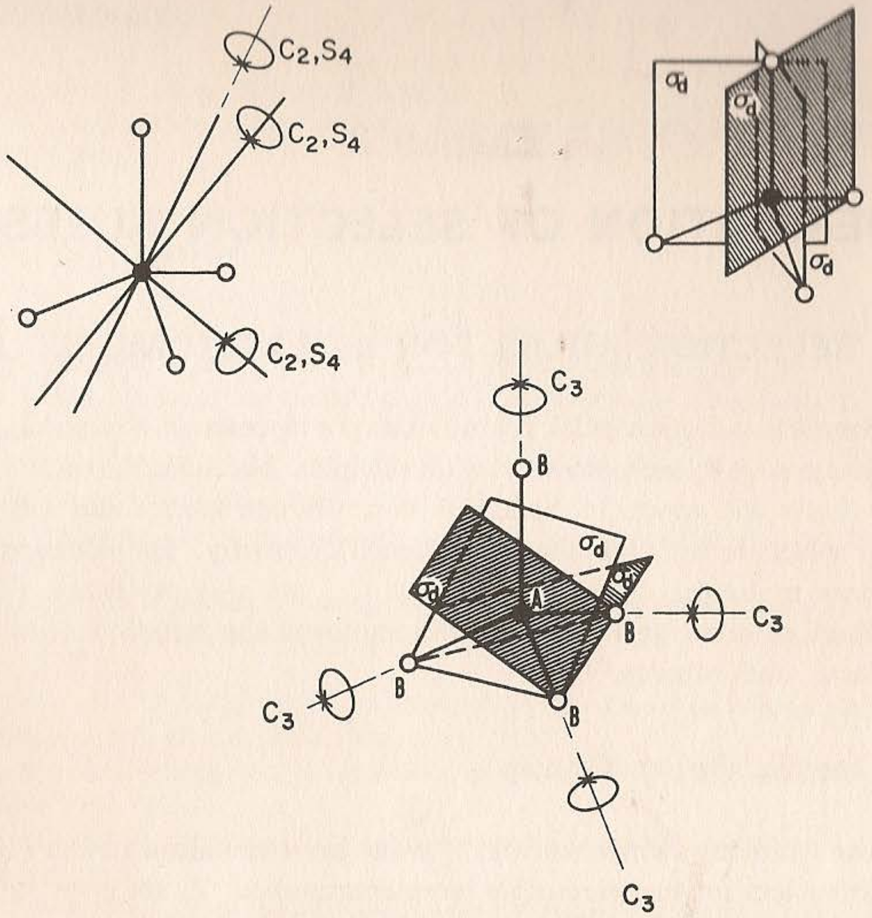


Fig. 2-1. Symmetry elements for the T_d point group ($4C_3$, $3C_2 \approx S_4$, $6\sigma_d$).

$$\begin{aligned}\Xi(R) &= (\mu_R - 2)(1 + 2\cos\varphi) \text{ for proper rotations}\\ &= (\mu_R)(-1 + 2\cos\varphi) \text{ for improper rotations}\end{aligned}$$

These relationships are applicable for molecules of different symmetries. Here φ is the angle associated with the proper or improper movement and μ_R is obtained from Table 2-1 and is the number of atoms left unchanged by the operation R. The number of vibrations of each type depends on the number of atoms contained in the molecule$^{(1,2)}$ and the symmetry involved.

The reduction formula used to obtain the number of frequencies of each species is

$$N_i = \frac{1}{N_G} \Sigma\, n_e \Xi(R) \chi_i(R) \tag{2-1}$$

where N_G is the number of elements in the group (e.g., $1 + 8 + 3 + 6 + 6$

= 24), n_e is the number of elements in each class (e.g., for E, $n_e = 1$), $\chi_i(R)$ is the character of the vibration species.

For T_d symmetry, and specifically for the CCl_4 molecule, the following results are obtained when the proper values are substituted into Eq. (2-1):

$$N_{A_1} = \tfrac{1}{24}[(1\times9\times1) + (8\times0\times1) + (3\times1\times1) + (6\times3\times1) + (6\times-1\times1)] = 1$$

$$N_{A_2} = \tfrac{1}{24}[(1\times9\times1) + (8\times0\times1) + (3\times1\times1) + (6\times3\times-1) + (6\times-1\times-1)] = 0$$

$$N_E = \tfrac{1}{24}[(1\times9\times2) + (8\times0\times-1) + (3\times1\times2) + (6\times3\times0) + (6\times-1\times0)] = 1$$

$$N_{F_2} = \tfrac{1}{24}[(1\times9\times3) + (8\times0\times0) + (3\times1\times-1) + (6\times3\times1) + (6\times-1\times-1)] = 2$$

$$N_{F_1} = \tfrac{1}{24}[(1\times9\times3) + (8\times0\times0) + (3\times1\times-1) + (6\times3\times-1) + (6\times-1\times1)] = 0$$

(Note that in the expansions here and below to save space and avoid confusion negative values have not been enclosed in parentheses; thus,

Table 2-1. Character Table for T_d Symmetry

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	
A_1	1	1	1	1	1	$\chi_i(R)$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	
F_2	3	0	−1	1	−1	
F_1	3	0	−1	−1	1	
φ	0°	120°	180°	0°	90°	
$2\cos\varphi$	2	−1	−2	2	0	
$\pm1 + 2\cos\varphi$	3	0	−1	1	−1	$\chi_M(R)$
2φ	0°	240°	360°	0°	180°	
$2\cos 2\varphi$	2	−1	2	2	−2	
$2 \pm 2\cos\varphi + 2\cos 2\varphi$	6	0	2	2	0	$\chi_a(R)$
μ_R	5	2	1	3	1	
$\Xi(R)$	9	0	1	3	−1	e.g., CCl_4
	Proper rotations			Improper rotations		