Symmetry and Group Theory

The symmetry properties of molecules and how they can be used to predict vibrational spectra, hybridization, optical activity, etc.

Point Groups

Molecules are classified and grouped based on their symmetry. Molecules with similar symmetry are but into the same *point group*. A point group contains all objects that have the same *symmetry elements*.

Symmetry Elements

Symmetry elements are mirror planes, axis of rotation, centers of inversion, etc.

A molecule has a given symmetry element if the operation leaves the molecule appearing as if nothing has changed (even though atoms and bonds may have been moved.)

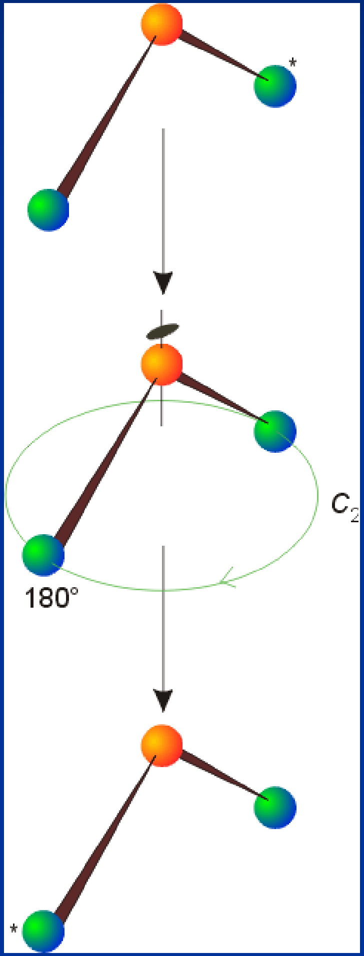
Symmetry Elements

Element	Symmetry Operation	Symbol
	Identity	E
n-fold axis	Rotation by $2\pi/n$	C_n
Mirror plane	Reflection	σ
Center of inversion	Inversion	i
n-fold axis of improper rotation	Rotation by $2\pi/n$ followed by reflection perpendicular to the axis of rotation	S_n

Identity, E

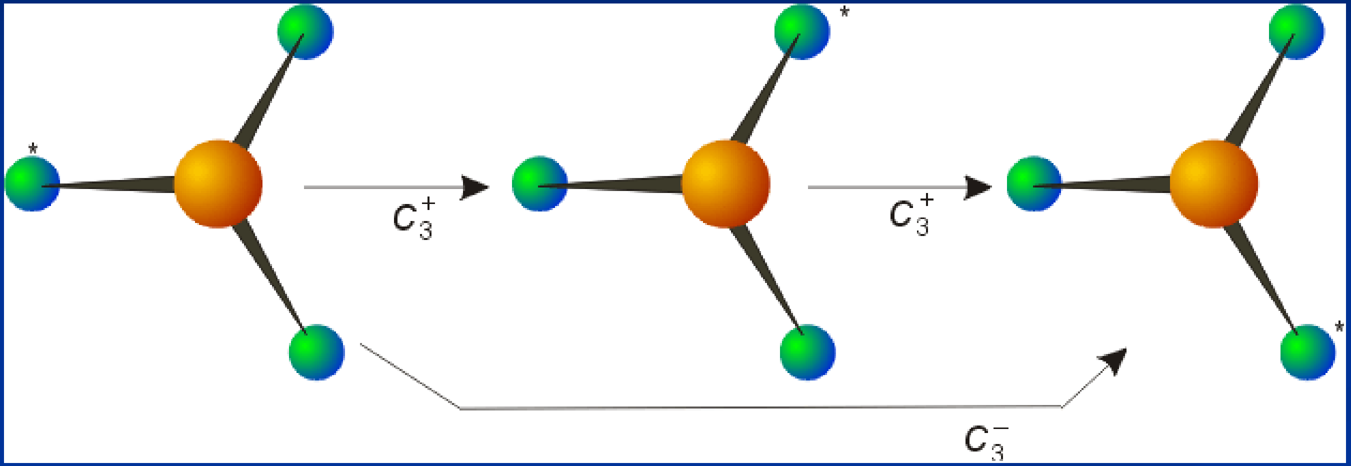
All molecules have Identity. This operation leaves the entire molecule unchanged. A highly asymmetric molecule such as a tetrahedral carbon with 4 different groups attached has only identity, and no other symmetry elements.

n-fold Rotation



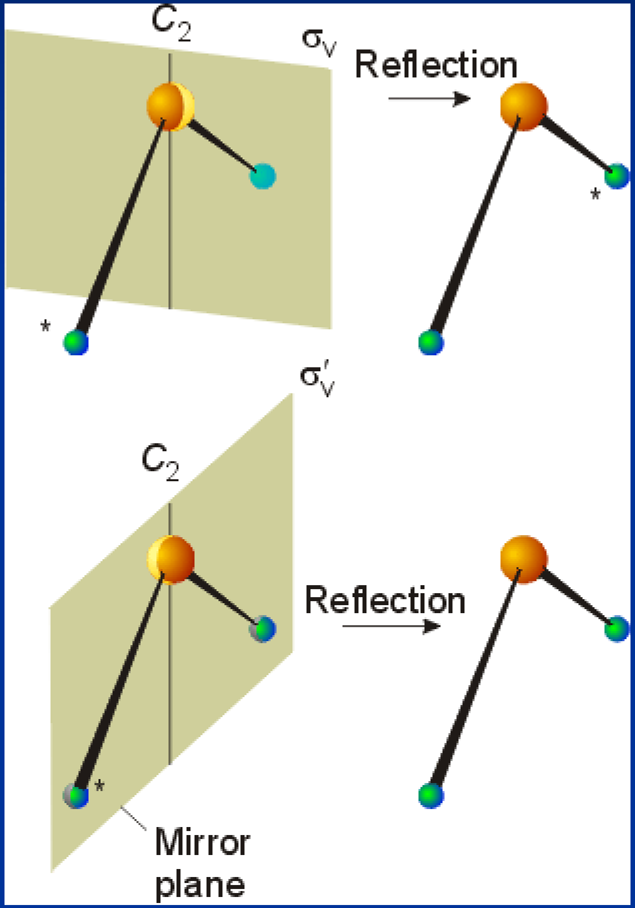
Water has a 2-fold axis of rotation. When rotated by 180°, the hydrogen atoms trade places, but the molecule will look exactly the same.

n-fold Axis of Rotation



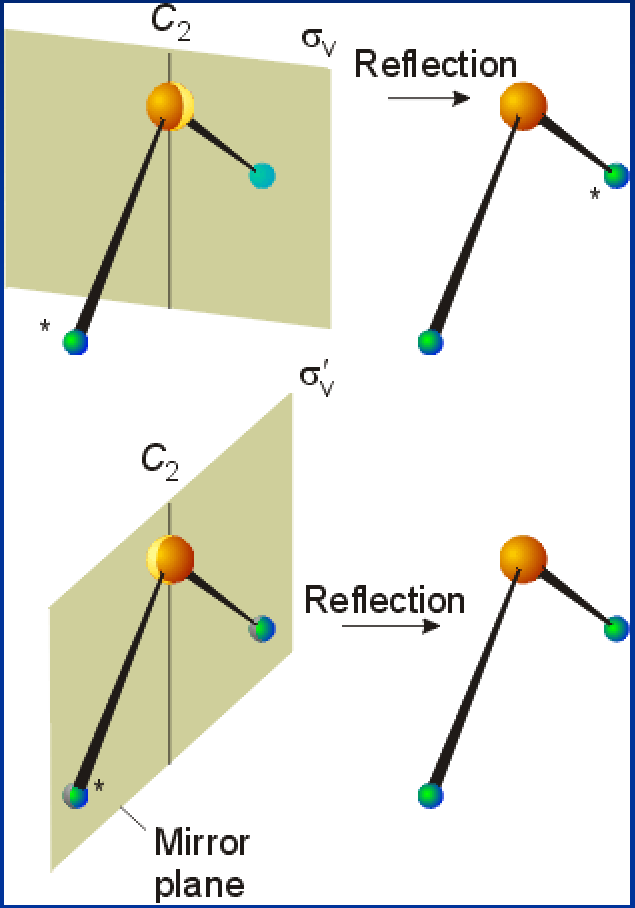
Ammonia has a C_3 axis. Note that there are <u>two</u> operations associated with the C_3 axis. Rotation by 120° in a clockwise or a counterclockwise direction provide two different orientations of the molecule.

Mirror Planes



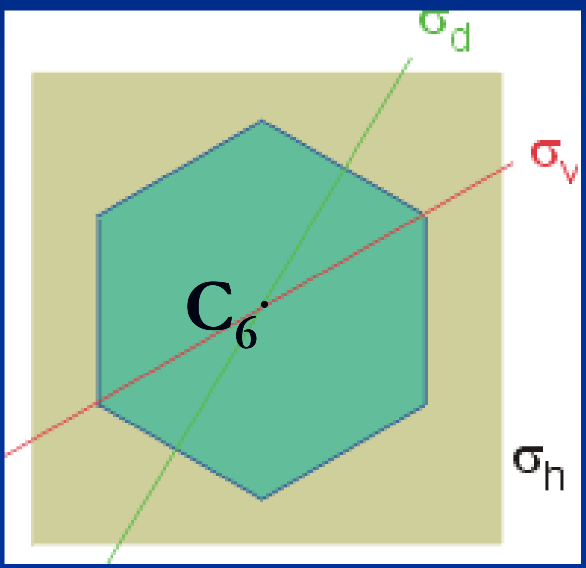
The reflection of the water molecule in either of its two mirror planes results in a molecule that looks unchanged.

Mirror Planes



The subscript "v" in σ_v, indicates a vertical plane of symmetry. This indicates that the mirror plane includes the principal axis of rotation (C_2).

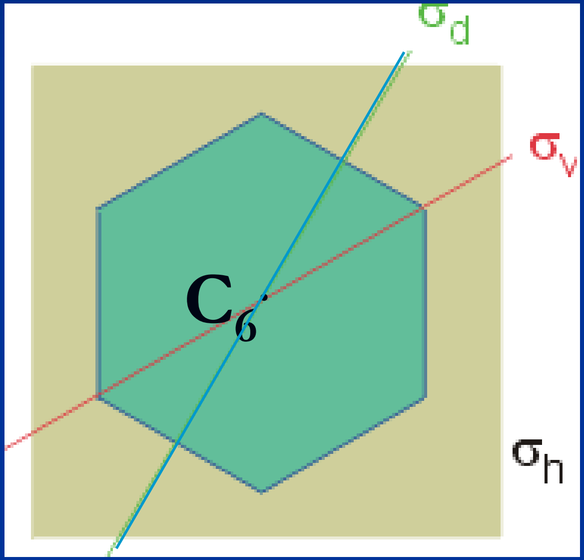
Mirror Planes



The benzene ring has a C_6 axis as its principal axis of rotation.

The molecular plane is perpendicular to the C_6 axis, and is designated as a horizontal plane, σ_h.

Mirror Planes

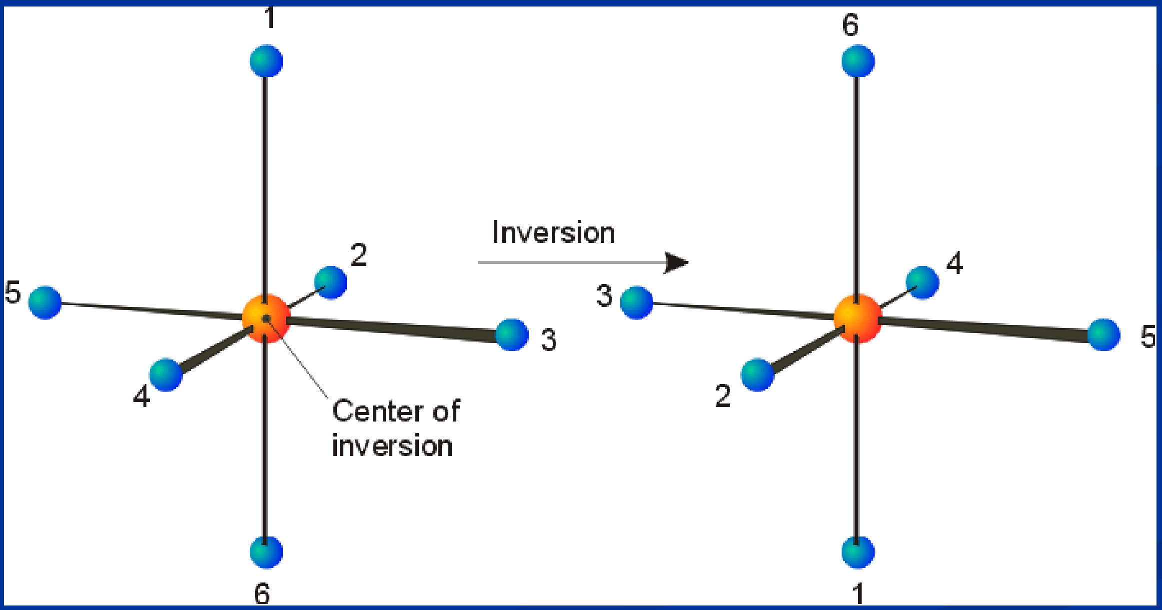


The vertical planes, σ_v, go through the carbon atoms, and include the C_6 axis.

The planes that bisect the bonds are called *dihedral* planes, σ_d.

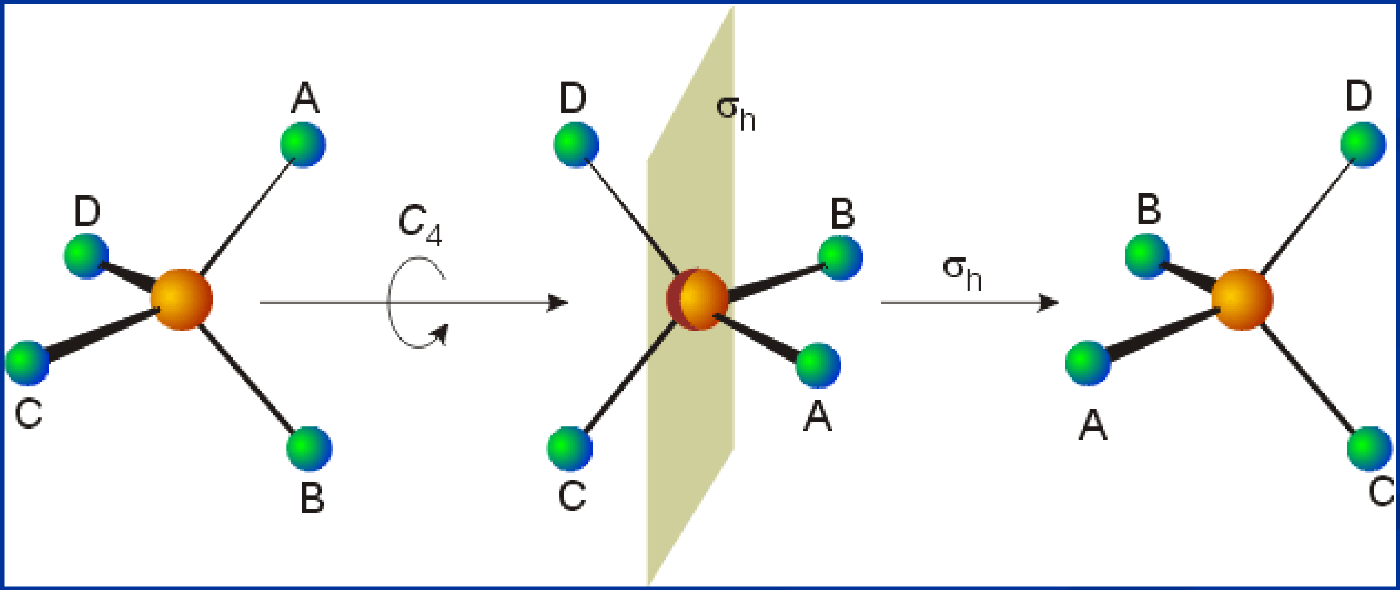
Inversion

The inversion operation projects each atom through the center of inversion, and across to the other side of the molecule.



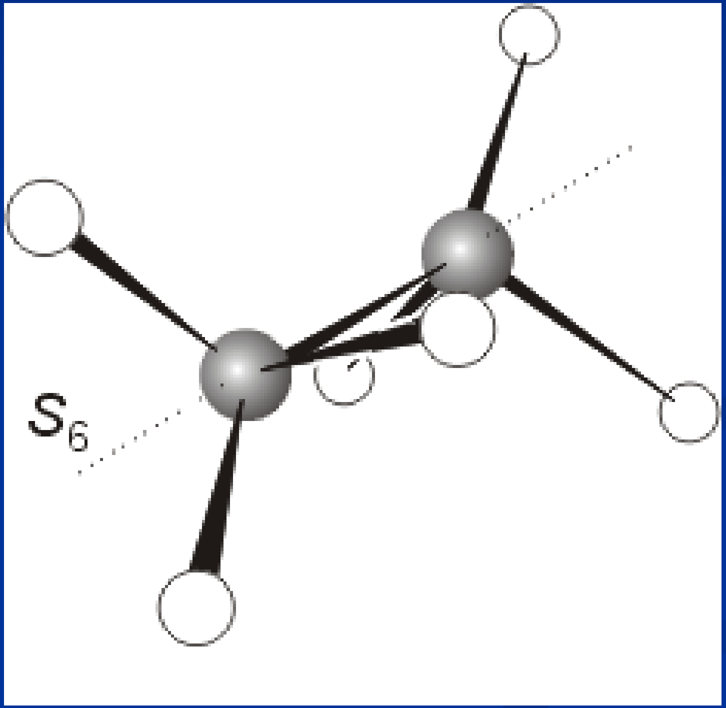
Improper Rotation

An improper rotation is rotation, followed by reflection in the plane perpendicular to the axis of rotation.



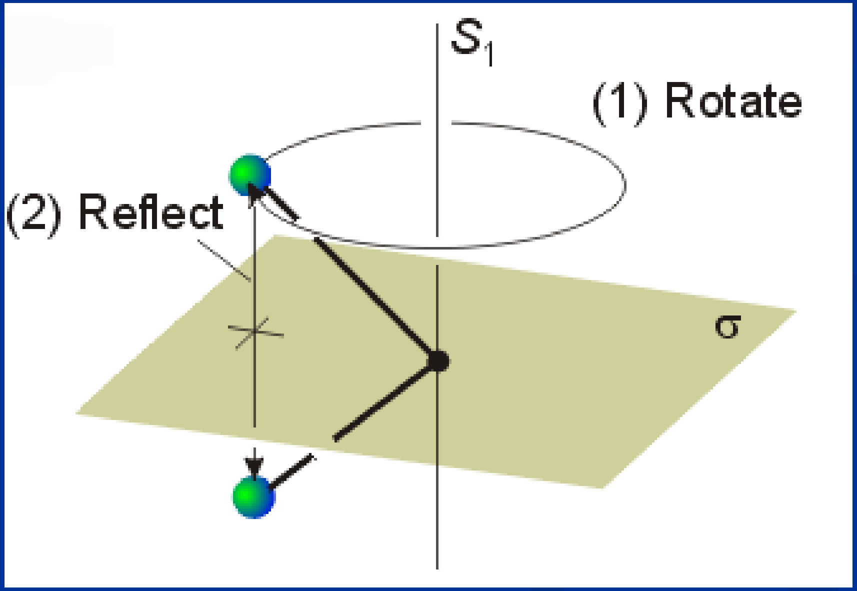
Improper Rotation

The staggered conformation of ethane has an S_6 axis that goes through both carbon atoms.



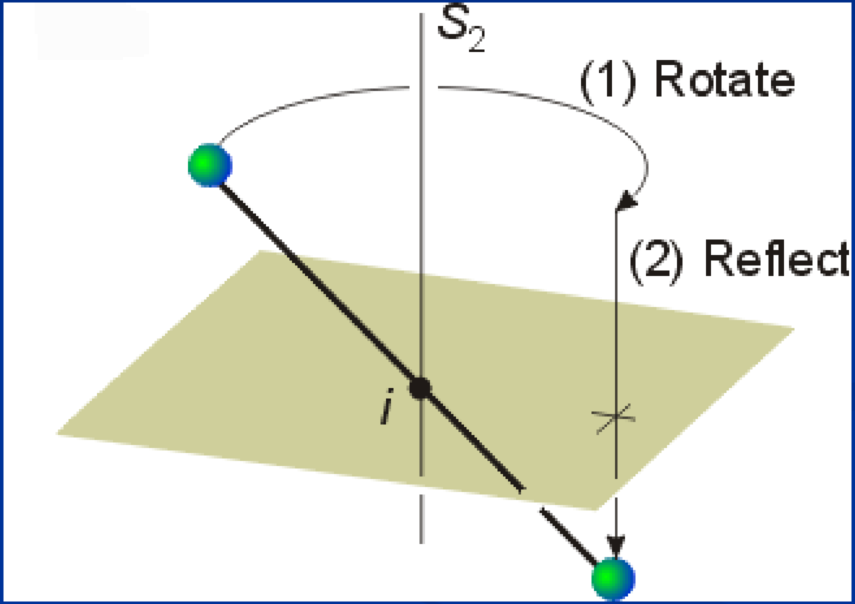
Improper Rotation

Note that an S_1 axis doesn't exist; it is same as a mirror plane.



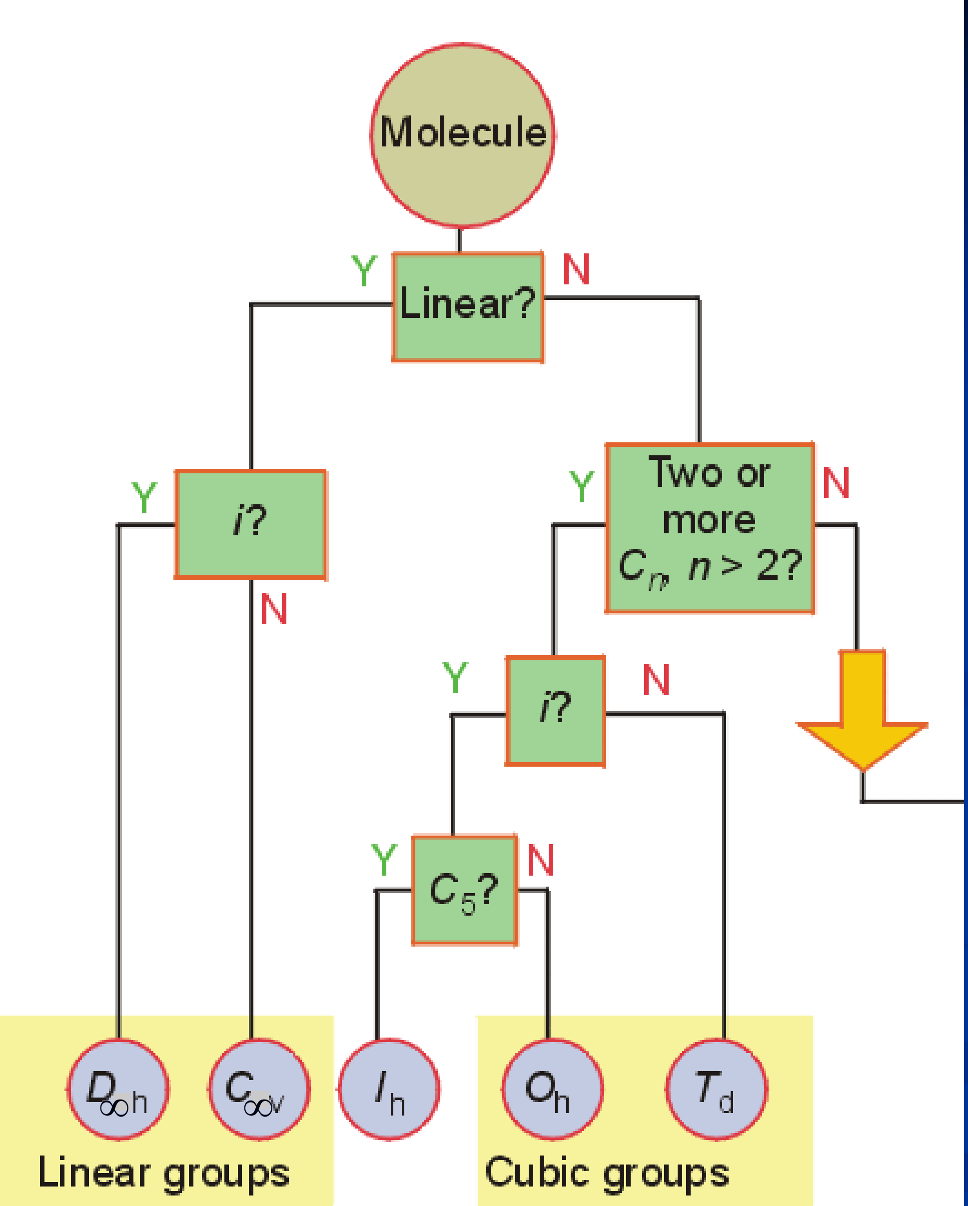
Improper Rotation

Likewise, an S_2 axis is a center of inversion.



Point Groups

Molecules with the same symmetry elements are placed into *point groups*.



Molecule

Linear?

Y

N

i?

Y

N

Two or more C_n, $n > 2$?

Y

N

i?

Y

N

C_5?

Y

N

$D_{\infty h}$

$C_{\infty v}$

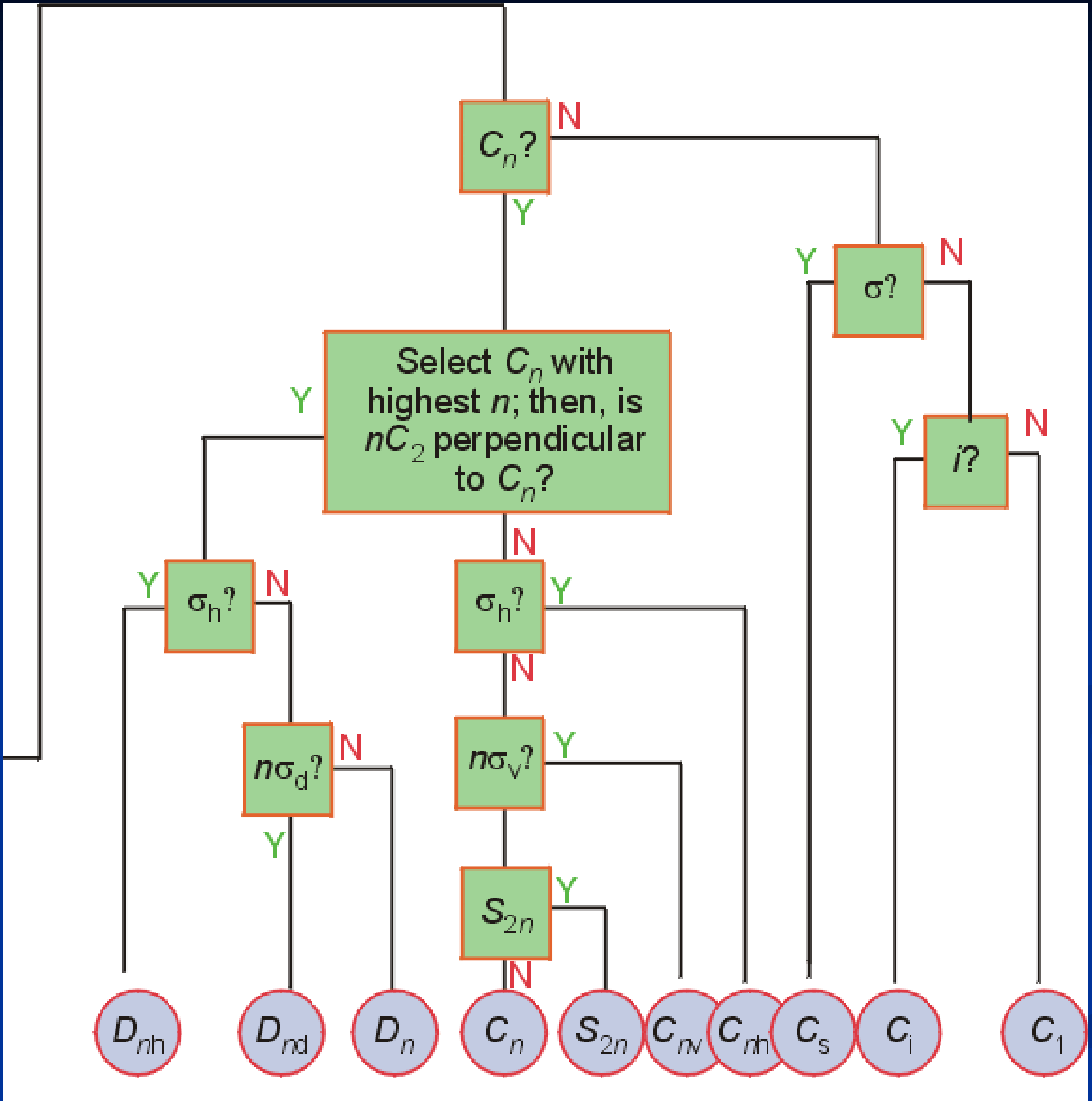
I_h

O_h

T_d

Linear groups

Cubic groups

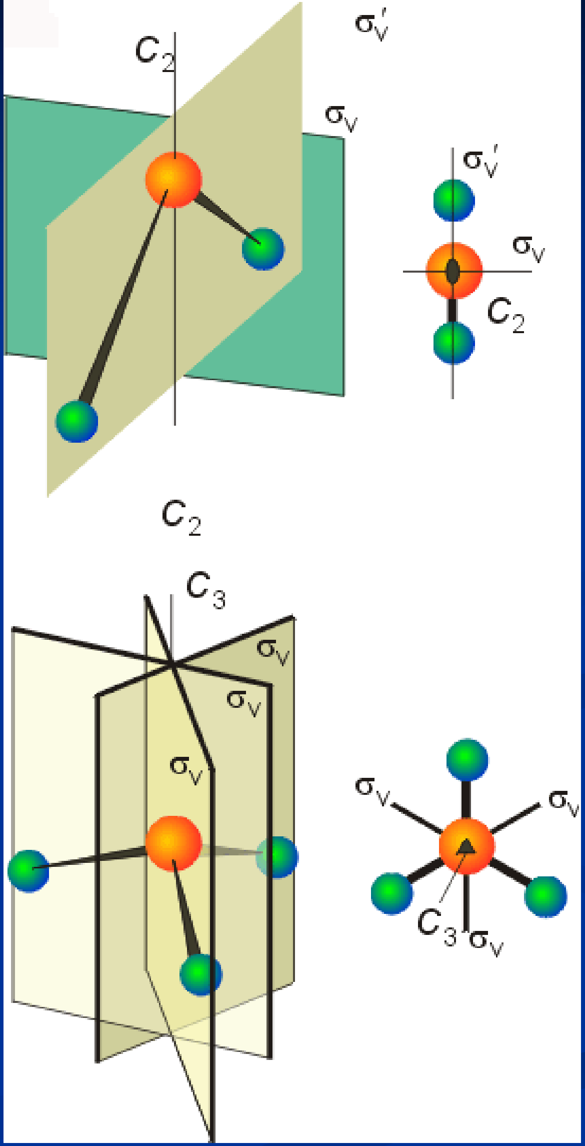

C_n?
N
Y
Y
σ?
N
Select C_n with highest n; then, is nC_2 perpendicular to C_n?
Y
Y
i?
N
N
Y
σ_h?
N
σ_h?
Y
N
$n\sigma_d$?
N
Y
$n\sigma_v$?
Y
S_{2n}
Y
N
D_{nh}
D_{nd}
D_n
C_n
S_{2n}
C_{nv}
C_{nh}
C_s
C_i
C_1

Point Groups

In general, you will not need to assign a molecule to its point group. Recognition of the features of some common point groups is useful.

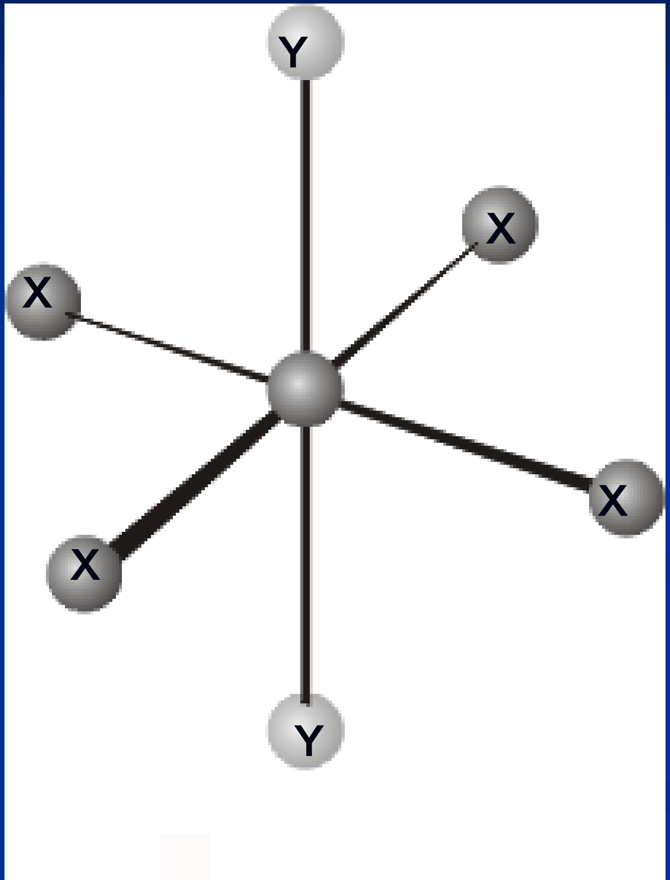
Point Groups

Water and ammonia both belong to the C_{nv} class of molecules. These have vertical planes of reflection, but no horizontal planes.



Point Groups

The D_{nh} groups have a horizontal plane in addition to vertical planes. Many inorganic complexes belong to these symmetry groups.



$[MX_4Y_2]$, D_{4h}

Point Groups

Highly symmetrical molecules, such as identically substituted tetrahedrons or octahedrons belong to their own point groups (T_d or O_h respectively).

Point Groups

In assigning a point group, we typically ignore the fine detail, such as conformation isomers, of the ligands.

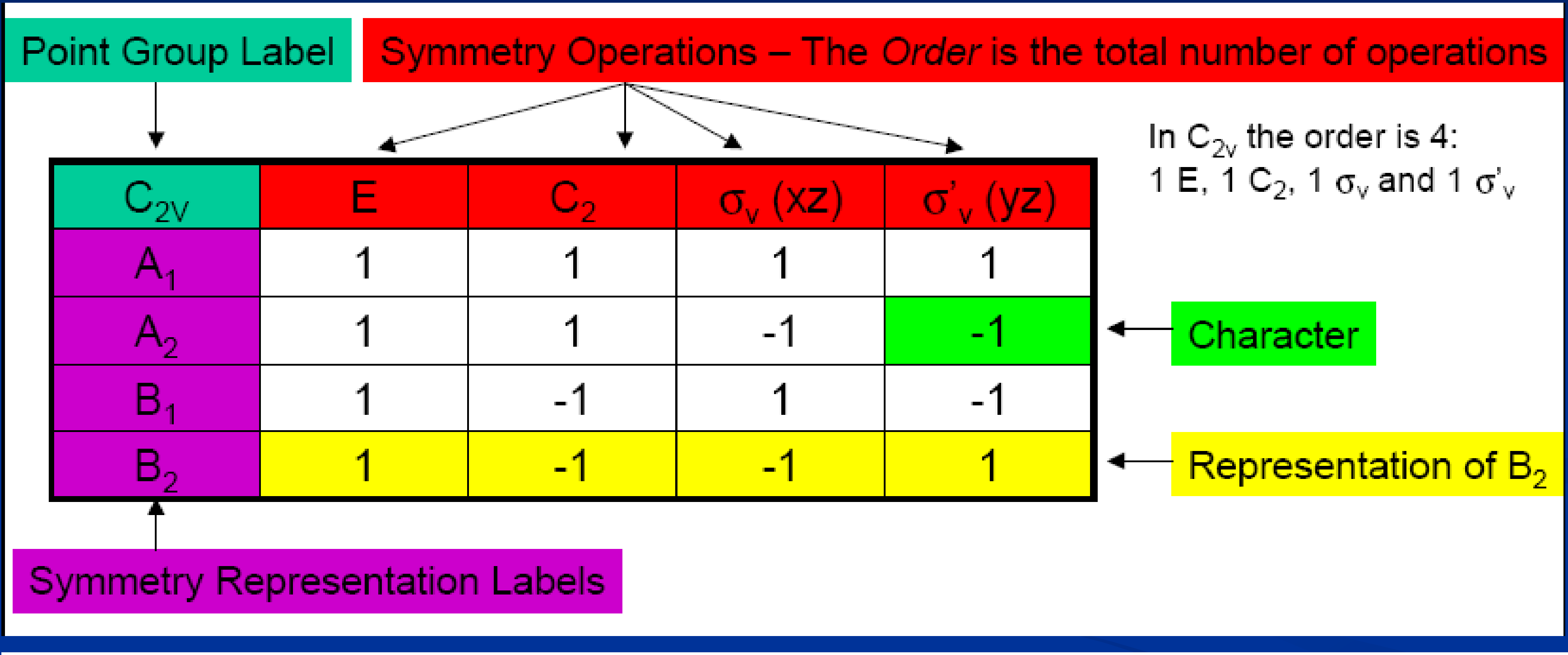
In working problems using group theory, the point group of the molecule will usually be provided to you.

Character Tables

The symmetry properties of each point group are summarized on a *character table*. The character table lists all of the symmetry elements of the group, along with a complete set of *irreducible representations*.

http://mutuslab.cs.uwindsor.ca/macdonald/250-LectureNotes/Fall2002/Bonding-Notes5.pdf

Character Table (C_{2v})



Point Group Label

Symmetry Operations – The *Order* is the total number of operations

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

In C_{2v} the order is 4:
1 E, 1 C_2, 1 σ_v and 1 σ'_v

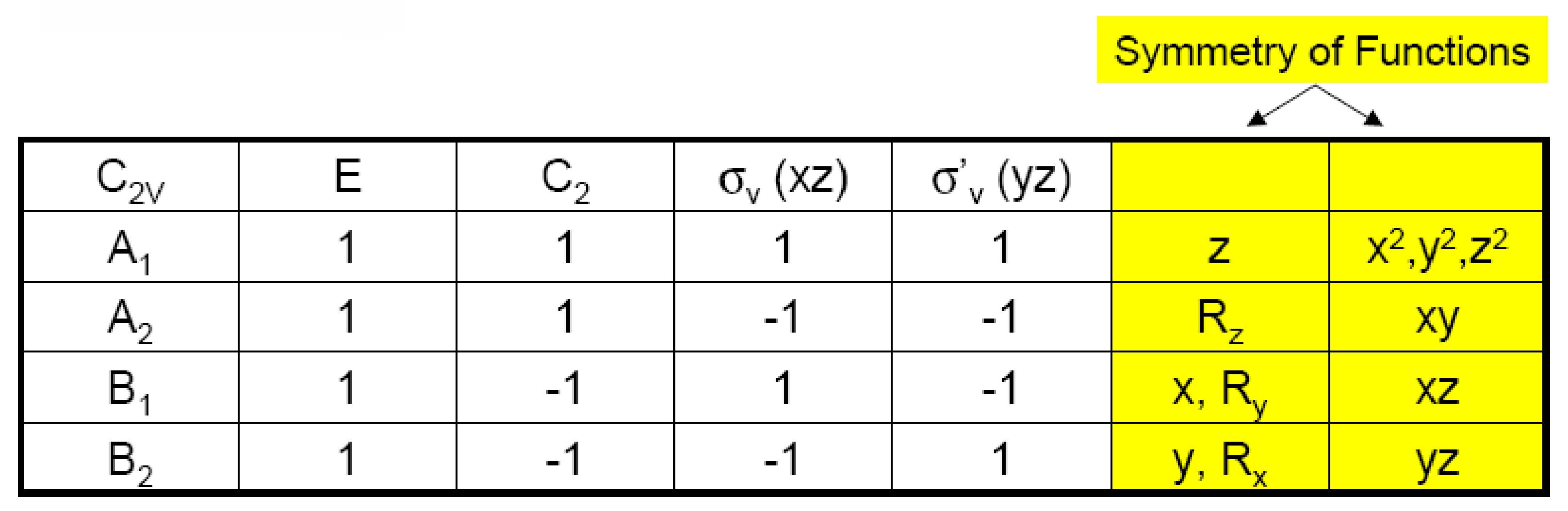
Character

Representation of B_2

Symmetry Representation Labels

"A" means symmetric with regard to rotation about the principle axis.
"B" means anti-symmetric with regard to rotation about the principle axis.
Subscript numbers are used to differentiate symmetry labels, if necessary.
"1" indicates that the operation leaves the function unchanged: it is called "symmetric".
"-1" indicates that the operation reverses the function: it is called "anti-symmetric".

Character Table (C_{2v})

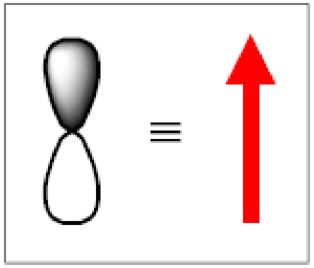


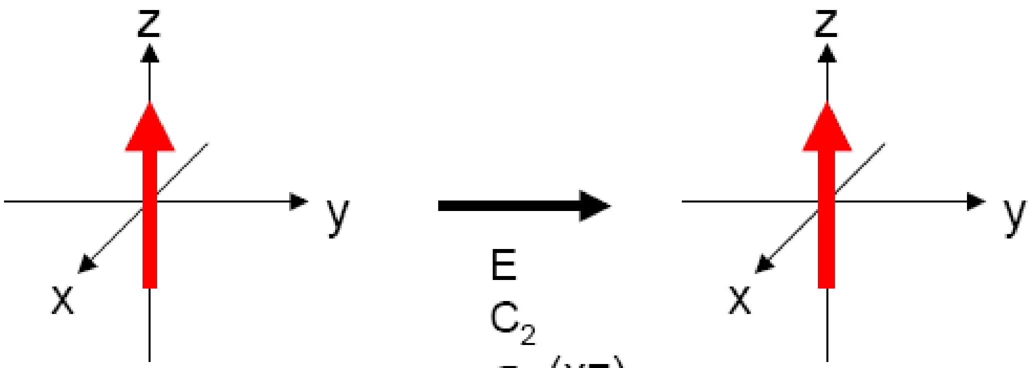
Symmetry of Functions

C_{2v}	E	C_2	σ_v (xz)	σ'_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

The functions to the right are called *basis functions.* They represent mathematical functions such as orbitals, rotations, etc.

A p_z orbital has the same symmetry as an arrow pointing along the z-axis.



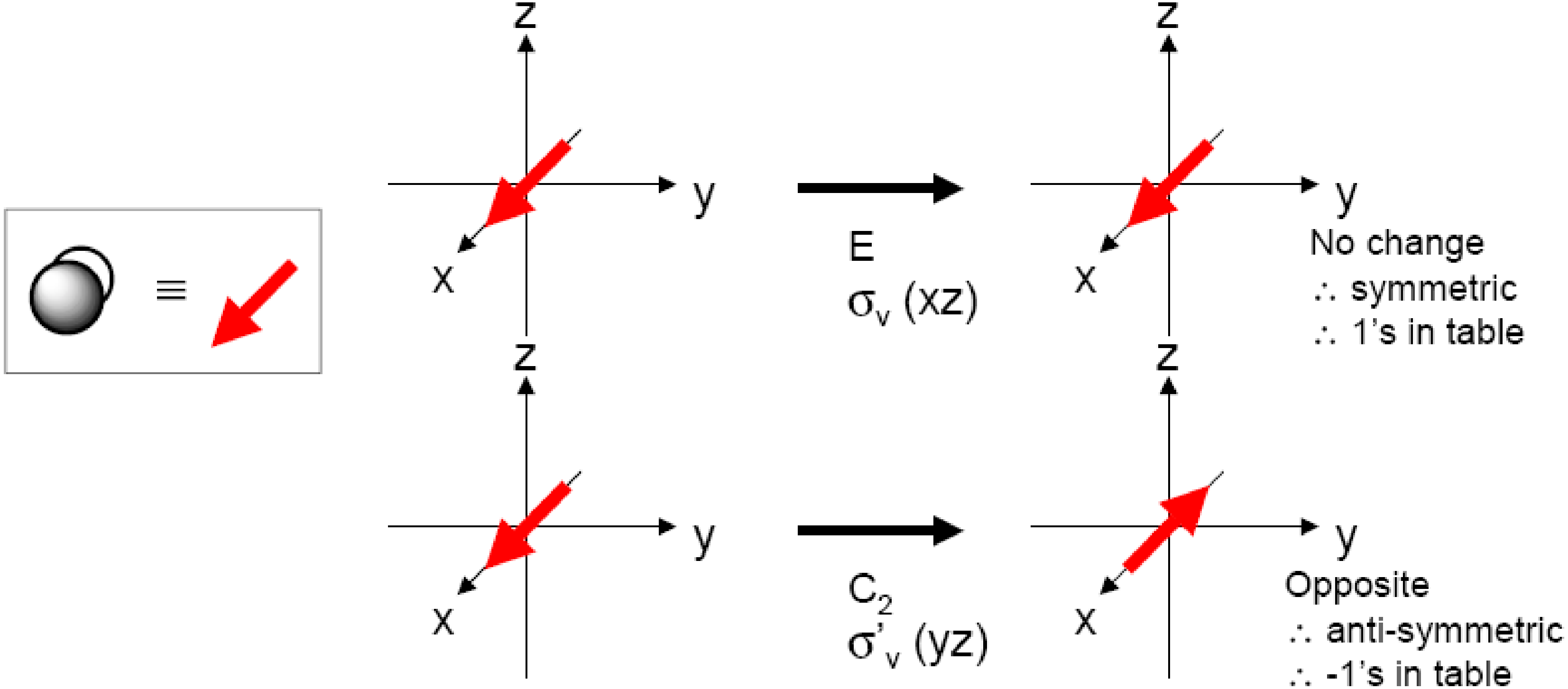


E
C_2
σ_v (xz)
σ'_v (yz)

No change
∴ symmetric
∴ 1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_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

A p_x orbital has the same symmetry as an arrow pointing along the x-axis.



E
σ_v (xz)

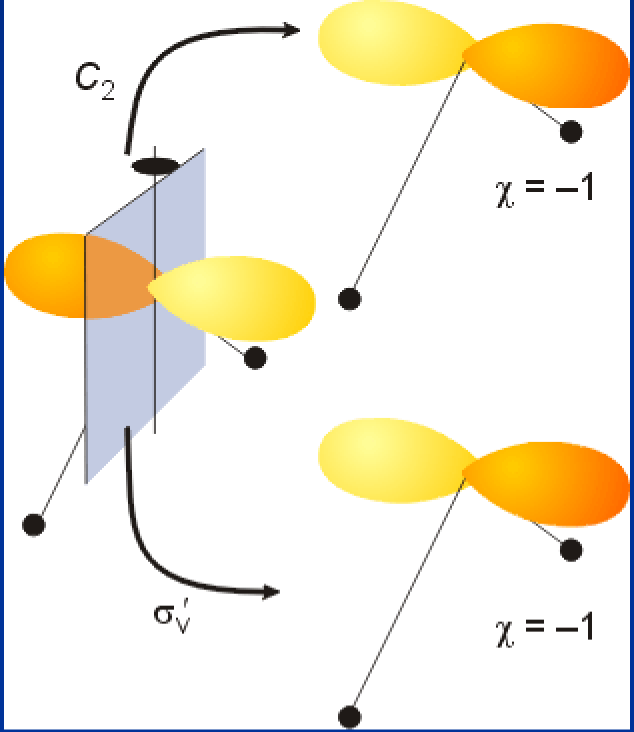
No change
∴ symmetric
∴ 1's in table

C_2
σ'_v (yz)

Opposite
∴ anti-symmetric
∴ -1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_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

The p_x orbital



If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is rotated about the C_2 axis, the orbital is reversed, so the character will be -1.

The p_x orbital

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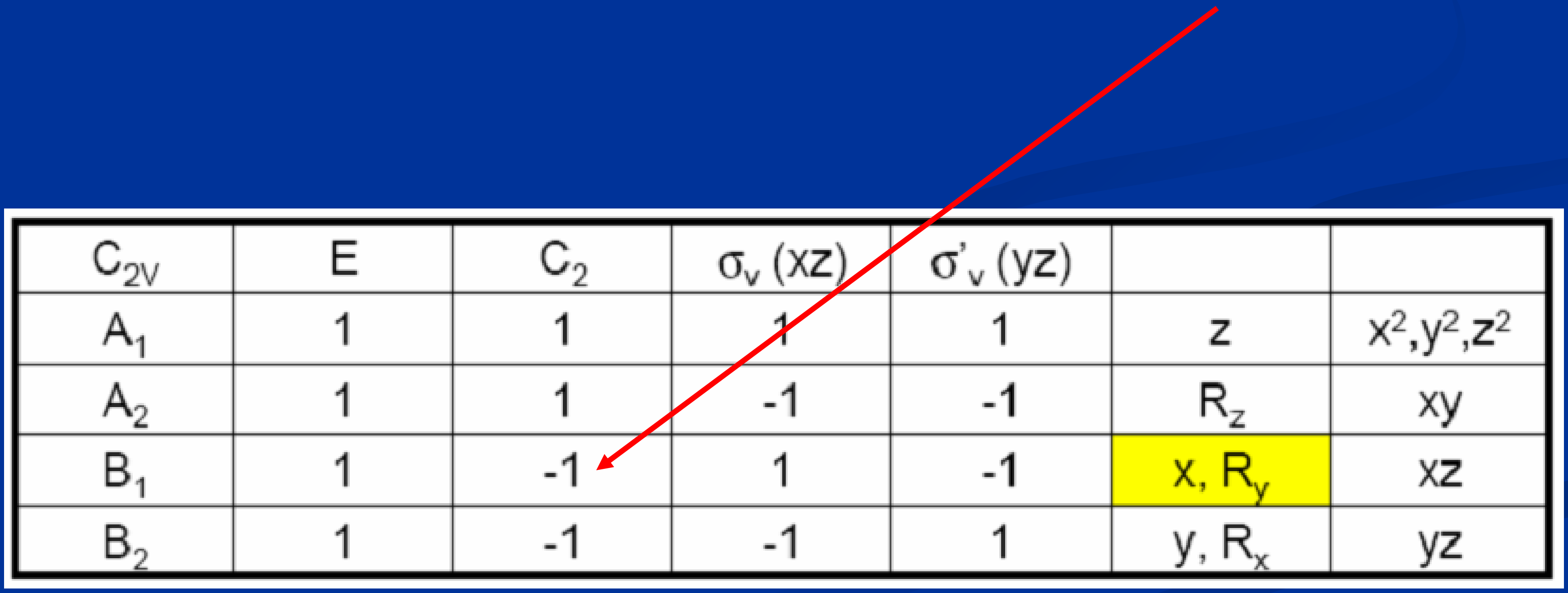
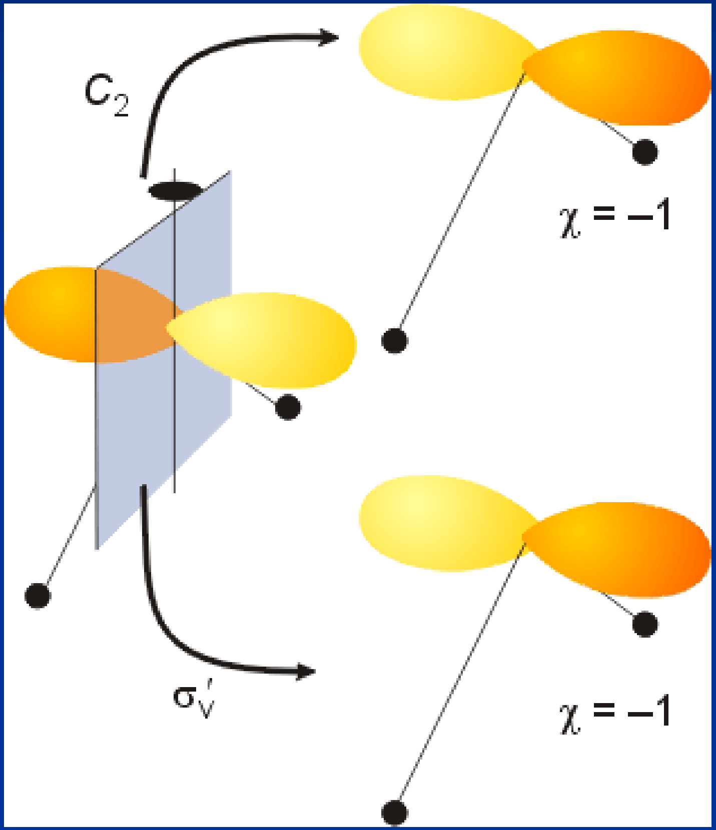


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The p_x orbital



If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is reflected in the yz plane, the orbital is also reversed, and the character will be -1.

The p_x orbital

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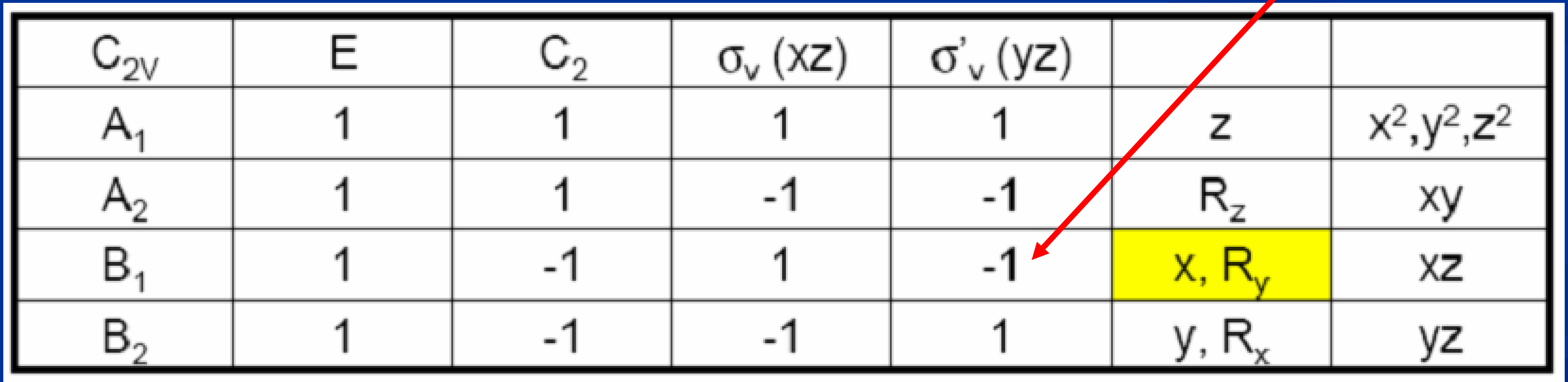
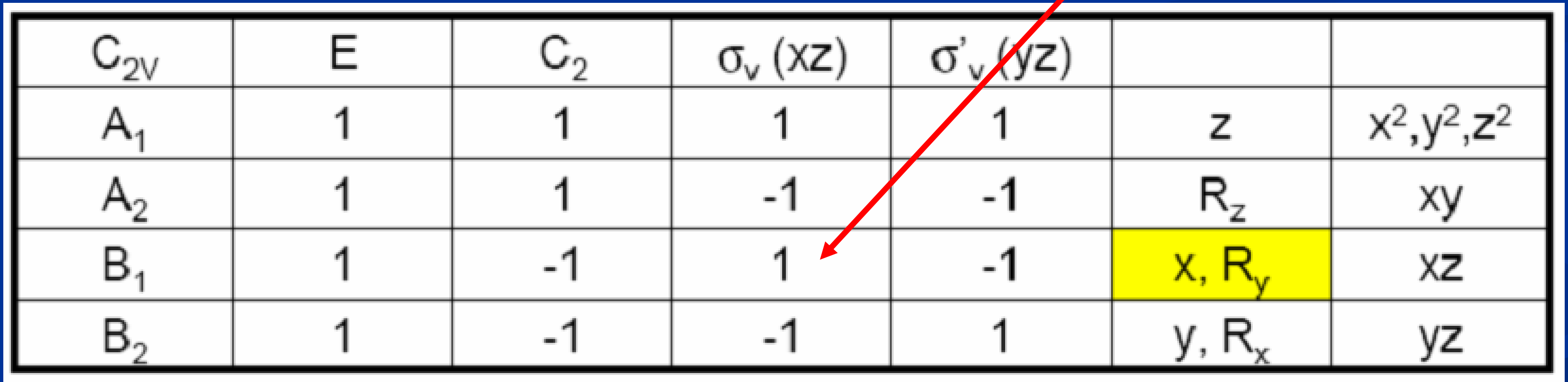


C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

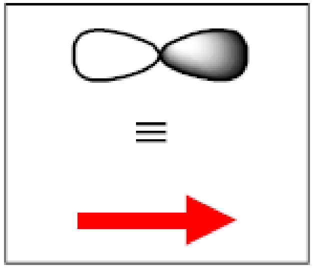
The p_x orbital

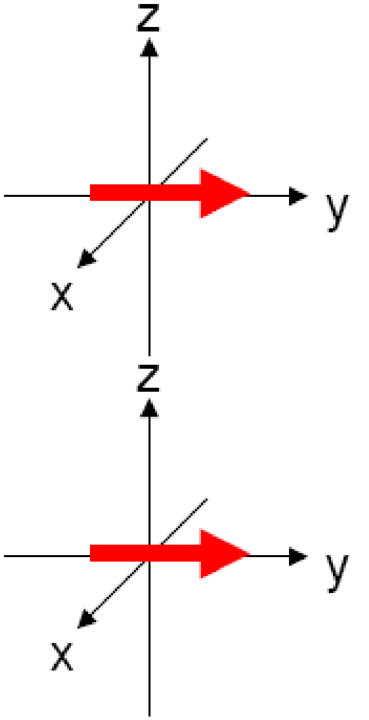
If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is reflected in the xz plane, the orbital is unchanged, so the character is +1.

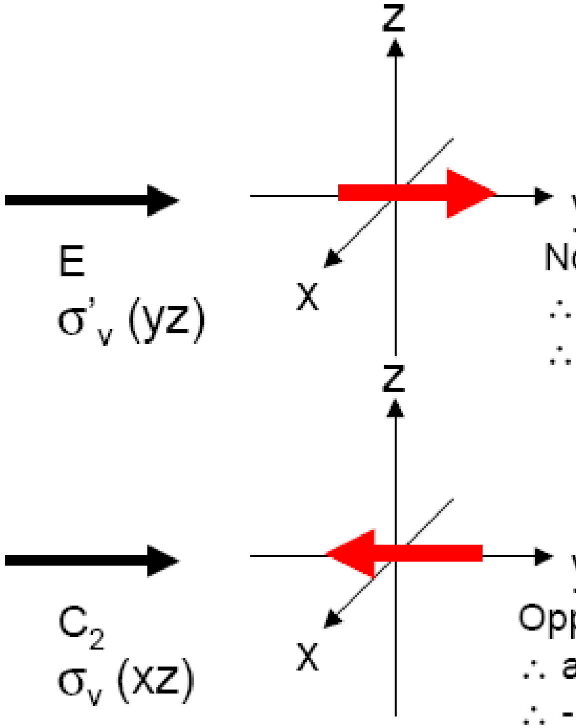


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

A p_y orbital has the same symmetry as an arrow pointing along the y-axis.







E
σ'_v (yz)

No change
∴ symmetric
∴ 1's in table

C_2
σ_v (xz)

Opposite
∴ anti-symmetric
∴ -1's in table

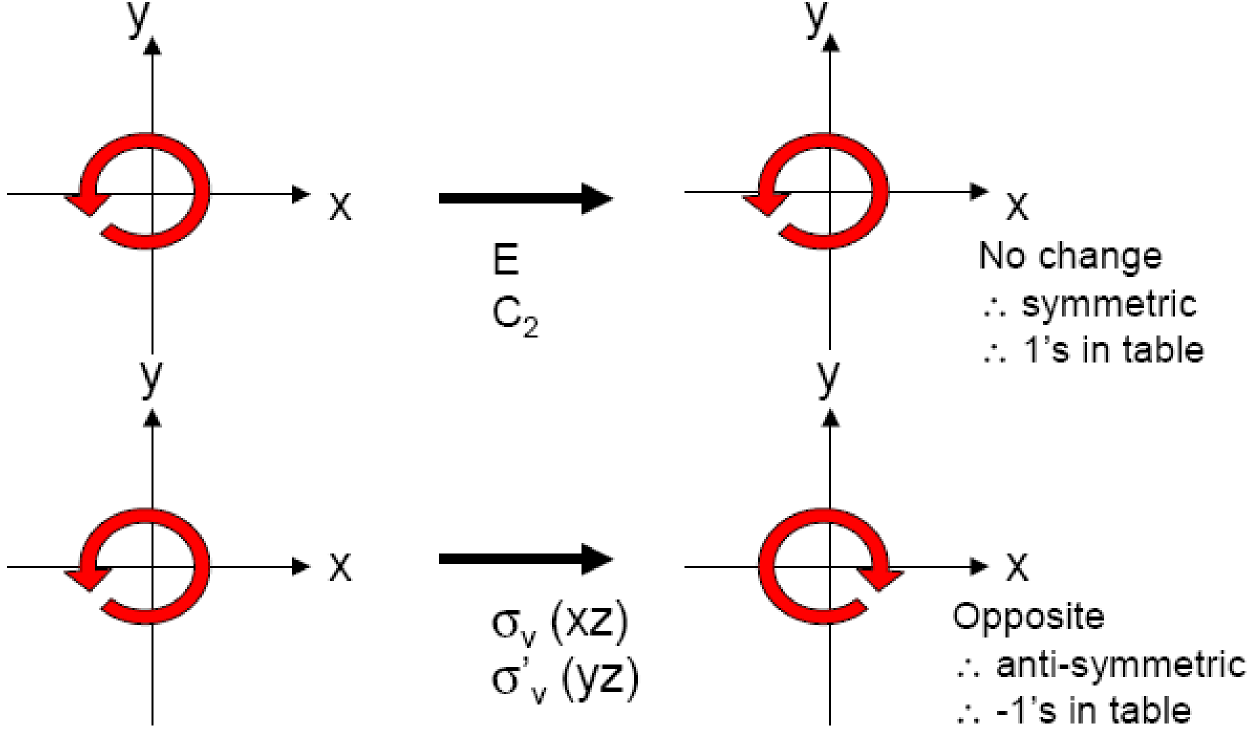
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Rotation about the n axis, R_n, can be treated in a similar way.

The z axis is pointing out of the screen!

If the rotation is still in the same direction (e.g. counter clock-wise), then the result is considered symmetric.

If the rotation is in the opposite direction (i.e. clock-wise), then the result is considered anti-symmetric.



E
C_2

No change
∴ symmetric
∴ 1's in table

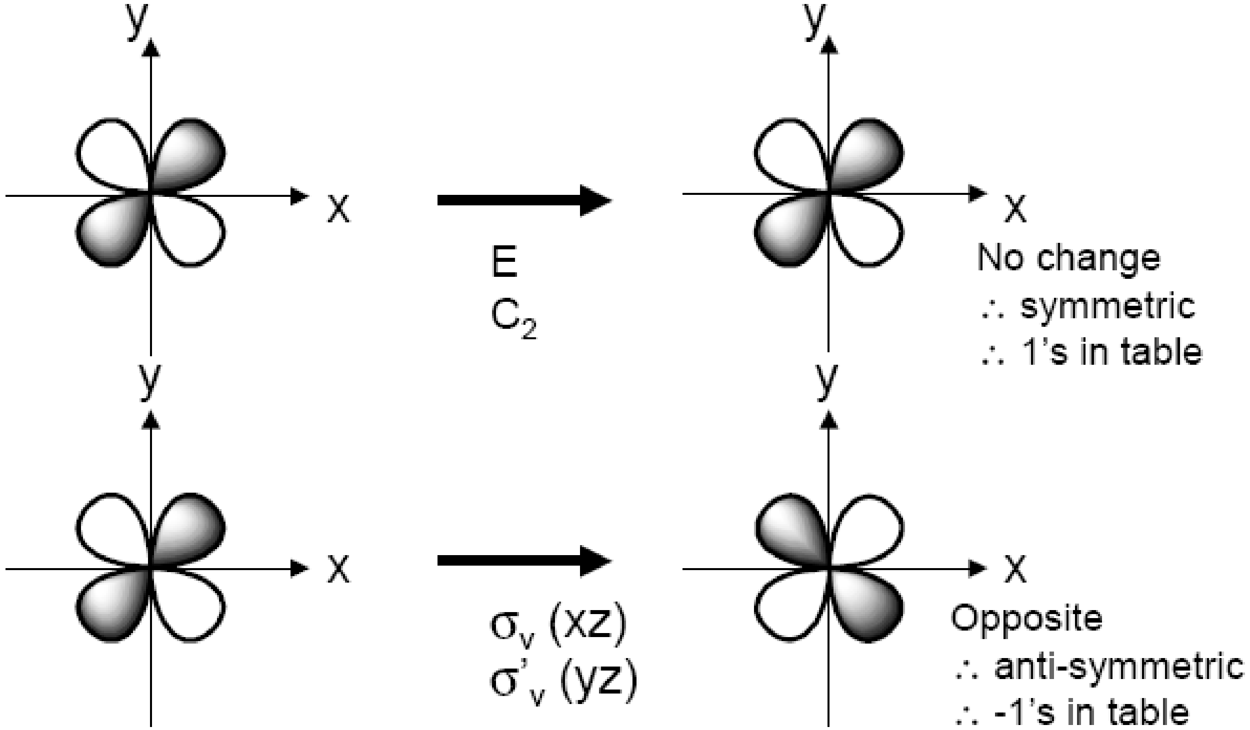
σ_v (xz)
σ'_v (yz)

Opposite
∴ anti-symmetric
∴ -1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_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

d orbital functions can also be treated in a similar way

The **z** axis is pointing out of the screen!



E
C_2

No change
∴ symmetric
∴ 1's in table

σ_v (xz)
σ'_v (yz)

Opposite
∴ anti-symmetric
∴ -1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_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

Character Table Representations

1. Characters of +1 indicate that the basis function is unchanged by the symmetry operation.
2. Characters of -1 indicate that the basis function is reversed by the symmetry operation.
3. Characters of 0 indicate that the basis function undergoes a more complicated change.

Character Table Representations

1. An *A* representation indicates that the functions are symmetric with respect to rotation about the principal axis of rotation.
2. *B* representations are asymmetric with respect to rotation about the principal axis.
3. *E* representations are doubly degenerate.
4. *T* representations are triply degenerate.
5. Subscrips *u* and *g* indicate asymmetric (*ungerade*) or symmetric (*gerade*) with respect to a center of inversion.

Applications of Group Theory

1. Predicting polarity of molecules. A molecule cannot have a permanent dipole moment if it
    - a) has a center of inversion
    - b) belongs to any of the D point groups
    - c) belongs to the cubic groups T or O

Applications of Group Theory

2. Predicting chirality of molecules. Chiral molecules lack an improper axis of rotation (S_n), a center of symmetry (i) or a mirror plane (σ).

Applications of Group Theory

3. Predicting the orbitals used in σ bonds. Group theory can be used to predict which orbitals on a central atom can be mixed to create hybrid orbitals.

Applications of Group Theory

4. Predicting the orbitals used in *molecular orbitals*. Molecular orbitals result from the combining or overlap of atomic orbitals, and they encompass the entire molecule.

Applications of Group Theory

5. Determining the symmetry properties of all molecular motion (rotations, translations and vibrations). Group theory can be used to predict which molecular vibrations will be seen in the infrared or Raman spectra.

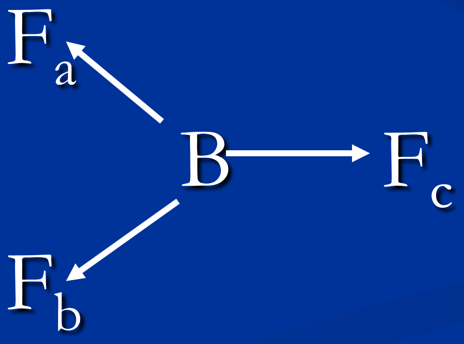
Determining Hybridization

1. Determine the point group of the molecule.
2. Consider the σ bonds as vectors, and determine how they are transformed by the symmetry operations of the group.
3. Obtain the characters for the bonds. For each symmetry operation, a bond which remains in place contributes a value of +1. If the bond is moved to another position, it contributes a value of 0.
4. *Reduce* the set of characters to a linear combination of the character sets of the point group.

Hybridization

- Determine the hybridization of boron in BF_3. The molecule is trigonal planar, and belongs to point group D_{3h}.

1. Consider the σ bonds as vectors.



Hybridization

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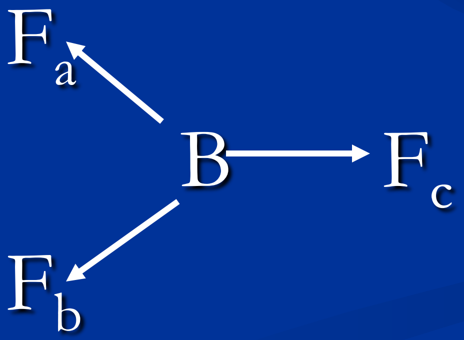
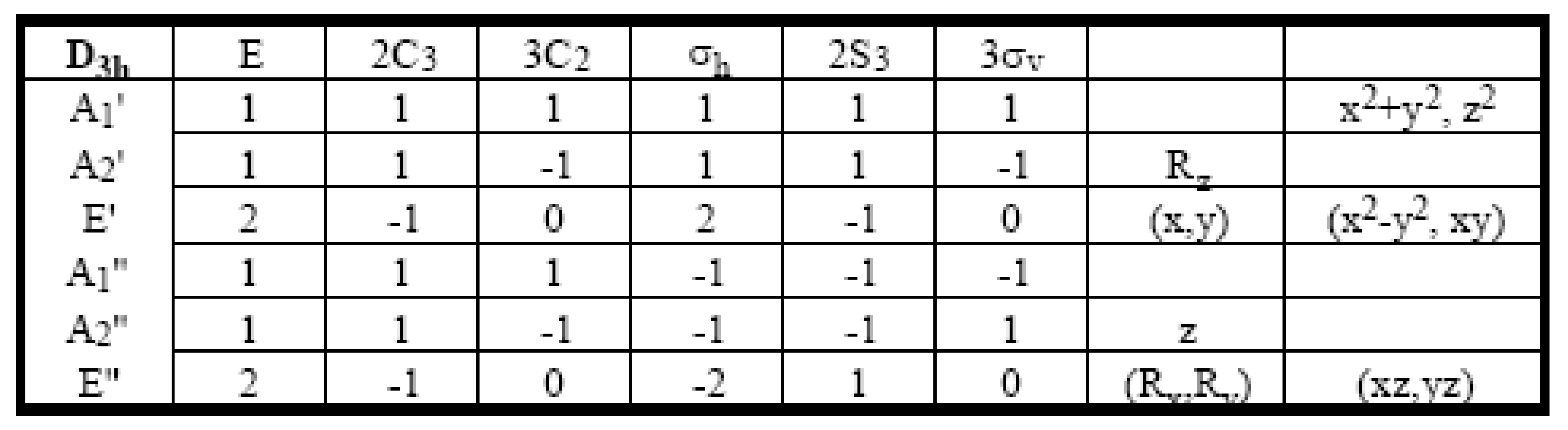
1. Consider the σ bonds as vectors.



Hybridization

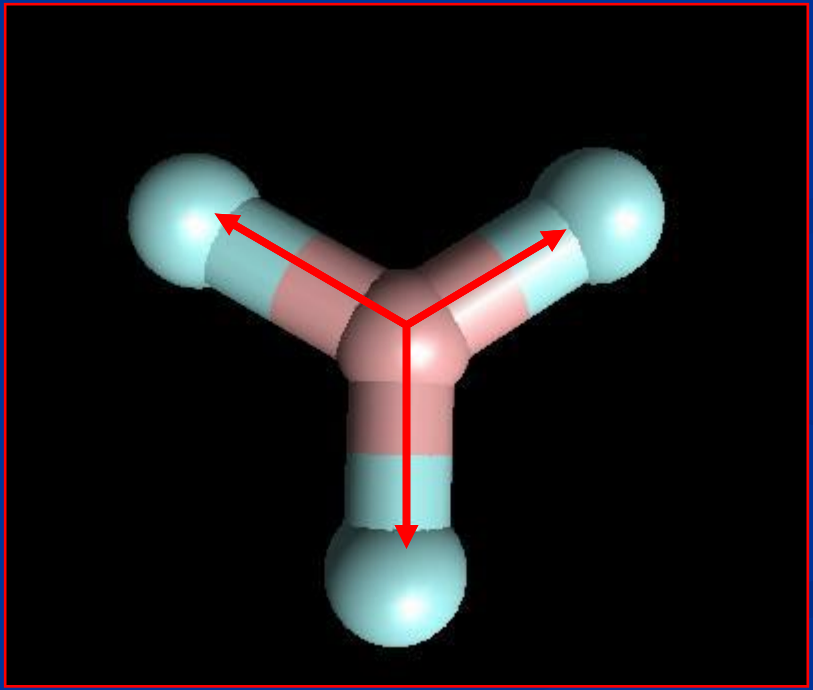
Determine how each vector (σ bond) is transformed by the symmetry operations of the group.



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x,R_y)	(xz,yz)

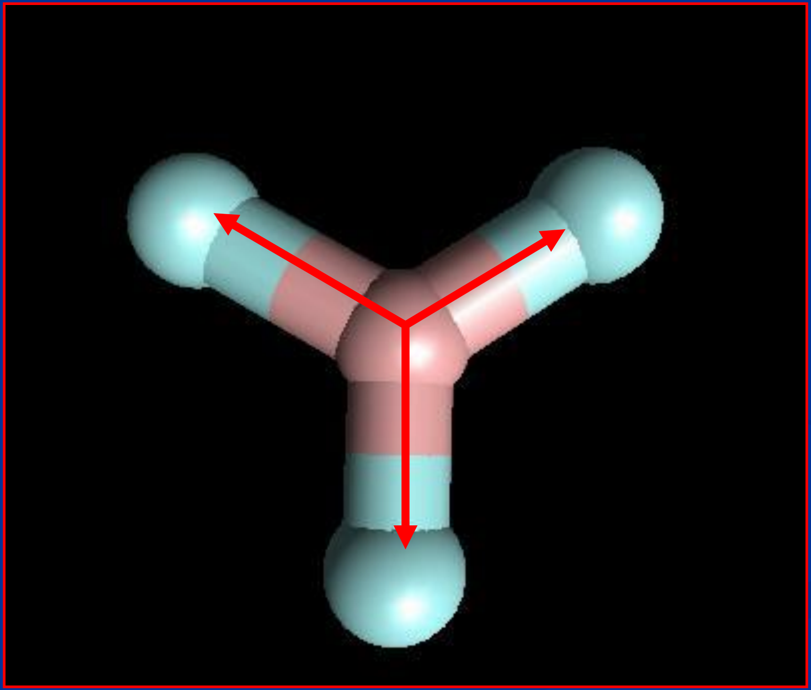
Determining Hybridization

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}						



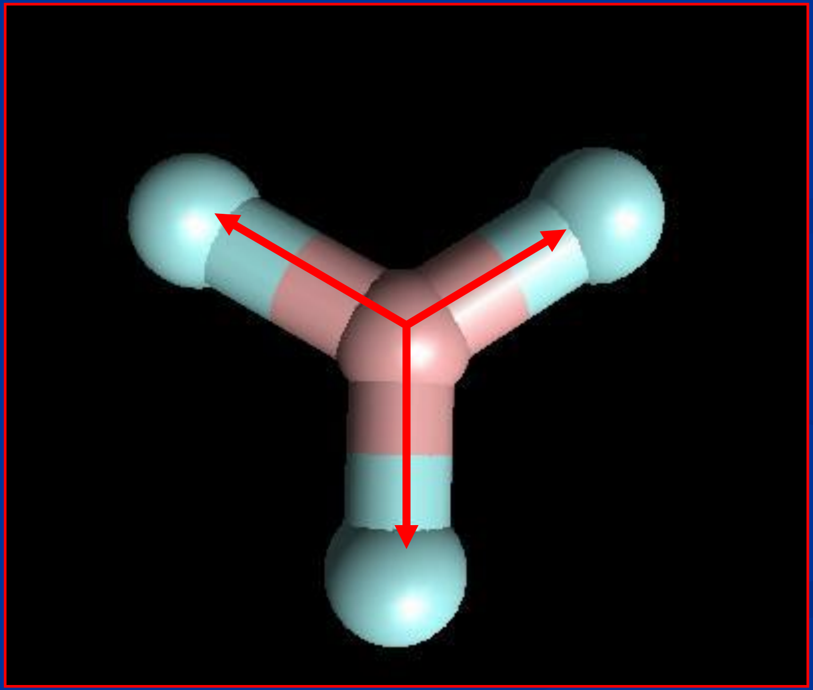
Determining Hybridization

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3					



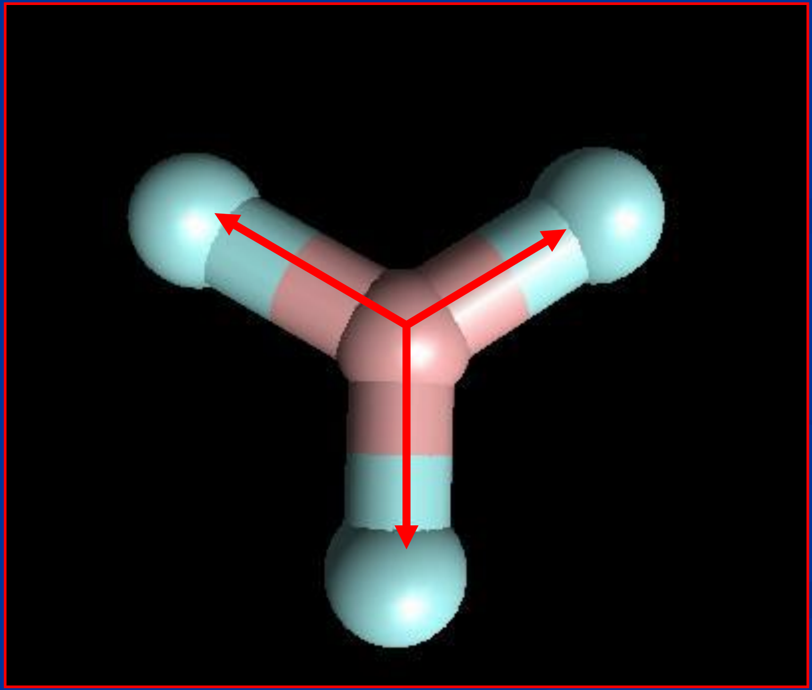
Determining Hybridization

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0				



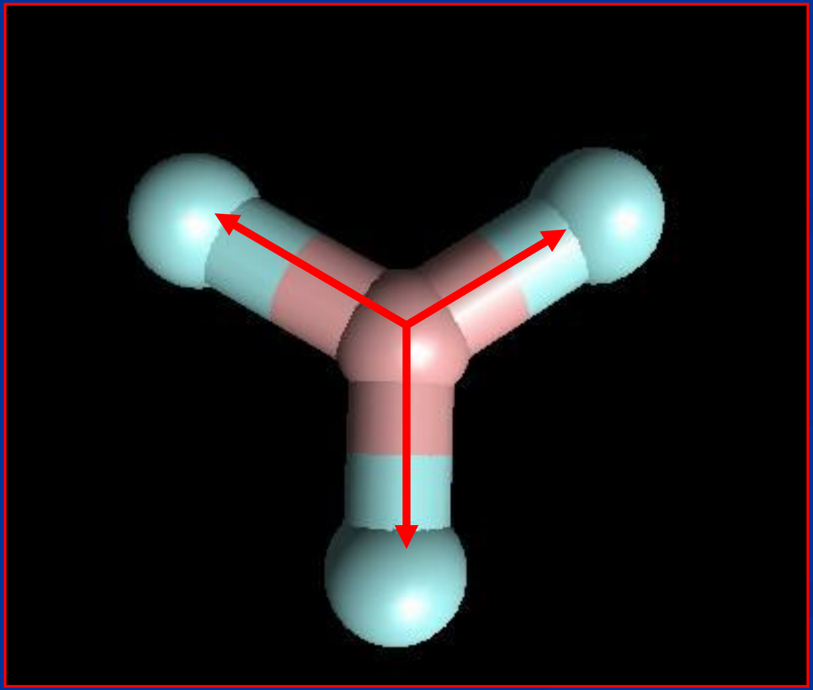
Determining Hybridization

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0	1			



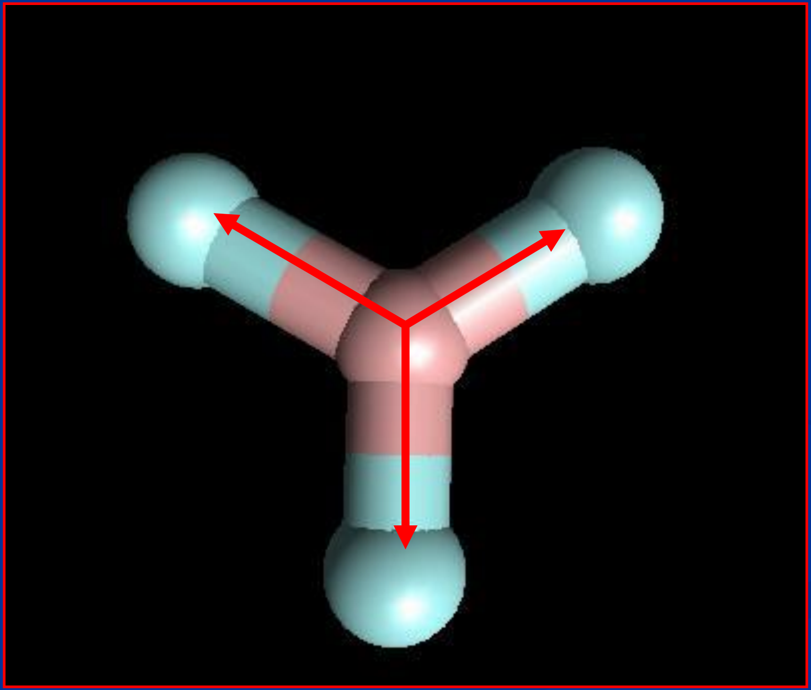
Determining Hybridization

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0	1			



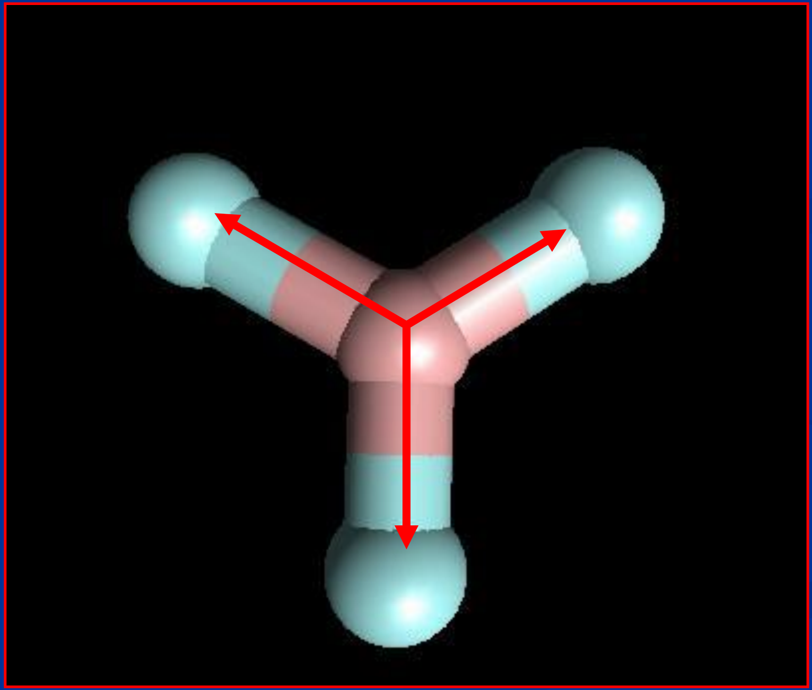
Determining Hybridization

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0	1	3		



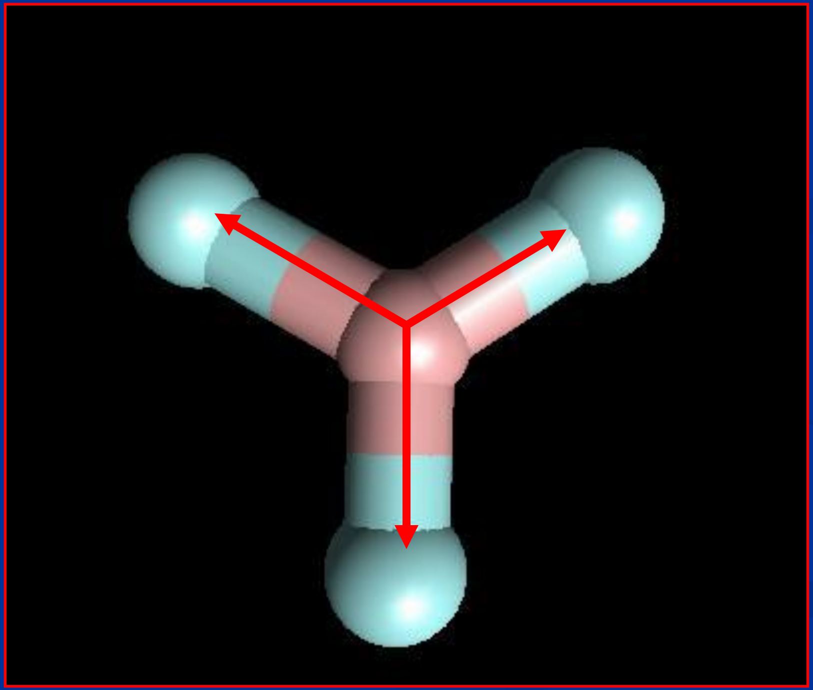
Determining Hybridization

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0	1	3	0	



Determining Hybridization

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{red}	3	0	1	3	0	1



Reducing a Representation

$$n_i = \frac{1}{h}\sum_{c} g_c \chi_i \chi_r$$

n_i = the number of times an irreducible representation *i* occurs in the reducible representation

h = the order of the group (the total number of operations in the point group)

c = the class (type) of operation

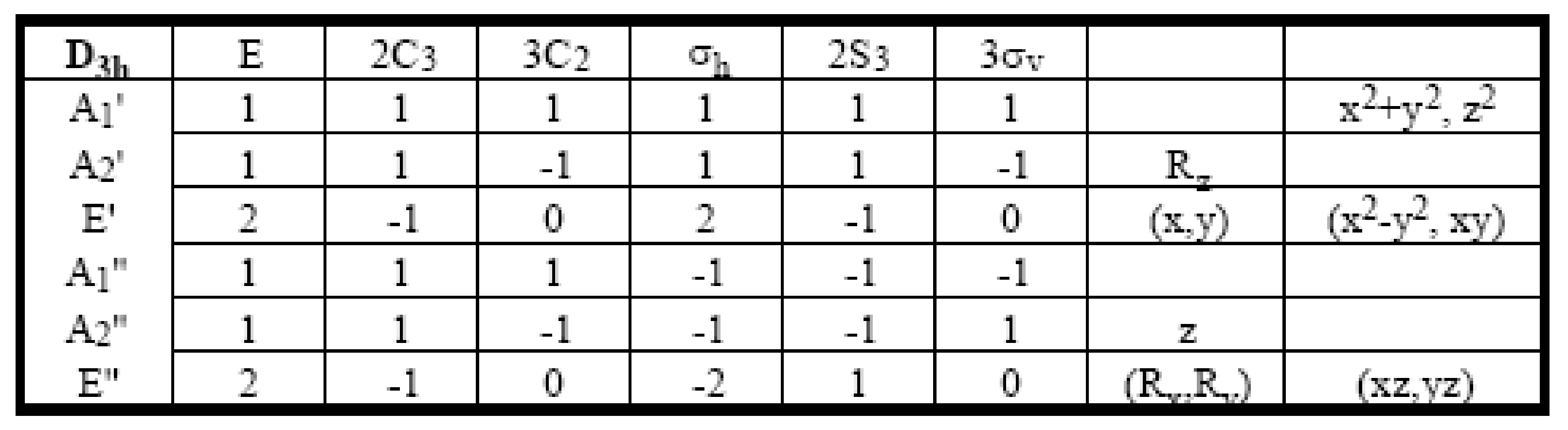
g_c= the number of operations in the class

χ_i = the character of the irreducible representation

χ_r = the character of the reducible representation

Reducing a Representation

$$n_i = \frac{1}{h}\sum_c g_c \chi_i \chi_r$$



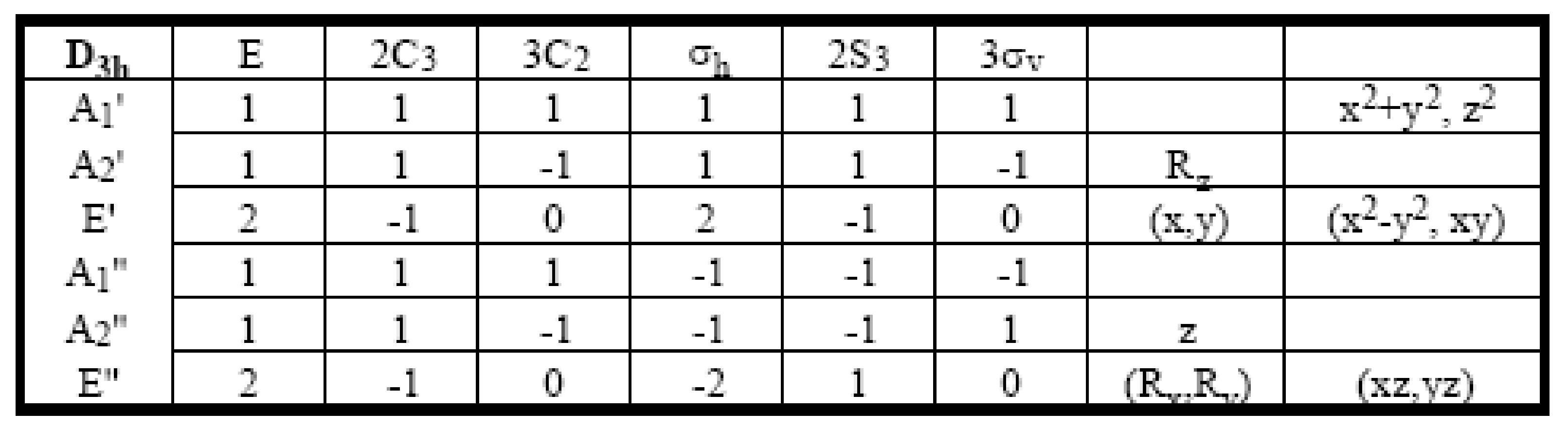
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x,R_y)	(xz,yz)

The order of the group, h, is the total number of operations.

$$h = 1+2+3+1+2+3=12$$

Hybridization of BF_3

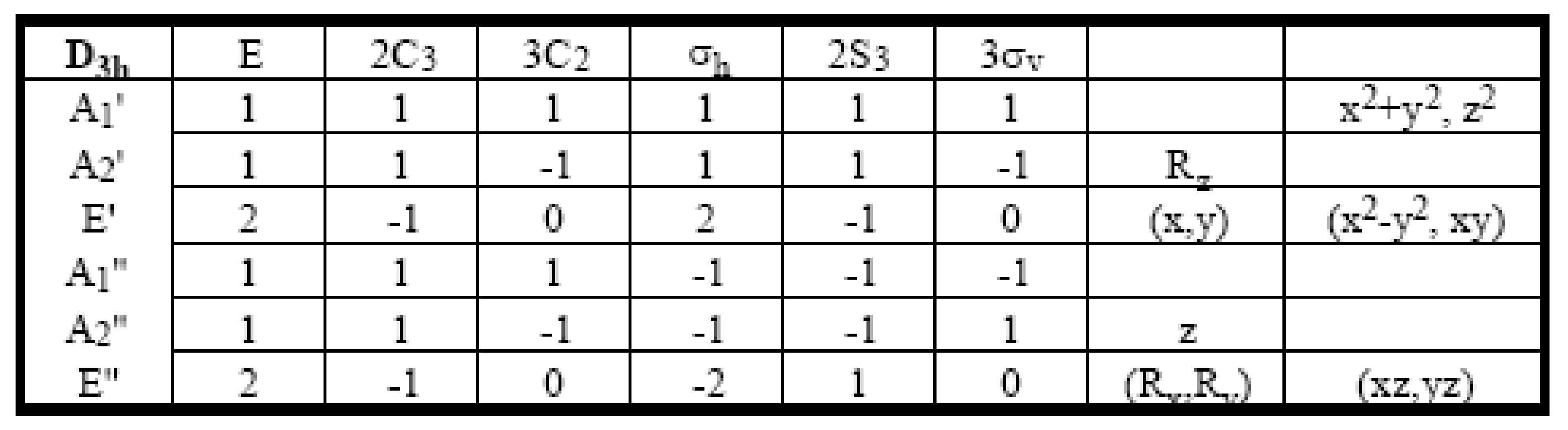
Γ_{red} reduces to $A_1' + E'$. The orbitals used in hybridization must have this symmetry.



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x,R_y)	(xz,yz)

Hybridization of BF_3

Γ_{red} reduces to A_1' + E'. The orbitals used in hybridization must have this symmetry.

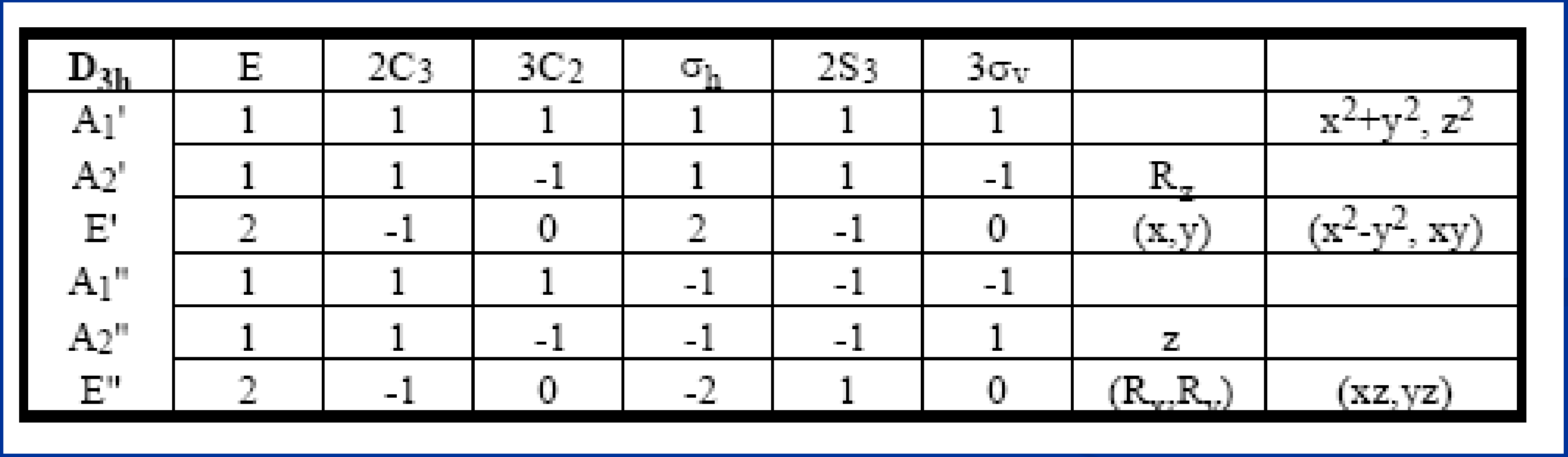


D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x,R_y)	(xz,yz)

The *s* orbital and the d_{z^2} orbitals on boron have A_1' symmetry. The 3 d_{z^2} orbital is too high in energy to hybridize.

Hybridization of BF_3

Γ_{red} reduces to A_1' + E '. The orbitals used in hybridization must have this symmetry.

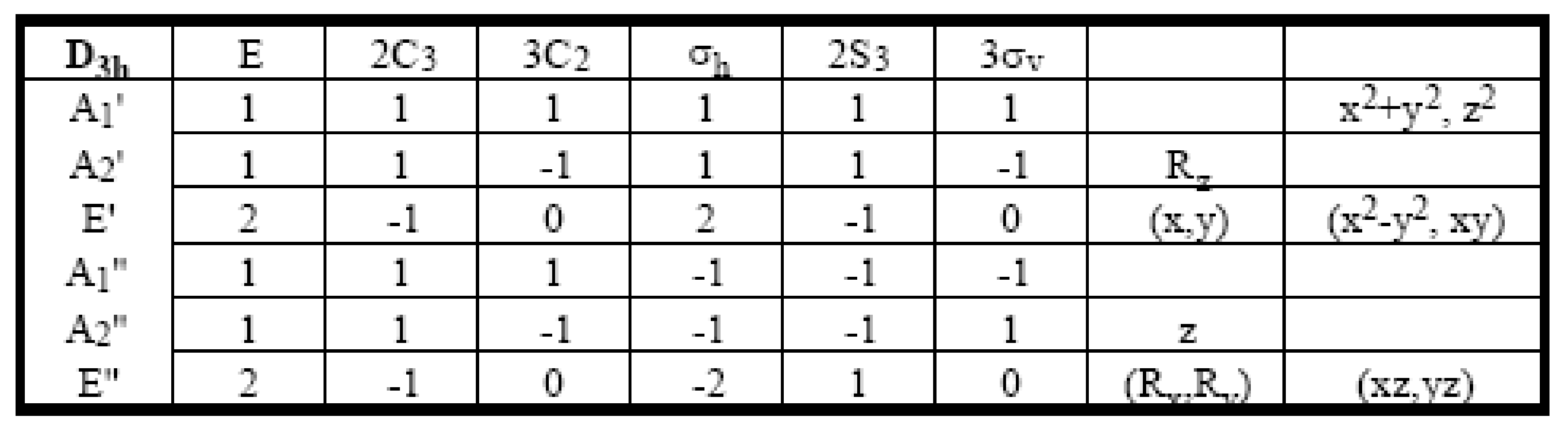


D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E"	2	-1	0	-2	1	0	(R_x,R_y)	(xz,yz)

The p_x and p_y orbitals and the $d_{x^2-y^2}$ and d_{xy} orbitals have E ' symmetry. Since the *d* orbitals on boron are too high in energy, they will not be used.

Hybridization of BF_3

Γ_{red} reduces to A_1' + E '. The orbitals used in hybridization must have this symmetry.



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x,R_y)	(xz,yz)

The hybridization of boron will sp^2 or, more specifically, sp_xp_y.

Molecular Vibrations

Molecular motion includes translations, rotations and vibrations. The total number of degrees of freedom (types of molecular motion) is equal to 3N, where N is the number of atoms in the molecule.

Molecular Vibrations

Of the 3N types of motion, three represent molecular translations in the x, y or z directions. Linear molecules have two rotational degrees of freedom, and non-linear molecules have three rotational degrees of freedom.

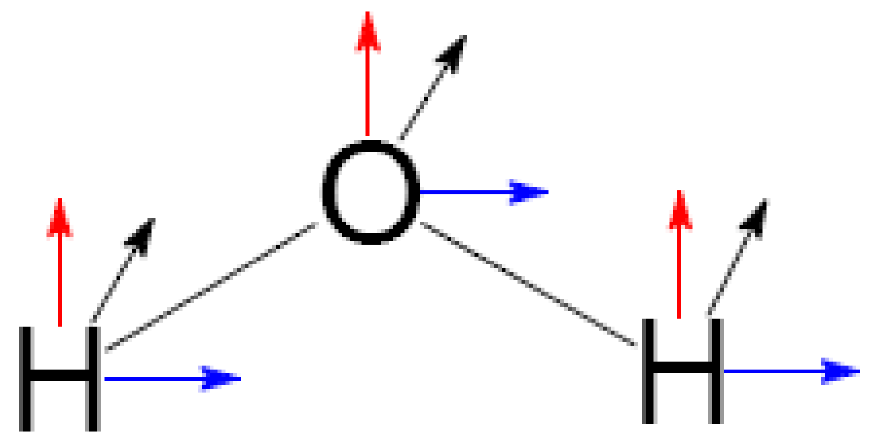
Molecular Vibrations

For linear molecules, the number of molecular vibrations = 3N-3-2 = 3N-5.

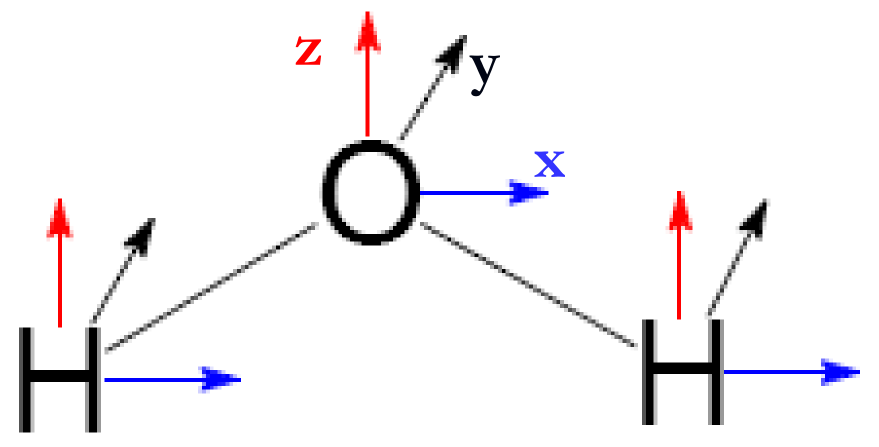
For non-linear molecules, the number of molecular vibrations = 3N-3-3= 3N-6.

Molecular Vibrations

To obtain Γ_{red} for <u>all</u> molecular motion, we must consider the symmetry properties of the three cartesian coordinates on <u>all</u> atoms of the molecule.

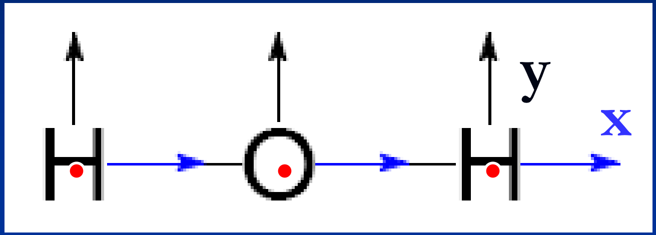


Molecular Vibrations



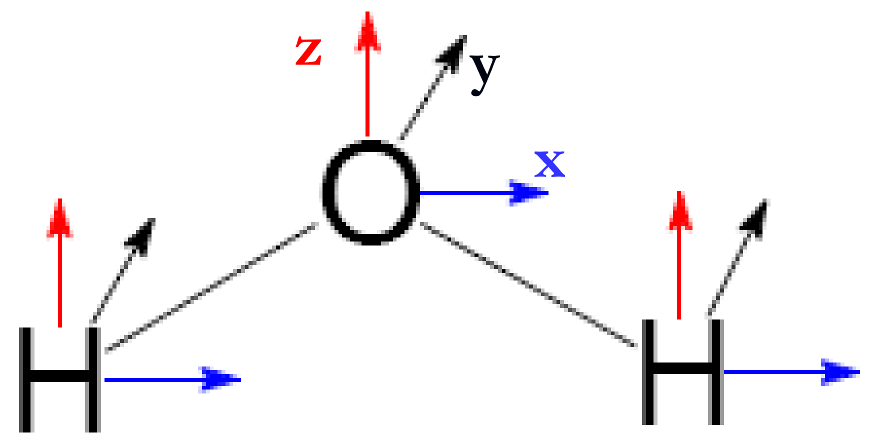
The molecule lies in the xz plane. The x axis is drawn in blue, and the y axis is drawn in black. The red arrows indicate the z axis.

Molecular Vibrations



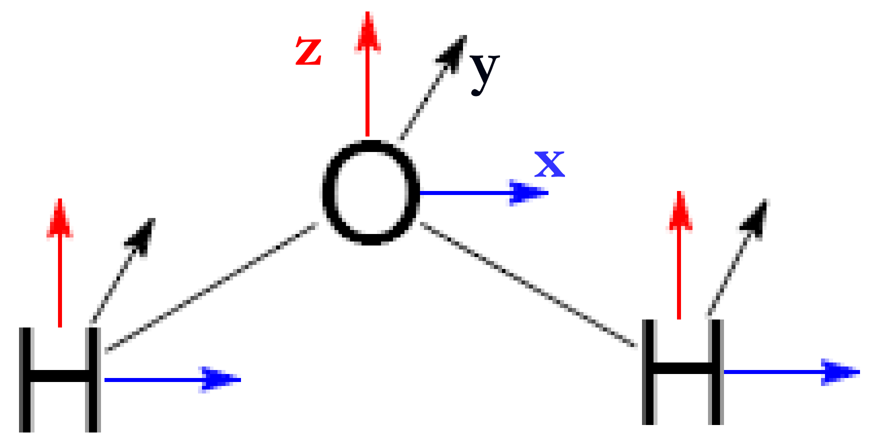
The molecule lies in the xz plane. The x axis is drawn in blue, and the y axis is drawn in black. The red arrows indicate the z axis.

Molecular Vibrations



If a symmetry operation changes the position of an atom, all three cartesian coordinates contribute a value of 0.

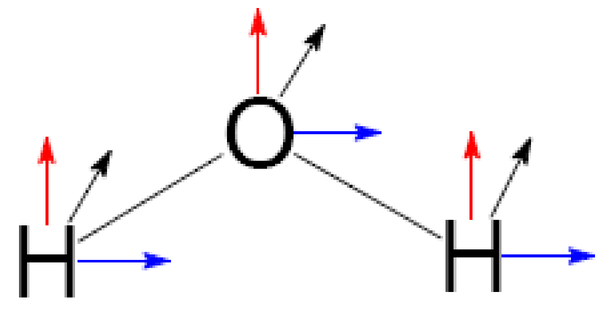
Molecular Vibrations



For operations that leave an atom in place, the character is +1 for an axis that remains in position, -1 for an axis that is reversed, and 0 for an axis that has been moved.

Molecular Vibrations

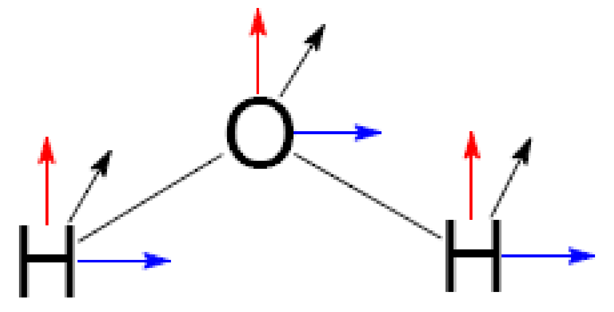
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$



Identity leaves all 3 atoms in position, so the character will be 9.

Molecular Vibrations

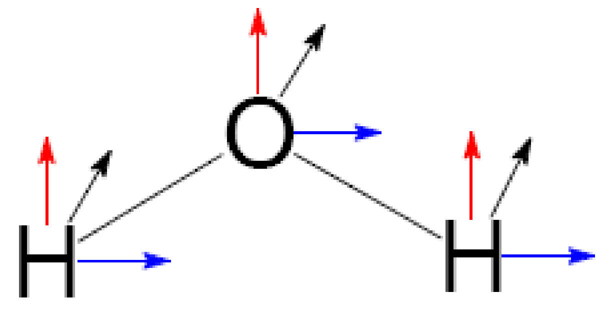
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9			



Identity leaves all 3 atoms in position, so the character will be 9.

Molecular Vibrations

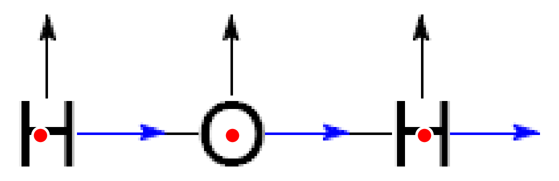
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9			



The C_2 axis goes through the oxygen atom, and exchanges the hydrogen atoms.

Molecular Vibrations

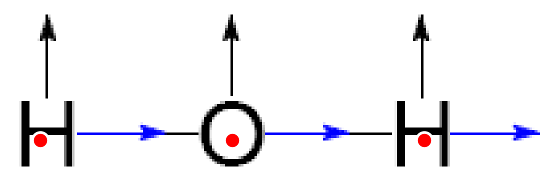
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9			

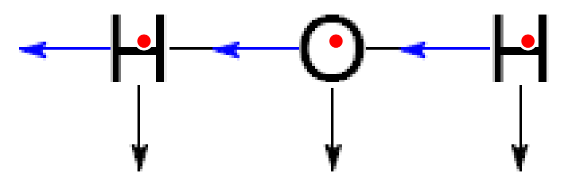


The z axis (red) on oxygen stays in position. This axis contributes +1 towards the character for C_2.

Molecular Vibrations

E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9			

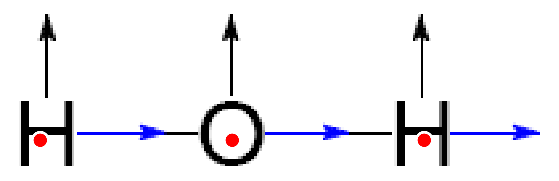


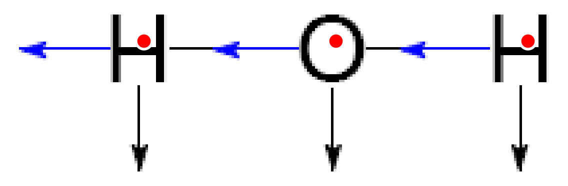


The y axis (black) on oxygen is rotated by 180°. This reverses the axis, and contributes -1 to the character for C_2.

Molecular Vibrations

E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9			





The x axis (blue) on oxygen is also rotated by 180°. This reverses the axis, and contributes -1 to the character for C_2.

Molecular Vibrations

E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9			

The character for the C_2 operation will be +1 (z axis on oxygen) -1 (y axis on oxygen) -1 (x axis on oxygen) = -1

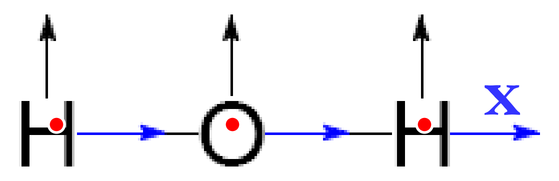
Molecular Vibrations

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

The character for the C_2 operation will be +1 (z axis on oxygen) -1 (y axis on oxygen) -1 (x axis on oxygen) = -1

Molecular Vibrations

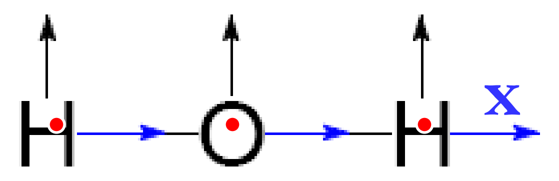
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9	-1		



The xz mirror plane is the molecular plane, and all three atoms remain in position.

Molecular Vibrations

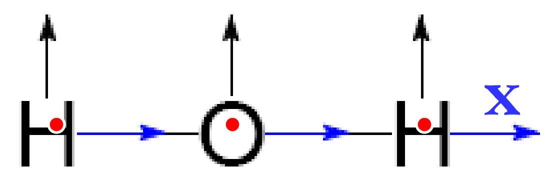
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9	-1		



The z axis and the x axis both lie within the xz plane, and remain unchanged.

Molecular Vibrations

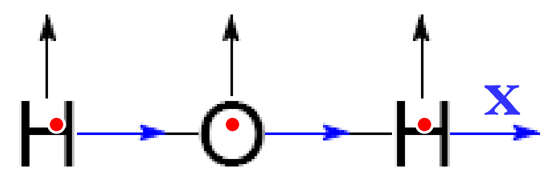
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9	-1		



Each unchanged axis contributes +1 to the character for the symmetry operation.

Molecular Vibrations

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

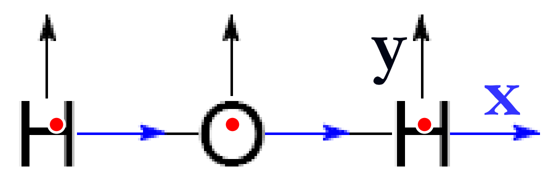


For 3 atoms, the contribution to the character will be:

$3(1+1) = 6$

Molecular Vibrations

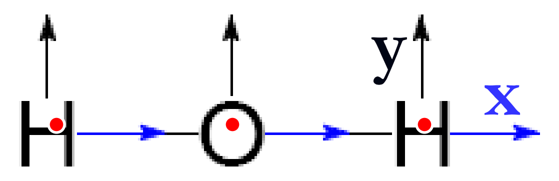
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9	-1		



The y axis will be reversed by the mirror plane, contributing a value of -1 for each of the three atoms on the plane.

Molecular Vibrations

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

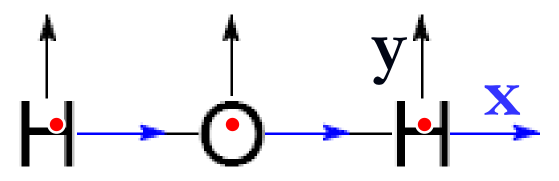


The character for the xz mirror plane will be:

6-3 = 3

Molecular Vibrations

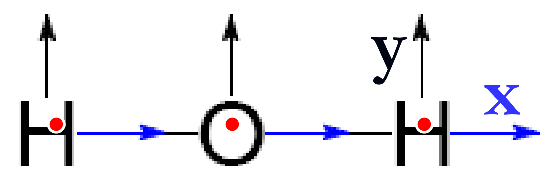
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9	-1	3	



The yz mirror plane bisects the molecule. Only the oxygen atom lies in the plane.

Molecular Vibrations

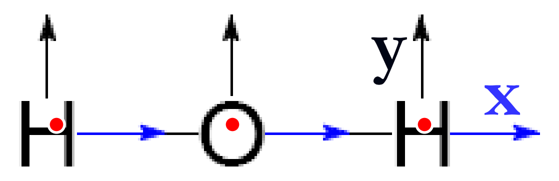
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9	-1	3	



The y and z axis lie within the yz plane, and each contributes +1 to the character.

Molecular Vibrations

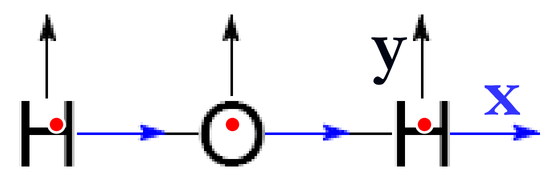
E	C_2	$\sigma_{v(xz)}$	$\sigma_{v'(yz)}$
9	-1	3	



The x axis on oxygen is reversed by the reflection, and contributes a -1 towards the character.

Molecular Vibrations

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



The character for reflection in the yz plane is:

1+1-1=1

Molecular Vibrations

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

The above reducible representation is sometimes called Γ_{3N}, because it reduces to all (3N) modes of molecular motion.

Γ_{3N} for water reduces to:

$$3A_1 + A_2 + 3B_1 + 2B_2$$

Molecular Vibrations

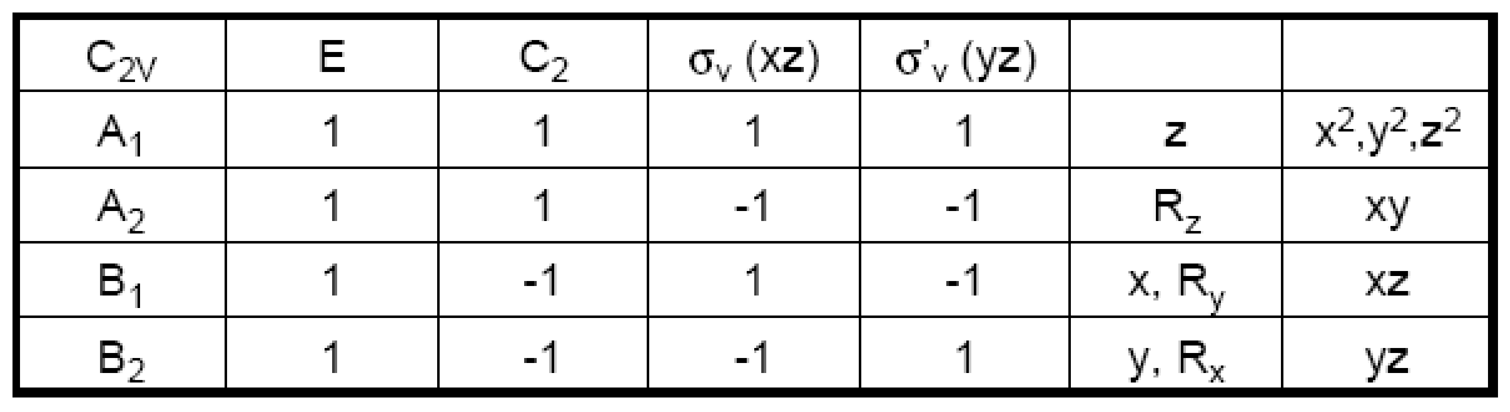
Γ_{3N} for water = $3A_1 + A_2 + 3B_1 + 2B_2$

Note that there are 9 modes of motion. These include vibrations, rotations and translations.

Molecular Vibrations

Γ_{3N} for water = $3A_1 + A_2 + 3B_1 + 2B_2$

Translations have the same symmetry properties as x, y and z.

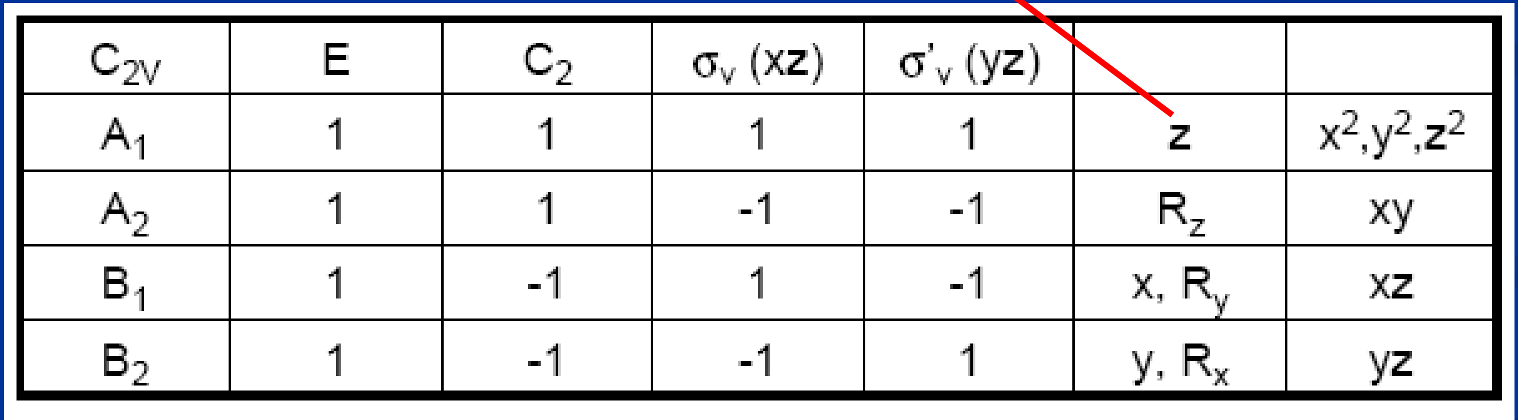


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Molecular Vibrations

Γ_{3N} for water = $3A_1 + A_2 + 3B_1 + 2B_2$

Translations have the same symmetry properties as x, y and z.

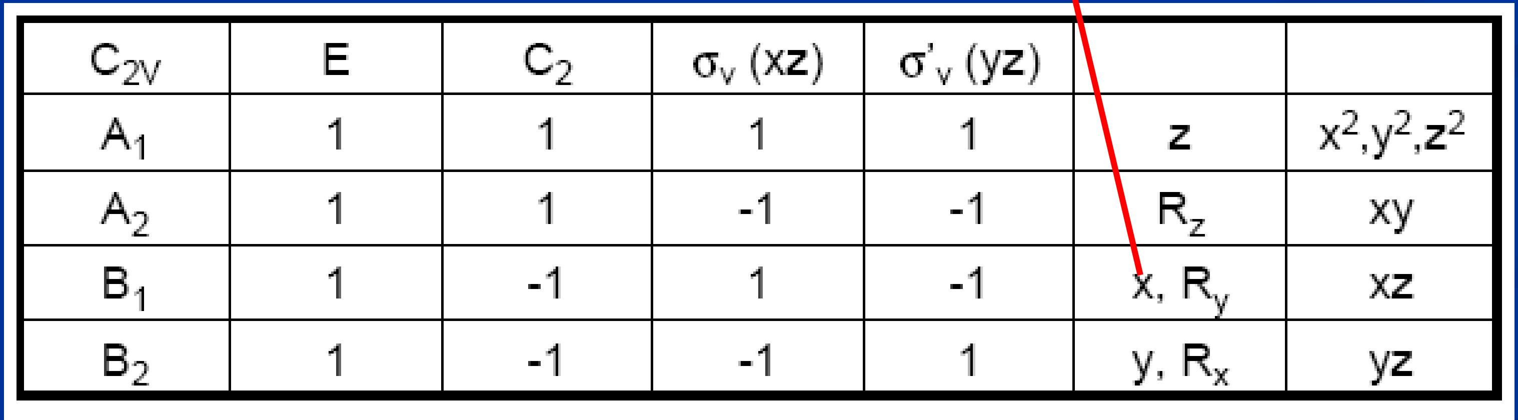


C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Molecular Vibrations

$$\Gamma_{3N} \text{ for water} = \overset{2}{\cancel{3}}A_1 + A_2 + 3B_1 + 2B_2$$

Translations have the same symmetry properties as x, y and z.



C_{2v}	E	C_2	σ_v (xz)	σ'_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

Molecular Vibrations

$$\Gamma_{3N} \text{ for water} = \overset{2}{\cancel{3}}A_1 + A_2 + \overset{2}{\cancel{3}}B_1 + 2B_2$$

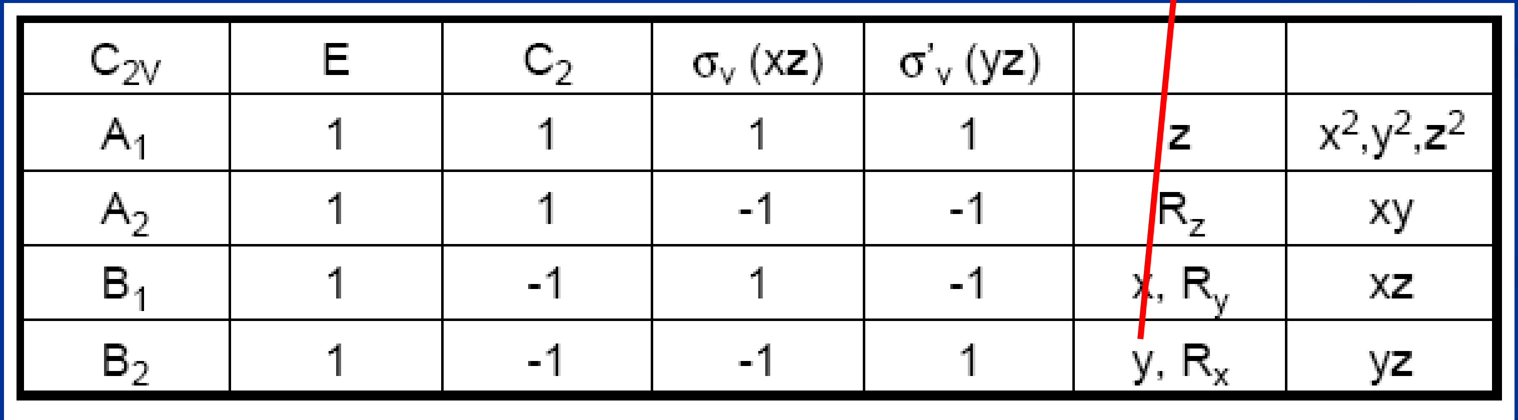
Translations have the same symmetry properties as x, y and z.

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

Molecular Vibrations

$$\Gamma_{3N} \text{ for water} = \overset{2}{\cancel{3}}A_1 + A_2 + \overset{2}{\cancel{3}}B_1 + 2B_2$$

Translations have the same symmetry properties as x, y and z.

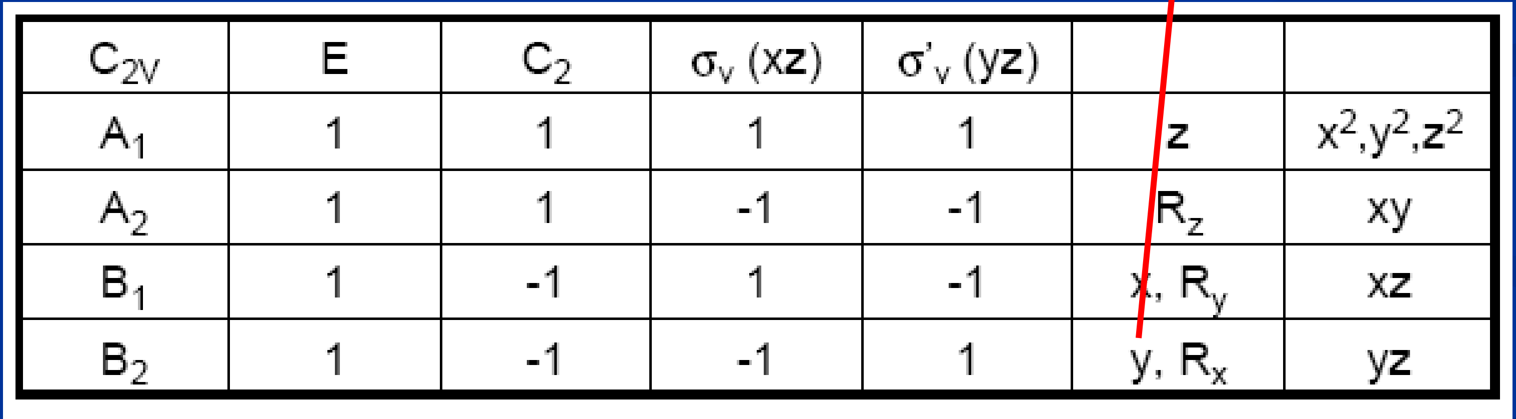


C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Molecular Vibrations

$$\Gamma_{3N} \text{ for water} = \overset{2}{\cancel{3}}A_1 + A_2 + \overset{2}{\cancel{3}}B_1 + \overset{1}{\cancel{2}}B_2$$

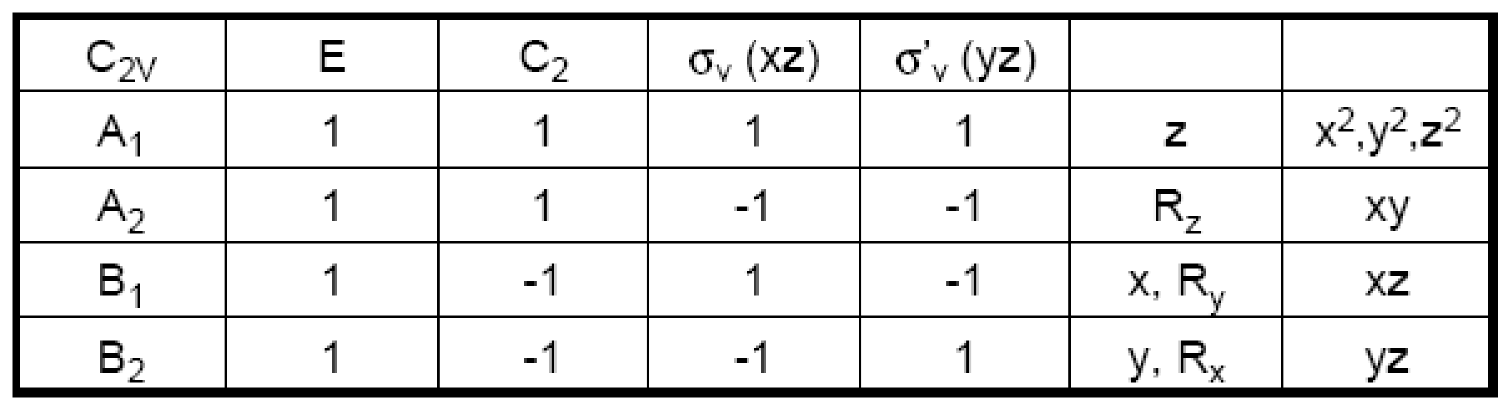
Translations have the same symmetry properties as x, y and z.



C_{2v}	E	C_2	σ_v (xz)	σ'_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

Molecular Vibrations

$$\Gamma_{\text{rot \& vib}} = 2A_1 + A_2 + 2B_1 + 1B_2$$

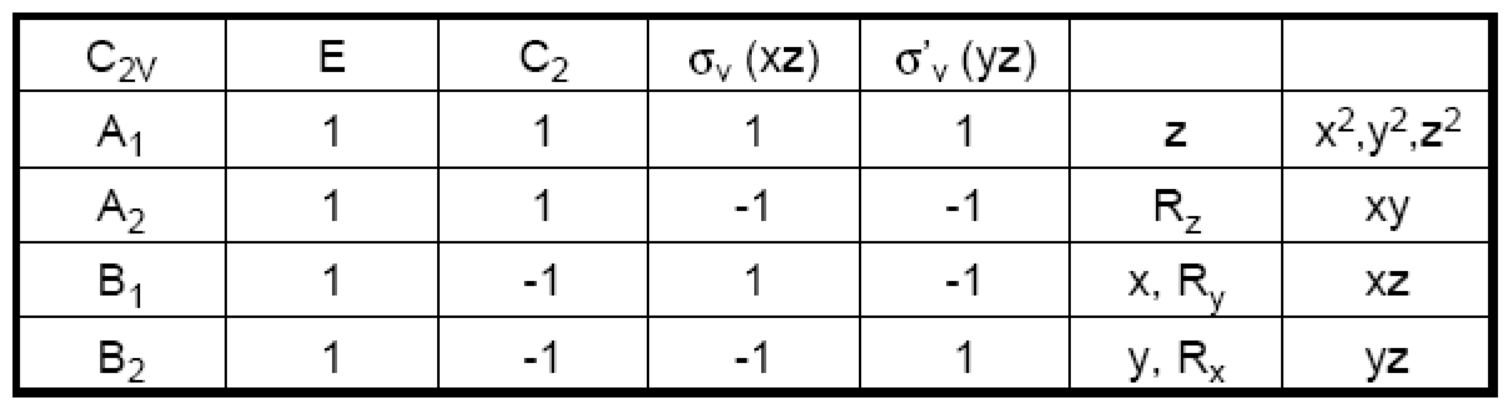


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Molecular Vibrations

$$\Gamma_{\text{rot \& vib}} = 2A_1 + A_2 + 2B_1 + 1B_2$$

Rotations have the same symmetry as R_x, R_y and R_z.

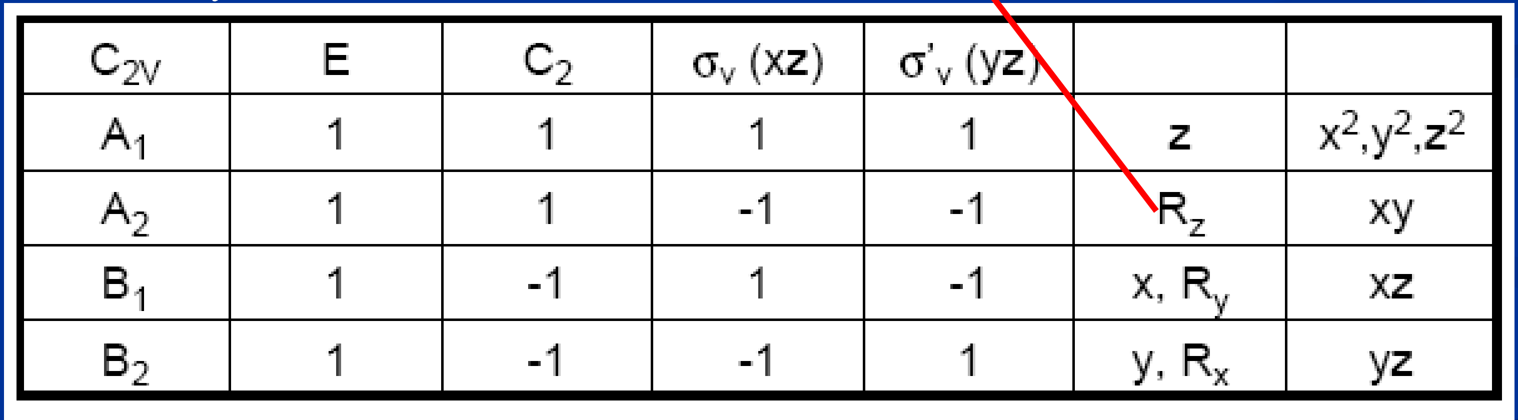


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Molecular Vibrations

$$\Gamma_{\text{rot \& vib}} = 2A_1 + \cancel{A_2} + 2B_1 + 1B_2$$

Rotations have the same symmetry as R_x, R_y and R_z.



C_{2v}	E	C_2	σ_v (xz)	σ'_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

Molecular Vibrations

$$\Gamma_{\text{rot \& vib}} = 2A_1 + \overset{1}{\cancel{2}}B_1 + 1B_2$$

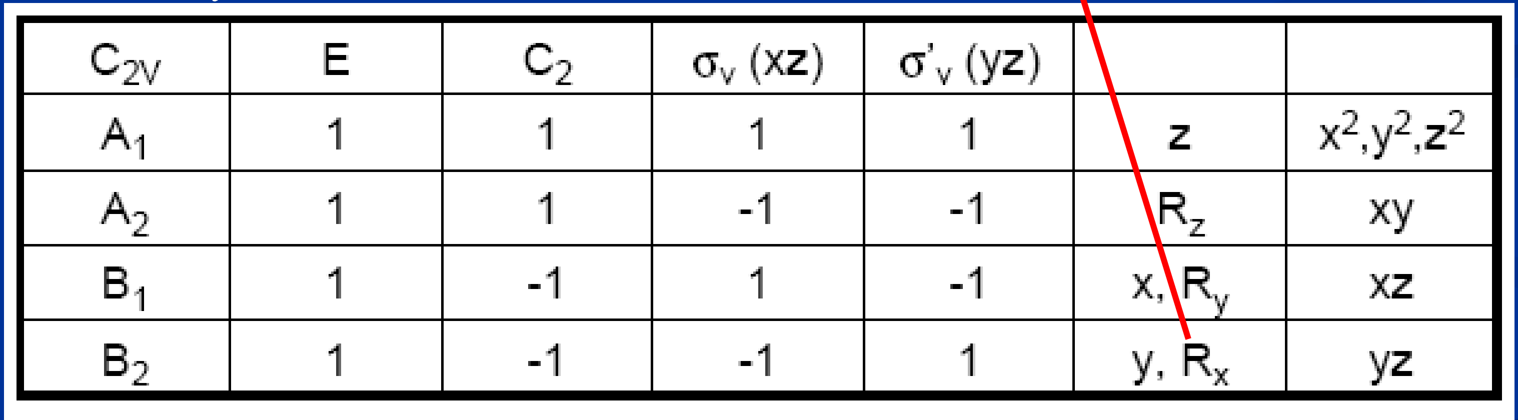
Rotations have the same symmetry as R_x, R_y and R_z.

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

Molecular Vibrations

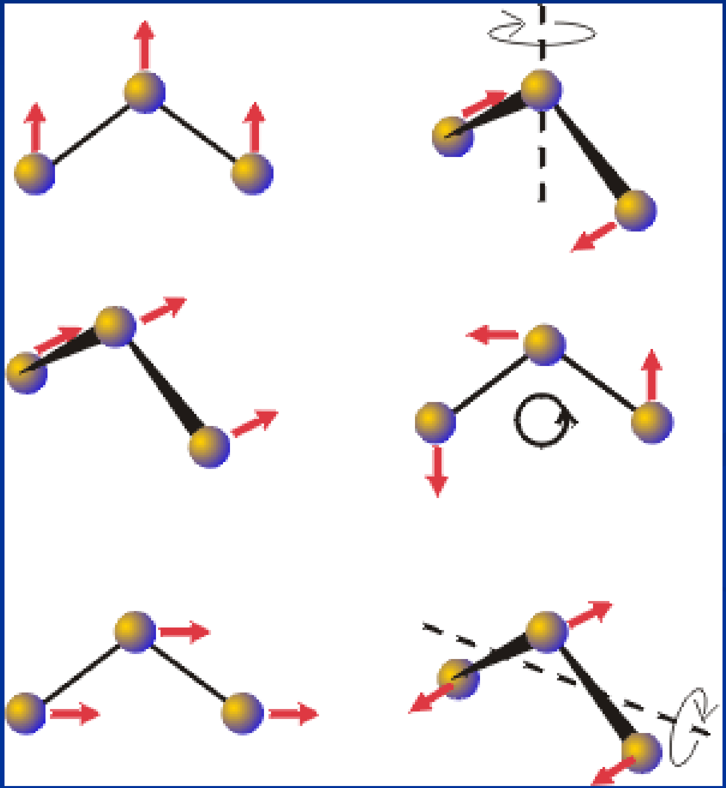
$$\Gamma_{\text{rot \& vib}} = 2A_1 + 1B_1 + \cancel{1}B_2$$

Rotations have the same symmetry as R_x, R_y and R_z.



C_{2v}	E	C_2	σ_v (xz)	σ'_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

Rotations and Translations



Trans_z R_z

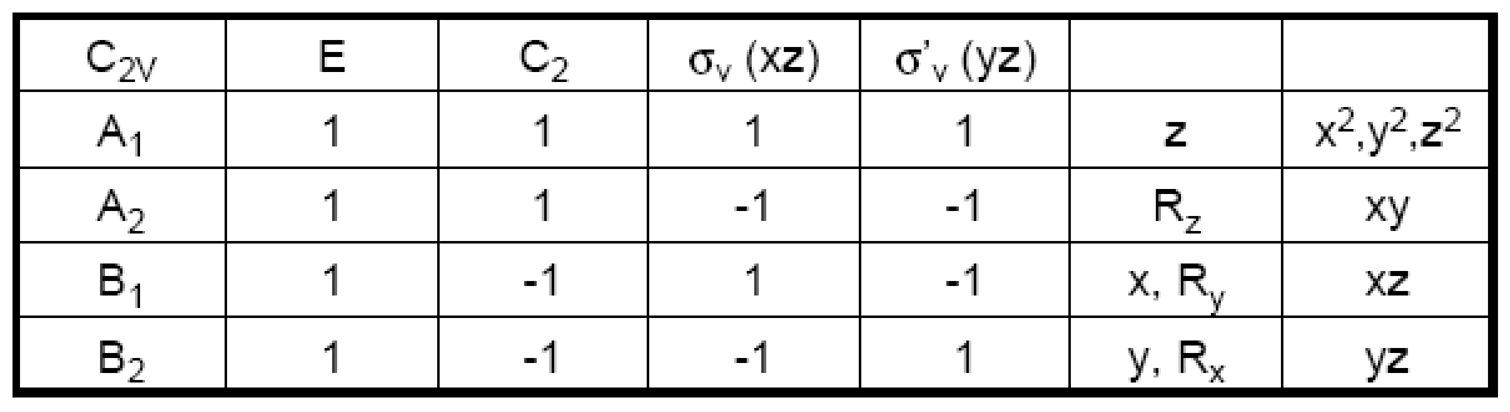
Trans_y R_x

Trans_x R_y

Molecular Vibrations

$$\Gamma_{vib} = 2A_1 + B_1$$

The three vibrational modes remain. Two have A_1 symmetry, and one has B_1 symmetry.

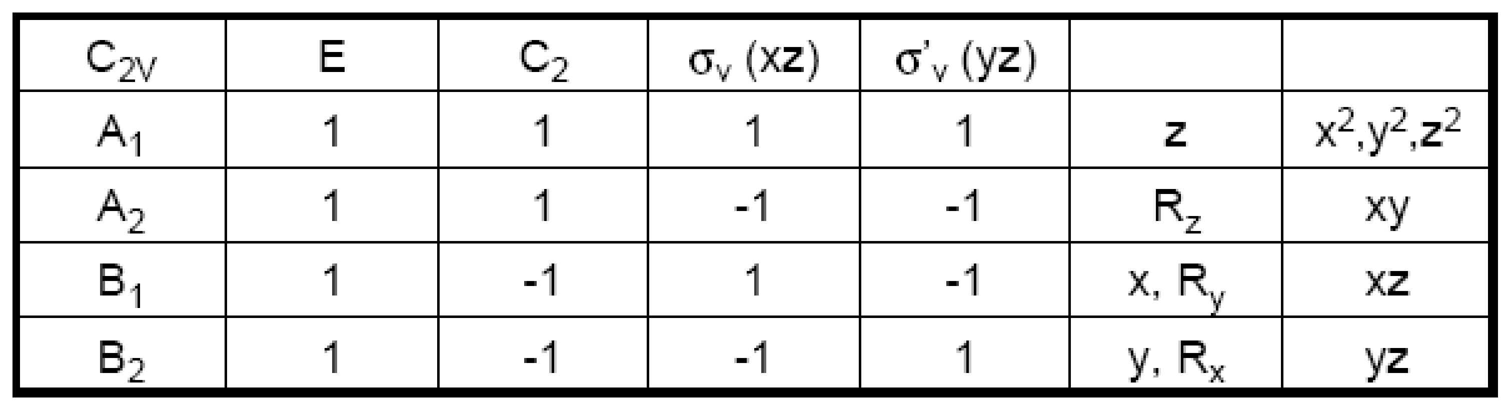


C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Molecular Vibrations

$$\Gamma_{vib} = 2A_1 + B_1$$

Two vibrations are symmetric with respect to all symmetry operations of the group.

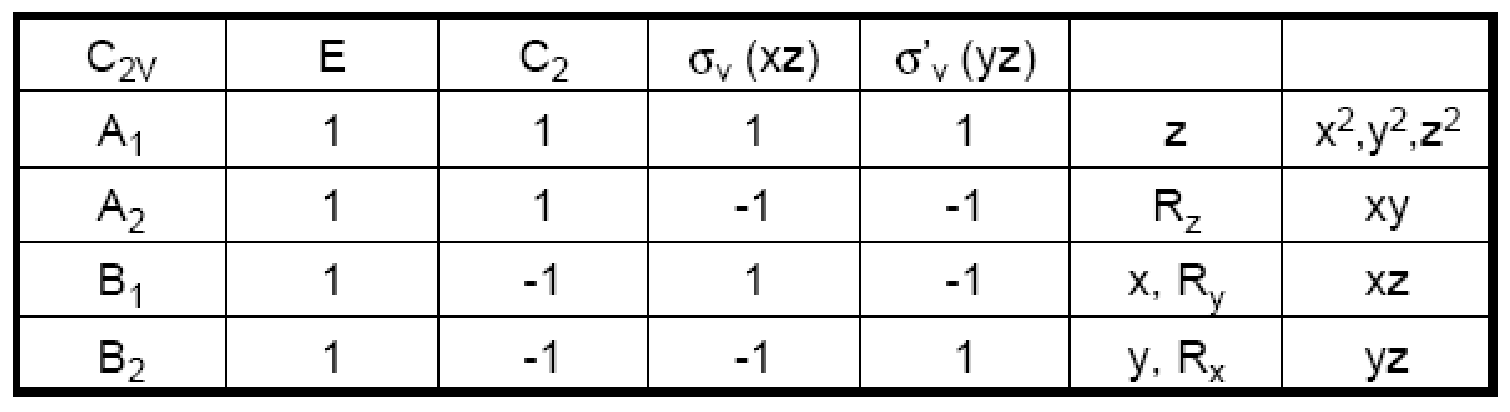


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Molecular Vibrations

$$\Gamma_{vib} = 2A_1 + B_1$$

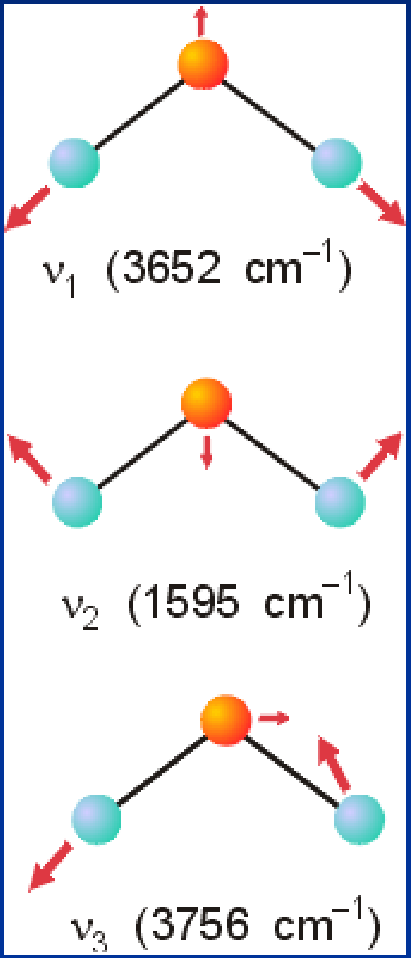
One vibration is asymmetric with respect to rotation and reflection perpendicular to the molecular plane.



C_{2V}	E	C_2	σ_v (xz)	σ'_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

Molecular Vibrations

$\Gamma_{vib} = 2A_1 + B_1$



A_1 symmetric stretch

A_1 bend

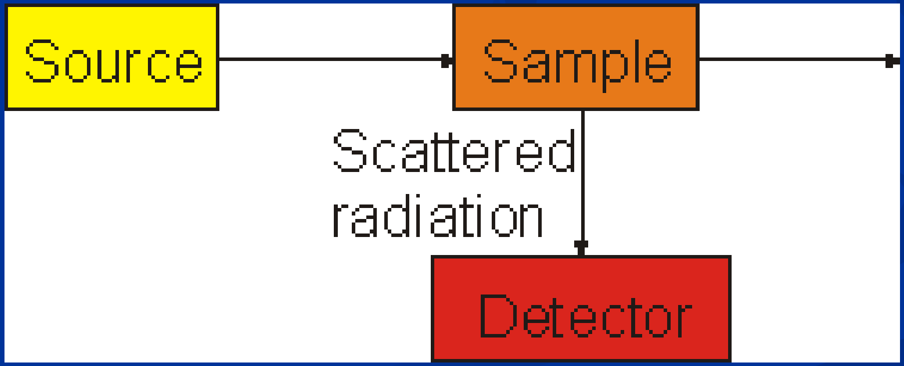
B_1 asymmetric stretch

Molecular Vibrations

For a molecular vibration to be seen in the infrared spectrum (IR active), it must change the dipole moment of the molecule. The dipole moment vectors have the same symmetry properties as the cartesian coordinates x, y and z.

Molecular Vibrations

Raman spectroscopy measures the wavelengths of light (in the IR range) scatted by a molecule. Certain molecular vibrations will cause the frequency of the scattered radiation to be less than the frequency of the incident radiation.



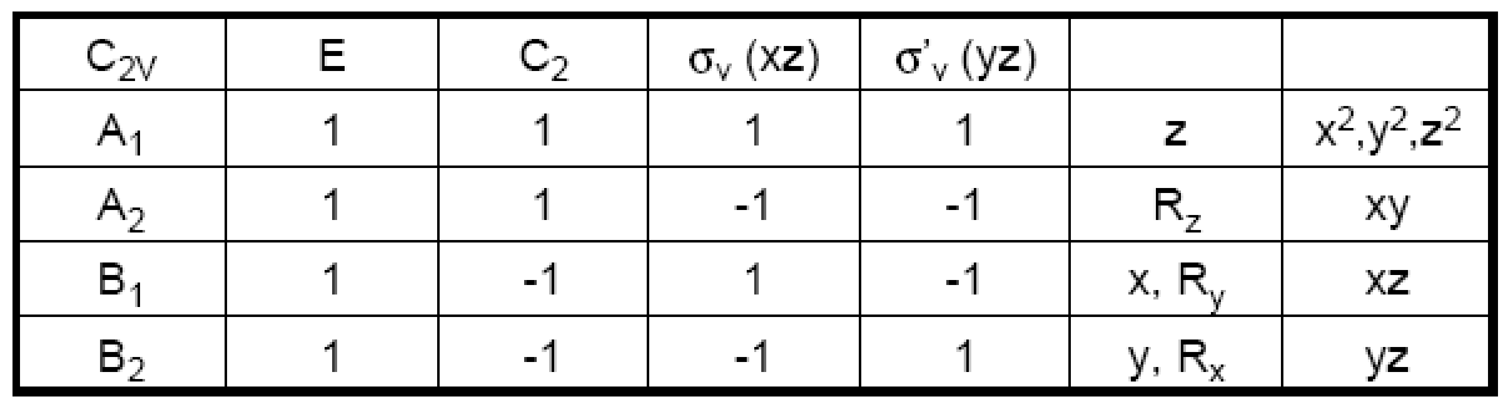
Molecular Vibrations

For a molecular vibration to be seen in the Raman spectrum (Raman active), it must change the polarizability of the molecule. The polarizability has the same symmetry properties as the quadratic functions:

$$xy, yz, xz, x^2, y^2 \text{ and } z^2$$

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$

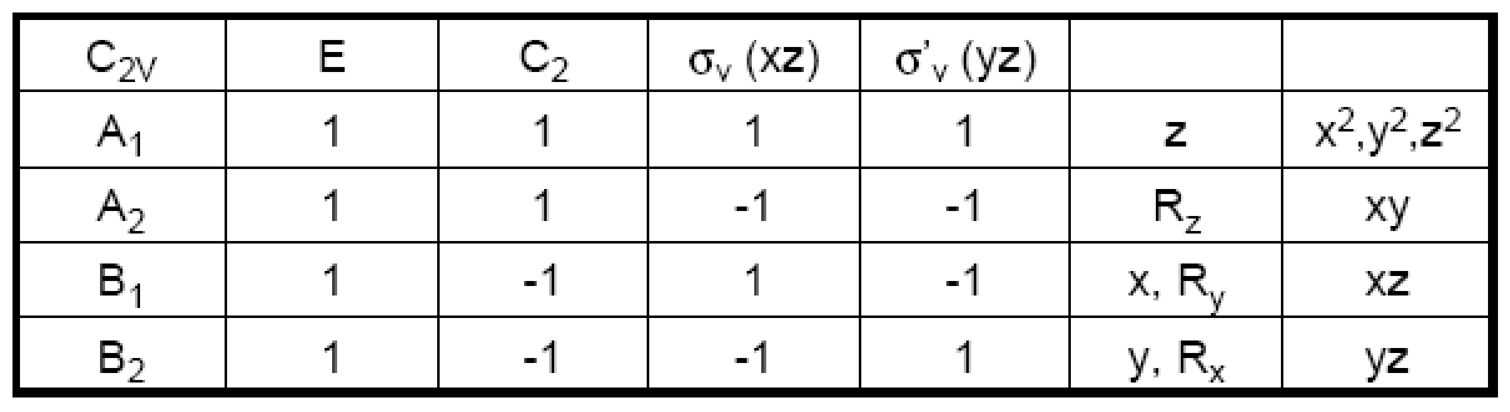


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The two vibrations with A_1 symmetry have z as a basis function, so they will be seen in the infrared spectrum of water. This will result in two peaks (at different frequencies) in the IR spectrum of water.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$

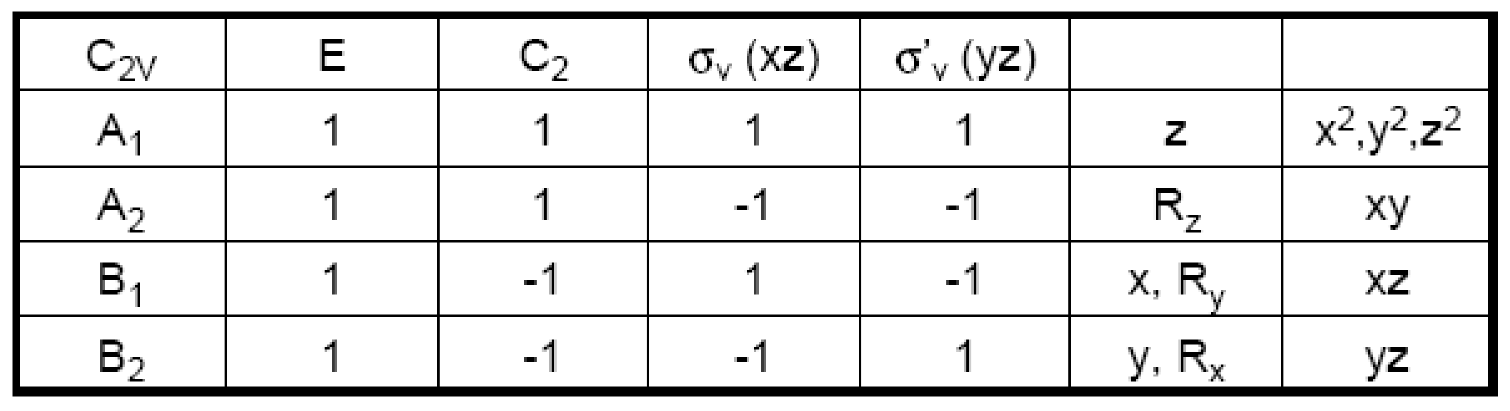


C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The two vibrations with A_1 symmetry also have quadratic basis functions, so they will be seen in the Raman spectrum of water as well.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$

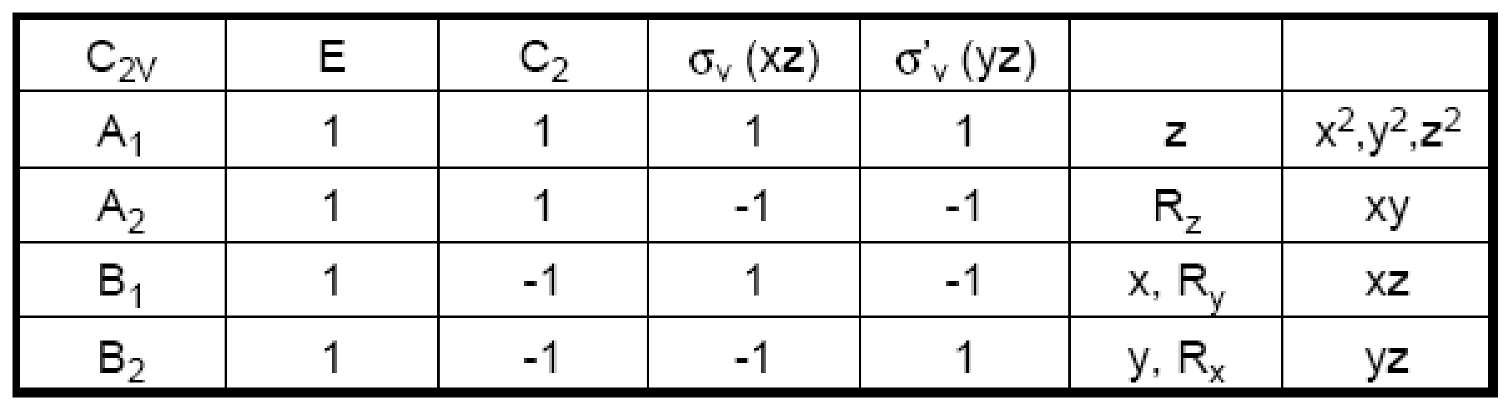


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The two vibrations with A_1 symmetry will appear as two peaks in both the IR and Raman spectra. The two frequencies observed in the IR and Raman for these vibrations will be the same in both spectra.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$

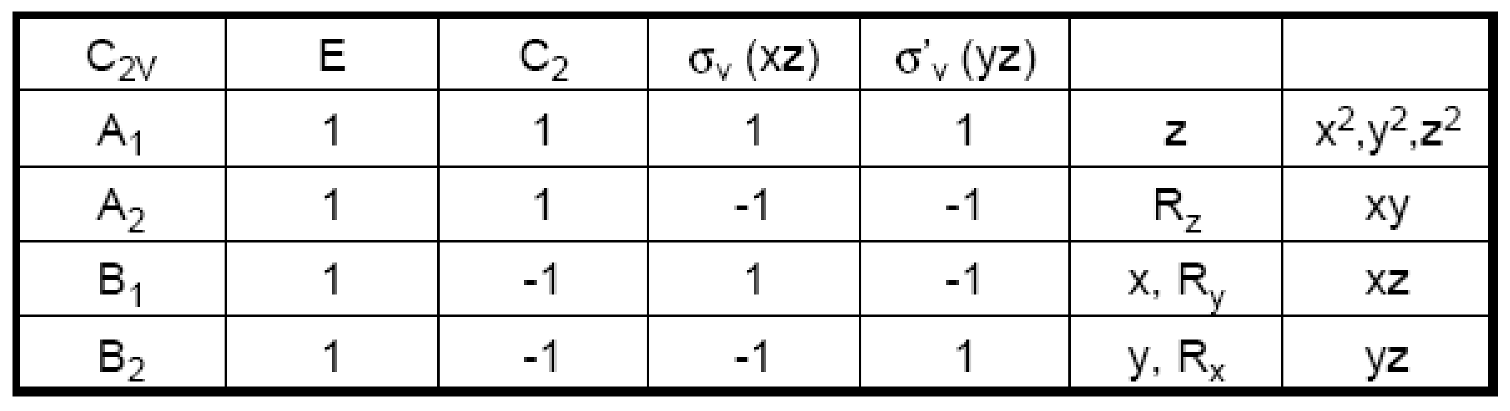


C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The vibration with B_1 symmetry has x and xz as basis functions. This vibration will be both IR active and Raman active. This vibration will appear as a peak (at the same frequency) in both spectra.

Molecular Vibrations of Water

$$\Gamma_{vib} = 2A_1 + B_1$$



C_{2v}	E	C_2	σ_v (xz)	σ'_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

Both the IR and Raman spectra should show three different peaks.

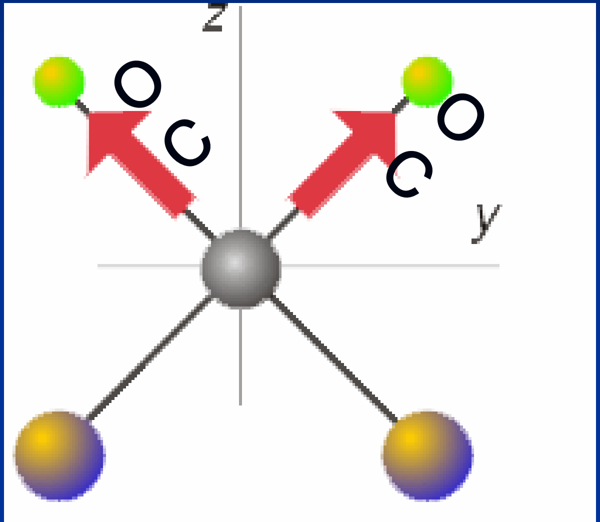
Summary

1. Obtain the point group of the molecule.
2. Obtain Γ_{3N} by considering the three cartesian coordinates on all atoms that aren't moved by the symmetry operation.
3. Reduce Γ_{3N} .
4. Eliminate translations and rotations.
5. Determine if remaining vibrations are IR and/or Raman active.

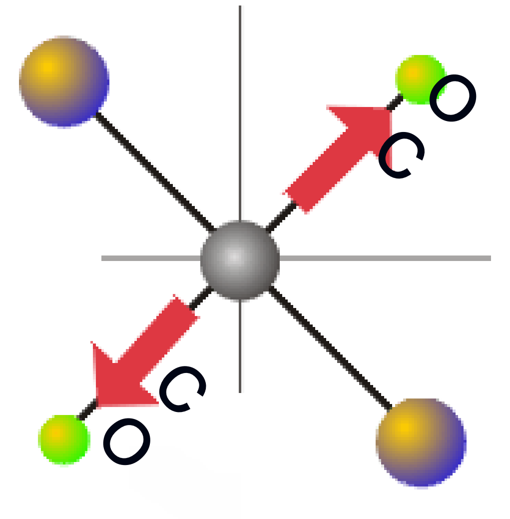
Application: Carbonyl Stretches

- Can IR and Raman spectroscopy determine the difference between two square planar complexes: *cis*-$ML_2(CO)_2$ and *trans*-$ML_2(CO)_2$?

cis and *trans* $ML_2(CO)_2$

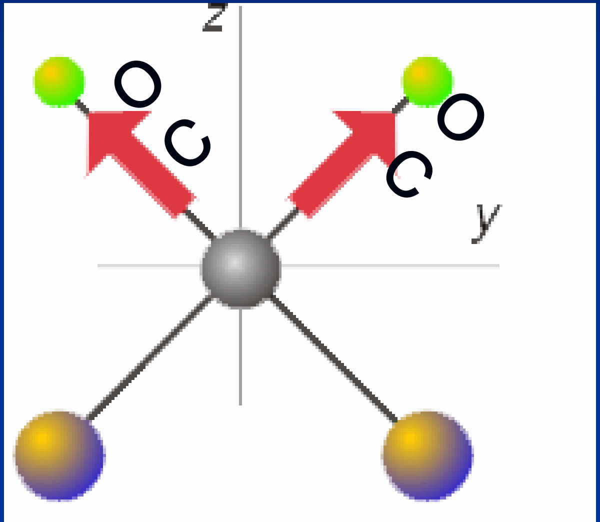


cis isomer – C_{2v}



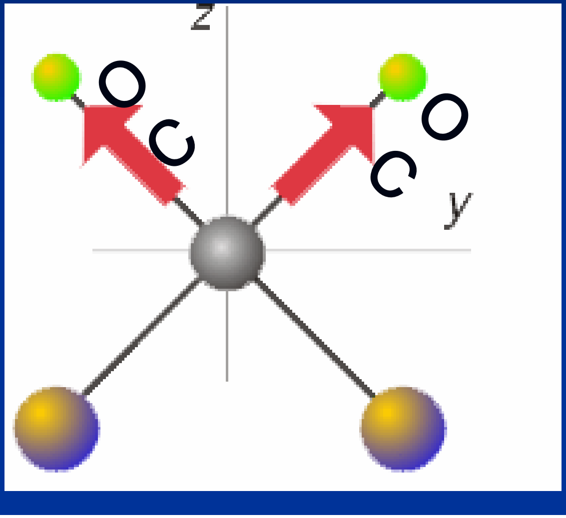
trans isomer – D_{2h}

cis - $ML_2(CO)_2$



C_{2v}:	$\underline{E}$	$\underline{C_2}$	$\underline{\sigma_{xz}}$	$\underline{\sigma_{yz}}$
Γ_{CO}:	2	0	2	0

cis - $ML_2(CO)_2$

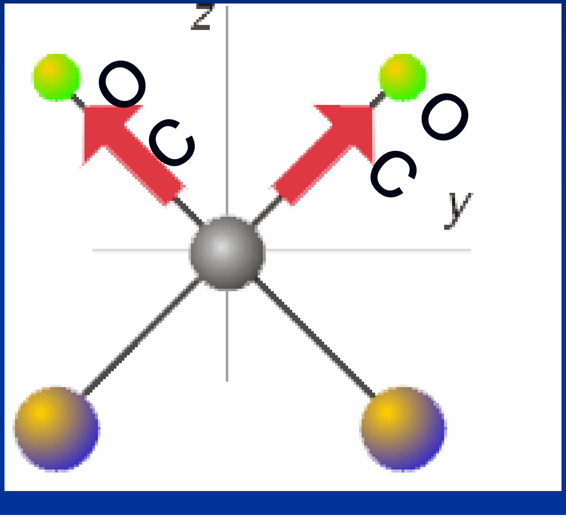


Γ_{CO} reduces to $A_1 + B_1$.

A_1 is a symmetric stretch, and B_1 is an asymmetric stretch.

C_{2V}	E	C_2	σ_v (xz)	σ'_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

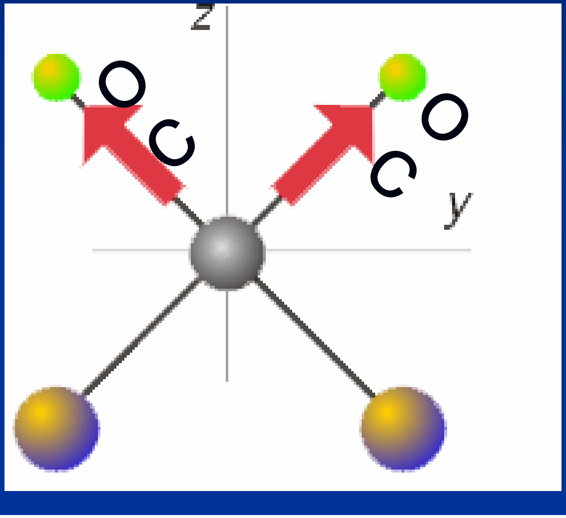
cis - $ML_2(CO)_2$



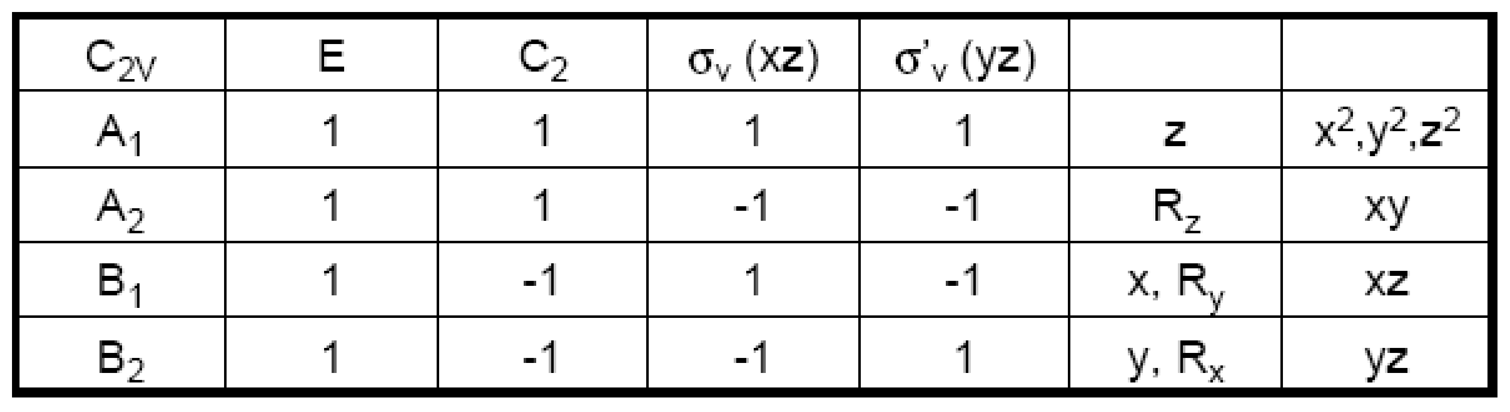
Γ_{CO} reduces to $A_1 + B_1$. The symmetric stretch (A_1) is IR and Raman active.

C_{2v}	E	C_2	σ_v (xz)	σ'_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

cis - $ML_2(CO)_2$



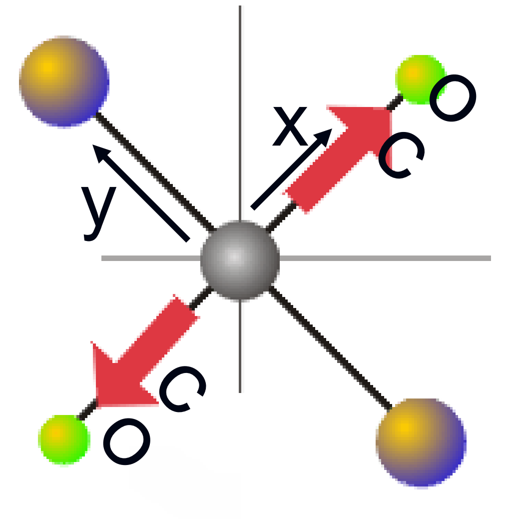
Γ_{CO} reduces to $A_1 + B_1$. The asymmetric stretch (B_1) is both IR and Raman active.



C_{2v}	E	C_2	σ_v (xz)	σ'_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

trans $ML_2(CO)_2$

The *trans* isomer lies in the xy plane. The point group D_{2h} has the following symmetry elements:

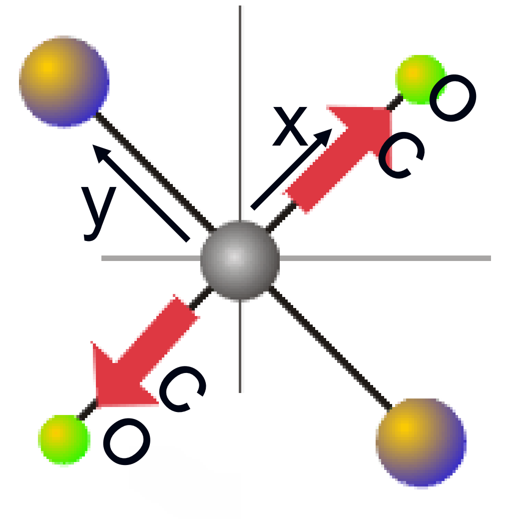


trans isomer – D_{2h}

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}

trans $ML_2(CO)_2$

The *trans* isomer lies in the xy plane. Γ_{CO} is obtained by looking only at the two C-O bonds.

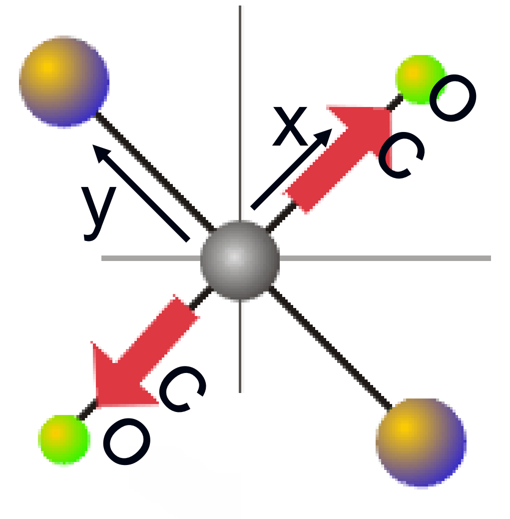


trans isomer – D_{2h}

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}
Γ_{CO}	2	0	0	2	0	2	2	0

trans $ML_2(CO)_2$

Γ_{CO} reduces to A_g (a symmetric stretch) and B_{3u}(an asymmetric stretch).

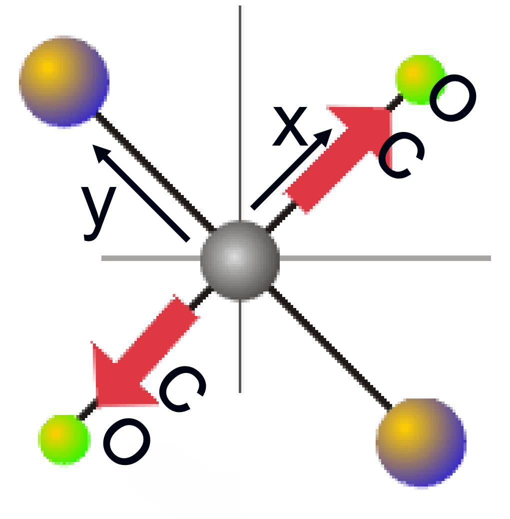


trans isomer – D_{2h}

trans $ML_2(CO)_2$

Γ_{CO} reduces to A_g (a symmetric stretch) and B_{3u}(an asymmetric stretch).

A_g has x^2, y^2 and z^2 as basis functions, so this vibration is Raman active.

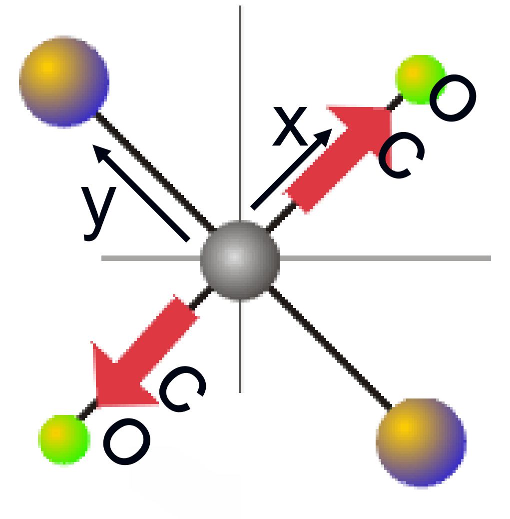


trans isomer – D_{2h}

trans $ML_2(CO)_2$

A_g has x^2, y^2 and z^2 as basis functions, so this vibration is Raman active.

B_{3u} has x as a basis function, so this vibration is IR active.



trans isomer – D_{2h}

trans $ML_2(CO)_2$

A_g has x^2, y^2 and z^2 as basis functions, so this vibration is Raman active.

B_{3u} has x as a basis function, so this vibration is IR active.

The IR and Raman spectra will each show one absorption at different frequencies.

Exclusion Rule

If a molecule has a center of symmetry, none of its modes of vibration can be both infrared and Raman active.

Exclusion Rule

If a molecule has a center of symmetry, none of its modes of vibration can be both infrared and Raman active.

The *cis* and *trans* isomers of square planar $ML_2(CO)_2$, can be easily distinguished using spectroscopy. The *cis* isomer has absorptions that are seen in both the IR and Raman spectra, whereas the *trans* isomer does not.