Lecture B3.1 Group Theory

#### **Covalent Bond Theories**

VSEPR (valence shell electron pair repulsion model).
A set of empirical rules for predicting a molecular geometry using, as input, a correct Lewis Dot representation.

#### 2. Valence Bond theory.

A more advanced description of orbitals in molecules. We emphasize just one aspect of this theory: Hybrid atomic orbitals. Works especially well for organic molecules.

3. Molecular Orbital theory.

The most modern and powerful theory of bonding. Based upon QM.

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#### **Covalent Bond Theories**

VSEPR (valence shell electron pair repulsion model).
A set of empirical rules for predicting a molecular geometry using, as input, a correct Lewis Dot representation.

Molecular Geometry is described by Group Theory!

## **Point Group Symmetry**

Point group symmetry is an important property of molecules widely used in some branches of chemistry: spectroscopy, quantum chemistry and crystallography.

An individual point group is represented by a set of symmetry "elements" or operations:

- E the identity (abbreviated to E, from the German 'Einheit' meaning Unity)
- $C_n$  rotation by  $2\pi/n$  angle  $^*$
- $\sigma_s$  reflection plane
- $\sigma_h$  horizontal reflection plane (perpendicular to the principal axis) \*\*
- $\sigma_v$  vertical reflection plane (contains the principal axis)
- $\sigma_d$  diagonal reflection plane (contains the principal axis and bisects the angle between two  $C_2$  axes perpendicular to the principal axis)
- i Center of symmetry or inversion center. A molecule has a center of symmetry when, for any atom in the molecule, an identical atom exists diametrically opposite this center an equal distance from it. There may or may not be an atom at the center.
- $S_n$  improper rotation (rotation by  $2\pi/n$  angle and reflection in the plane perpendicular to the axis)
- \* n is an integer
- $\ast\ast$  principal axis is a  $C_n$  axis with the biggest n.

A molecule belongs to a symmetry point group if it is unchanged under all the symmetry operations of this group.

I. <u>Identity</u> is indicated as E does nothing, has no effect All molecules/objects possess the identity operation, i.e., possess E.

E has the same importance as the number I does in multiplication (E is needed in order to define inverses).



2. <u>n-Fold Rotations</u>:  $C_n$ , where n is an integer

rotation by 360°/n about a particular axis defined as the n-fold rotation axis.

 $C_2 = 180^\circ$  rotation,  $C_3 = 120^\circ$  rotation,  $C_4 = 90^\circ$  rotation,  $C_5 = 72^\circ$  rotation,  $C_6 = 60^\circ$  rotation, etc.

Rotation of  $H_2O$  about the axis shown by  $180^{\circ}$  (C<sub>2</sub>) gives the same molecule back.

Therefore  $H_2O$  possess the  $C_2$  symmetry element.



3. <u>Reflection</u>:  $\sigma_s$  (the symmetry element is called a mirror plane or plane of symmetry)

If reflection about a mirror plane gives the same molecule/ object back than there is a plane of symmetry ( $\sigma_s$ ).

If plane contains the principle rotation axis (i.e., parallel), it is a vertical plane ( $\sigma_v$ )

If plane is perpendicular to the principle rotation axis, it is a horizontal plane ( $\sigma_h$ )

If plane is parallel to the principle rotation axis, but bisects angle between 2 C<sub>2</sub> axes, it is a diagonal plane ( $\sigma_d$ )

H<sub>2</sub>O possesses 2  $\sigma_v$  mirror planes of symmetry because they are both parallel to the principle rotation axis (C<sub>2</sub>)



4. <u>Inversion</u>: i (the element that corresponds to this operation is a center of symmetry or inversion center)

The operation is to move every atom in the molecule in a straight line through the inversion center to the opposite side of the molecule.

XeF<sub>4</sub>

Therefore  $XeF_4$  possesses an inversion center at the Xe atom.



5. Improper Rotations: S<sub>n</sub>

n-fold rotation followed by reflection through mirror plane perpendicular to rotation axis

Note: n is always 3 or larger because  $S_1 = s$  and  $S_2 = i$ .



# An example: H<sub>2</sub>O





The water molecule has one  $C_2$  axis and two  $\sigma_v$  symmetry planes.

### It's point group is: $C_{2v}$



### The $C_{2v}$ Character Table:

## C<sub>2v</sub> Point Group

Abelian, 4 irreducible representations Subgroups of  $C_{2v}$  point group:  $C_s, C_2$ 

Character table for C2v point group

	E	$C_2(z)$	$\sigma_v^{(xz)}$	$\sigma_v^{}(yz)$	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
<b>B</b> <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz





	E	$C_2(z)$	σ <sub>v</sub> (xz)	σ <sub>v</sub> (yz)	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
<b>B</b> <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

Symmetry elements





	E	$C_2(z)$	$\sigma_v^{(xz)}$	$\sigma_v^{}(yz)$	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	xy
В <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
В <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

#### Irreducible Representations



Character table for C<sub>2v</sub> point group

	E	$C_2(z)$	$\sigma_v^{(xz)}$	$\sigma_v^{}(yz)$	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
<b>B</b> <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

 $C_{2v}$ 

Number of vibrations: 3N - 6 = 3

IR activity is denoted by x, y or z Normal mode vibrations:  $2 A_1 + B_2$ 



Character	table	for	C <sub>2v</sub>	point	group
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	E	$C_2(z)$	$\sigma_v^{(xz)}$	$\sigma_v^{}(yz)$	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	ху
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
<b>B</b> <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

 $C_{2v}$ 

Number of vibrations: 3N - 6 = 3

Raman activity is denoted by this column. Normal mode vibrations:  $2 A_1 + B_2$ 



Character table for C2v point group

	E	C <sub>2</sub> (z)	$\sigma_v^{(xz)}$	$\sigma_v^{}(yz)$	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
В <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

 $C_{2v}$ 

Number of vibrations: 3N - 6 = 3

Each normal mode vibration has an irreducible representation:

Normal mode vibrations:  $2A_1 + B_2$ 

Character table for C2v point group



	E	$C_2(z)$	$\sigma_v^{(XZ)}$	$\sigma_v^{}(yz)$	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
<b>B</b> <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

Number of vibrations: 3N - 6 = 3

## $v_1$ vibration: 3657 cm<sup>-1</sup> A<sub>1</sub> symmetry, OH symmetric stretch

Both IR and Raman active.

Character table for C<sub>2v</sub> point group



	E	$C_2(z)$	$\sigma_v^{(xz)}$	$\sigma_v^{}(yz)$	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
<b>B</b> <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

Number of vibrations: 3N - 6 = 3

# $V_2$ vibration: 1595 cm<sup>-1</sup> A<sub>1</sub> symmetry, OH bend



Both IR and Raman active.

#### Character table for C2v point group



	E	$C_2(z)$	$\sigma_v^{(xz)}$	$\sigma_v^{}(yz)$	linear, rotations	quadratic
A <sub>1</sub>	1	1	1	1	Z	$x^{2}, y^{2}, z^{2}$
A_2	1	1	-1	-1	R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	XZ
B <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

Number of vibrations: 3N - 6 = 3

## $V_3$ vibration: 3756 cm<sup>-1</sup> B<sub>2</sub> symmetry, OH asymmetric stretch

IR and Raman active.

# There are only a finite number of molecular symmetry groups.

Nonaxial	C <sub>n</sub>	C <sub>nv</sub>	C <sub>nh</sub>	D <sub>n</sub>	D <sub>nh</sub>	D <sub>nd</sub>	S <sub>n</sub>	Higher	Linear
$C_1$	C <sub>2</sub>	$C_{2v}$	C <sub>2h</sub>	D <sub>2</sub>	D <sub>2h</sub>	D <sub>2d</sub>	S <sub>4</sub>	T <sub>d</sub>	$C_{_{\infty_V}}$
C <sub>s</sub>	C <sub>3</sub>	C <sub>3v</sub>	C <sub>3h</sub>	D <sub>3</sub>	D <sub>3h</sub>	D <sub>3d</sub>	S <sub>6</sub>	O <sub>h</sub>	$D_{\infty h}$
C <sub>i</sub>	C <sub>4</sub>	$C_{4v}$	C <sub>4h</sub>	D <sub>4</sub>	$D_{4h}$	D <sub>4d</sub>	S <sub>8</sub>	$\mathbf{I}_{\mathbf{h}}$	
	C <sub>5</sub>	C <sub>5v</sub>	C <sub>5h</sub>	D <sub>5</sub>	$D_{5h}$	D <sub>5d</sub>	<b>S</b> <sub>10</sub>		
	C <sub>6</sub>	C <sub>6v</sub>	C <sub>6h</sub>	D <sub>6</sub>	D <sub>6h</sub>	D <sub>6d</sub>			

We can use a flowchart to find them if we can find all of the symmetry elements. We can use a flowchart to find them if we can find all of the symmetry elements.







## $\mathsf{SF}_4$





#### Seesaw Geometry



## $CO_2$



















