(14) **Today**

4.1 Symmetry elements and Operations

4.2 Point Groups

4.3 Properties and Representations of Groups

Next Class (15)

4.3 Properties and Representations of Groups

(16) **Second Class from Today**

4.3 Properties and Representations of Groups

4.4 Uses of Character Tables

Chap 5

Third Class from Today (17)

4.4 Uses of Character Tables

Summary of all the symmetry

irreducible representation

symmetry operations

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

matching functions

same symmetry as moving something along the z axis

characters

Muliken Labels - symmetry labels

label that describes the symmetry of the band

σ bond

π bond

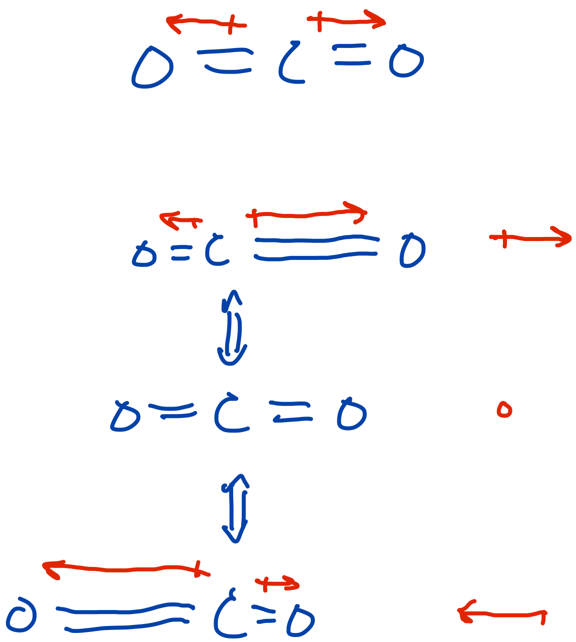
same symmetry as rotating something or the z axis anything that relates to symmetry

How do we use Character Tables.

To examine the symmetry of the thing we are interested in (molecular motions, orbitals, symmetry adapted linear combinations of atomic orbitals...) we create a reducible representation of the symmetry elements of the thing we are interested in.		For each operation add 1, 0 or -1 to the value for χ based on whether there is no change (1), the items changes position (0), or doesn't change position but changes sign (-1).
We use linear algebra to determine the irreducible representations that must be combined to for the reducible one that we just found.		
We use the functions in the character tables to interpret our results.		

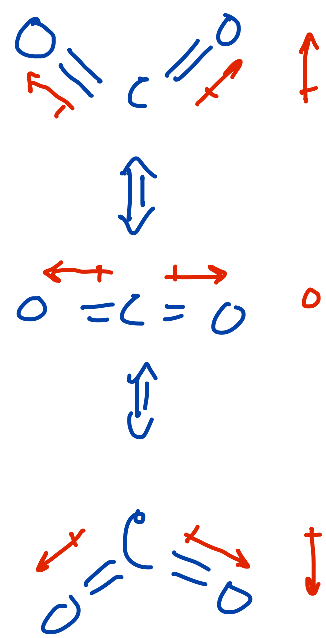
 vibrational spectroscopy

a vibration that changes the dipole of the molecule can interact with and absorb IR light



IR active

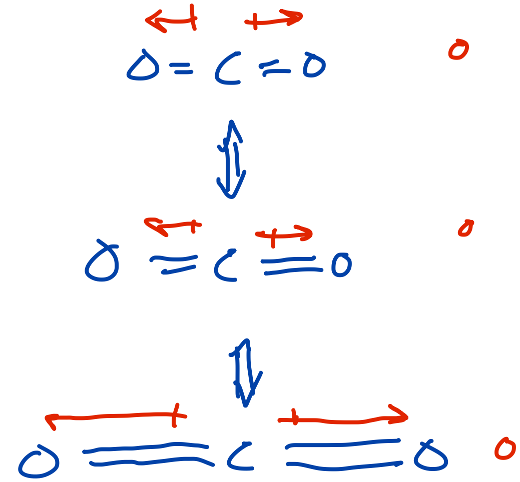
stretching mode



IR active

this one but out of the plane

bending mode



not IR active

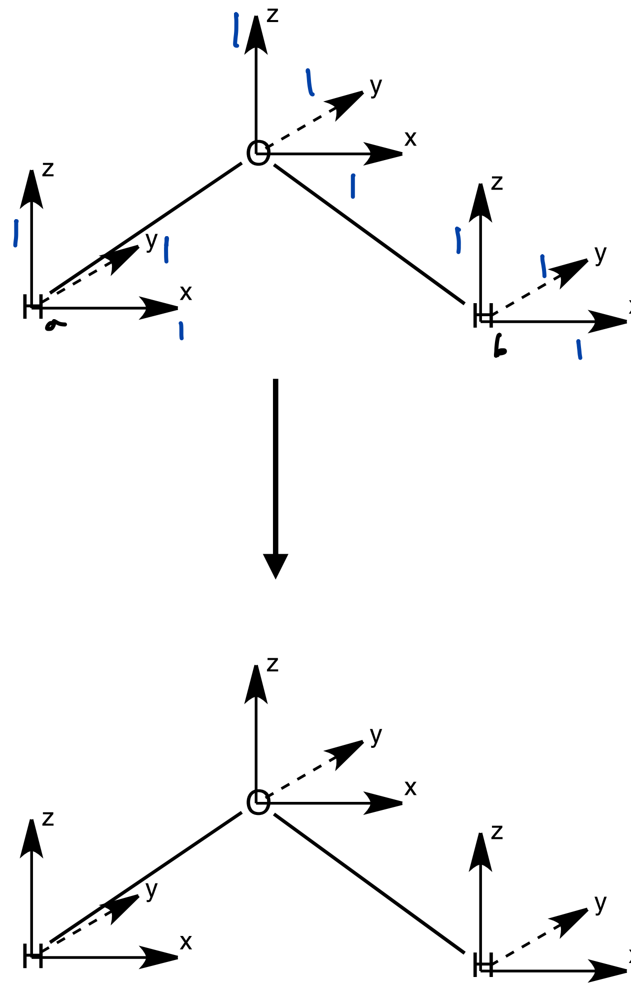
stretching mode

Thing we are interested in .... atomic motions of the atoms in a molecule

Number of IR Active Vibrational Modes for Water

C_{2v}	**E**	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ	9			

$$\begin{array}{cc} \mathrm{O} & x'_{O} \\ & y'_{O} \\ & z'_{O} \\ \mathrm{H_a} & x'_{Ha} \\ & y'_{Ha} \\ & z'_{Ha} \\ \mathrm{H_b} & x'_{Hb} \\ & y'_{Hb} \\ & z'_{Hb} \end{array} = \begin{array}{|ccccccccc|} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array} \begin{array}{c} x_{O} \\ y_{O} \\ z_{O} \\ x_{Ha} \\ y_{Ha} \\ z_{Ha} \\ x_{Hb} \\ y_{Hb} \\ z_{Hb} \end{array}$$

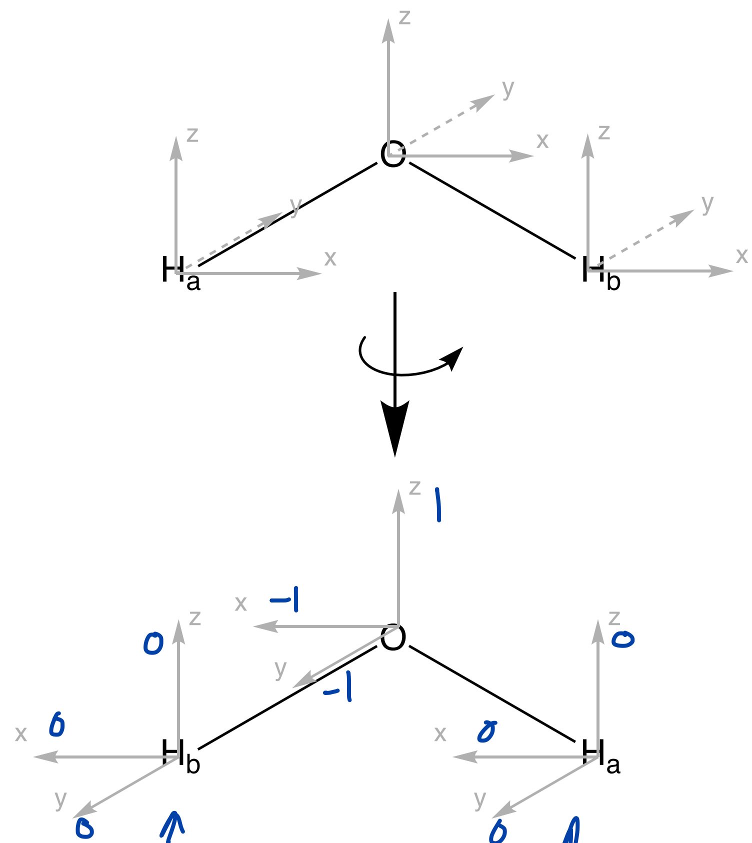


trace of this matrix is 9

the sum of the diagonal elements

C_{2v}	E	$\mathbf{C_2}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$
	9	-1		

$$\begin{array}{cc} O & x'_O \\ & y'_O \\ & z'_O \\ H_a & x'_{Ha} \\ & y'_{Ha} \\ & z'_{Ha} \\ H_b & x'_{Hb} \\ & y'_{Hb} \\ & z'_{Hb} \end{array} = \begin{bmatrix} -1 & & & & & & & & \\ & -1 & & & & & & & \\ & & 1 & & & & & & \\ & & & 0 & & & -1 & & \\ & & & & 0 & & & -1 & \\ & & & & & 0 & & & 1 \\ & -1 & & & & & 0 & & \\ & & -1 & & & & & 0 & \\ & & & 1 & & & & & 0 \end{bmatrix} \begin{array}{c} x_O \\ y_O \\ z_O \\ x_{Ha} \\ y_{Ha} \\ z_{Ha} \\ x_{Hb} \\ y_{Hb} \\ z_{Hb} \end{array}$$



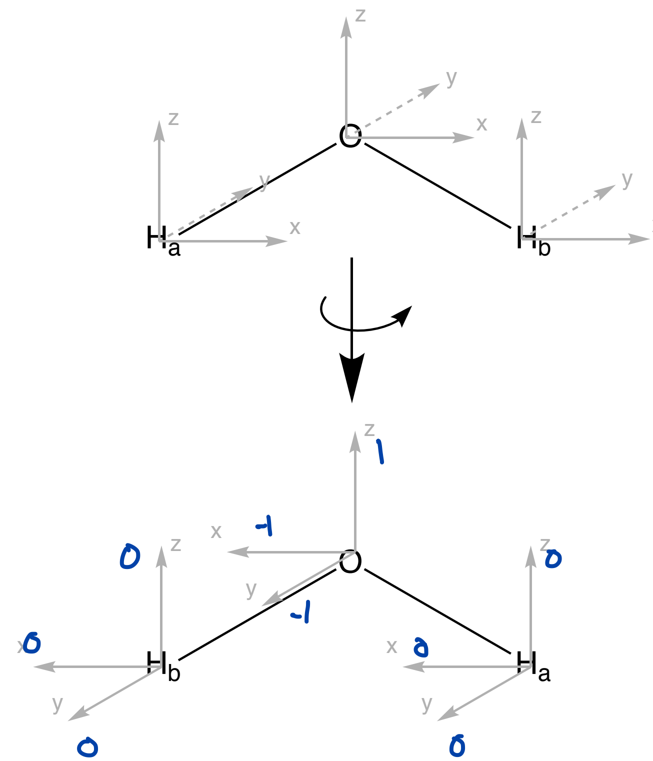
trace -1 + -1 + 1

when the atoms move

Easier way to determine the trace?

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
	9	-1		

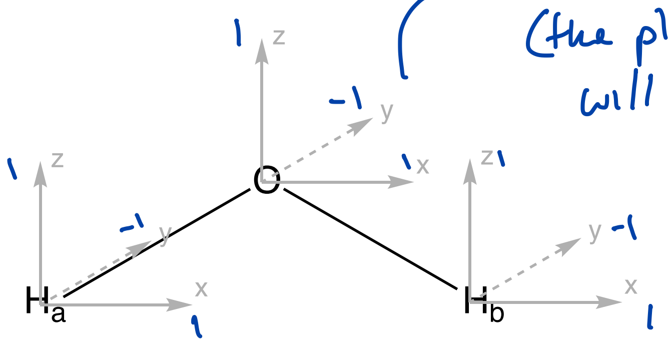
$$
\begin{array}{cc}
\mathrm{O} & x'_{O} \\
 & y'_{O} \\
 & z'_{O} \\
\mathrm{H_a} & x'_{Ha} \\
 & y'_{Ha} \\
 & z'_{Ha} \\
\mathrm{H_b} & x'_{Hb} \\
 & y'_{Hb} \\
 & z'_{Hb}
\end{array}
=
\begin{array}{|c|c|c|c|c|c|c|c|c|}
-1 & & & & & & & & \\
 & -1 & & & & & & & \\
 & & 1 & & & & & & \\
 & & & 0 & & & -1 & & \\
 & & & & 0 & & & -1 & \\
 & & & & & 0 & & & 1 \\
 & & & -1 & & & 0 & & \\
 & & & & -1 & & & 0 & \\
 & & & & & 1 & & & 0
\end{array}
\begin{array}{c}
x_{O} \\ y_{O} \\ z_{O} \\ x_{Ha} \\ y_{Ha} \\ z_{Ha} \\ x_{Hb} \\ y_{Hb} \\ z_{Hb}
\end{array}
$$



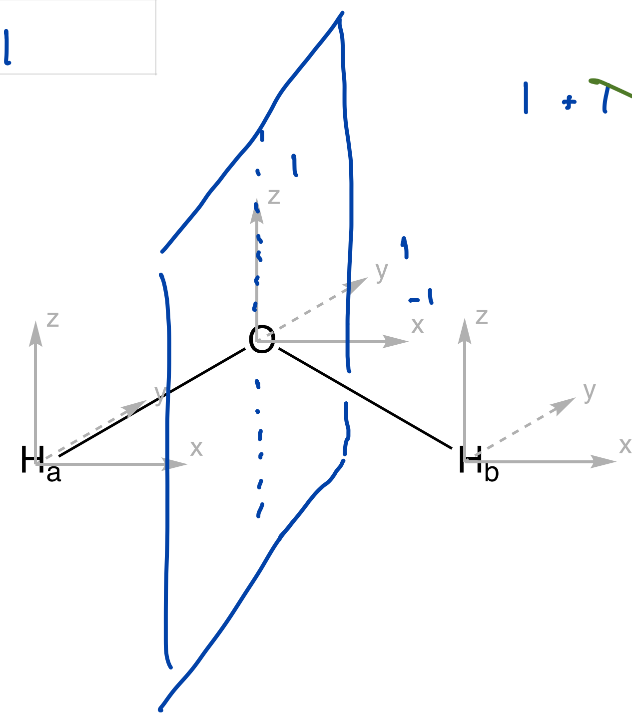
For each operation add 1, 0 or -1 to the value for χ based on whether there is no change (1), the items changes position (0), or doesn't change position but changes sign (-1).

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ	9	-1	3	1

reflection on the xz plane (the plane of the screen) will cause motion on the y axis to flip

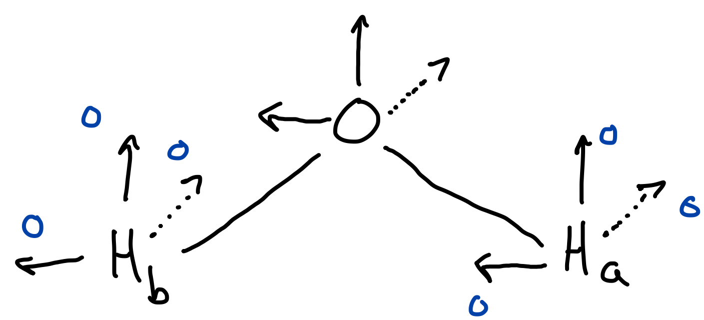


1 + ~~-1 +1~~ + 1 + ~~-1 +1~~ + 1 + ~~-1 +1~~



1 + ~~1 + -1~~

For each operation add 1, 0 or -1 to the value for χ based on whether there is no change (1), the items changes position (0), or doesn’t change position but changes sign (-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
Γ	9	-1	3	1		

now that we have the reducible representation we need to find which irreducible representations are used to make it

Extracting the Symmetry in formation by reducing the reducible representation   Section 4.4

sum of the squares of the characters under E

$$\text{number of irreducible representations of a given type needed} = \frac{1}{\text{order}} \sum_{\text{classes}} \left[\left(\begin{array}{c} \# \\ \text{operations} \\ \text{in class} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{irreducible} \\ \text{representation} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{reducible} \\ \text{representation} \end{array} \right) \right]$$

or sum accross all classes

class

$9 + \cancel{-1} + 3 \cancel{+} 1$

$$n(A_1) = 1/4 \bullet [(1)(1)(9) + (1)(1)(-1) + (1)(1)(3) + (1)(1)(1)]$$

$n = 3$

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		

$$\text{number of irreducible representations of a given type needed} = {}^{1}/_{\text{order}} \Sigma_{\text{classes}} \left[\left(\begin{array}{c} \# \\ \text{operations} \\ \text{in class} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{irreducible} \\ \text{representation} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{reducible} \\ \text{representation} \end{array} \right) \right]$$

$$n(A_2) = {}^{1}/\quad \bullet [(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )]$$

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		

$$\text{number of irreducible representations of a given type needed} = {}^{1}/_{\text{order}}\ \Sigma_{\text{classes}} \left[\left(\begin{array}{c} \# \\ \text{operations} \\ \text{in class} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{irreducible} \\ \text{representation} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{reducible} \\ \text{representation} \end{array} \right) \right]$$

$$n(B_1) = {}^{1}/\quad \bullet [(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )]$$

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		

$$\text{number of irreducible representations of a given type needed} = {}^{1}/_{\text{order}} \Sigma_{\text{classes}} \left[\left(\begin{array}{c} \# \\ \text{operations} \\ \text{in class} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{irreducible} \\ \text{representation} \end{array} \right) \left(\begin{array}{c} \chi \text{ of the} \\ \text{reducible} \\ \text{representation} \end{array} \right) \right]$$

$$n(B_2) = {}^{1}/\quad \bullet [(\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ ) + (\ )(\ )(\ )]$$

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		

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		

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

all possible motions = vibration + translation + rotation

$$\text{number of vibrational modes} = \left(\begin{array}{c}\text{\# of ways}\\ \text{of moving}\end{array}\right) - \left(\begin{array}{c}\text{translational}\\ \text{movement}\end{array}\right) - \left(\begin{array}{c}\text{rotational}\\ \text{movement}\end{array}\right)$$