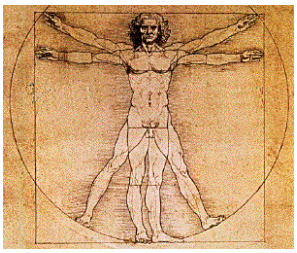
Symmetry and group theory

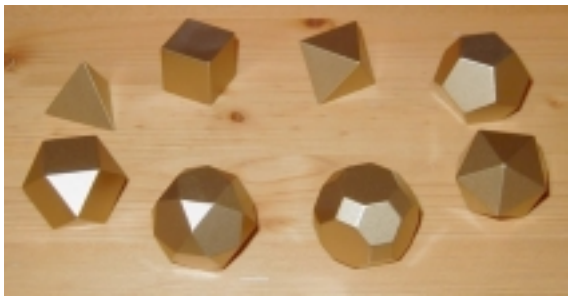
or
How to Describe the Shape of
a Molecule with two or three letters

Natural symmetry in plants

Symmetry
in animals

Symmetry in the human body





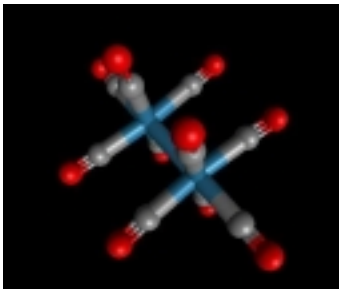
The platonic solids

Symmetry in modern art
M. C. Escher

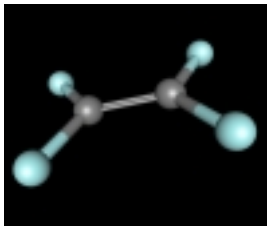
Symmetry in arab architecture
La Alhambra, Granada (Spain)

Symmetry in baroque art
Gianlorenzo Bernini
Saint Peter's Church
Rome

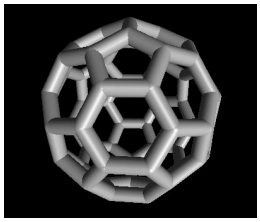
Symmetry in words, music



$Re_2(CO)_{10}$



C_2F_4



C_{60}

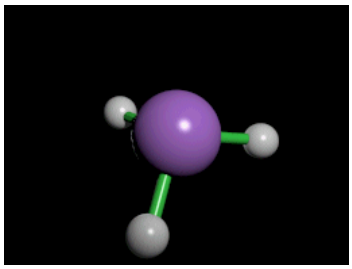
Symmetry in chemistry

- Molecular structures
- Wave functions
- Description of orbitals and bonds
- Reaction pathways
- Optical activity
- Spectral interpretation (electronic, IR, NMR)

...

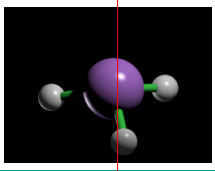
Molecular structures

A molecule is said to have symmetry if some parts of it may be interchanged by others without altering the identity or the orientation of the molecule



Symmetry Operation:

Movement of an object into an equivalent or indistinguishable orientation



Symmetry Elements:

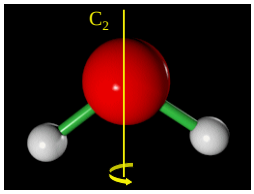
A point, line or plane about which a symmetry operation is carried out

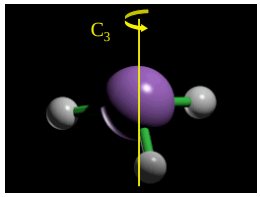
5 types of symmetry operations/elements

Identity: this operation does nothing, symbol: E

Element is entire object

Proper Rotation:
Rotation about an axis by an angle of 2π/n

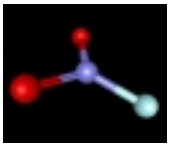




H_2O

NH_3

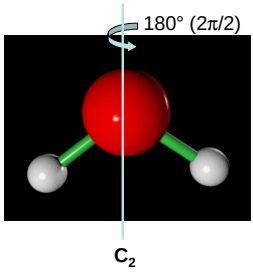
How about:



NFO_2?

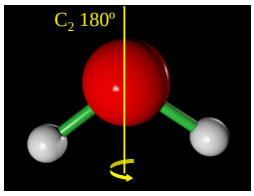
The Operation: Proper rotation C_n is the movement ($2\pi/n$)

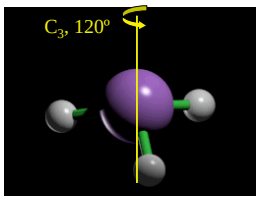
The Element: Proper rotation axis C_n is the line



Applying C_2 twice
Returns molecule to original oreintation
$C_2^2 = E$

Proper rotation axes

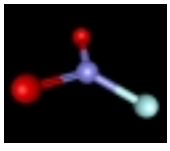




H_2O

NH_3

How about:

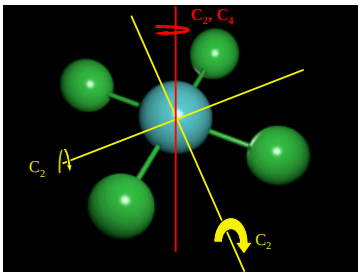


NFO_2?

Rotation angle	Symmetry operation
60º	C_6
120º	C_3 (= C_6^2)
180º	C_2 (= C_6^3)
240º	C_3^2(= C_6^4)
300º	C_6^5
360º	E (= C_6^6)

Proper Rotation:
Rotation about an axis by an angle of 2π/n

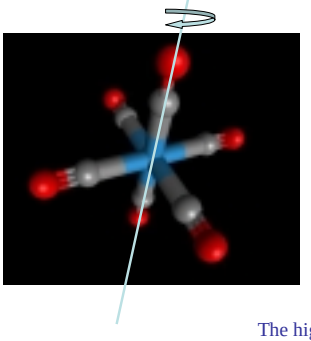
$PtCl_4$



C_n^m
Rotation 2πm/n

$C_n^n = E$

$C_n^{n+1} = C_n$

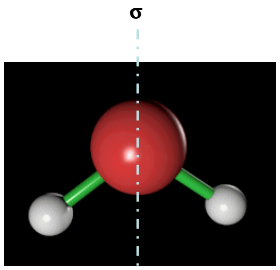


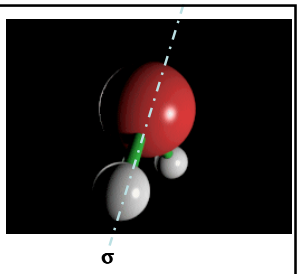
2π/2 = **C_2**
2π/4 = **C_4**

$C_n^n = E$

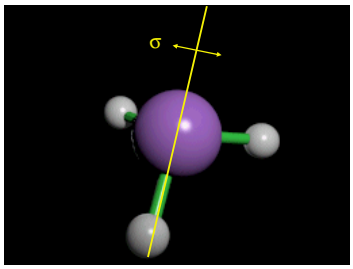
The highest order rotation axis
is the *principal* axis
and it is chosen as the z axis

Reflection and reflection planes (mirrors)





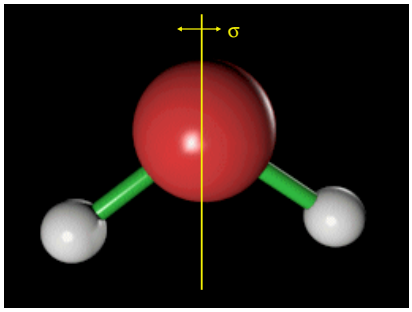
σ (reflection through a mirror plane)



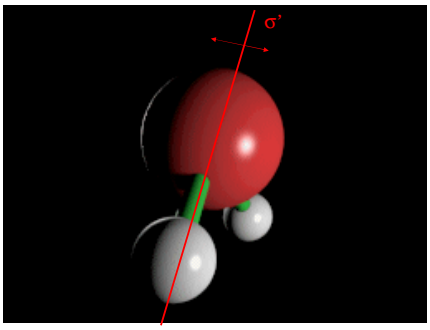
NH_3

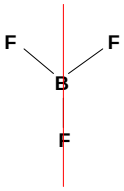
Only one σ?

H_2O



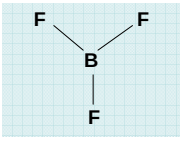
H_2O





If the plane contains the principal axis it is called σ_v

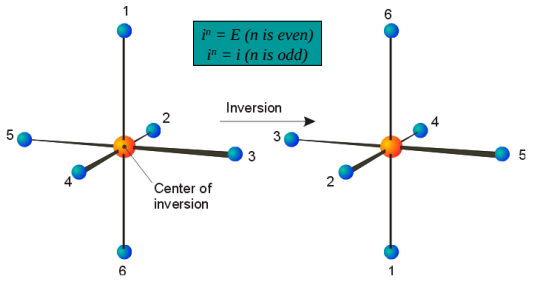
If the plane is perpendicular to the principal axis it is called σ_h



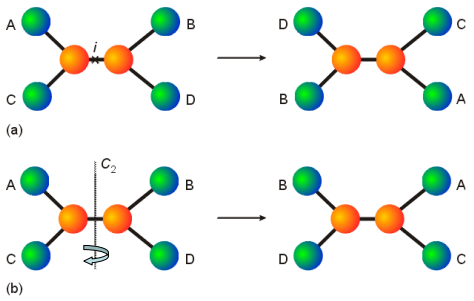
$\sigma^n = E$ (n = even)
$\sigma^n = \sigma$ (n = odd)

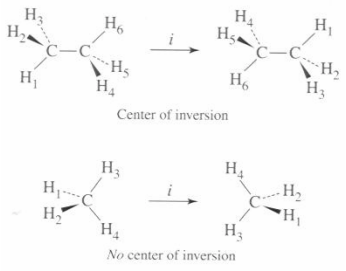
Inversion: *i*

Center of inversion or center of symmetry
(x,y,z) → (-x,-y,-z)

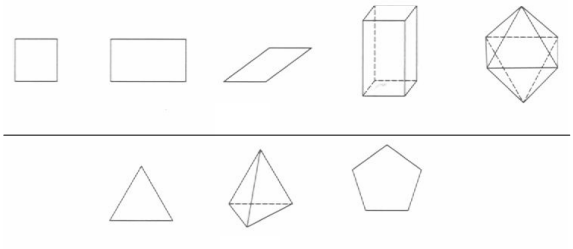


Inversion not the same as C_2 rotation !!





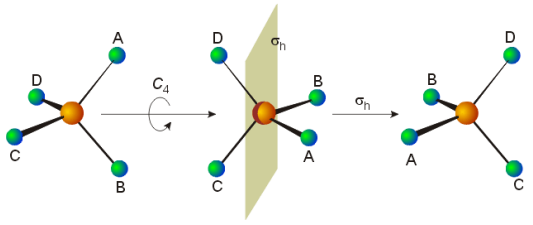
Figures with center of inversion



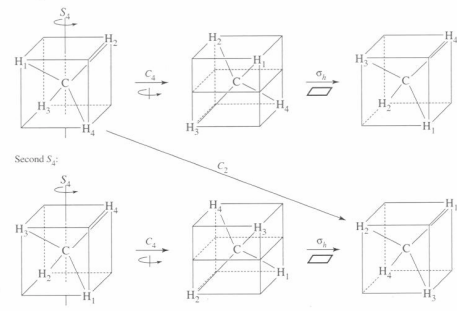
Figures without center of inversion

Improper rotation (and improper rotation axis): S_n

rotation about an axis by an angle $2\pi/n$
followed by reflexion through perpendicular plane



$S_4^2 = C_2$



Also, $S_4^4 = E$; $S_2 = i$; $S_1 = \sigma$

Symmetry operations and elements

Operation	Element
proper rotation	axis (C_n)
improper rotation	axis (S_n)
reflection	plane (s)
inversion	center (i)
Identity	Molecule (E)

Symmetry point groups

The set of all possible symmetry operations on a molecule is called the point group (there are 28 point groups)

The mathematical treatment of the properties of groups is Group Theory

In chemistry, group theory allows the assignment of structures, the definition of orbitals, analysis of vibrations, ...

See: Chemical applications of group theory by F. A. Cotton

Point Groups – Special Shapes

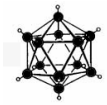
Linear

C_2

$D_{\infty h}$ – O=C=O — C_∞

$C_{\infty v}$ – H-Cl — C_∞

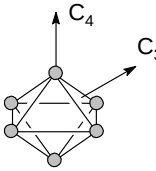
Icosahedral Group, I_h – rare
The platonic solid with 20 triangular faces



e.g. $B_{12}H_{12}^{2-}$

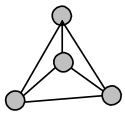
common symmetry for viruses (human rhinovirus, polio virus, T-3 viruses)

Two of the most common



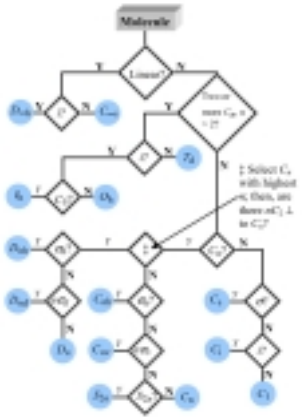
Octahedral Group, O_h – common
e.g. most MX_6 species
Lots of symmetry

Tetrahedral, T_d
Most non-transitional AX_4 species.

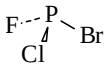


But…for
Intermediate Symmetries
(Flow Chart)

To determine the point group of a molecule

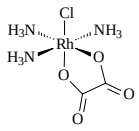


Low Symmetry (no C_n) C_1 : only E

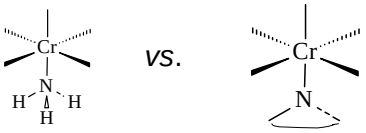


C_s: E and σ only

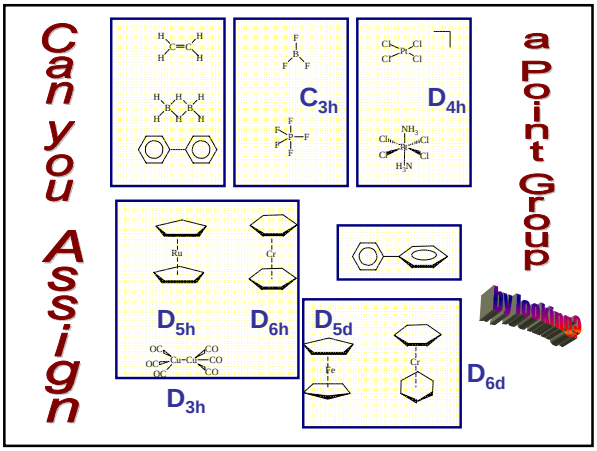
CHFICl

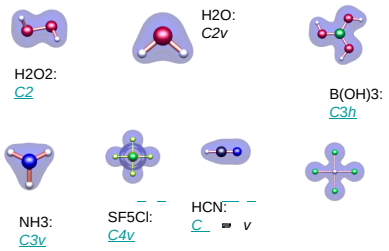


The C_4 vs. C_3 paradox? – $[Cr(NH_3)_6]^{3+}$



$[Fe(OH_2)_6]^{2+}$, $Si(CH_3)_4$, $Pb(C_2H_5)_4$





...and the purpose of this is.....?

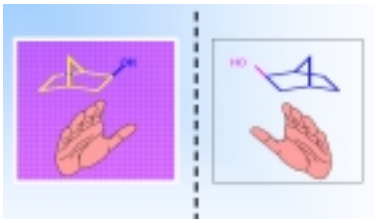
Here's two examples

Chirality

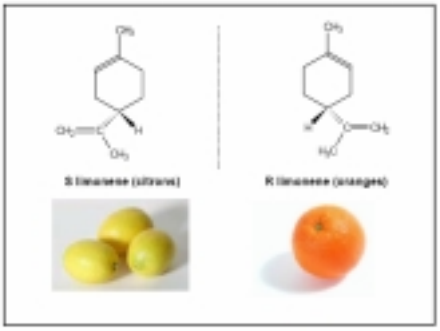
Dipole Moments

Raman Spectroscopy

Chirality



No Mirror Planes or Mirror Centers



Symmetry and Dipole Moments

Permanent Dipoles: Never have an inversion center (i) or a S_n

Molecules which belong to: Ci, Sn, Dn, Cnh, Dnh, Dnd, Td, Oh, Ih, Dinfh NEVER Have permanet dipoles.

Only those molecules which belong to C1, Cn, Cs, Cn, Cnv can have a permanent dipole moment.

C_{2v}

Character Table

Point group

Symmetry operations

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

Mülliken symbols

Characters
+1 symmetric behavior
-1 antisymmetric

Each row is an irreducible representation

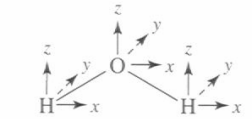
Naming of Irreducible representations

- One dimensional (non degenerate) representations are designated A or B.
- Two-dimensional (doubly degenerate) are designated E.
- Three-dimensional (triply degenerate) are designated T.
- Any 1-D representation symmetric with respect to C_n is designated *A;* antisymmétric ones are designated *B*
- Subscripts 1 or 2 (applied to A or B refer) to symmetric and antisymmetric representations with respect to $C_2 \perp C_n$ or (if no C_2) to $\perp \sigma_v$ respectively
- Superscripts ‘ and ‘‘ indicate symmetric and antisymmetric operations with respect to σ_h, respectively
- In groups having a center of inversion, subscripts *g* (gerade) and *u* (ungerade) indicate symmetric and antisymmetric representations with respect to *i*

Character Tables

- Irreducible representations are the generalized analogues of σ or π symmetry in diatomic molecules.
- Characters in rows designated *A, B*,..., and in columns other than *E* indicate the behavior of an orbital or group of orbitals under the corresponding operations (+1 = orbital does not change; -1 = orbital changes sign; anything else = more complex change)
- Characters in the column of operation *E* indicate the degeneracy of orbitals
- Symmetry classes are represented by CAPITAL LETTERS (*A, B, E, T*,...) whereas *orbitals* are represented in lowercase (*a, b, e, t*,...)
- The identity of orbitals which a row represents is found at the extreme right of the row
- Pairs in brackets refer to groups of degenerate orbitals and, in those cases, the characters refer to the properties of the set

Let's use character tables!
Symmetry and molecular vibrations



# of atoms	degrees of freedom	Translational modes	Rotational modes	Vibrational modes
N (linear)	3 x 2	3	2	3N-5 = 1
Example 3 (HCN)	9	3	2	4
N (non-linear)	3N	3	3	3N-6
Example 3 (H_2O)	9	3	3	3

Symmetry and molecular vibrations

A molecular vibration is IR active
only if it results in a change in the dipole moment of the molecule

A molecular vibration is Raman active
only if it results in a change in the polarizability of the molecule

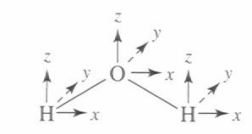
In group theory terms:

A vibrational motion is IR active if it corresponds to an irreducible representation with the same symmetry as an *x, y, z* coordinate (or function)

and it is Raman active if the symmetry is the same as
x^2, y^2, z^2, or one of the rotational functions R_x, R_y, R_z

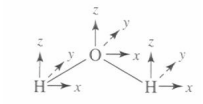
How many vibrational modes belong to each irreducible representation?

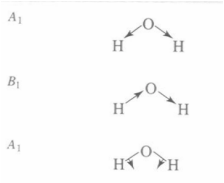
You need the molecular geometry (point group) and the character table



Symmetry of molecular movements of water

All Motions	*Translation* (x, y, z)	*Rotation* (R_x, R_y, R_z)	*Vibration (Remaining Modes)*
$3A_1$	A_1		$2A_1$
A_2		A_2	
$3B_1$	B_1	B_1	B_1
$2B_2$	B_2	B_2	





Vibrational modes

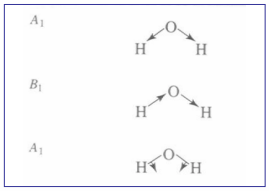
If the symmetry label of a normal mode corresponds to x, y, or z, then the fundamental transition for this normal mode will be IR active.

If the symmetry label of a normal mode corresponds to products of x, y, or z (such as x^2 or yz) then the fundamental transition for this normal mode will be Raman active.

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, Ry	xz	IR	Raman
B_2	1	-1	-1	1	y, Rx	yz	IR	Raman

Water has three normal modes: two of A_1 symmetry and one of B_2 symmetry. All of these are IR and Raman active. We would expect water to have three peaks corresponding to fundamental vibrations in the IR spectrum. There also would be three peaks in its Raman spectrum at the same frequencies as in the IR.

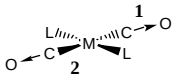
Which of these vibrations having A_1 and B_1 symmetry are IR or Raman active?



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

Raman active *IR active*

What about the trans isomer?



D_{2h}	E	C_2(z)	C_2(y)	C_2(x)	i	σ_v(xy)	σ_v(xz)	σ_v(yz)	
A_g	1	1	1	1	1	1	1	1	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x
Γ	2	0	0	2	0	2	2	0	

Only one IR active band and no Raman active bands

Remember cis isomer had two IR active bands and one Raman active