$$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$		
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_y	xz
B_2	1	-1	-1	1	y,R_x	yz

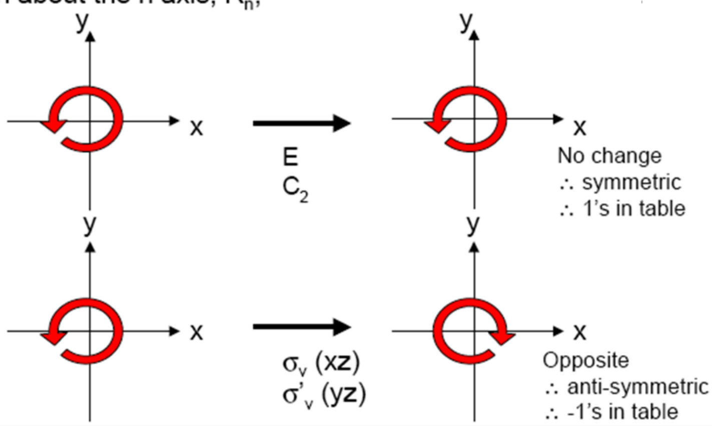
Characters of the irreducible representation

Rotation about the n axis, R_n,

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.



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

C_{3v}	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)

$$\Gamma \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} \cos 2\pi/3 & -\sin 2\pi/3 & 0 \\ \sin 2\pi/3 & \cos 2\pi/3 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma_{x,y} \quad \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \begin{pmatrix} \cos 2\pi/3 & -\sin 2\pi/3 \\ \sin 2\pi/3 & \cos 2\pi/3 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\Gamma_z \quad 1 \quad 1 \quad 1$$

C_{3v}	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)

Mulliken symbol

1D → A, B
2D → E
3D → T

$\chi(C_n) = 1 \longrightarrow$ A
$\chi(C_n) = -1 \longrightarrow$ B

Subscript 1,2 : C_2 or σ_v
Subscript g, u: i

Character Tables

	symmetry operation classes		
area #1	area #2	area #3	area #4

area #1 Symmetry Labels ("Mulliken Symbols") for irreducible representations. See rules for assigning these labels according to symmetry behavior.

area #2 Characters, the "mathematical essence" of symmetry behavior, equal to the traces of symmetry transformation matrices. Roughly, +1 = symmetrical behavior, and -1 = antisymmetrical behavior. Higher dimensional representations can have higher integers; less easily related to symmetry.

area #3 Translational axes (x,y,z) and rotational axes (R_x, R_y, R_z) grouped according to irreducible representations.

area #4 Polynomials, grouped according to irreducible representations. The symmetry of atomic orbitals is equivalent to the symmetry of the corresponding polynomials.

C_{2v} Character Table

C_{2v} symmetry elements grouped into classes

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

Mulliken symbol for irreducible representation

single entry is a character (χ)

entire row is a representation

orbital, function, or other spatial property (each has a characteristic representation)

R_z - rotation about *z*
T_z - translation along *z*

Note: no. of irreducible representations of a group = no. of classes

C_{3v}	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)

Mulliken symbol

Basis:
Coordinates: x,y,z
R: rotation
p_x,p_y,p_z

All the squares, binary products
d orbitals

Mulliken Symbol Notation

1) All representations described by one basis function (i.e., one dimensional matrices) are given either **A** or **B** symbols.

Two dimensional representations are given the symbol **E**
Three-dimensional representations are given the symbol **T**

2) Representations that are symmetric w.r.t. the principle axis C_n are **A**
Representations that are antisymmetric w.r.t. the principle axis C_n are **B**

3) **Subscripts:** 1, when representation is symmetric w.r.t. $\perp$ C_2's *or* σ_v's
2, when representation is antisymmetric w.r.t. $\perp$ C_2's *or* σ_v's

4) **Superscripts:** "prime", when representation is symmetric w.r.t. σ_h
"double-prime", when representation is antisymmetric w.r.t. σ_h

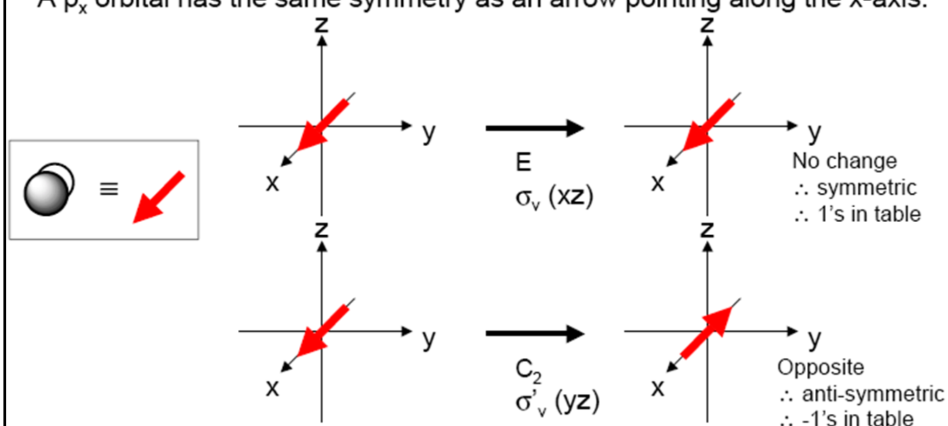
5) **Subscripts:** g (gerade), when representation is symmetric w.r.t. inversion, *i*
u (ungerade), when representation is antisymmetric w.r.t. inversion, *i*

NOTES:

When inversion symmetry is present, (5) supercedes (4)
When multiple $\perp$ C_2 and σ_v classes are present, it is not readily apparent which classes have precedence for rule (3)

C_{2h}	E	C_2	i	σ_h	–	–
A_g	1	1	1	1	R_z	x^2; y^2; z^2; xy
B_g	1	-1	1	-1	R_x;R_y	xz;yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x;y	

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



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

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Basis

e. g. in C_{2v}, the p_x orbital transforms as x, and is represented by the irreducible representation Γ_x.

C_{2v}	E	C_2	σ_v	σ_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_y	xz
B_2	1	-1	-1	1	y,R_x	yz

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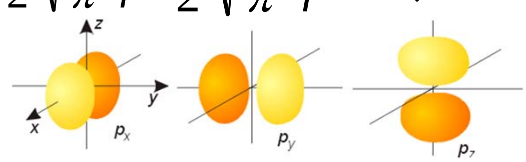
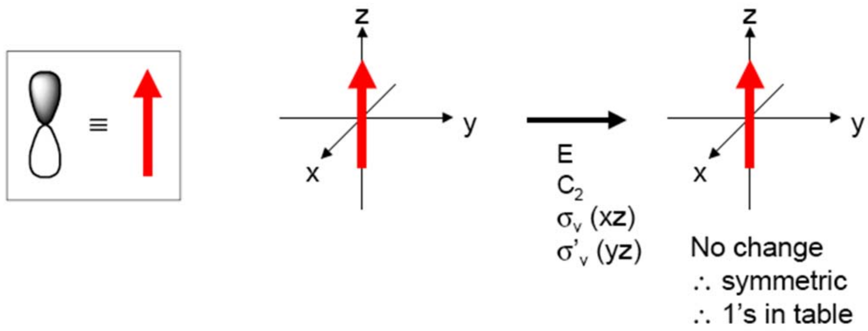
$$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r} \quad \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r} \quad \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$$



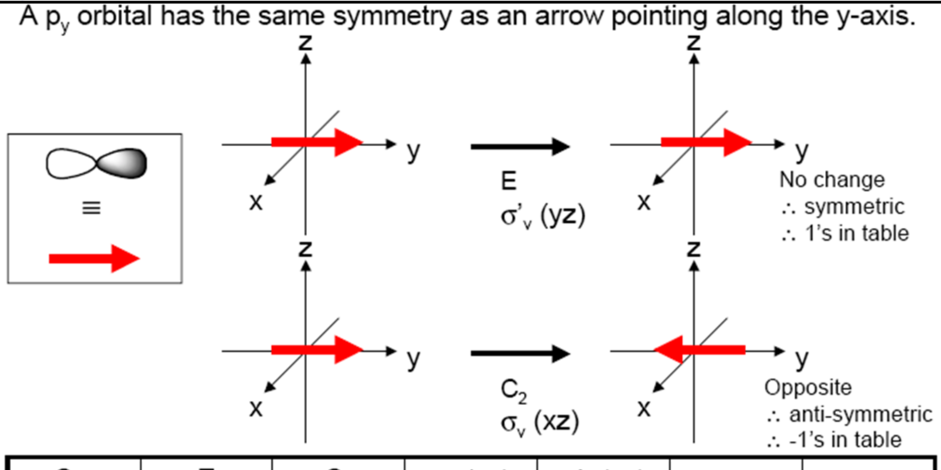
In cartesian coordinates

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

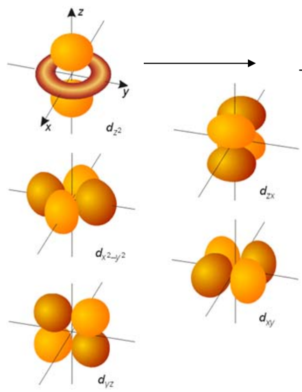


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

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



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

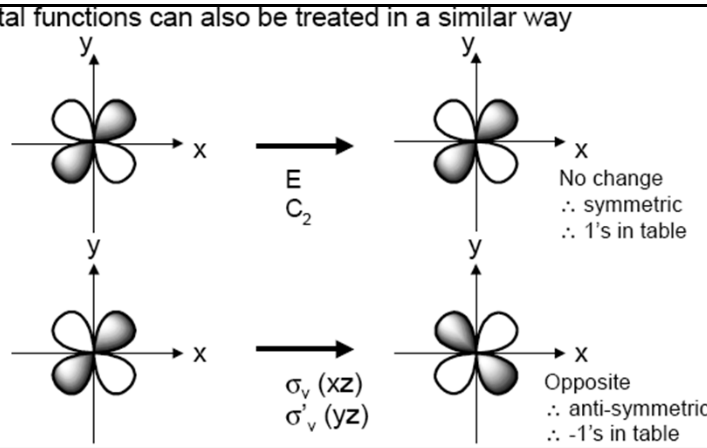


$$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{2z^2-x^2-y^2}{r^2}$$

$$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$$

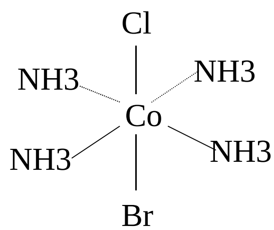
d orbital functions can also be treated in a similar way

The z axis is pointing out of the screen!



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

If application of a symmetry operation does not change the total energy but interconvert two orbitals, they must be identical, we call them degenerate orbitals



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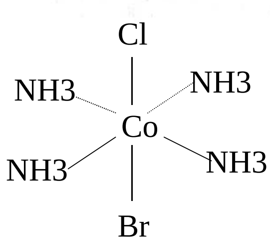
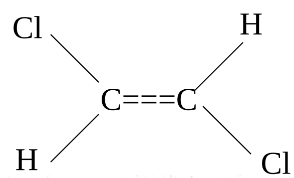
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)



p_x, p_y degenerate orbitals

Note: in the same round bracket



C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

p_x, p_y : NOT degenerate orbitals

NOT bracketed together!

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Properties of Character Table

C_{3v}	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)

C_{3v}	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)

Irreducible representation

the sum of the squares of the dimensions of the irreducible representations of a group equals to the order of the group:

$h=\Sigma\, l_i^2$

$$\sum l_i^{\,2} = 1+1+4=6=h$$

C_{3v}	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)

Irreducible representation

the sum of the squares of the characters multiplied by the number of operations in the class in any irreducible representation equals h.

$$\sum_R N\chi_i(R)^2 = h$$

$$A_1: 1^2+2(1^2)+3(1^2)=6$$
$$A_2: 1^2+2(1^2)+3(-1)^2=6$$
$$E: 2^2+2(-1)^2+3(0)^2=6$$

C_{3v}	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)

Irreducible representation

Irreducible representations are orthogonal to each other.

$$\sum_R N\chi_i(R)\chi_j(R)=0 \quad \text{for } i\neq j.$$

$$A_2\times E:(1)2+2(1)(-1)+3(-1)(0)=0$$

C_{3v}	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)

Irreducible representation

A totally symmetric representation is included in all groups with characters of 1 for all operations.

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$		
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_y	xz
B_2	1	-1	-1	1	y,R_x	yz

$$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

Reducible

$$\Gamma = \{3,-1,1,1\} = A_1 + B_1 + B_2$$

Irreducible

Much of the group theory to solve real problems (including molecular vibration) involves generating a reducible representation and then reducing it to its constituent irreducible representation.

Reduction Formula:

Number of times an irreducible representation occurs in the reducible representation =
$$\frac{1}{h}\sum_{over \cdot all \cdot class} \chi_R \chi_I N$$

C_{3v}	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)
Γ	4	1	-2		

$$\# of \ldots A_1 = \frac{1}{6}[4\bullet 1\bullet 1 + 1\bullet 1\bullet 2 + (-2)\bullet 1\bullet 3] = 0$$

$$\# of \ldots A_2 = \frac{1}{6}[4\bullet 1\bullet 1 + 1\bullet 1\bullet 2 + (-2)\bullet(-1)\bullet 3] = 2$$

$$\# of \ldots E = \frac{1}{6}[4\bullet 2\bullet 1 + 1\bullet(-1)\bullet 2 + (-2)\bullet 0\bullet 3] = 1$$

$$\Gamma = 2A_2 + E$$

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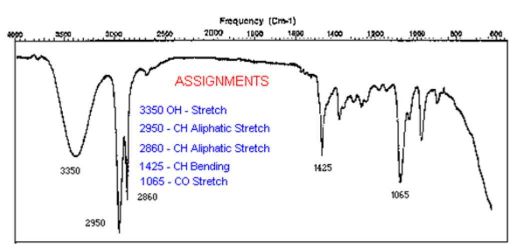
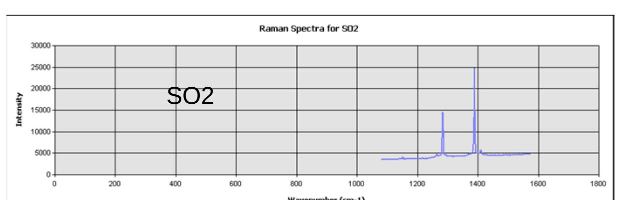
Vibrational Spectroscopy

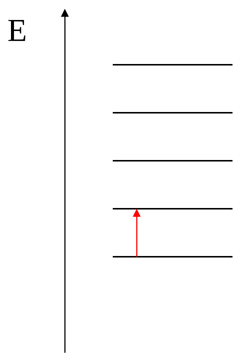
IR,
Raman





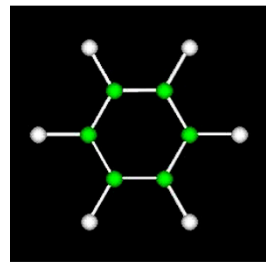
Vibrational Spectroscopy

IR: a photon of IR radiation of frequency *v* is absorbed and molecules/solids are promoted to higher vibrational states. For this absorption to occur, the energy of the photon must match the energy separation.

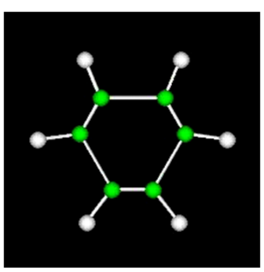


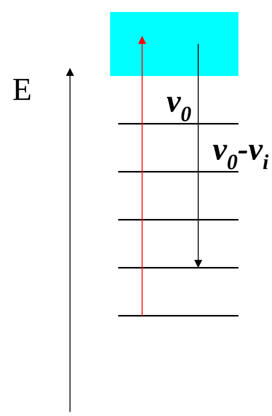
$$E_v = (v + \frac{1}{2})\hbar\omega$$

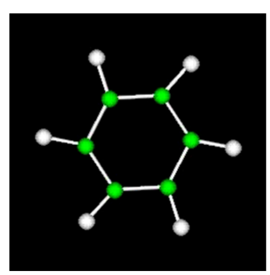
$$\omega = \sqrt{\frac{k}{m}}$$



Raman spectroscopy: a photon of frequency v_0 is scattered inelastically, giving up a part of energy and emerging from the sample with a lower frequency v_0-v_i, where v_i is the vibrational frequency of the molecule.







Group theory is instrumental in predicting the vibrational spectra of molecules, or conversely from spectra to molecular geometry.

A nonlinear molecule with N atoms has 3N-6 vibrational modes (3N-5 if linear): normal modes of vibration

How many vibration modes for XeF_4?

Molecule or Atom	Geometry	Number of Vibrational Modes
Ar	point	3N - 3 = 0
H_2	linear	3N - 5 = 1
CO_2	linear	3N - 5 = 4
H_2S	non-linear	3N - 6 = 3
CH_4	tetrahedral	3N - 6 = 9
C_4H_{10}	non-linear	3N - 6 = 36
C_6H_6	cyclic	3N - 6 = 30

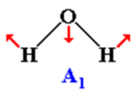
Basis

e. g. in C_{2v}, the p_x orbital transforms as x, and is represented by the irreducible representation Γ_x.

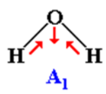
C_{2v}	E	C_2	σ_v	$\sigma_{v'}$		
A_1	1	1	1	1	z	$x^2; y^2; z^2$
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y,R_x	yz

Important relationship between symmetry & Vibrations

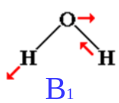
Each normal mode of vibration forms a basis for an irreducible representation of the point group of the molecule.



Bend

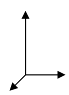


Symmetric Stretch



Anti-symmetric stretch

Bent (C_{2v})

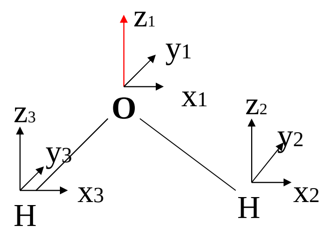


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

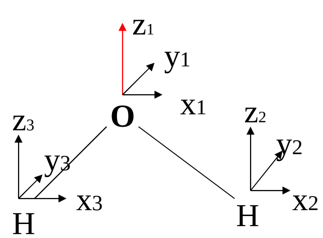
Can the symmetry of the normal vibration mode be determined without any previous knowledge of the actual forms of the modes?

Vibrational Spectroscopy

To find out the symmetry of all possible molecular motions,
Step 1. use x, y, z coordinates at each atom as a basis to generate a reducible representation of the group.



$$\begin{pmatrix} x_1' \\ y_1' \\ z_1' \\ x_2' \\ y_2' \\ z_2' \\ x_3' \\ y_3' \\ z_3' \end{pmatrix} = \begin{pmatrix} 1 & & & & & & & & \\ & 1 & & & & & & & \\ & & 1 & & & 0 & & & \\ & & & 1 & & & & & \\ & & & & 1 & & & & \\ & & & & & 1 & & & \\ & 0 & & & & & 1 & & \\ & & & & & & & 1 & \\ & & & & & & & & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

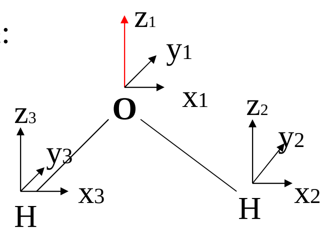


For E:

$$\chi^E = 9$$

$$\begin{pmatrix} x_1' \\ y_1' \\ z_1' \\ x_2' \\ y_2' \\ z_2' \\ x_3' \\ y_3' \\ z_3' \end{pmatrix} = \left(\begin{array}{ccc|ccc|ccc} -1 & & & & & & & & \\ & -1 & & & 0 & & & 0 & \\ & & 1 & & & & & & \\ \hline & & & 0 & & & -1 & & \\ & 0 & & & 0 & & & -1 & \\ & & & & & 0 & & & 1 \\ \hline & & & -1 & & & 0 & & \\ & 0 & & & -1 & & & 0 & \\ & & & & & 1 & & & 0 \end{array}\right) \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

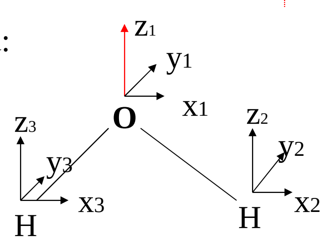
For C_2:



$$\chi^{C2} = -1$$

$$\begin{pmatrix} x_1' \\ y_1' \\ z_1' \\ x_2' \\ y_2' \\ z_2' \\ x_3' \\ y_3' \\ z_3' \end{pmatrix} = \left(\begin{array}{ccc|ccc|ccc} 1 & & & & & & & & \\ & -1 & & & 0 & & & 0 & \\ & & 1 & & & & & & \\ \hline & & & 1 & & & & & \\ & 0 & & & -1 & & & 0 & \\ & & & & & 1 & & & \\ \hline & & & & & & 1 & & \\ & 0 & & & 0 & & & -1 & \\ & & & & & & & & 1 \end{array}\right) \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

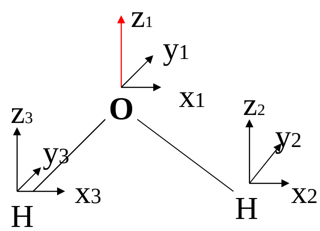
For σ_v:



$$\chi^{\sigma v(xz)} = 3$$

General rules:

1. A nonzero entry appears along the diagonal of the matrix only for an atom that does not change position upon symmetry operation.
2. If the atom position changes, 0 is entered.
3. If the atom position unchanged and the vector direction is unchanged: enter 1
   vector direction reversed: enter -1



$$\chi^{\sigma v(xz)} = 3$$

$$\chi^{\sigma v'(yz)} = 1$$

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$
Γ_{3N}	9	-1	3	1

Step 2. Reduce the reducible representation into the irreducible representation for the group. (Use reduction formula)

$$\# = \frac{1}{h} \sum_{overallclass} \chi_R \chi_I N$$

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

$$\frac{1}{h}\sum_{overallcla\ ss}\chi_R \chi_I N$$

$$\#of \ldots A_1 = \frac{1}{4}[9\bullet 1\bullet 1 + (-1)\bullet 1\bullet 1 + 3\bullet 1\bullet 1 + 1\bullet 1\bullet 1] = 3$$

$$\#of \ldots A_2 = \frac{1}{4}[9\bullet 1\bullet 1 + (-1)\bullet 1\bullet 1 + 3\bullet (-1)\bullet 1 + 1\bullet (-1)\bullet 1] = 1$$

$$\#of \ldots B_1 = \frac{1}{4}[9\bullet 1\bullet 1 + (-1)\bullet (-1)\bullet 1 + 3\bullet 1\bullet 1 + 1\bullet (-1)\bullet 1] = 3$$

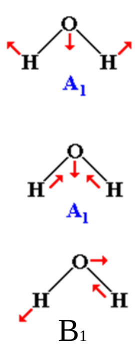
$$\#of \ldots B_2 = \frac{1}{4}[9\bullet 1\bullet 1 + (-1)\bullet (-1)\bullet 1 + 3\bullet (-1)\bullet 1 + 1\bullet 1\bullet 1] = 2$$

$$\Gamma_{3N} = 3A_1 + A_2 + 3B_1 + 2B_2$$

$$\Gamma_{vib} = \Gamma_{3N} - \Gamma_{translation} - \Gamma_{rotation}$$

$$\ldots\ldots = (3A_1 + A_2 + 3B_1 + 2B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2)$$

$$\ldots\ldots = 2A_1 + B_1$$



Bent (C_{2v})

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

Activity rule:

A vibration is IR active if it belongs to the same irreducible representation as x, y, z (i. e. it involves a change in dipole moment).

A vibration is Raman active if it belongs to the same irreducible representation as a binary product (xy, xz, yz, z^2, x^2,y^2){component of polarizability tensor).

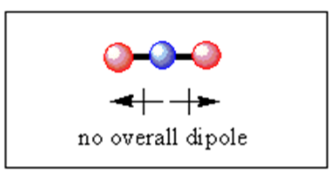
$$\Gamma_{vib} = 2A_1 + B_1$$

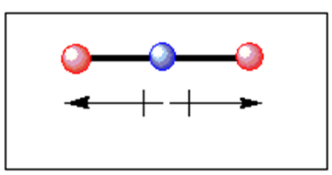
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$				
A_1	1	1	1	1	z	x^2, y^2, z^2	IR	Raman
A_2	1	1	-1	-1	R_z	xy		Raman
B_1	1	-1	1	-1	x, R_y	xz	IR	Raman
B_2	1	-1	-1	1	y, R_x	yz	IR	Raman

In IR spectroscopy, the molecule interacts with the oscillating electric fields of the light and for energy to be transferred,

the dipole moment of the molecule must *change* during the vibration for the vibration to be seen in the IR spectrum

This rule (*selection rule*) controls the number of bands seen in the IR spectrum.





ν_{asym} occurs at 2349 cm^{-1}.

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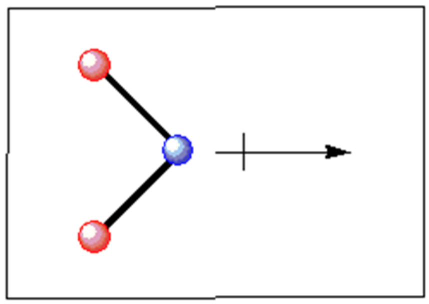

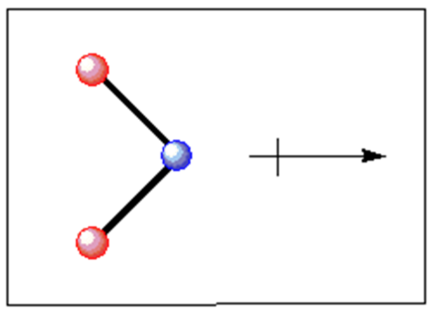

ν_{sym} occurs at 3652 cm^{-1}

ν_{asym} occurs at 3756 cm^{-1}

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When light is scattered inelastically from the molecule, the light interacts with the molecule by distorting the electron cloud surrounding the molecule to produce a dipole. The ease with which the electron cloud can be distorted is called the *polarizability*. For the distortion to produce a dipole, the polarizability of the molecule must change during the vibration. The selection rule for Raman spectroscopy is,

the polarizability of the molecule must *change* during the vibration for the vibration to be seen in the Raman spectrum