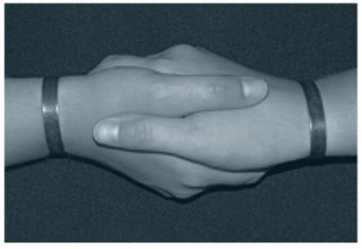
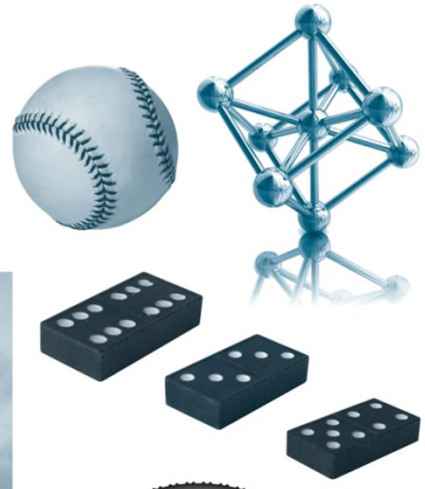
Chapter 4. Symmetry and Group Theory

- Symmetry is every where, in **nature** and in **engineering achievements**.

  e.g.) flowers, plants, snowflakes, insects,,,

  pyramid, Eiffel tower,,,





- symmetry concept in chemistry: symmetry of molecule
  - predict **infrared spectra**
  - predict **orbital activity**
  - describe the type of **orbitals in bonding**
  - interpret **electronic spectra**
  - other **molecular properties**

- in Chapter 4: 1) five symmetry operations

  2) molecular classification based on the symmetry

  3) how to use to predict optical activity

  4) to determine IR- & Raman-active molecular vibrations

Chapter 4. Symmetry and Group Theory

Symmetry Elements vs.

Symmetry Operations:

- Name, symbols, roles etc,,,

Point group & Group theory:

- 6 steps to determine point groups (Table 4.6)

- C vs. D groups

4 properties of group

Matrix & Character:

- Multiplicity

- Symmetry operations

Reducible vs. irreducible representation

Character table

Molecular vibrations

- Reduction formula

- IR active vs. Raman active

4.1 Symmetry Elements and Operations

- **symmetry element:** geometrical **entity** (a line, a plane, or a point) with respect to which one or more symmetry operations can be carried out

- **symmetry operation:** a **movement** applied to a molecule

  → **no overall change** in the overall positions of the atoms (except for the labels we put on atoms)

- A molecule must have **exactly the same** appearance after the operation as before, if there is a symmetry elements!!

  ↳ **indistinguishable** before & after the operation

4.1 Symmetry Elements and Operations

Table of Symmetry Elements and Symmetry Operations

Elements	Symbols	Operations
1. Identity	E	Identity operation
2. Proper Axis	C_n	Rotation operation by 360°/n
3. Reflection Plane	σ	Reflection operation (in the plane)
4. Inversion Center	i	Inversion (of the point x, y, x to $-x$, $-y$, $-z$)
5. Improper Axis	S_n	Improper rotation (= rotation-reflection operation) 1. Rotation by 360°/n 2. Reflection in plane perpendicular to rotation axis

4.1 Symmetry Elements and Operations

- ***E*: identity (identity operation)**
  - no change in the molecule
  - needed for mathematical completeness
  - every molecule has this operation!!

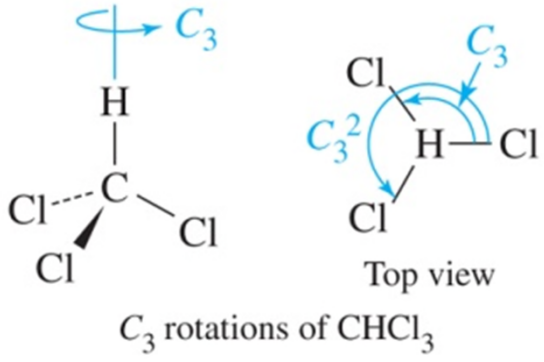


Fig.4.2

- **C_n: proper axis (rotation operation)**
  - rotation through 360°/*n* about a rotation axis (counterclockwise: +)
  - $CHCl_3$: threefold (C_3) axis
    - rotation axis → parallel to C-H axis
    - C_3: rotation angle: 360°/3 = 120°
    - C^2_3: two consecutive rotation → 360° x (2/3) = 240°
    - $C^3_3 \equiv E$ (*E is included in all molecules!!)

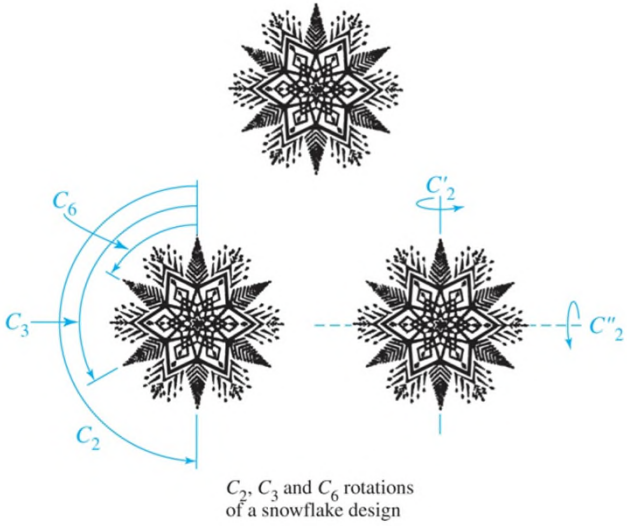
- **C_n: proper axis (rotation operation)**

  - **multiple** rotation axes

  e.g.) snowflake (Fig.4.2): hexagonal, planar

  1) C_6: along the axis through the center of molecule

Rotation Angle	Symmetry Operation
60°	C_6
120°	C_3 ($\equiv C_6^2$)
180°	C_2 ($\equiv C_6^3$)
240°	C_3^2 ($\equiv C_6^4$)
300°	C_6^5
360°	E ($\equiv C_6^6$)



C_2, C_3 and C_6 rotations of a snowflake design

Fig.4.2

  2) two sets of three C_2: C_2'(x3), C_2"(x3)

  3) principal axis (= **highest order** of rotation axis): C_n axis w/ the largest n value

  ↳ for snowflake → C_6

  ↳ principal axis → z axis in Cartesian coordinate

▪ **σ : reflection plane (reflection operation in the mirror plane)**

- **move a point** to a opposite and equidistance point **through a plane**

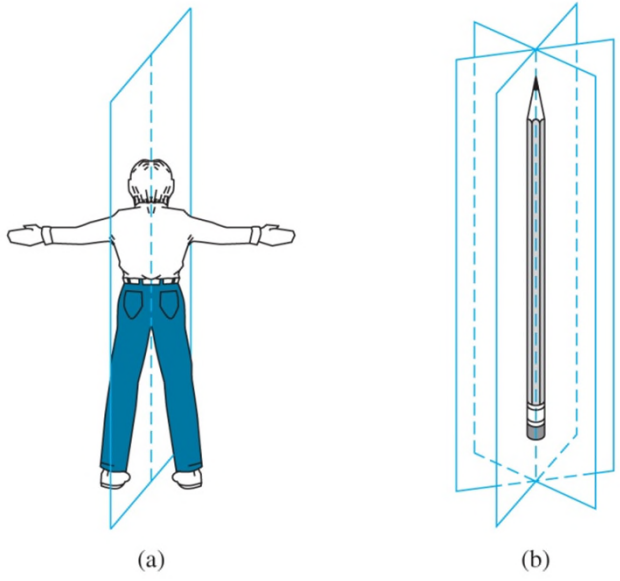


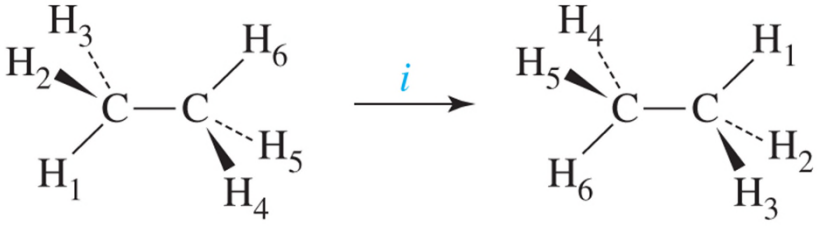
Fig.4.3

e.g.) human body: one mirror plane switching left to right

round pencil: infinite # mirror planes at the center of the object (e.g. acetylene, CO_2)

- { if perpendicular to the principal axis, → σ_h (horizontal)
  { if contain the principal axis, → σ_v (vertical), σ_d (dihedral)

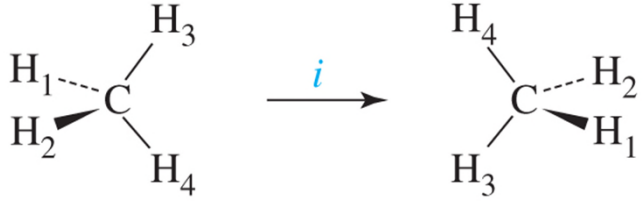
- ***i*** **: inversion center (inversion of the point)**
  - **move a point** to a opposite and equidistance position **through a common central point**
  - e.g.) ethane (staggered conformation) (Fig.4.4)



Center of inversion

Fig.4.4

  - methane ?? → No inversion center!!



No center of inversion

Fig.4.4

- *i* : inversion center (inversion of the point)

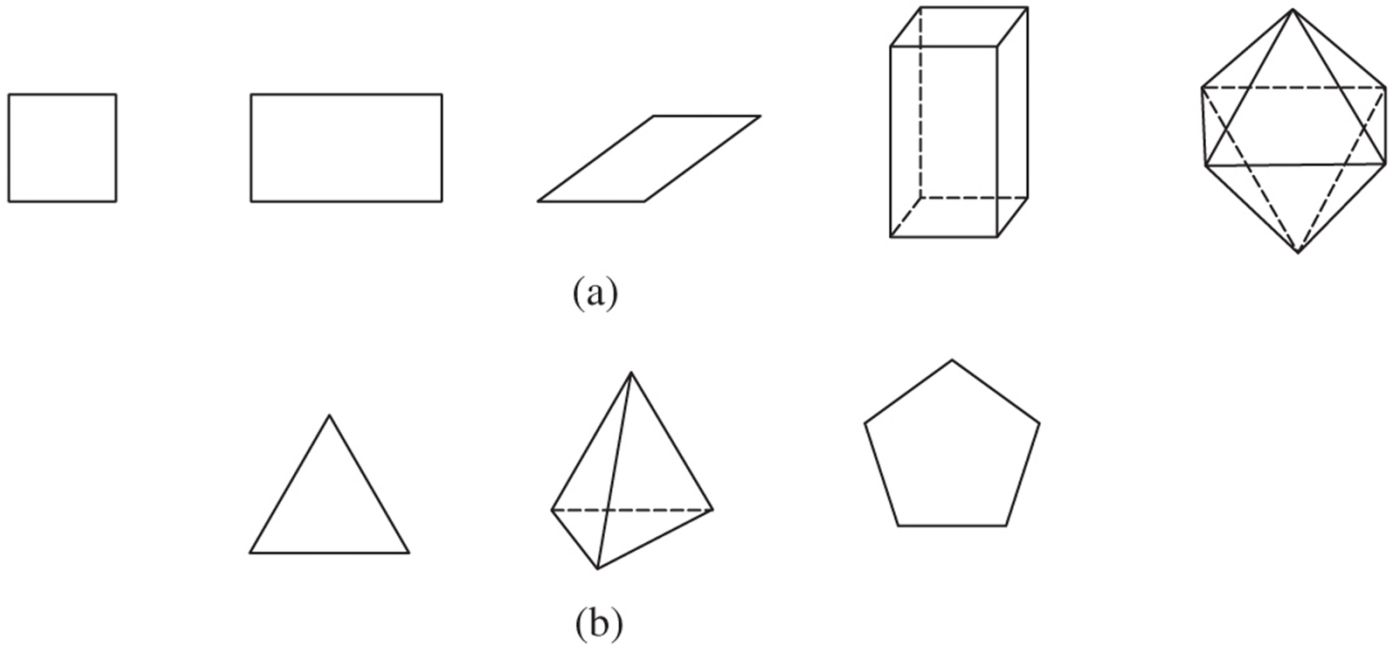
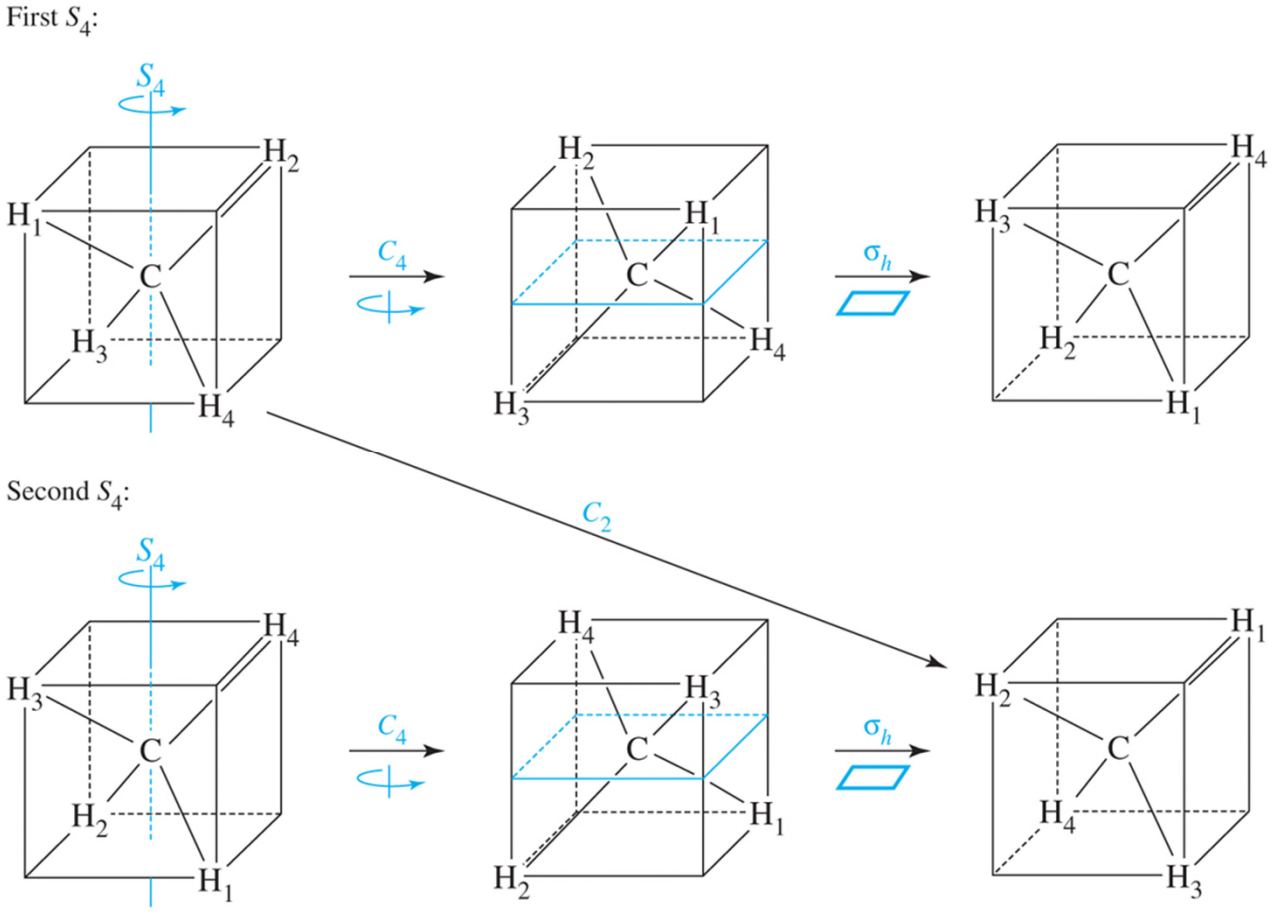


Fig.4.5

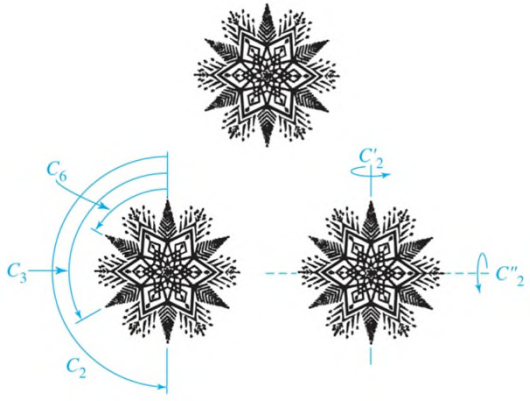
- **S_n : improper axis (improper rotation, rotation-reflection operation)**
  - rotation by 360°/n + reflection through a perpendicular plane
  - e.g.) methane → S_4 (x3) (through C & bisecting the angle b/w two H)

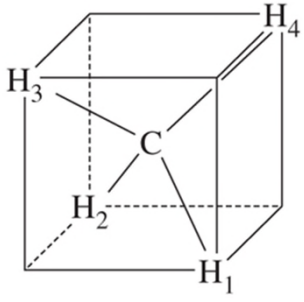
Fig.4.6



- **S_n : improper axis (improper rotation, rotation-reflection operation)**

  - S_n axis coincident w/ a C_n axis: (e.g.) snowflake: $S_2(= i)$, S_3; S_6 coincides w/ C_6
  - S_{2n} axis coincident w/ a C_n axis: (e.g.) methane: S_4 coincides w/ C_2
  - $S_2 = i$, $S_1 = \sigma$ } → i, σ notations are preferred.

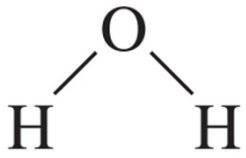




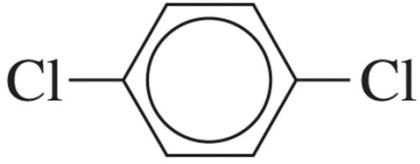
- see **Table 4.1** Symmetry Table of Symmetry Elements and Operations

- **Examples 4.1:** Find all symmetry elements!!

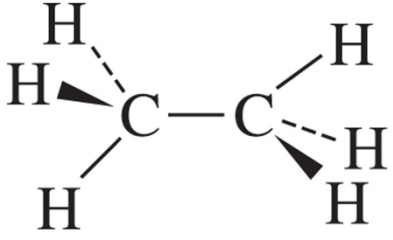
1) H_2O: E, C_2 axis, planes of symmetry (x 2)



2) *p*-Dichlorobenzene: E, C_2 axis (x 3), mirror plane (x 3), i



3) ethane (staggered conformation): E, C_3 axis, C_2 axis (x 3), σ (x 3), i, S_6 axis



4.2 Point Groups

- **Point Group**: the set of symmetry operations (describing the molecule's symmetry)
- **Group Theory**: the mathematical treatment of the properties of groups

  ↳ used for molecular orbitals, vibrations, other properties,,,

- **How to ??**: follow **six steps** shown in Figure 4.7 until final classification of the molecule

  1) Determine whether low or high symmetry

  2) Find the rotation axis w/ the highest *n* (the principal axis)

  3) Does the molecule have any C_2 axes perpendicular to the C_n axis?

  4) Does the molecule have a mirror plane (σ_h) perpendicular to the C_n axis?

  5) Does the molecule have any mirror plane (σ_v or σ_d) that contain the C_n axis?

  6) Is there an S_{2n} axis collinear w/ the C_n axis?

4.2 Point Groups

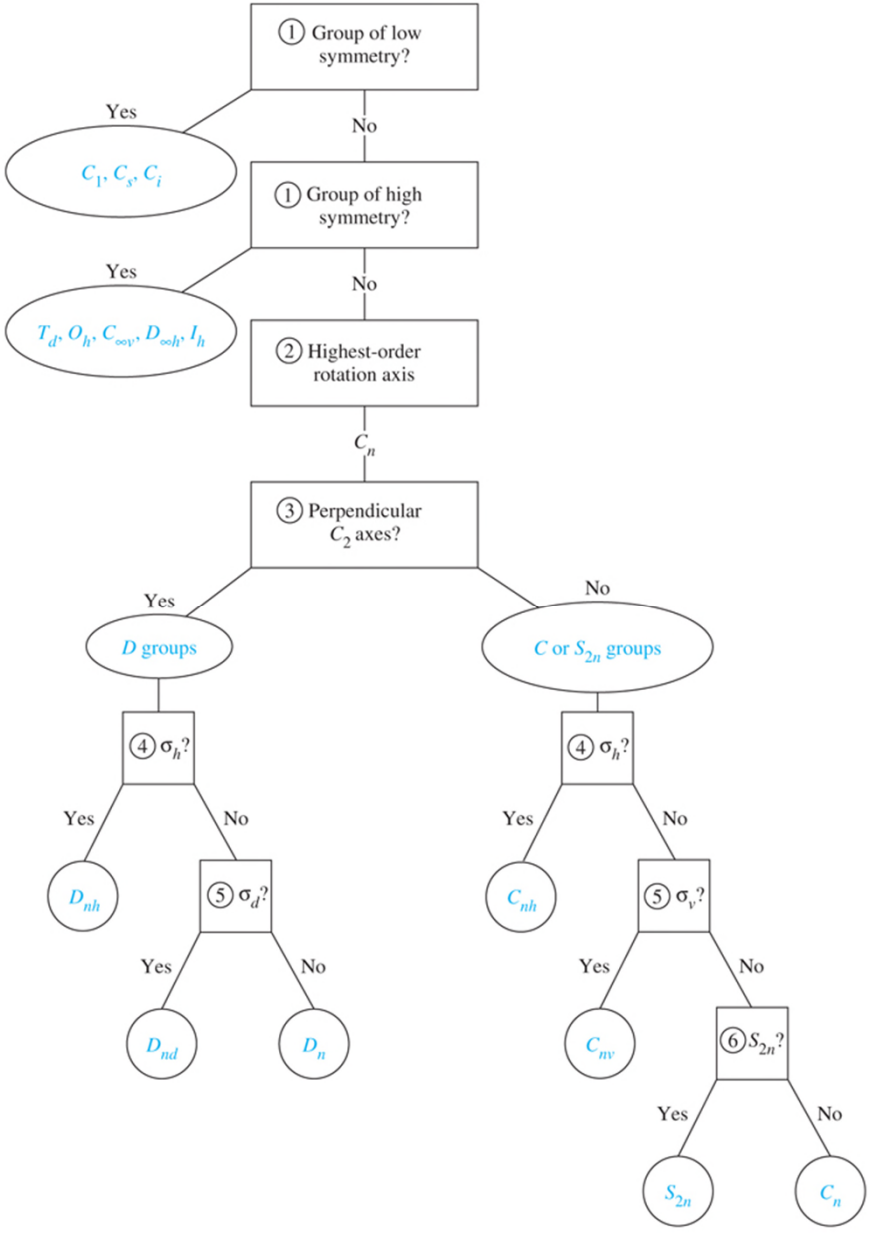


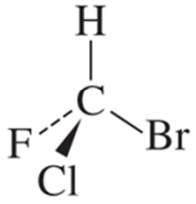
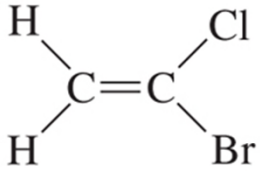
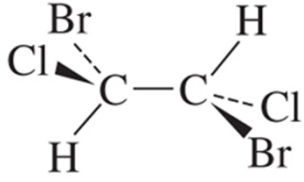
Fig.4.7 Diagram of the Point Group Assignment Method.

4.2.1 Groups of Low and High Symmetry

1. Determine whether the molecule belongs to one of the special cases of low or high symmetry

1) **Low symmetry**: few or no symmetry operations

TABLE 4.2 Groups of Low Symmetry

Group	Symmetry	Examples	
C_1	No symmetry other than the identity operation	CHFClBr	
C_s	Only one mirror plane	$H_2C{=}CClBr$	
C_i	Only an inversion center; few molecular examples	HClBrC—CHClBr (staggered conformation)	

4.2.1 Group of Low and High Symmetry

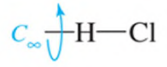
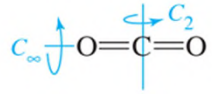
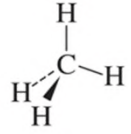
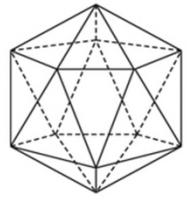
1. Determine whether the molecule belongs to one of the special cases of low or high symmetry

2) **High symmetry**:

contain many symm. operations

↳ linear, tetrahedral, octahedral, icosahedral

TABLE 4.3 Groups of High Symmetry

Group	Description	Examples
$C_{\infty v}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.	
$D_{\infty h}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular C_2 axes, a perpendicular reflection plane, and an inversion center.	
T_d	Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d planes. They have no C_4 axes.	
O_h	These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four C_3 rotations, three C_4 rotations, and an inversion.	
I_h	Icosahedral structures are best recognized by their six C_5 axes, as well as many other symmetry operations—120 in all.	 $B_{12}H_{12}^{2-}$ with BH at each vertex of an icosahedron

In addition, there are four other groups, T, T_h, O, and I, which are rarely seen in nature. These groups are discussed at the end of this section.

4.2.2 Other Groups

2. Find the rotation axis w/ the highest *n*, the highest order C_n axis for the molecule. This is principal axis of the molecule.

- If all equivalent, choose one passing through the **most # atom** as a principal axis

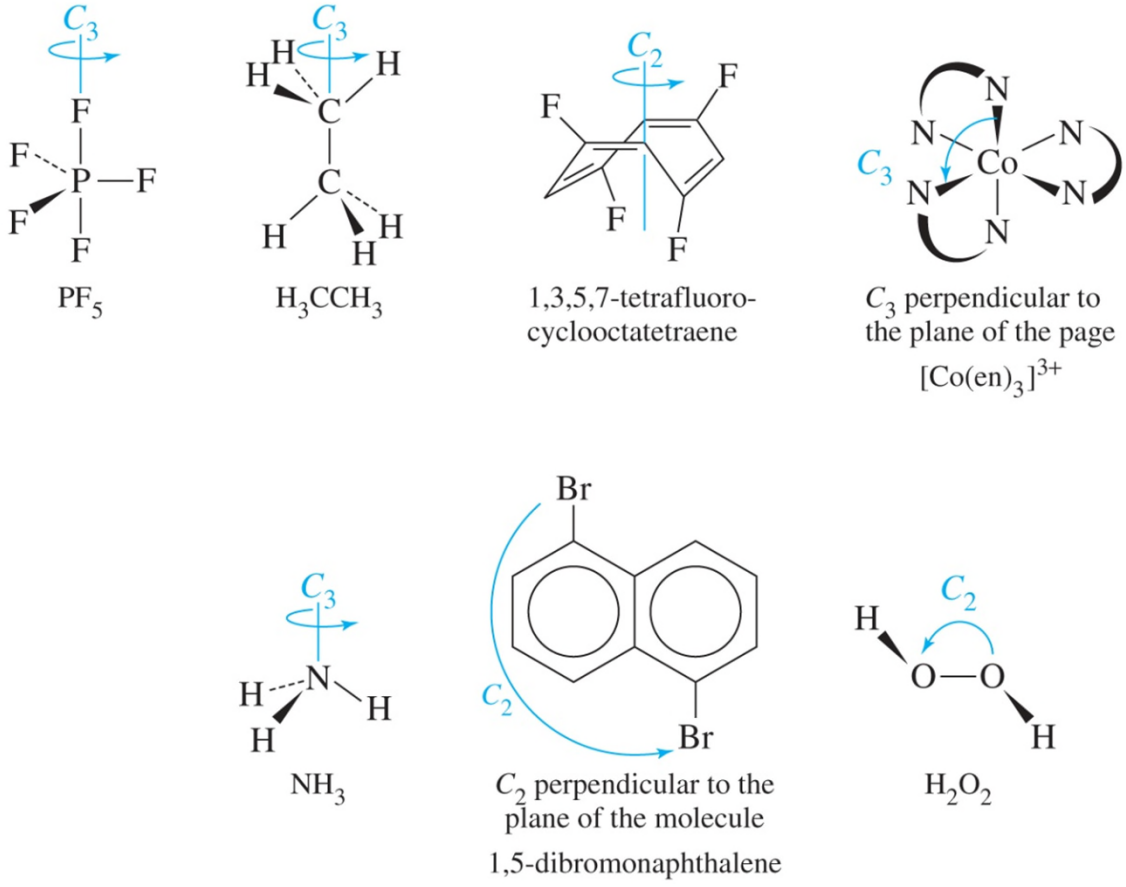


Fig.4.8

4.2.2 Other Groups

3. Does the molecule have any C_2 axes perpendicular to the C_n axis?

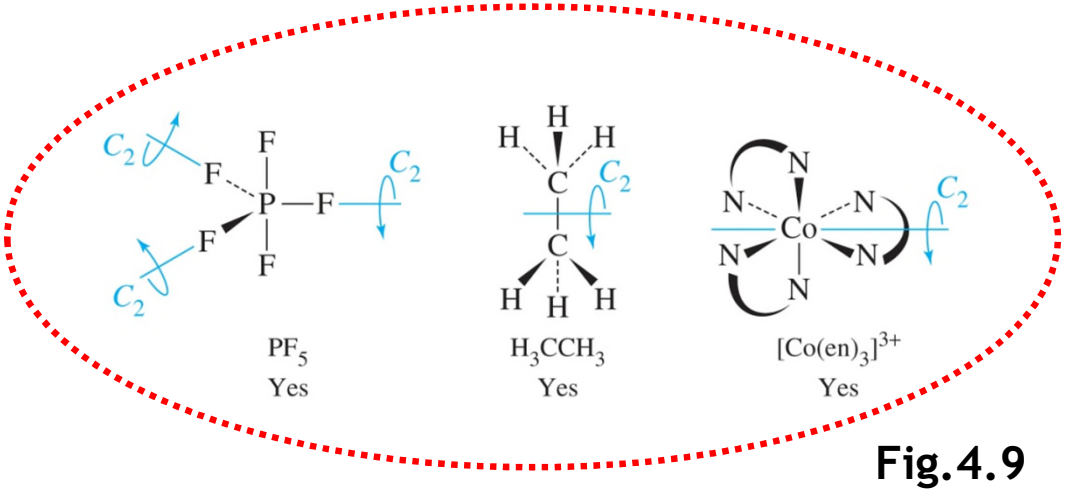


Fig.4.9

YES

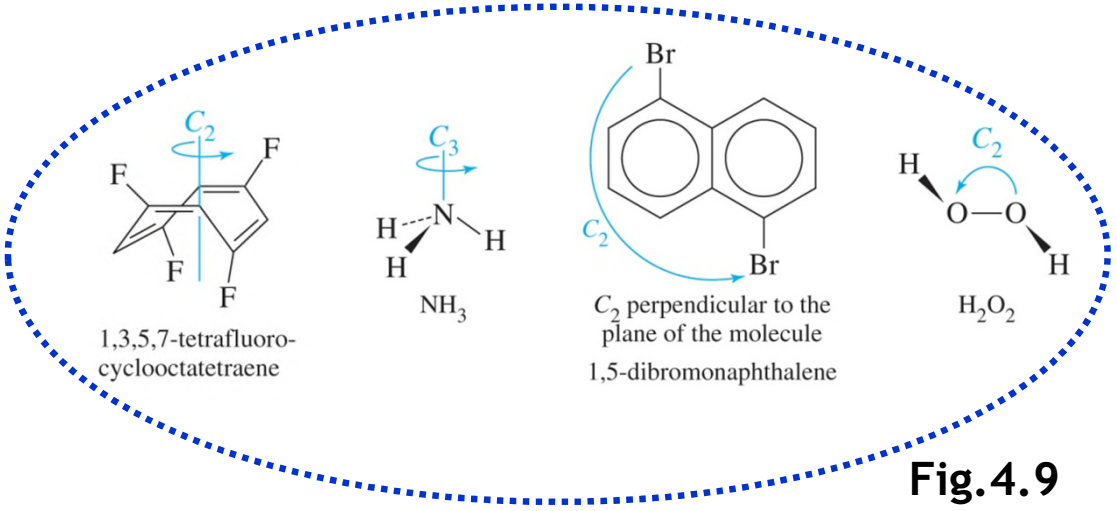


Fig.4.9

NO

D Group

C or *S* Group

* There are nC_2 axes !!

4. Does the molecule have a mirror plane (σ_h horizontal plane) **perpendicular** to the C_n axis?

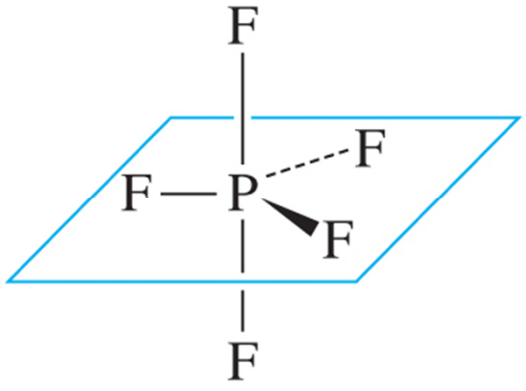
D Groups

H_3CCH_3

No

$[Co(en)_3]^{3+}$

No



PF_5
Yes
D_{3h}

C or *S* Groups

NH_3

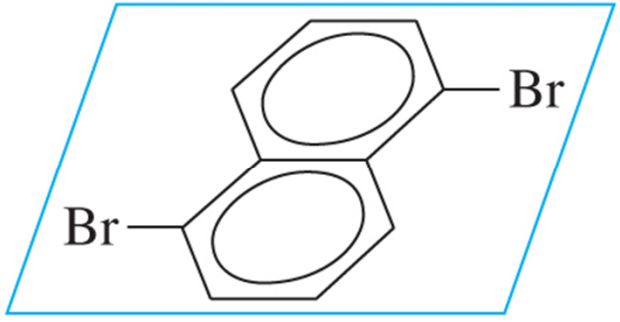
No

H_2O_2

No

1,3,5,7-tetrafluoro-cyclooctatetraene

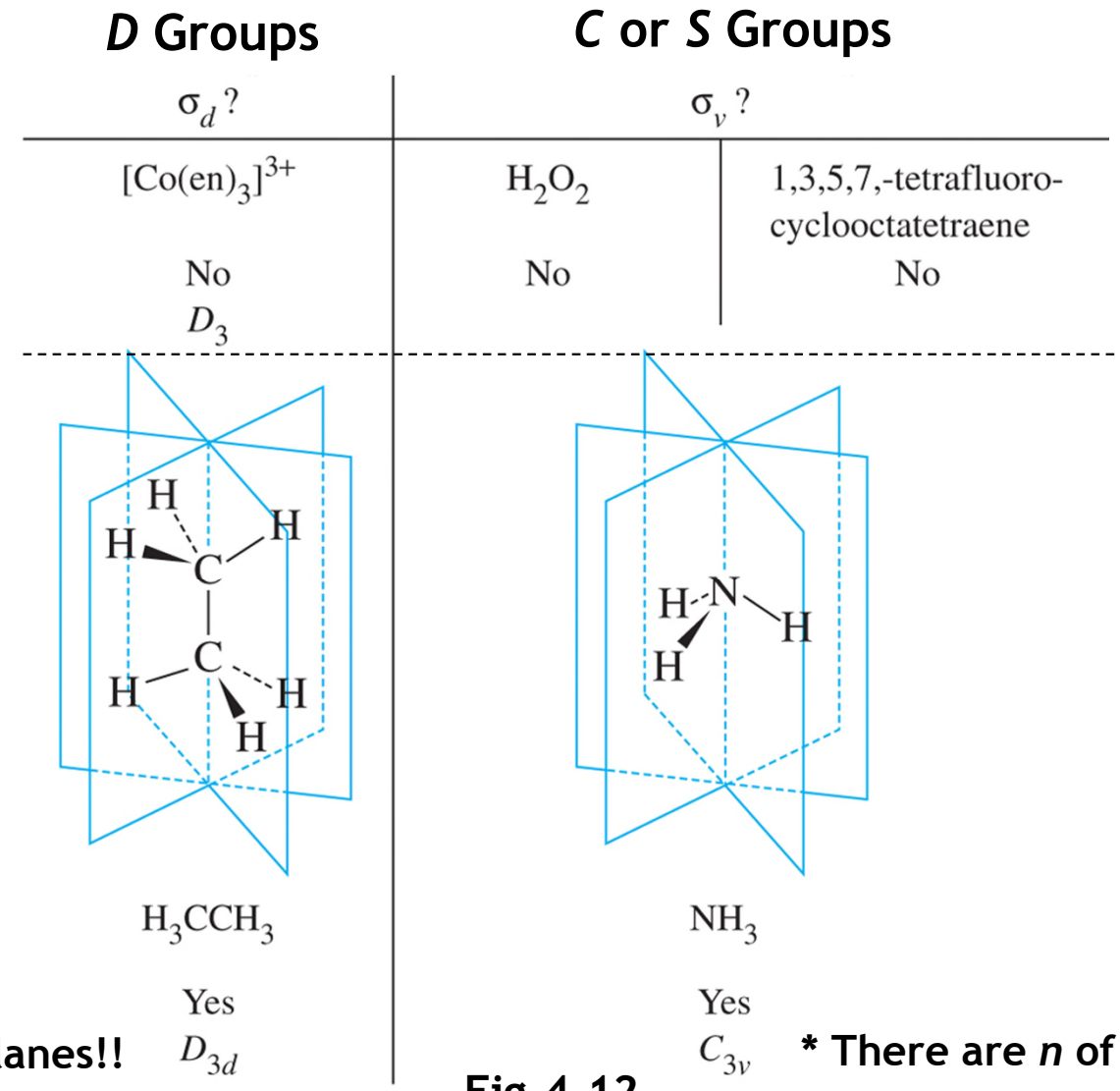
No



1,5-dibromonaphthalene
Yes
C_{2h}

Fig.4.11

5. Does the molecule have any mirror plane (σ_v or σ_d) that **contain** the C_n axis?



* There are *n* of these planes!!

* There are *n* of these planes!!

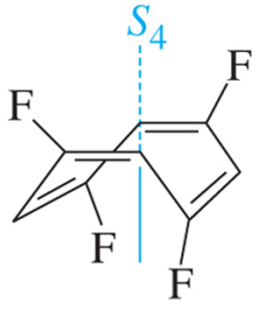
Fig.4.12

4.2.2 Other Groups

6. Is there an S_{2n} axis collinear with the C_n axis?

C or *S* Groups

S_{2n} ?
H_2O_2
No
C_2



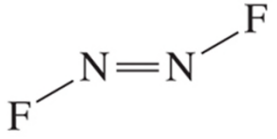
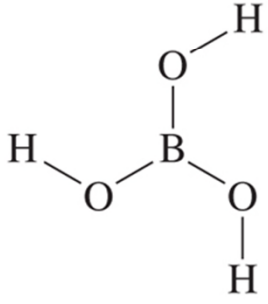
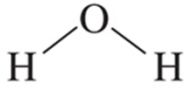
1,3,5,7,-tetrafluoro-cyclooctatetraene
Yes
S_4

Fig.4.12

4.2.2 Other Groups

- **More Examples**

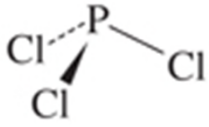
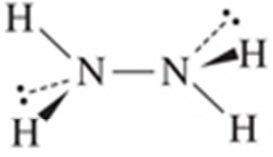
TABLE 4.4 Further Examples of *C* and *D* Point Groups

General Label	Point Group and Example		
C_{nh}	C_{2h}	difluorodiazene	
	C_{3h}	$B(OH)_3$, planar	
C_{nv}	C_{2v}	H_2O	

4.2.2 Other Groups

- More Examples

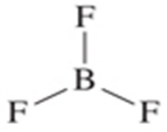
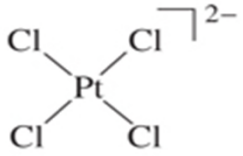
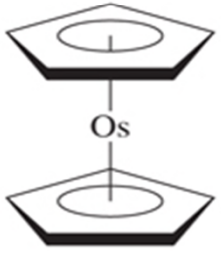
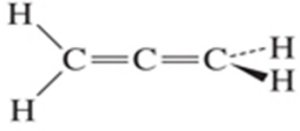
TABLE 4.4 Further Examples of *C* and *D* Point Groups—continued

General Label	Point Group	and Example
	C_{3v}	PCl_3 
	C_{4v}	BrF_5 (square pyramid) 
	$C_{\infty v}$	HF, CO, HCN 
C_n	C_2	N_2H_4, which has a *gauche* conformation 
	C_3	$P(C_6H_5)_3$, which is like a three-bladed propeller distorted out of the planar shape by a lone pair on the P 

4.2.2 Other Groups

- More Examples

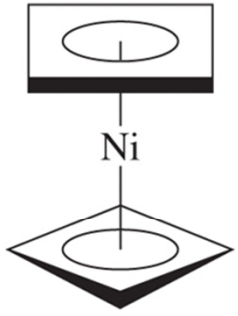
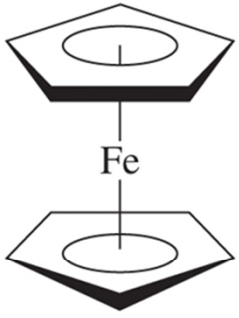
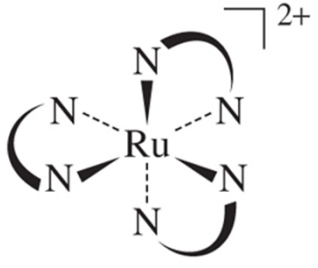
TABLE 4.4 Further Examples of *C* and *D* Point Groups—continued

General Label	Point Group and Example		
D_{nh}	D_{3h}	BF_3	
	D_{4h}	$PtCl_4^{2-}$	
	D_{5h}	$Os(C_5H_5)_2$ (eclipsed)	
	D_{6h}	benzene	
	$D_{\infty h}$	F_2, N_2	
		acetylene (C_2H_2)	
D_{nd}	D_{2d}	$H_2C=C=CH_2$, allene	

4.2.2 Other Groups

- More Examples

TABLE 4.4 Further Examples of *C* and *D* Point Groups—continued

General Label	Point Group	Example
	D_{4d}	$Ni(cyclobutadiene)_2$ (staggered) 
	D_{5d}	$Fe(C_5H_5)_2$ (staggered) 
D_n	D_3	$[Ru(NH_2CH_2CH_2NH_2)_3]^{2+}$ (treating the $NH_2CH_2CH_2NH_2$ group as a planar ring) 

- **Example 4.2:**

1) XeF_4: 1. no low or high symm.

2. C_4

3. perpendicular C_2 (x 4) → *D* Group

4. horizontal plane → D_{4h}

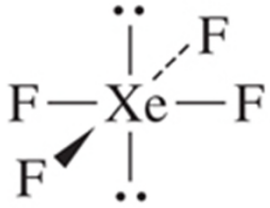


Fig.3.13

2) SF_4: 1. no low or high symm.

2. C_2

3. no other C_2 → *C* or *S* Group

4. no σ_h

5. σ_v (x 2) → C_{2v}

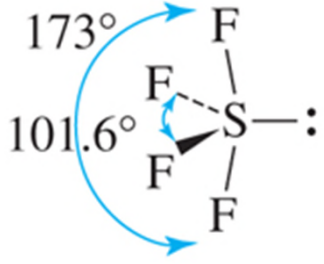


Fig.3.13

3) IOF_3: 1. no low or high symm.

2. σ_h

3. C_s

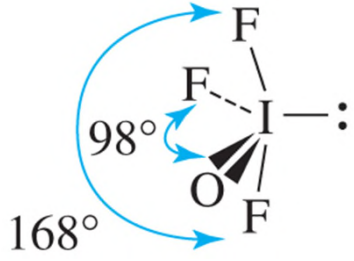


Fig.3.16

4.2.2 Other Groups

- ***C* versus *D* Point Group Classification**

	***D* Classifications**	***C* Classifications**
General Case:		
Look for C_2 axes perpendicular to the highest order C_n axis.	nC_2 axes $\perp$ C_n axis	No C_2 axes $\perp$ C_n axis
Subcategories:		
If a horizontal plane of symmetry exists:	$\boldsymbol{D_{nh}}$	$\boldsymbol{C_{nh}}$
If *n* vertical planes exist:	$\boldsymbol{D_{nd}}$	$\boldsymbol{C_{nv}}$
If no planes of symmetry exist:	$\boldsymbol{D_n}$	$\boldsymbol{C_n}$

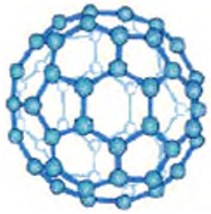
NOTES:

1. Vertical planes contain the highest order C_n axis. In the D_{nd} case, the planes are designated *dihedral* because they are between the C_2 axes—thus, the subscript d.
2. The presence of a C_n axis does not guarantee that a molecule will be in a D or C category; the high-symmetry T_d, O_h, and I_h point groups and related groups have a large number of C_n axes.
3. When in doubt, you can always check the character tables (Appendix C) for a complete list of symmetry elements for any point group.

4.2.2 Other Groups

- **Group Related to I_h, O_h and T_d Group**

  - I_h: C_{60},
    O_h: SF_6
    T_d: CH_4



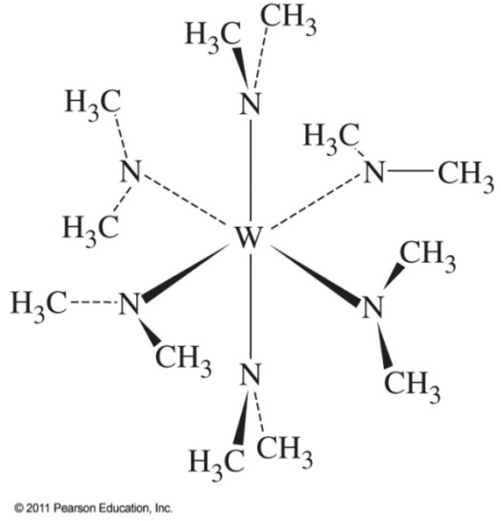


Fig.4.13

  - purely rotational subgroup: I, O, T

    ↳ E + only proper axes w/o i, σ, S_n

  - T_h: T + i → S_6, S^5_6, σ_h (e.g. $W[N(CH_3)_2]_6$

TABLE 4.5 Symmetry Operations for High-Symmetry Point Groups and Their Rotational Subgroups

Point Group	Symmetry Operations									
I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ
I	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2\ (\equiv C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2\ (\equiv C_4^2)$					
T_d	E	$8C_3$	$3C_2$				$6S_4$			$6\sigma_d$
T	E	$\overbrace{4C_3\ 4C_3^2}$	$3C_2$							
T_h	E	$4C_3\ 4C_3^2$	$3C_2$			i	$4S_6$	$4S_6^5$	$3\sigma_h$	

- **Properties of Group**

  - symmetry operations for ammonia

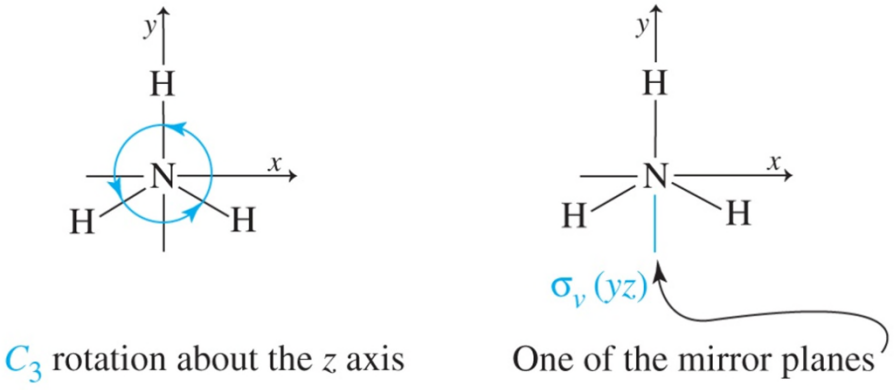
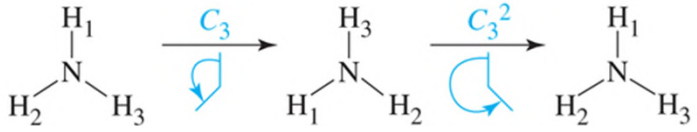
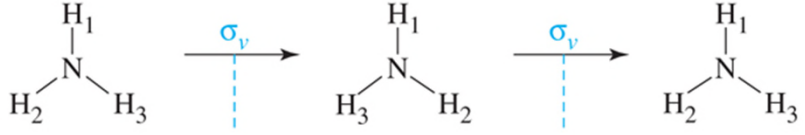
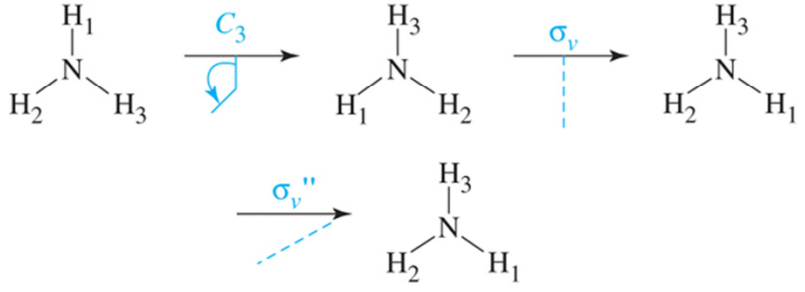


Fig.4.14

4.3 Properties and Representations of Groups

TABLE 4.6 Properties of a Group

Property of Group	Examples from Point Group
1. Each group must contain an **identity** operation that commutes (in other words, $EA = AE$) with all other members of the group and leaves them unchanged ($EA = AE = A$).	C_{3v} molecules (and *all* molecules) contain the identity operation E.
2. Each operation must have an **inverse** that, when combined with the operation, yields the identity operation (sometimes a symmetry operation may be its own inverse). *Note:* By convention, we perform combined symmetry operations *from right to left* as written.	 $C_3^2 C_3 = E$ (C_3 and C_3^2 are inverses of each other)  $\sigma_v\sigma_v = E$ (mirror planes are shown as dashed lines; σ_v is its own inverse)
3. The product of any two group operations must also be a member of the group. This includes the product of any operation with itself.	 $\sigma_v C_3$ has the same overall effect as σ_v'', therefore we write $\sigma_v C_3 = \sigma_v''$. It can be shown that the products of any two operations in C_{3v} are also members of C_{3v}.
4. The associative property of combination must hold. In other words, $A(BC) = (AB)C$.	$C_3(\sigma_v\,\sigma_v') = (C_3\,\sigma_v)\sigma_v'$

4.3.1 Matrices

- Important information about the **symmetry aspect** of **point group** is summarized,,,

in **character table !!**

↑

to understand character table,,,, **properties of matrices** should be considered !!

(basis of the tables)

- **matrix:** an ordered array of numbers

e.g.) $\begin{bmatrix} 3 & 7 \\ 2 & 1 \end{bmatrix}$ or [2 0 1 3 5]

4.3.1 Matrices

- **Multiplication**

1) # vertical column of the 1st matrix = # of horizontal rows of the 2nd matrix

2) match term by term – each term in a row must be multiplied by its corresponding term in the appropriate column of the 2nd matrix

3) product's { # row (determined by the row of the 1st matrix)
             { # column (determined by the column of the 2nd matrix)

$$C_{ij} = \Sigma (A_{ik} \times B_{kj})$$

{ C_{ij} = product matrix, w/ i row & j column
{ A_{ik} = initial matrix, w/ i rows & k column
{ B_{kj} = initial matrix, w/ k row & j column

- **Examples**

4.3.2 Representation

- **Symmetry operations: matrix representations**

- e.g.) **H_2O**: C_{2v} point group – E, C_2, $\sigma_v(xz)$, $\sigma_v'(yz)$

z axis xz plane as the plane of molecule

: **symmetry operation** may be expressed as a **transformation matrix**

[new coordinates] = [**transformation matrix**] [old coordinates]

1) C_2:

$$\begin{cases} x' = \text{new } x = -x \\ y' = \text{new } y = -y \\ z' = \text{new } z = z \end{cases} \qquad \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

in matrix notation,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

$$\begin{pmatrix} \text{new} \\ \text{coordinates} \end{pmatrix} = \begin{pmatrix} \text{transformation} \\ \text{matrix} \end{pmatrix} \begin{pmatrix} \text{old} \\ \text{coordinates} \end{pmatrix} = \begin{pmatrix} \text{new coordinates} \\ \text{In terms of old} \end{pmatrix}$$

4.3.2 Representation

2) $\sigma_v(xz)$: $\begin{cases} x' = \text{new } x = x \\ y' = \text{new } y = -y \\ z' = \text{new } z = z \end{cases}$ $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

in matrix notation

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

The transformation matrices for the four symmetry operations.

E: $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ C_2: $\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ $\sigma_v(xz)$: $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ $\sigma_v'(yz)$: $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

4.3.2 Representation

- **Matrix representation**: satisfies the properties of group

  : each matrix corresponds to an operation

  e.g.) multiplying **two matrices** ↔ multiplying **two corresponding operations**

  (* carrying out to left, $C_2\sigma_v$ means σ_v followed by C_2)

$$C_2 \mathbf{X} \sigma_v(xz) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \sigma'_v(yz)$$

- **Character:** only for a square matrix

  ↳ the **sum of the # on the diagonal** from upper left to lower right

  e.g.) for C_{2v} from the above operation

E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
3	-1	1	1

  ↳ **reducible** representation (Γ)

  ↳ can be reduced to **irreducible** representations

4.3.2 Representation

- **Reducible and irreducible representations**

  - **transformation matrix** is 'block diagonalized' → broken into smaller matrices along the diagonal

$$E: \begin{pmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix} \quad C_2: \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix} \quad \sigma_v(xz): \begin{pmatrix} [1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix} \quad \sigma_v'(yz): \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix}$$

1x1 matrix along the principal diagonal

  - *x*, *y*, *z* coordinates are independent each other

    - each **1, 1** position → result of the ***x* coordinate**
    - each **2, 2** position → result of the ***y* coordinate**
    - each **3, 3** position → result of the ***z* coordinate**

4.3.2 Representation

- **Reducible and irreducible representations**

four matrix elements for x → representation of the group
four matrix elements for y → representation of the group
four matrix elements for z → representation of the group

	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Coordinate Used
	1	−1	1	−1	x
	1	−1	−1	1	y
	1	1	1	1	z
Γ	3	−1	1	1	

each row: **irreducible representation** → cannot simplified further

Σ of irreducible representation: **reducible representation**

4.3.3 Character Table

- **Character table**: a complete set of **irreducible representations** for a point group

- C_{2v} character table w/ the irreducible representations

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

- The labels used w/ character tables

x, y, z	transformations of the x, y, z coordinates or combinations thereof
R_x, R_y, R_z	rotation about the x, y, and z axes
$\boldsymbol{R}$	any symmetry operation, such as C_2 or $\sigma_v(xz)$
χ	character of an operation
i and j	designation of different representations, such as A_1 or A_2
h	order of the group (the total number of symmetry operations in the group)

4.3.3 Character Table

TABLE 4.7 Properties of Characters of Irreducible Representations in Point Groups

Property	Example: C_{2v}
1. The total number of symmetry operations in the group is called the **order (*h*)**. To determine the order of a group, simply total the number of symmetry operations listed in the top row of the character table.	Order = 4 four symmetry operations: E, C_2, $\sigma_v(xz)$, and $\sigma_v'(yz)$
2. Symmetry operations are arranged in **classes**. All operations in a class have identical characters for their transformation matrices and are grouped in the same column in character tables.	Each symmetry operation is in a separate class; therefore, there are four columns in the character table.
3. The number of irreducible representations equals the number of classes. This means that character tables have the same number of rows and columns (they are square).	Because there are four classes, there must also be four irreducible representations—and there are.
4. The sum of the squares of the **dimensions** (characters under E) of each of the irreducible representations equals the order of the group.	$1^2 + 1^2 + 1^2 + 1^2 = 4 = h$, the order of the group.

$$h = \sum_i [\chi_i(E)]^2$$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

4.3.3 Character Table

TABLE 4.7 Properties of Characters of Irreducible Representations in Point Groups

5. For any irreducible representation, the sum of the squares of the characters multiplied by the number of operations in the class (see Table 4.8 for an example), equals the order of the group. $h = \sum_R [\chi_i(R)]^2$	For A_2, $1^2 + 1^2 + (-1)^2 + (-1)^2 = 4 = h$. Each operation is its own class in this group.
6. Irreducible representations are **orthogonal** to each other. The sum of the products of the characters, multiplied together for each class, for any pair of irreducible representations is 0. $\sum_R \chi_i(R)\chi_j(R) = 0, \text{when } i \neq j$ Taking any pair of irreducible representations, multiplying together the characters for each class, multiplying by the number of operations in the class (see Table 4.8 for an example), and adding the products gives zero.	B_1 and B_2 are orthogonal: $(1)(1) + (-1)(-1) + (1)(-1) + (-1)(1) = 0$ $E \quad C_2 \quad \sigma_v(xz) \quad \sigma_v'(yz)$ Each operation is its own class in this group.
7. A **totally symmetric representation**, with characters of 1 for all operations, is included in all groups.	C_{2v} has A_1, in which all characters = 1.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

4.3.3 Character Table

- **Understanding A_2 representation of the C_{2v} group using properties of group**

  - 4 columns → thus,, 4 classes (property 2) of symmetry operations (property 3)

  - orthogonality (property 6)

    ↳ a product of A_1 and unknown → must have { irreducible rep. 1 (X 2) / irreducible rep. -1 (X 2) } → 0

  - the character of *E* operation → 1 ($\because 1^2 + 1^2 + 1^2 + x^2 = 4$, $x = 1$ (property 4))

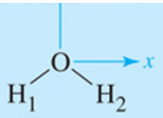
  - no two operations can be the same

    ↳ $\therefore A_2$: 1 1 -1 -1

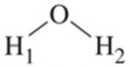
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	???					
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

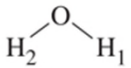
4.3.3 Character Table

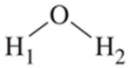
TABLE 4.8 Representation Flow Chart: (H_2O) (C_{2v})

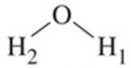


Symmetry Operations


after E


after C_2


after $\sigma_v(xz)$


after $\sigma_v'(yz)$

Matrix Representations (Reducible)

$$E:\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} \quad C_2:\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix} \quad \sigma_v(xz):\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix} \quad \sigma_v'(yz):\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

Characters of Matrix Representations

3	−1	1	1

Block Diagonalized Matrices

$$\begin{bmatrix}[1]&0&0\\0&[1]&0\\0&0&[1]\end{bmatrix} \quad \begin{bmatrix}[-1]&0&0\\0&[-1]&0\\0&0&[1]\end{bmatrix} \quad \begin{bmatrix}[1]&0&0\\0&[-1]&0\\0&0&[1]\end{bmatrix} \quad \begin{bmatrix}[-1]&0&0\\0&[1]&0\\0&0&[1]\end{bmatrix}$$

Irreducible Representations

E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Coordinate Used
1	−1	1	−1	x
1	−1	−1	1	y
1	1	1	1	z
3	−1	1	1	

Character Table

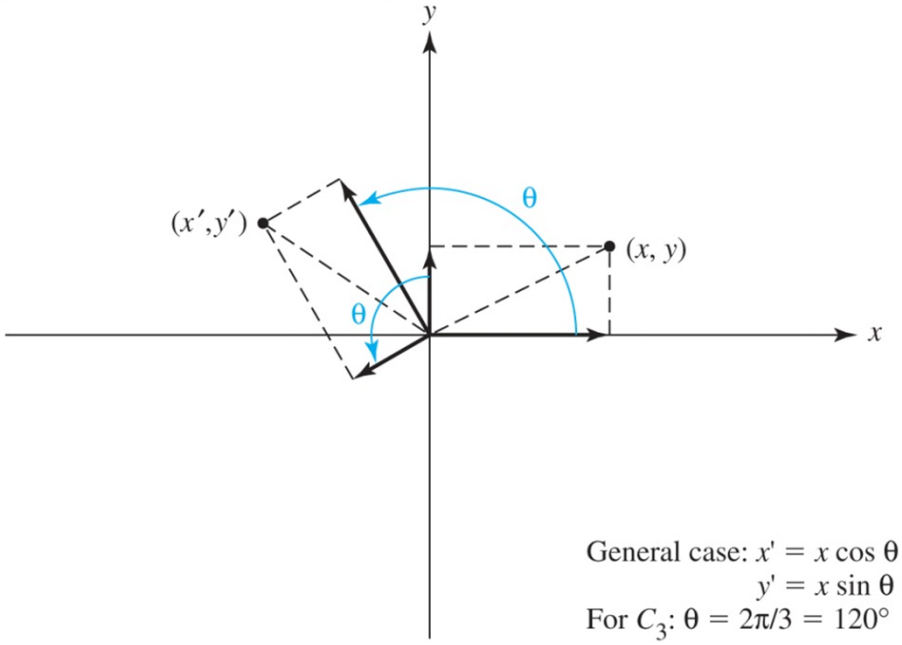
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Matching Functions	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

4.3.3 Character Table

- **Another Example: C_{3v} (NH_3)**

  - C_3 (120° rotation) : *x*', *y*' can be described by using **trigometric functions** of *x* and *y*.

  - $\begin{cases} x' = x\cos(2\pi/3) - y(\sin(2\pi/3) = -1/2x - \sqrt{3}/2y \\ y' = x\sin(2\pi/3) + y\cos(2\pi/3) = \sqrt{3}/2x - 1/2y \end{cases}$



General case: $x' = x\cos\theta - y\sin\theta$
$y' = x\sin\theta + y\cos\theta$
For C_3: $\theta = 2\pi/3 = 120°$

- E, C_3, $\sigma_{v(xz)}$ → cannot be block diagonalized into 1 X 1 (∵ 2 X 2, 1 X 1)

for the **C_3 matrix** must be blocked in the **2 X 2 matrix.**
(∵ **(x, y) combination** is needed for the new x' and y')

- $\begin{cases} \text{2 X 2 matrices} \rightarrow \text{E representation} \\ \text{1 X 1 matrices} \rightarrow A_1 \text{ representation} \end{cases}$ ⟶ How about A_2 ?

4.3.3 Character Table

TABLE 4.9 Properties of the Characters for the C_{3v} Point Group

Property	C_{3v} Example
1. Order	6 (6 symmetry operations)
2. Classes	3 classes: E $2C_3$ $(= C_3, C_3^2)$ $3\sigma_v$ $(= \sigma_v, \sigma_v', \sigma_v'')$
3. Number of irreducible representations	3 (A_1, A_2, E)
4. Sum of squares of dimensions equals the order of the group	$1^2 + 1^2 + 2^2 = 6$
5. Sum of squares of characters multiplied by the number of operations in each class equals the order of the group	$E \quad 2C_3 \quad 3\sigma_v$ A_1: $1^2 + 2(1)^2 + 3(1)^2 = 6$ A_2: $1^2 + 2(1)^2 + 3(-1)^2 = 6$ E: $2^2 + 2(-1)^2 + 3(0)^2 = 6$ (Multiply the squares by the number of symmetry operations in each class.)
6. Orthogonal representations	The sum of the products of any two representations multiplied by the number of operations in each class equals 0. Example of $A_2 \times E$: $(1)(2) + 2(1)(-1) + 3(-1)(0) = 0$
7. Totally symmetric representation	A_1, with all characters = *1*

4.3.3 Character Table

- **Additional Features of Character Table**

1. C_3, C^2_3 are in the **same class** → clockwise and counter-clockwise direction
2. C_2 perpendicular to the principal axis → { C_2': pass through **several atoms**; C_2": pass **b/w the atoms** }
3. { horizontal plane: σ_h; vertical plane: σ_v, σ_d }
4. in the right side of the column in the character table,

{ x, y, z; R_x, R_y, R_z; xy, xz, yz } in the character table ⟶ { p_x, p_y, p_x; d_{xy}, d_{xz}, d_{yz} }

totally symmetric ⟶ s

in C_{3v} ⟶ (x, y) have the same symm. properties as the *E* irreducible rep.

4.3.3 Character Table

- **Additional Features of Character Table**

5. matching the symm. operation w/ list in the top row

↳ confirm any point group

6. labeling of irreducible representation (symm. → 1, antisymm. → -1)

a) **letter**: dimension of the irreducible representation

Dimension	Symm. label
1	A, B
2	E
3	T

b) subscript: 1 → **symmetric to a C_2** rotation **perpendicular to the principal axis**

2 → **antisymm. to the C_2**

* if no perpendicular C_2,,,

1 – **symm.** to a **vertical plane**

2 – **antisymm.** to a **vertical plane**

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

4.3.3 Character Table

- **Additional Features of Character Table**

6. c) subscript: { g (gerade) → symm. to i
                 { u (ungerade) → antisymm. to i

   d) { single prime (‘) → symm to σ_h
      { double prime (“) → antisymm. to σ_h

4.4.1 Chirality

- chiral/dissymmetric: molecules that are not superimposable on their mirror image

e.g.) { CBrClFI
propeller (C_3 axis)

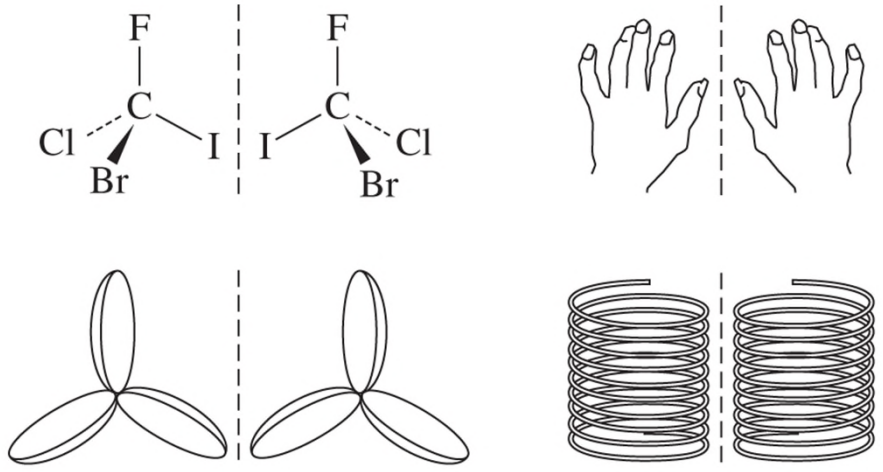


Fig.4.18

↳ condition for chirality: { no symm. operation other than *E* *or*,,,
only **proper rotation**

4.4.1 Chirality

- **optical activity**: the ability of chiral molecules **to rotate plane-polarized light**

  1) clockwise rotation: dextrorotatory

  2) anticlockwise rotation: levorotatory

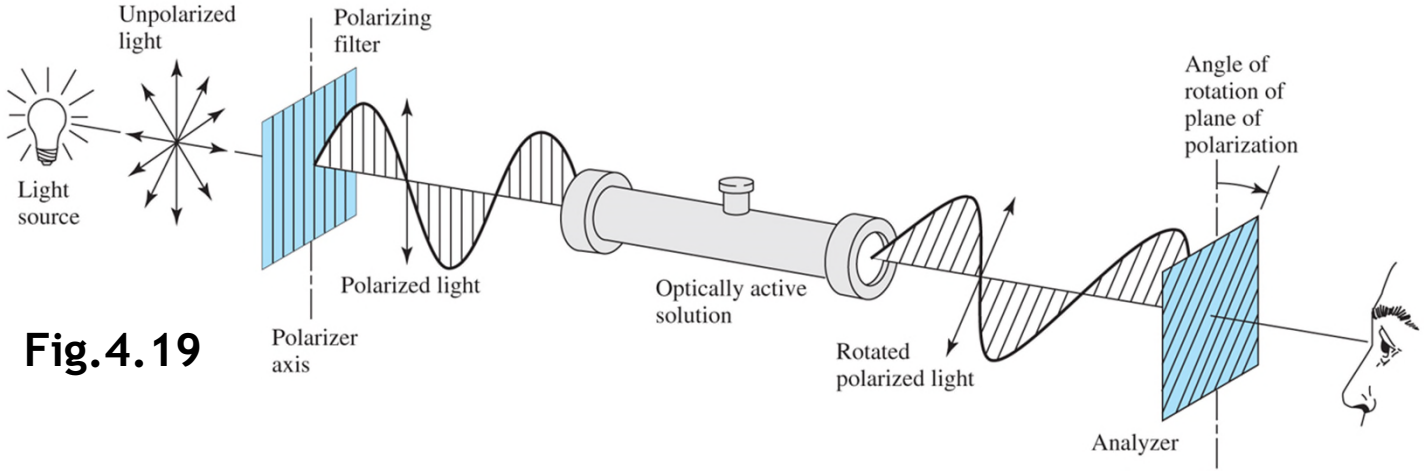


Fig.4.19

e.g.) $[Ru(NH_2CH_2CH_2NH_2)_3]^{2+} \rightarrow D_3$

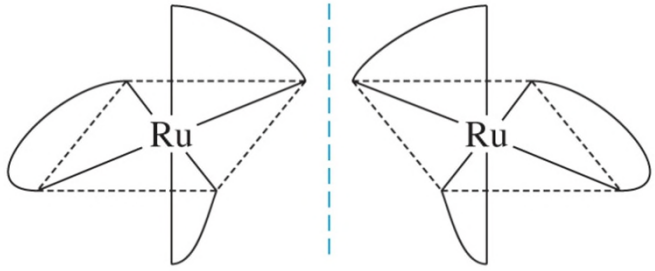


Fig.4.20

4.4.2 Molecular Vibrations

: Symmetry can help to determine **the mode of vibration** of molecule

- water (C_{2v} symm.): x, y, z coordinates should be used for each atom.

x – plane of molecule

y – perpendicular to plane ⟶ Total 9 transformation

(motion of each atom in x, y, z directions)

z – C_2 axes

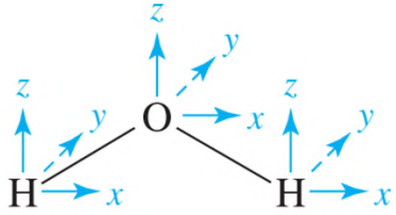


Fig.4.21

TABLE 4.10 Degrees of Freedom

Number of Atoms	Total Degrees of Freedom	Translational Modes	Rotational Modes	Vibrational Modes
N (linear)	3*N*	3	2	3*N* − 5
3 (HCN)	9	3	2	4
N (nonlinear)	3*N*	3	3	3*N* − 6
3 (H_2O)	9	3	3	3

4.4.2 Molecular Vibrations

- to assign translation, rotation, vibration motion → use a **transformation matrix** for a symm. operation !!

  ↳ for H_2O w/ 9 transformation → e.g.) 9 x 9, C_2 matrix

[new axes] = **[transformation matrix (9 x 9)]** [initial axes]

↳
- **if position changes (during the operation) → 0**
- **if unchanged changes → 1**
- **if vector direction changes → -1**

- use the **character** of the representation matrices instead of individual matrix

  ↳ sum of along the diagonal

    ↳ no-zero entry appears along the diagonal of the matrix only for an atom that does not change position.

4.4.2 Molecular Vibrations

- reducible representation Γ

- E: **9** → no change
- C_2:
  - 2H → **0**: change position
  - O → (-1) + (-1) + 1 = **-1**:
    - x, y – reversed
    - z – remains same
- σ_v(xz) (plane of molecule): 3 – 3 + 3 = **3** :
  - x, z – unchanged
  - y – change the direction
- σ_v'(yz):
  - 2H → **0**: changed position
  - O →
    - x – change direction
    - y, z – unchanged

⟶ -1 + 1 + 1 = **1**

4.4.2 Molecular Vibrations

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz
Γ	9	−1	3	1		

reducible representation

∵ Because all **nine directions vectors** are included in this representation,,
it represents **all the motions** of molecules: { 3 translations, 3 rotations, 3 vibrations

4.4.2 Molecular Vibrations

- **Reducing** a reducible representation to irreducible representations

  : separate the reducible representation **into its component irreducible representations**

  - reduction formula

$$\left[\begin{array}{c}\text{\# irreducible}\\ \text{representation of}\\ \text{a given type}\end{array}\right] = (1/\text{order})\Sigma\left\{\left[\begin{array}{c}\text{\# operations}\\ \text{in the class}\end{array}\right] \times \left[\begin{array}{c}\text{character of}\\ \text{reducible}\\ \text{representation}\end{array}\right] \times \left[\begin{array}{c}\text{character of}\\ \text{irreducible}\\ \text{representation}\end{array}\right]\right\}$$

- For H_2O,,

$$n_{A1} = 1/4[(9)(1) + (-1)(1) + (3)(1) + (1)(1)] = 3$$

$$n_{A2} = 1/4[(9)(1) + (-1)(1) + (3)(-1) + (1)(-1)] = 1$$

$$n_{B1} = 1/4[(9)(1) + (-1)(-1) + (3)(1) + (1)(-1)] = 3$$

$$n_{B2} = 1/4[(9)(1) + (-1)(-1) + (3)(-1) + (1)(1)] = 2$$

$$\longrightarrow \quad \Gamma = 3A_1 + A_2 + 3B_1 + +2B_2$$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz
Γ	9	−1	3	1		

4.4.2 Molecular Vibrations

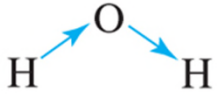
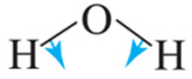
- according to the character table,,,

  - translation along x, y, z: $A_1 + B_1 + B_2$
  - rotation (R_x, R_y, R_z): $A_2 + B_1 + B_2$
  - **vibration mode: $2A_1 + B_1$**

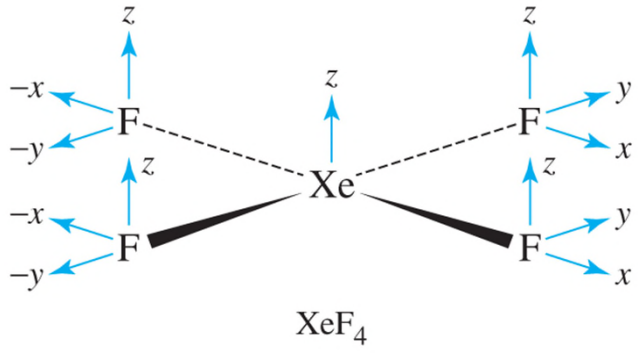
TABLE 4.11 Symmetry of Molecular Motions of Water

All Motions	Translation (x, y, z)	Rotation (R_x, R_y, R_z)	Vibration (Remaining Modes)
$3A_1$	A_1		$2A_1$
A_2		A_2	
$3B_1$	B_1	B_1	B_1
$2B_2$	B_2	B_2	

TABLE 4.12 The Vibrational Modes of Water

A_1		Symmetric stretch: change in dipole moment; more distance between positive hydrogens and negative oxygen *IR active*
B_1		Antisymmetric stretch: change in dipole moment; change in distances between positive hydrogens and negative oxygen *IR active*
A_1		Symmetric bend: change in dipole moment; angle between H—O vectors changes *IR active*

Example 4.4) Using the x, y, z coordinates for each atom in XeF_4, **determine the reducible representation** for all molecular motions; **reduce** this representation to its irreducible components; and classify these representations into **translational, rotational, and vibrational** mode.



XeF_4

Fig.4.22

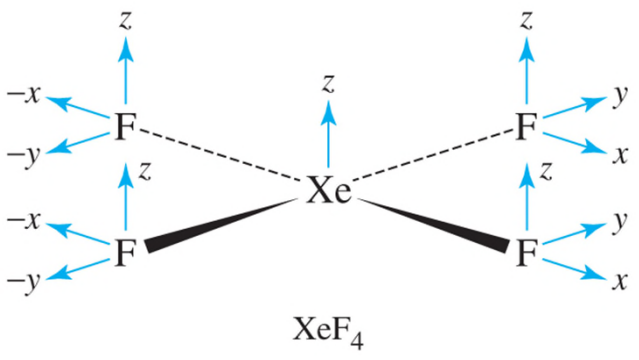
sol) only the coordinates on atoms that **do not move** when symmetry operations are applied can give rise to nonzero elements along the diagonals of transformation matrices.

if unchanged → 1

if reverse the direction → -1

if move to another coordinate → 0

4.4.2 Molecular Vibrations



XeF_4

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		$x^2 + y^2, z^2$
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		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	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	(x, y)	

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	15	1	−1	−3	−1	−3	−1	5	3	1

There are 15 possible motions to be considered.

If reduced,,

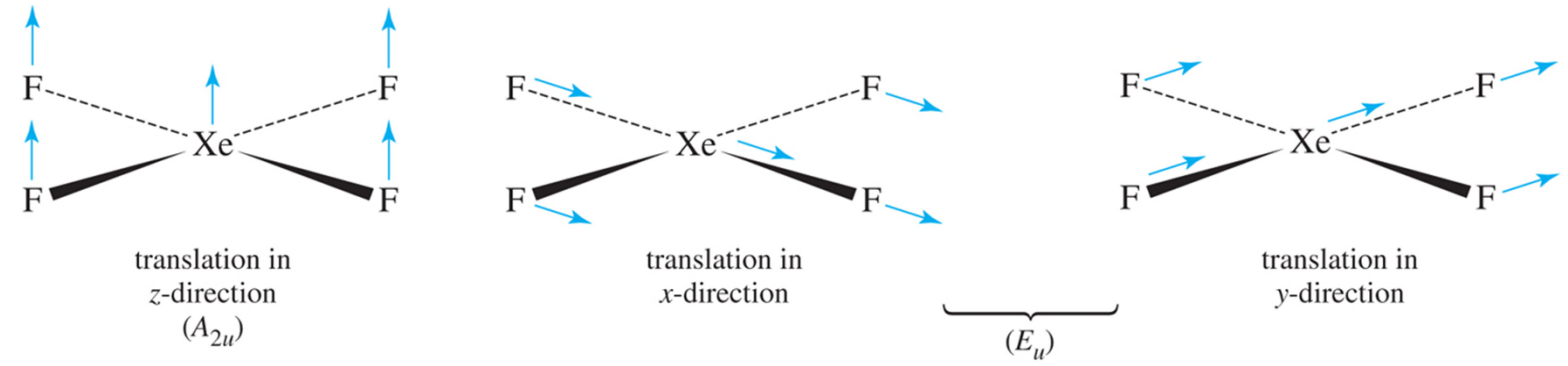
$\Gamma = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$

4.4.2 Molecular Vibrations

- translational motion: motion through space w/ x, y, z components

$\left\{\begin{array}{l} z \quad : A_{2u} \\ x,\ y: E_u \end{array}\right.$

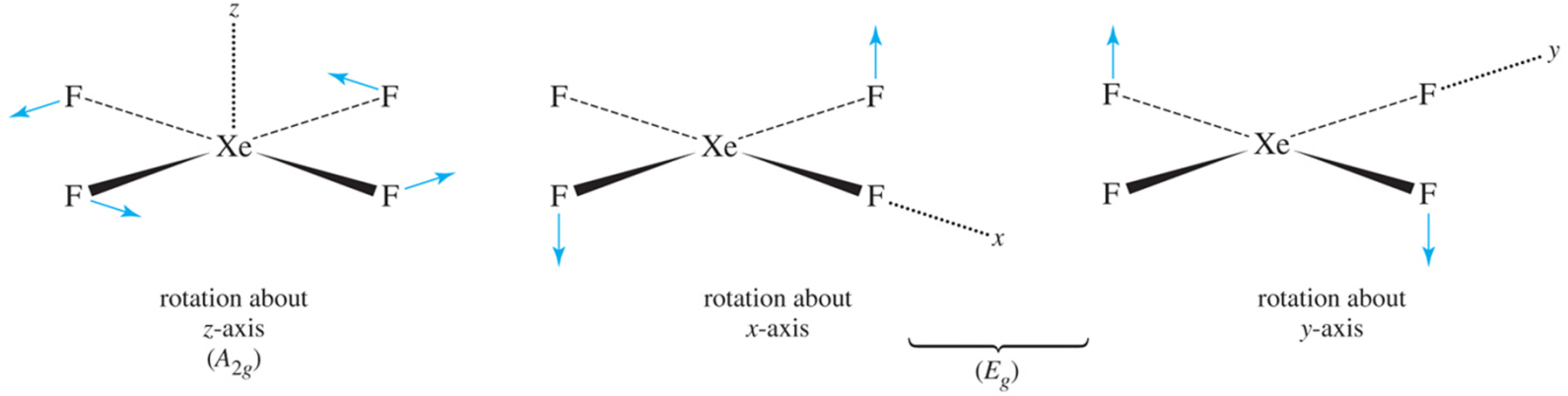
Fig.4.23



- Rotationl motion: rotation about the x, y, z axis (R_x, R_y, R_z)

$\left\{\begin{array}{l} R_z \quad : A_{2g} \\ (R_x,\ R_y): E_g \end{array}\right.$

Fig.4.24



4.4.2 Molecular Vibrations

- vibrational motion: 15 – 3 – 3 = 9

  : { change in bond length & angles
    { motion both within and out of the molecular place

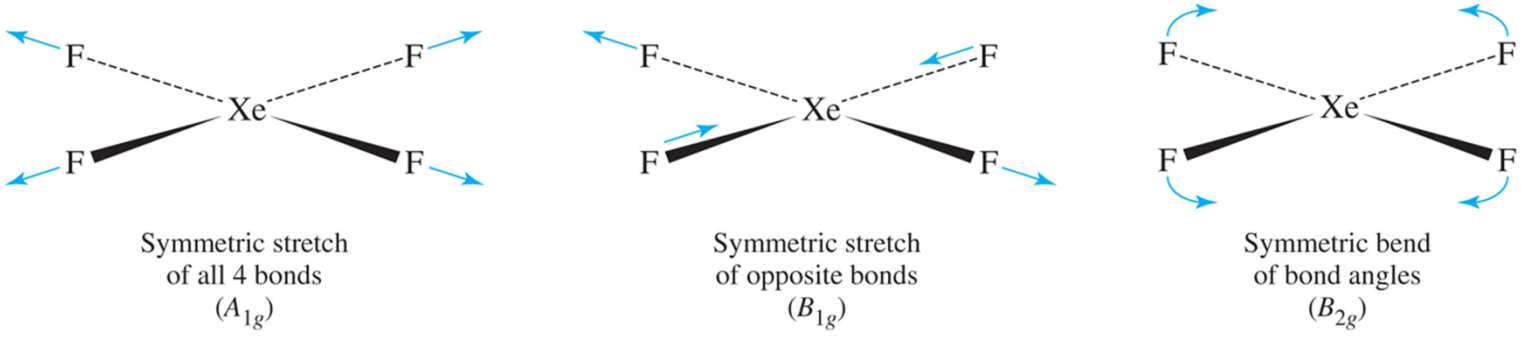


Fig.4.25

TABLE 4.13 Symmetry of Molecular Motions of XeF_4

	Γ (all modes)	Translation	Rotation	Vibration
	A_{1g}			A_{1g}
	A_{2g}		A_{2g}	
	B_{1g}			B_{1g}
	B_{2g}			B_{2g}
	E_g		E_g	
	2 A_{2u}	A_{2u}		A_{2u}
	B_{2u}			B_{2u}
	3 E_u	E_u		2 E_u
Total	15	3	3	9

4.4.2 Molecular Vibrations

Example 4.5) Reduce the following representation to their irreducible representation in the point group indicated (refer to the character table in Appendix C).

C_{2h}	E	C_2	i	σ_h
Γ	4	0	2	2

4.4.2 Molecular Vibrations

- **Infrared Spectra**

  - **infrared active**: if there is any change in the **dipole moment** of the molecule

    ↳ using group theory: *infrared active if it corresponds to an irreducible representation that has the **same symmetry** (or transformation) as the Cartesian coordinates **x, y, z***

  ∵ vibrational motion → change the center of charge → change in dipole moment

- We can **select particular vibrational modes!!!**

  e.g.) C-O stretching bands *cis*- and *trans*-dicarbonyl square planar complex

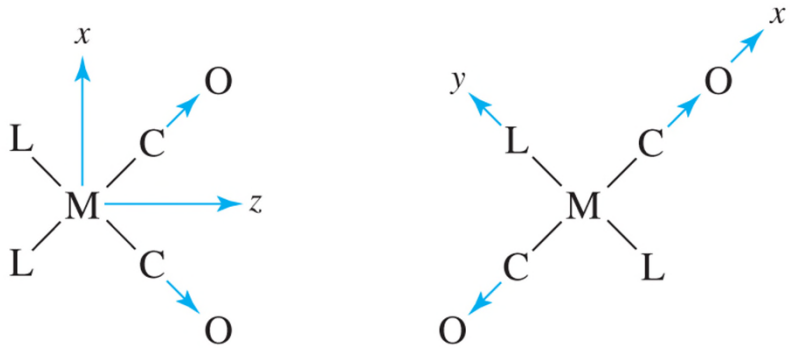


Fig.4.26 *Cis*-dicarbonyl complex *Trans*-dicarbonyl complex

1) *cis*-$ML_2(CO_2)$ point group C_{2v}:

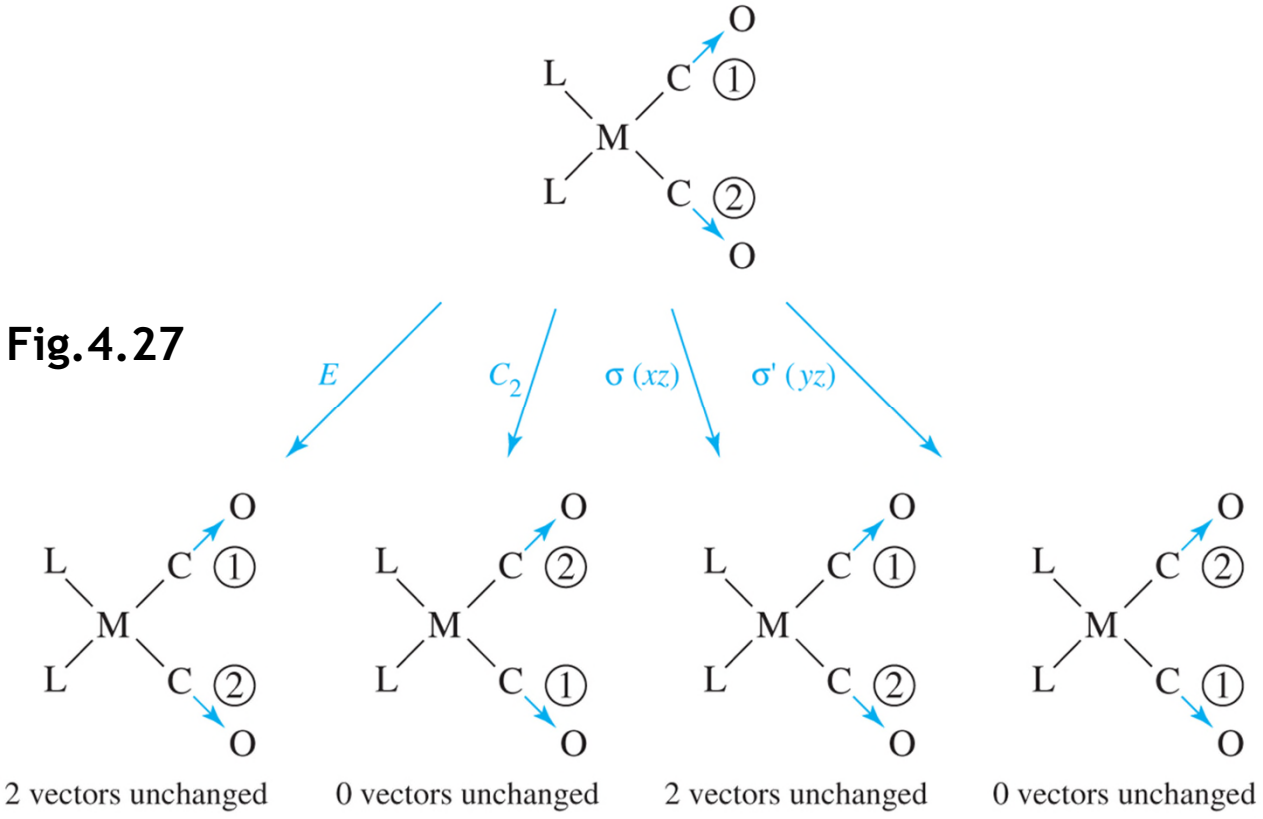


Fig.4.27

- either an increase or decrease in the C-O distance

  ↳ generate the reducible representation usign C-O bond as shown in Fig.4.27

4.4.2 Molecular Vibrations

1) *cis*-$ML_2(CO_2)$ point group C_{2v}.

	E	C_2	$\sigma\,(xz)$	$\sigma'\,(yz)$
Γ	2	0	2	0

reduction

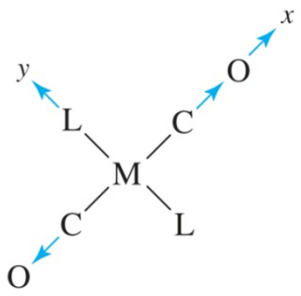
$\Gamma = A_1 + B_1$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ	2	0	2	0		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_1	1	−1	1	−1	x, R_y	xz

$\begin{cases} A_1 \rightarrow z \\ B_1 \rightarrow x \end{cases}$ → Both A_1, B_1 transforms as the Cartesian coordinates z, x

∴ There are two IR active vibrational modes!!

2) *trans*-$ML_2(CO_2)$ point group D_{2h}:



Trans-dicarbonyl complex

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
Γ	2	0	0	2	0	2	2	0	

reduction

$\Gamma = A_g + B_{3u}$

A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

$A_g \rightarrow$ No $\rightarrow$ IR-inactive

$B_{3u} \rightarrow x \rightarrow$ IR-active

∴ There are one IR active vibrational modes!!

∴ **Therefore, to distinguish *cis*- & *trans*-$ML_2(CO)_2$ by IR.**

- **one C-O stretching band → *trans***
- **two C-O stretching band → *cis***

Example 4.6) Determine the # of **IR active CO stretching** modes for *fac*-$Mo(CO)_3(CH_3CH_2CN)_3$

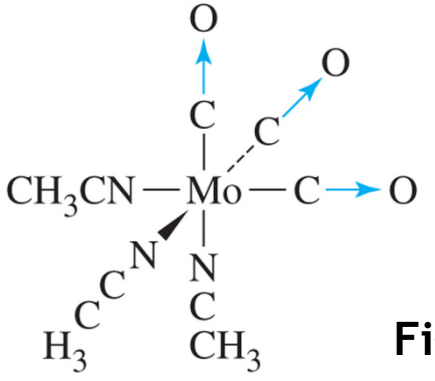


Fig.4.28

- **Raman Spectra**

  - laser → excite molecule to higher electronic states ("virtual" states)

    → decay of excited states to various vibrational states → provide info. about vibrational *E*

  - Raman active if there is a change in **polarizability**!!!

    ↳ **xy, yz, xz, x^2, y^2, z^2 functions** or linear combination of any of these.

e.g.) XeO_4 (T_d) → two Raman bands at 778 & 878 cm^{-1}. Confirm these bands!!

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ	4	1	0	0	2

reduction → $\Gamma = A_1 + T_2$

A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

∴ Both the A_1 & T_2 → two Raman active bands!!