19. Introduction To Group Theory

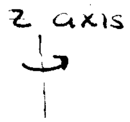
– used to represent states and to determine selection rules

(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)

Elements

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



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

Bernath : $\hat{C}$

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

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

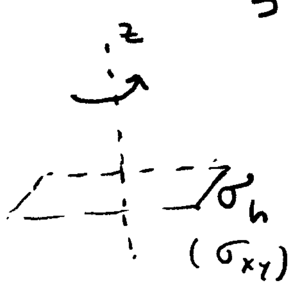
(xy) b) σ_h means reflect through a plane $\perp$ to C_p axis. (normally xy)

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

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

5. S_p (improper rotation)

– proper rotation (C_p) followed by σ_h reflection.



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

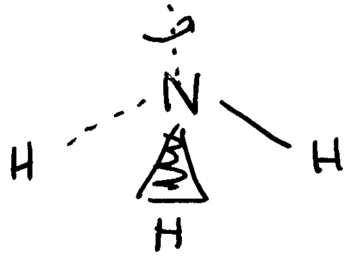
$= -x - y - z = i(x,y,z)$

Examples of "Point" Groups

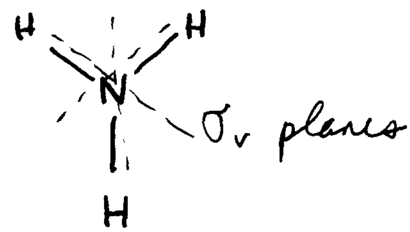
1. "C_{3v}" consists of E, $\underbrace{C_3, C_3^2}_{2C_3}$, $3\sigma_v$ planes

refers to molecules such as ammonia

Side View



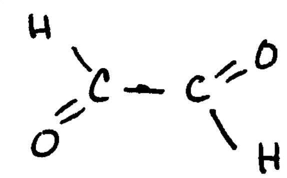
Top View



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

refers to molecules such as glyoxal

(planar)



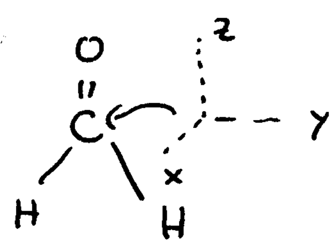
$C_2(z)$ axis is out of paper

$(S_2 = C_2\sigma_h = i)$

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

refers to molecules such as formaldehyde

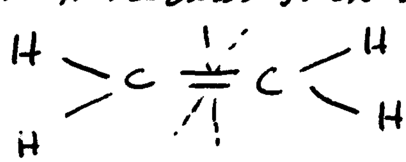
(planar)



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

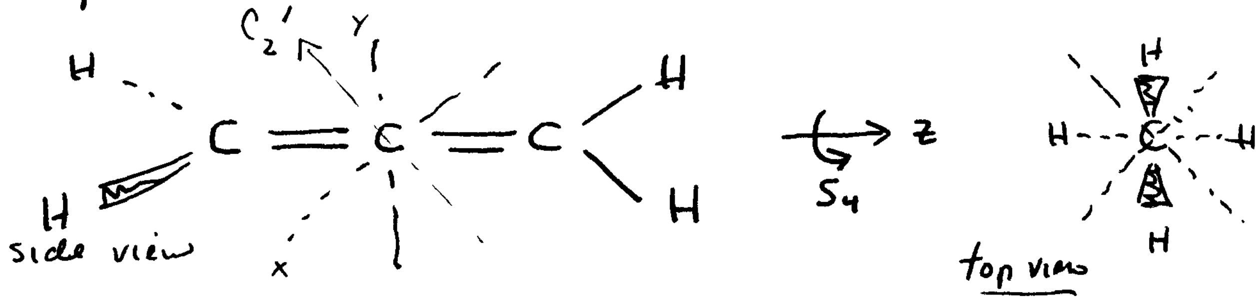
refers to molecules such as ethylene

(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.

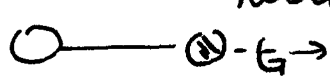
6. Some groups with fewer symmetry elements:

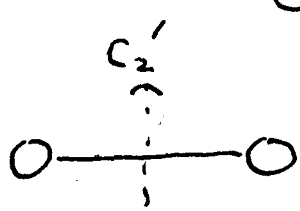
$C_1 = E$ $\quad C_s : E, \sigma$ $\quad C_i : E, i$

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

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

heteronuclear diatomics





$D_{\infty h} \; (E, 2C(\phi), \infty\sigma_v, i, 2S(\phi), \infty C_2')$ $\quad \sigma_h$?

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
$R_1(R_2R_3) = (R_1R_2)R_3 = R_1R_2R_3$

3. a unique identity $ER_i = R_iE = R_i$

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. $[1, -1, i, -i]$

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".

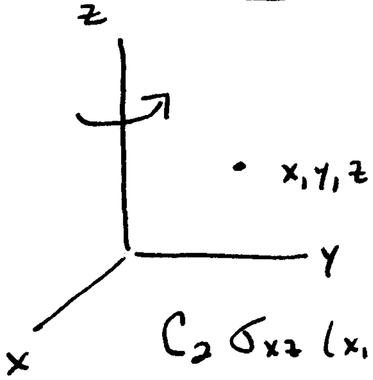
Consider the group C_{2v} $(E, C_2(z), \sigma_{xz}, \sigma_{yz})$ $h = 4$

	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)

$\boxed{\text{obeys closure}}$

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 analogous elements.

Mathematically:

A, B are in the same class if $\exists\, k_i$ such that

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

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