Chapter 17 – Symmetry

<u>Symmetry elements</u>

E	-	identity
C_n	-	n-fold rotation
σ	-	mirror plane
i	-	inversion
S_n	-	n-fold rotation-reflection

H_2O $\quad E, \sigma_v, \sigma_v', C_2 \quad \Rightarrow C_{2v}$

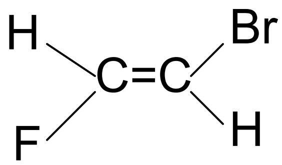
NH_3 $\quad E, \sigma_v(1), \sigma_v(2), \sigma_v(3)$

$C_3, C_3^2 = C_3^{-1} \quad \Rightarrow C_{3v}$

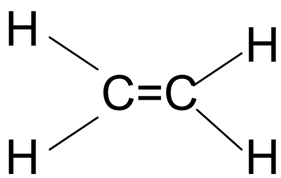
$CHFClBr$ $\quad E \quad \Rightarrow C_1$

$\sigma_v \Rightarrow$ mirror plane contains princ. rotational axis

$\sigma_h \Rightarrow$ mirror plane $\perp$ to the princ. axis



$E, \sigma \qquad \Rightarrow C_s$

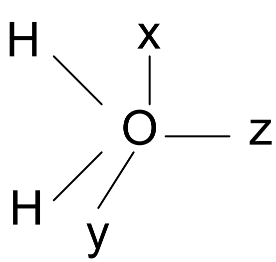


$E, C_2, C_2^{'}, 2C_2^{''} \qquad \Rightarrow D_{2h}$

$\sigma, \sigma^{'}, \sigma^{''}, i \qquad \uparrow$

group

Symmetry operators can be represented by matrices
Example:



, x $\perp$ to the plane of the molecule

$$\hat{E}: \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{C}_2: \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma}_v: \begin{pmatrix} 1 & 0 & 1 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma}_v^{'}: \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{C}_2 \bullet \hat{C}_2 = \hat{E}$$

$$\hat{C}_2 \bullet \hat{\sigma}_v = \hat{\sigma}_v^{'}$$

etc.

form a representation
fro the C_{2v} group

TABLE 17.3

Multiplication Table for Operators of the C_{2v} Group

Second Operation	First Operation: $\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

In this case, there are simpler representations

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_2$	$\hat{\sigma}_v'$		
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	$x,\ R_x$	xz
B_2	1	-1	-1	1	y, R_x	yz

character table

↑ irreducible representations

$O \quad p_z \rightarrow a_1$

A_1 = totally symmetric representation

$O \quad p_x \rightarrow b_1$

$O \quad p_y \rightarrow b_2$

for C_{2V} all irreducible representations are one-dimensional

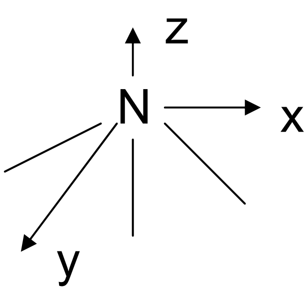
$\Rightarrow$ no degeneracies

C_{3V} is an example of a group with a degenerate representation

TABLE 17.4

The C_{3v} Character Table

	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2-y^2, xy),(xz, yz)$



rotate 120°, "mixes" x and y

E is a two-fold degenerate representation

The different representations are orthogonal

$$A_1 x A_2 = 1 \bullet 1 + 2 \bullet 1 \bullet 1 + 3 \bullet 1 \bullet (-1) = 0$$

$$A_2 x E = 1 \bullet 2 + 2(1)(-1) + 0 = 0$$

Electronic structure

C_{2v} group

$$a_2^2 \rightarrow A_1$$

$$b_1 b_2 \rightarrow A_2$$

$$a_2 b_2 \rightarrow A_1$$

$$b_1 a_2 \rightarrow B_2$$

$$\int \psi_1 \hat{H} \psi_2 d\tau = 0$$

if ψ_1, ψ_2 not the same symmetry

$$\int \psi_1 \hat{A} \psi_2 d\tau = 0$$

if $\psi_1 \hat{A} \psi_2$ does not contain totally symmetric representation

Selection rules

$$\int a_1 z a_1 d\tau \neq 0 \qquad a_1 \rightarrow a_1$$

$$\int a_1 z b_2 d\tau = 0 \qquad a_1 \rightarrow b_1$$

$$\int a_1 x b_1 d\tau \neq 0$$

etc.
allowed transitions

$$C_{3v} \qquad e^2 \rightarrow 4 \quad 1 \quad 0$$

$$= C_1(1 \quad 1 \quad 1) + C_2(1 \quad 1 \quad -1) + C_3(2 \quad -1 \quad 0)$$

$$C_1 = C_2 = C_3 = 1 \quad \Rightarrow \quad e^2 \rightarrow e, a_1, a_2$$

two electrons in an *e* orbital → *E*, A_1, A_2 states

Symmetries of vibrational normal modes

$$V = \frac{1}{2}\sum_i \left(\frac{\partial^2 V}{2Q_i^2} \right) Q_i^2, \qquad Q_i \text{ are normal coordinates}$$

$$\Psi = \psi_1(Q_1)\psi_2(Q_2)\ldots\psi_N(Q_N)$$

$$E = \sum_j \left(n_j + \frac{1}{2} \right) h\nu_j$$

Procedure (p. 404-405) for determining how many normal modes there are of each symmetry

$$H_2O = A_1, A_1, B_2$$

$$\psi_0\left(Q_j\right)Q_j\underbrace{\psi_m\left(Q_j\right)}$$

must belong to the same representation as *x, y,* or *z* to be IR active

C_{2V}: A_1 vibrations are IR active
B_2 vibration is also IR active

T_d: example CH_4: $\underbrace{A_1, E}$, $2T_2$ vibrations

A_1, E: IR forbidden

$2T_2$: IR active