19. <u>Introduction To Group Theory</u>

- used to represent states and to determine selection rules

(Discrete) Point Group: group of rotations/reflections etc. that leave a molecule unchanged; i.e., put it in an equivalent configuration.

"Point": operations all leave at least a point fixed (origin) (center of mass)

<u>Elements</u>

1. E (identity) $E(\underbrace{x,y,}_{\text{basis}}z) = (x,y,z)$

z axis

Bernath: $\hat{C}$

2. C_p (rotation) $C_p(r,\theta,z) \rightarrow (r, \theta + \frac{2\pi}{p}, z)$

e.g. C_3: rotate by $2\pi/3$, ~ 120°

C_3^2: rotate by $2\pi/3$ twice ~ 240°

C_3^3: E $\qquad C_6^2 = C_6 C_6 = C_3$

3. σ (reflections)

a) σ_{ij} means reflect through ij plane

$\sigma_{xz}(xyz) = x, -y, z$, etc.

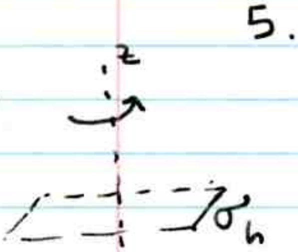
(xy) b) σ_h means reflect through a plane $\perp$ to C_p axis. (normally xy)

c) σ_v means reflect through a plane containing C_p axis ~~(normally xz, yz)~~

4. i (inversion) $i(x,y,z) = -x,-y,-z$

5. S_p (improper rotation)

- proper rotation (C_p) followed by σ_h reflection.



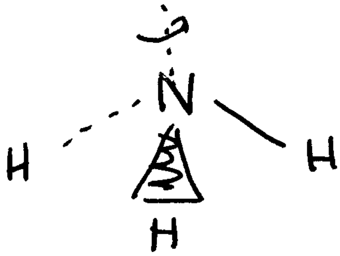
$S_2 = i$ Proof $\sigma_h C_2(x,y,z) = \sigma_h(-x,-y,z)$
$= -x,-y,-z = i(x,y,z)$

Examples of "Point" Groups

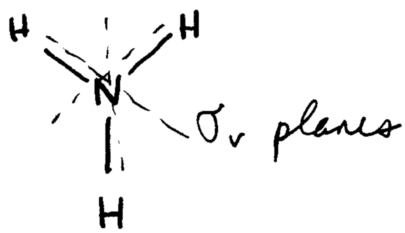
1. "C_{3v}" consists of E, $\underbrace{C_3, C_3^2}_{2C_3}$, $3\sigma_v$ planes

refers to molecules such as ammonia

Side View



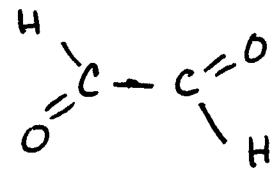
Top View



2. "C_{2h}" consists of E, C_2, i, σ_h

refers to molecules such as glyoxal

(planar)

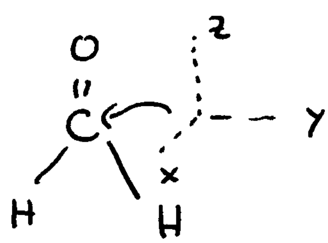


$C_2(z)$ axis is out of paper
($S_2 = C_2\sigma_h = i$)

3. "C_{2v}" consists of E, C_2, σ_{xz}, σ_{yz}

refers to molecules such as formaldehyde

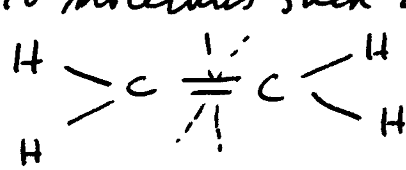
(planar)



4. "D_{2h}" consists of E, $C_2(z)$, $C_2(x)$, $C_2(y)$, i, σ_{xz}, σ_{yz}, σ_{xy}

refers to molecules such as ethylene

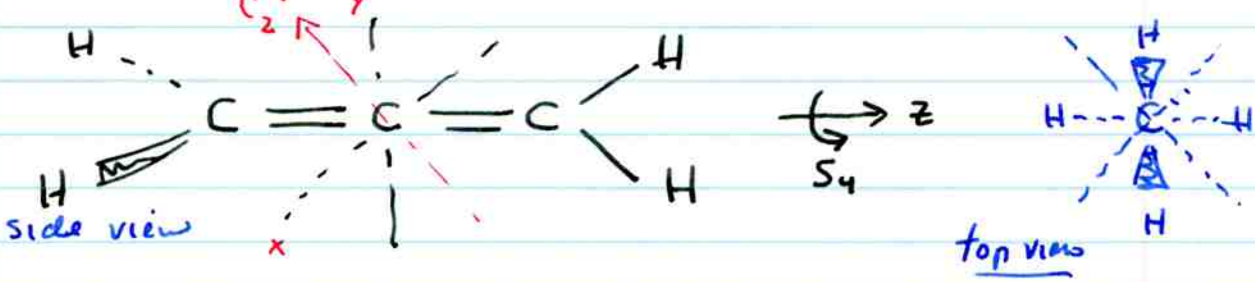
(planar)



5. "D_{2d}" consists of $E, \underbrace{S_4, S_4^3}_{2S_4}, \underbrace{S_4^2}_{C_2}\ \ 2C_2', \ 2\sigma_d$

↑ dihedral

refers to molecules such as allene



C_2' axes difficult to see. They lie ⊥ to the z axis and at 45° to the σ_d planes.

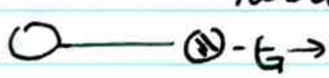
6. Some groups with fewer symmetry elements:

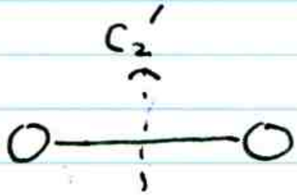
$C_1 = E \qquad C_s : E, \sigma \qquad C_i : E, i$

$C_n : \ E, (n-1)C_n \quad (C_n, C_n^2, C_n^3 \dots)$

7. Linear groups (infinite) $\quad C_{\infty v}\,(E, 2C(\varphi), \infty\sigma_v)$

heteronuclear diatomics





$D_{\infty h}\,(E, 2C(\varphi), \infty\sigma_v, i, 2S(\varphi), \infty C_2')$ σ_h?

homonuclear diatomics

Group Properties

h operations such that the following properties are obeyed:

1. closure $R_i \in G \quad R_j \in G \Rightarrow R_i R_j = R_k \in G$

2. "multiplication" is associative
$R_1(R_2 R_3) = (R_1 R_2) R_3 = R_1 R_2 R_3$

3. a unique identity $E R_i = R_i E = R_i$

4. each element has an inverse R_i^{-1}

$$R_i R_i^{-1} = E = R_i^{-1} R_i$$

e.g. $R_i = C_3 \quad C_3^2 = R_i^{-1}$ e.g. $[1, -1, i, -i]$

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Commutation of group elements is not required. A group with commuting elements is known as Abelian.

The group properties are illustrated by means of a so-called "multiplication table".

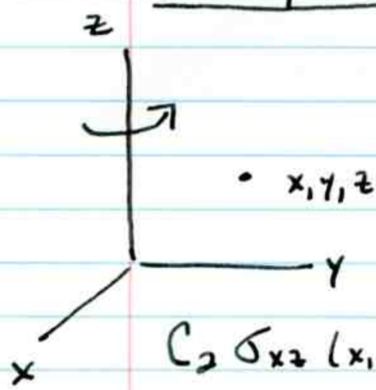
Consider the group C_{2v} (E, $C_2(z)$, σ_{xz}, σ_{yz}) $h = 4$

	E	C_2	σ_{xz}	σ_{yz}
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

(Abelian)

obeys closure

C_{2v} Operations



$$C_2(x,y,z) = -x, -y, z$$
$$\sigma_{xz}(x,y,z) = x, -y, z$$
$$\sigma_{yz}(x,y,z) = -x, y, z$$

$$C_2\,\sigma_{xz}(x,y,z) = C_2(x,-y,z) = -x, y, z = \sigma_{yz}(x,y,z)$$

$$C_2\,\sigma_{yz}(x,y,z) = C_2(-x,y,z) = x, -y, z = \sigma_{xz}(x,y,z)$$

$$\sigma_{xz}\,C_2(x,y,z) = \sigma_{xz}(-x,-y,z) = -x, y, z = \sigma_{yz}(x,y,z)$$

$$\sigma_{xz}\,\sigma_{yz}(x,y,z) = \sigma_{xz}(-x,y,z) = -x,-y,z = C_2(x,y,z)$$

$$\sigma_{yz}\,C_2(x,y,z) = \sigma_{yz}(-x,-y,z) = x,-y,z = \sigma_{xz}(x,y,z)$$

$$\sigma_{yz}\,\sigma_{xz}(x,y,z) = \sigma_{yz}(x,-y,z) = -x,-y,z = C_2(x,y,z)$$

Classes of Elements

- these consist of physically similar elements.

Mathematically:
A, B in the same class if $\exists\, R_i$ such that

$$R_i A R_i^{-1} = B$$

For an Abelian group $R_i A R_i^{-1} = R_i R_i^{-1} A = A$ so that each element is in a class by itself.

20. <u>Representations</u> (Γ)

Defn. sets of numbers or matrices that follow the group multiplication table.

$$R \underset{\sim}{B} = (\ \ ) B$$ representation

basis : function, axis helpful

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ_5	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	(x, y)

Example : 2-D matrices with x, y as basis.

$$R\begin{pmatrix} x \\ y \end{pmatrix} = (\quad)\begin{pmatrix} x \\ y \end{pmatrix} \qquad E\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

$$C_2\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ -y \end{pmatrix} \doteq \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

$$\sigma_{xz}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ -y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

$$\sigma_{yz}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ y \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

and $C_2\sigma_{xz} = \sigma_{yz}$ etc.

Example : numbers with z axis as basis $\uparrow$

$$C_2 \uparrow = \uparrow = 1 \uparrow \qquad \text{or coordinate}$$
$$\sigma_{xz} \uparrow = \uparrow = 1 \uparrow$$
$$\sigma_{yz} \uparrow = \uparrow = 1 \uparrow$$

One Dimensional Representations:

A_1 $\chi_1 = \Gamma_1$	1	1	1	1	z axis <u>symmetric</u>	
A_2 $\chi_2 = \Gamma_2$	1	1	-1	-1	xy	
B_1 $\chi_3 = \Gamma_3$	1	-1	1	-1	x	xz
B_2 $\chi_4 = \Gamma_4$	1	-1	-1	1	y	yz

Although the number of representations is infinite, virtually all are "reducible" in the sense that they

a) are diagonal matrices consisting of 1-D representations (see Γ_5) Γ_5 breaks down into $\Gamma_3 + \Gamma_4$

b) can be transformed into such diagonal matrices or into matrices with $n \times n$ blocks where $n <$ dimensionality of matrix.

<u>Irreducible Representations</u> : cannot be reduced

Some theorems:

(1) The number of irreducible representations can be shown to be equal to the number of classes s in a group.

For C_{2v} $s = h = 4 \Rightarrow 4$ irreducible representations ($\Gamma_1 - \Gamma_4$)

(2) $$\underbrace{h}_{\text{no. group elements "order of group"}} = \underbrace{\sum_{i=1}^{s}}_{\text{sum over classes}} l_i^2 \qquad l_i : \text{dimensionality of irreducible representation}$$

For C_{2v} $h = 4 = l_1^2 + l_2^2 + l_3^2 + l_4^2$

$l_i = 1 \Rightarrow 4$ 1-D irreducible representations

($h = s \Rightarrow$ 1-D reps only)

Representations are normally tabulated in terms of "<u>characters</u>" χ (<u>traces of matrices</u>)

	E	C_2	σ_{xz}	σ_{yz}	
$\chi(\Gamma_5)$	2	-2	0	0	$= \chi(\Gamma_3) + \chi(\Gamma_4)$
~~$\chi(\Gamma_6)$~~	~~2~~	~~0~~	~~0~~	~~2~~	~~$= \chi(\Gamma_1) + \chi(\Gamma_4)$~~

(3) Matrices representing group elements in the same class have the same trace.

<u>Proof</u> $RAR^{-1} = B$ $\quad R, A, B$ matrices