Chapter 16 – Symmetry

Symmetry elements

E - identity

C_n - n-fold rotation

σ - mirror plane

i - inversion

S_n - n-fold rotation-reflection

Principal rotation axis – axis of the highest symmetry

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

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

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

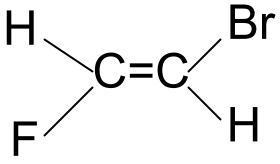
$CHFClBr$ $\quad E \quad \Rightarrow C_1$

Symmetry operations

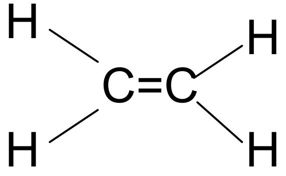
group

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

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



$E, \sigma \qquad \Rightarrow C_s$



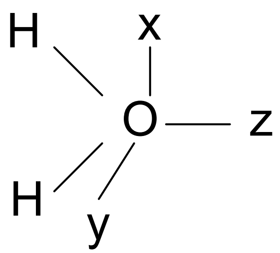
$E, C_2, C_2^{'}, 2C_2^{''} \qquad \Rightarrow D_{2h}$

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

↑

group

Symmetry operators can be represented by matrices
Example:



, x ⊥ to the plane of the molecule

$$\left.\begin{array}{l}
\hat{E}:\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}\\[1em]
\hat{C}_2:\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix}\\[1em]
\hat{\sigma}_v:\begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix}\\[1em]
\hat{\sigma}_v^{'}:\begin{pmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}
\end{array}\right\}$$

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

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

etc.

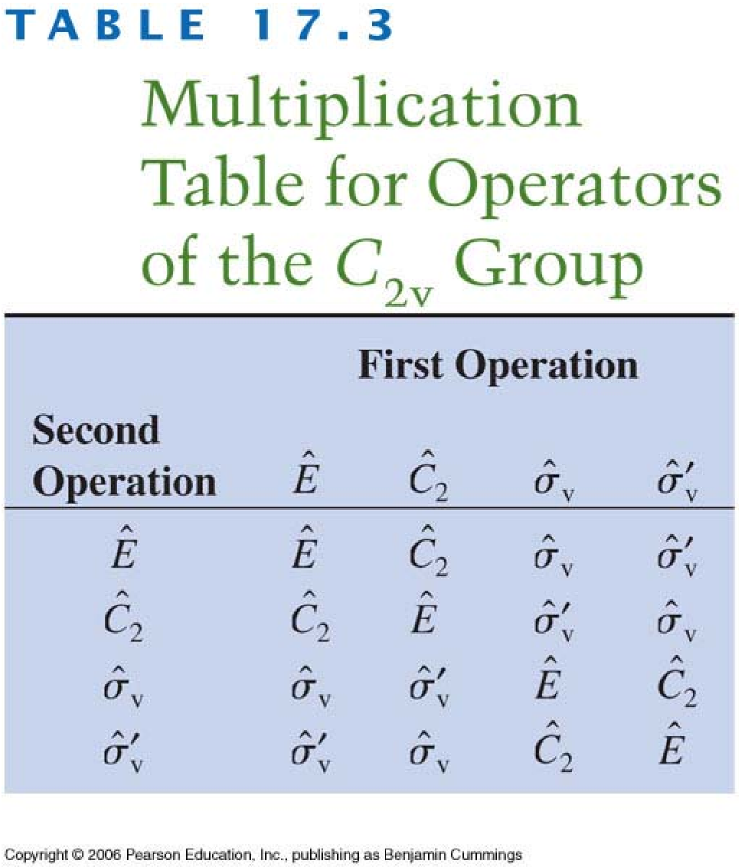


TABLE 17.3

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

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

form a representation
for the C_{2v} group

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

R$_i$ = rotation about I axis

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

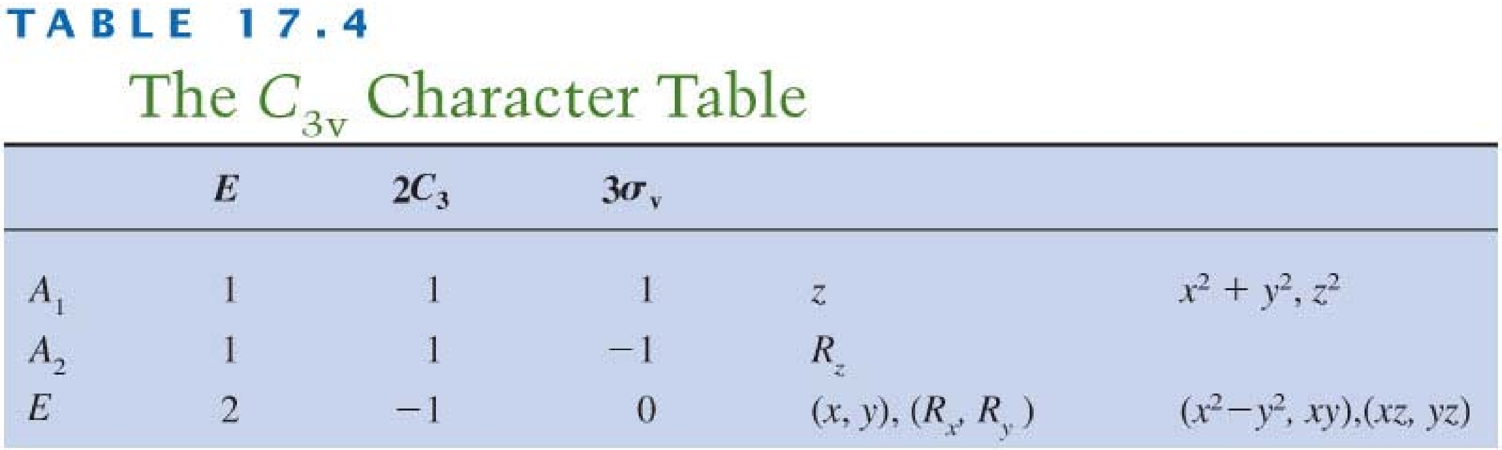
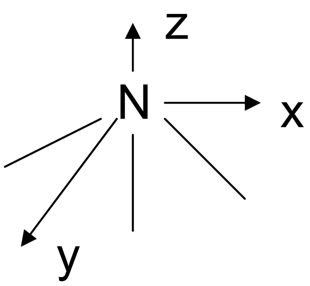


TABLE 17.4

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

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

$$= c_1(1 \quad 1 \quad 1) + c_2(1 \quad 1 \quad -1) + c_3(2 \quad -1 \quad 0)$$

$$\mathrm{c}_1 = c_2 = c_3 = 1 \quad \Rightarrow \quad e^2 \rightarrow e, a_1, a_2$$

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

Symmetries of vibrational normal modes

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

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

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

Procedure (p. 396) 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: $\underbrace{A_1,\ E,}_{\text{IR forbidden}}\ 2T_2$ vibrations

IR active