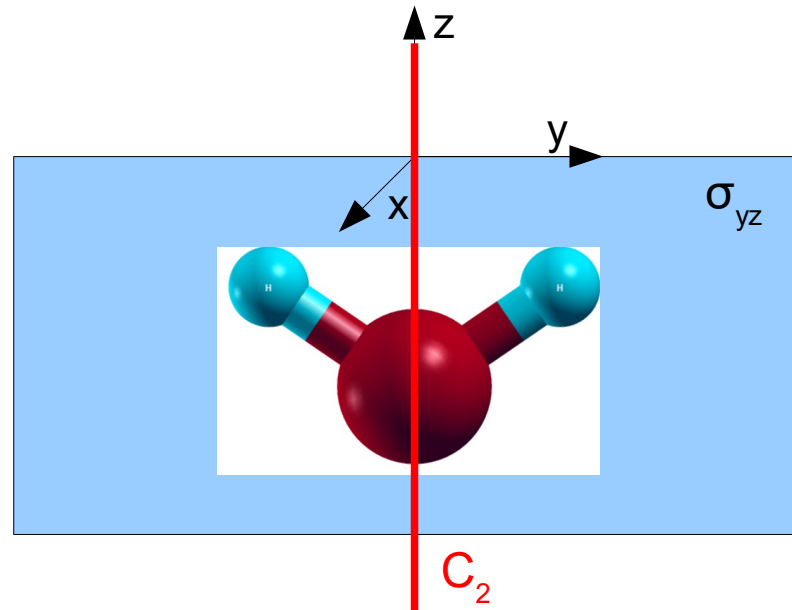


Group Theory applied to Molecules



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Topics you hopefully already know

- Matrix properties and operations
- Formal aspects of group theory:
 - groups, order of groups,
 - characters,
 - reducible and irreducible representations,
 - orthogonality theorem
- Basic quantum mechanics (H-atom, s-, p-, d-orbitals)
- Vibrations (normal modes)
- Whatever else I forgot to mention
- ...

If you have any questions please ask!

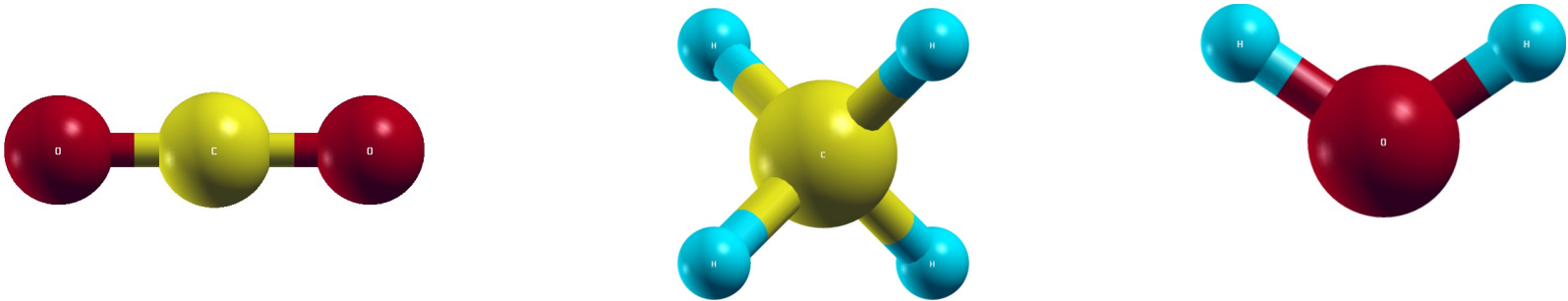
Wherrett, Brian S.: “Group theory for atoms, molecules and solids”
Englewood Cliffs NJ : Prentice-Hall Internat., 1986

Yu, P.Y., Cardona, M. “Fundamentals of Semiconductors” Springer:
Chapter “A Pedestrian’s Guide to Group Theory”

Character tables: <http://symmetry.jacobs-university.de/>

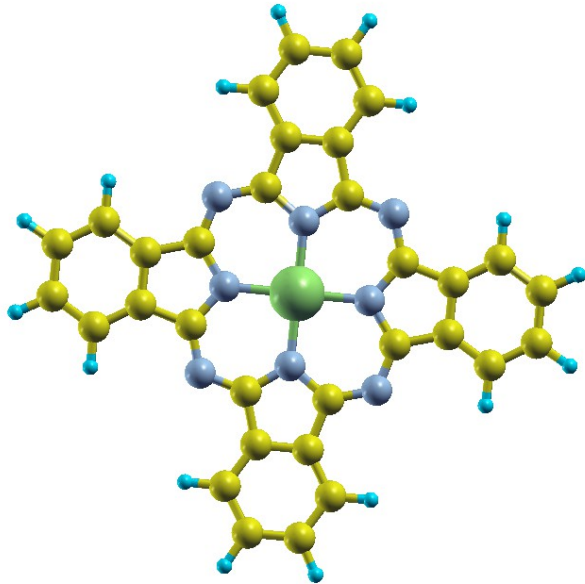
Motivation

- Molecules may have symmetries described by point groups, which leave the molecule invariant under these operations.
- The symmetries can be represented by matrices.
→ representation theory
- The functions describing the physical properties must show corresponding behavior under the symmetry operation of the molecule.
 - electronic wavefunctions
 - normal vibrational modes
 - dipole moments
 - whatever ...

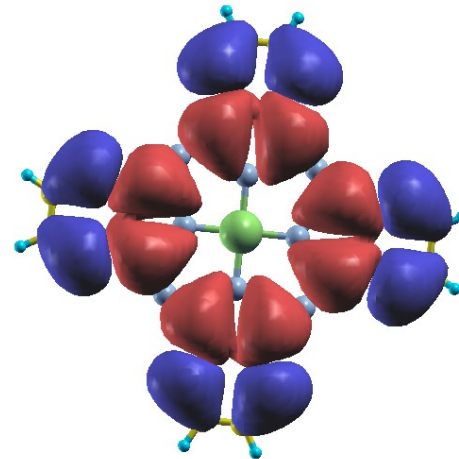


No dipole moment for molecules with inversion.

Symmetry of molecule determines symmetry of electronic wavefunctions



There exist a whole family of phthalocyanine with different metal atoms (Cu, Co, Ni, Fe, Zn ...).



The HOMO for CoPc involves ligand states. The molecule has spin $\frac{1}{2}$.

Schönflies notation

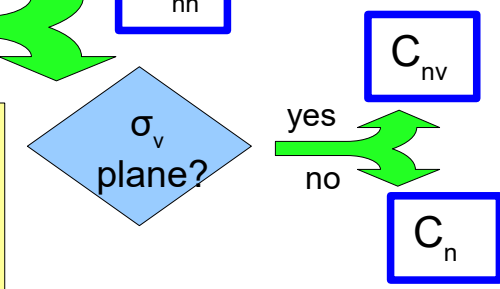
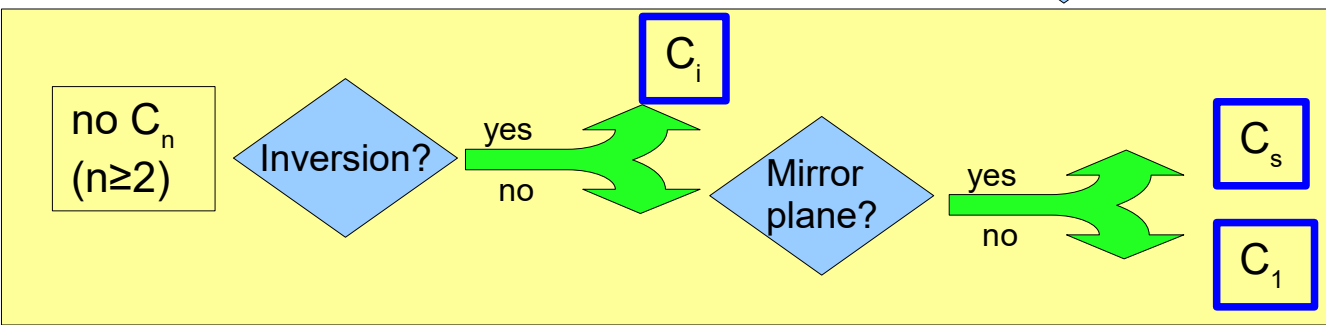
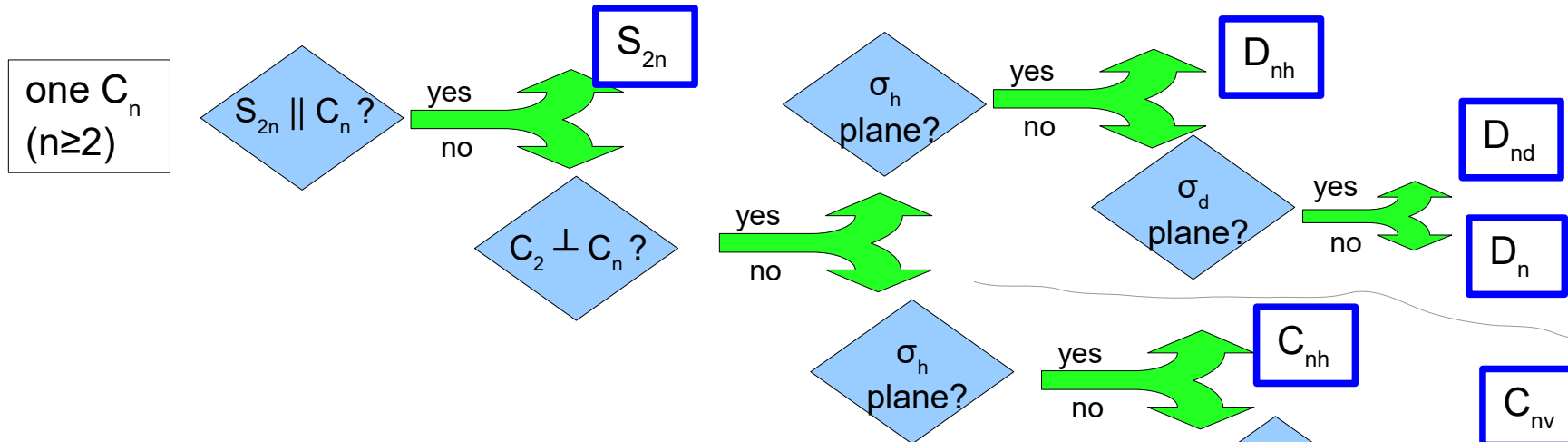
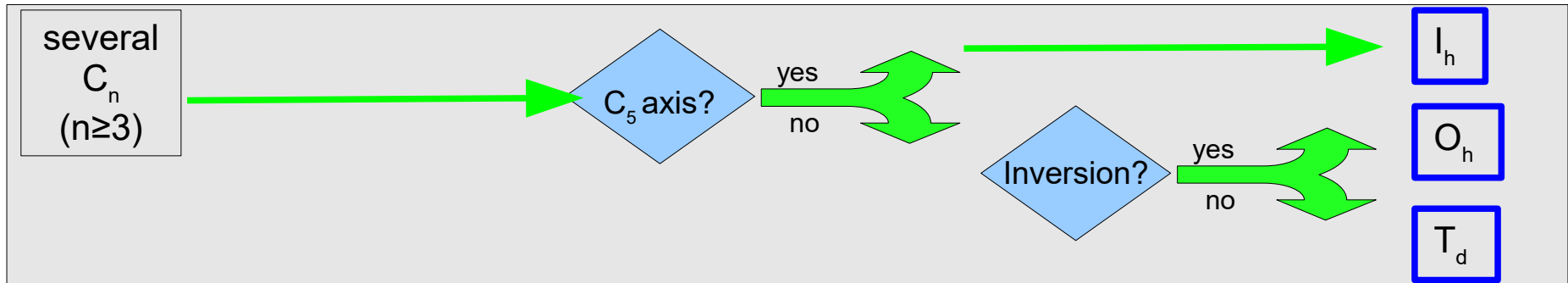
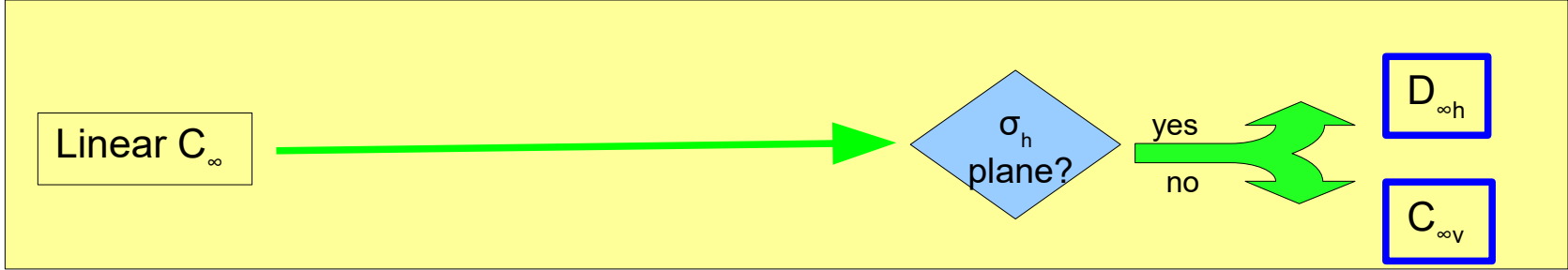
- E: identity
I: inversion
 σ : reflection
 σ_v plane is parallel to principal axis
 σ_h plane is perpendicular to principal axis
- C_n : clockwise rotation around an axis by $2\pi/n$ (n-fold axis)
For molecules with more than one symmetry axis, the axis with the largest n is called the principal axis.
- S_n : rotation C_n followed by a reflection through a plane perpendicular to the rotation axis (improper rotation)

Definitions:

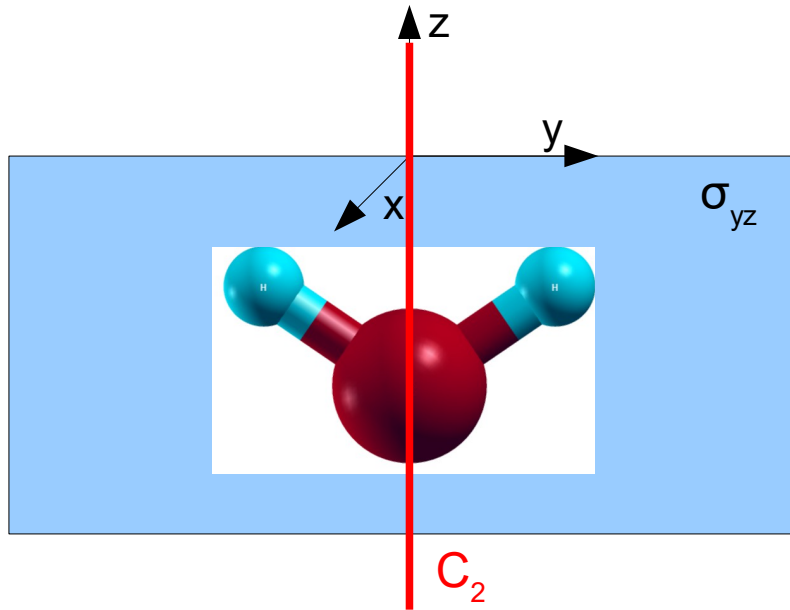
Order: total number of symmetry operations in a group

Class: subset of symmetry operations that transform into each other
e.g. any C_n axis will have a subgroup of order n

Character: trace = sum of diagonal elements in a matrix



Symmetry group: C_{2v} (water)



Symmetry elements:

E: identity

C_2 : rotation by π

σ_{yz} : mirror plane (yz)

σ_{xz} : mirror plane (xz)

Multiplication table C_{2v} :

C_{2v}	E	C_2	σ_{yz}	σ_{xz}
E	E	C_2	σ_{yz}	σ_{xz}
C_2	C_2	E	σ_{xz}	σ_{yz}
σ_{yz}	σ_{yz}	σ_{xz}	E	C_2
σ_{xz}	σ_{xz}	σ_{yz}	C_2	E

C_{2v} (water): Identity E as 9x9 matrix

$$E \circ H_2O = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x(H1) \\ y(H1) \\ z(H1) \\ x(O) \\ y(O) \\ z(O) \\ x(H2) \\ y(H2) \\ z(H2) \end{pmatrix} = \begin{pmatrix} x(H1) \\ y(H1) \\ z(H1) \\ x(O) \\ y(O) \\ z(O) \\ x(H2) \\ y(H2) \\ z(H2) \end{pmatrix}$$

$$\chi(E) = 9$$

C_{2v} (water): Rotation C_2 as 9x9 matrix

$$C_2 \circ H_2O = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x(H1) \\ y(H1) \\ z(H1) \\ x(O) \\ y(O) \\ z(O) \\ x(H2) \\ y(H2) \\ z(H2) \end{pmatrix} = \begin{pmatrix} -x(H2) \\ -y(H2) \\ z(H1) \\ -x(O) \\ -y(O) \\ z(O) \\ -x(H1) \\ -y(H1) \\ z(H2) \end{pmatrix}$$

$$\chi(C_2) = -1$$

C_{2v} (water): mirror plane xz as 9x9 matrix

$$\sigma_{xz} \circ H_2 O = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x(H1) \\ y(H1) \\ z(H1) \\ x(O) \\ y(O) \\ z(O) \\ x(H2) \\ y(H2) \\ z(H2) \end{pmatrix} = \begin{pmatrix} x(H2) \\ -y(H2) \\ z(H1) \\ x(O) \\ -y(O) \\ z(O) \\ x(H1) \\ -y(H1) \\ z(H2) \end{pmatrix}$$

$$\chi(\sigma_{xz}) = 1$$

C_{2v} (water): mirror plane yz as 9×9 matrix

$$\sigma_{yz} \circ H_2O = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x(H1) \\ y(H1) \\ z(H1) \\ x(O) \\ y(O) \\ z(O) \\ x(H2) \\ y(H2) \\ z(H2) \end{pmatrix} = \begin{pmatrix} -x(H2) \\ y(H2) \\ z(H1) \\ -x(O) \\ y(O) \\ z(O) \\ -x(H1) \\ y(H1) \\ z(H2) \end{pmatrix}$$

$$\chi(\sigma_{yz}) = 1$$

C_{2v} (water): reducible representation as 9x9 matrix

These four 9×9 matrices reproduce our multiplication table (**check as homework**). They form a reducible representation of the group C_{2v} .

Is this representation unique? No!

The following set of four 3x3 matrices will also reproduce our multiplication table (**check as homework**):

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{xz} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{yz} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

They are also a representation of point group C_{2v} .

$$\Gamma(C_{2v}) = \{E, C_2, \sigma_{xz}, \sigma_{yz}\}$$

C_{2v} (water): irreducible representations

Can we even find simpler representations? Note that z is not changing, therefore we can break the 3×3 matrices in 2×2 and 1×1 blocks further. We get two representations (Γ_z and Γ_A) both reproducing our multiplication table:

$$\Gamma_z(C_{2v}) = \{(1), (1), (1), (1)\}$$

$$\Gamma_A(C_{2v}) = \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \right\}$$

Γ_z can not be reduced any further, it is an **irreducible representation** of C_{2v} .

However Γ_A can be reduced into two 1×1 representations according to x and y .

$$\Gamma_x(C_{2v}) = \{(1), (-1), (1), (-1)\}$$

$$\Gamma_y(C_{2v}) = \{(1), (-1), (-1), (1)\}$$

C_{2v} : character table

There is still one irreducible representation missing.

$$\Gamma_{A_2}(C_{2v}) = \{(1), (1), (-1), (-1)\}$$

The point group C_{2v} has four irreducible representations resulting in the following **character table**

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	generators
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

Mulliken symbols = symmetry labels: A, B: 1D e: 2D t: 3D

A: 1D symmetric with respect to principal axis (C_2)

B: 1D anti-symmetric with respect to principal axis (C_2)

Reducing a reducible representation

$$a_i = \frac{1}{h} \sum_R \chi_\Gamma(R) * \chi_{\Gamma_i}(R) N_R$$

a_i = the number of times the irreducible representation is in the reducible representation

h = order of group, N_R = number of elements in class

R = symmetry operation (sum of all symmetry operations)

χ_Γ = character of reducible representation

χ_{Γ_i} = character of irreducible representation (from character table)

For example our 3x3 matrices can be reduced:

$$\Gamma(C_{2v}) = \{E, C_2, \sigma_{xz}, \sigma_{yz}\} \quad \chi_\Gamma = \{3, -1, 1, 1\}$$

$$A1: \frac{1}{4} (3 \cdot 1 + (-1) \cdot 1 + 1 \cdot 1 + 1 \cdot 1) = 1$$

$$A2: \frac{1}{4} (3 \cdot 1 + (-1) \cdot 1 + 1 \cdot (-1) + 1 \cdot (-1)) = 0$$

$$B1: \frac{1}{4} (3 \cdot 1 + (-1) \cdot (-1) + 1 \cdot 1 + 1 \cdot (-1)) = 1$$



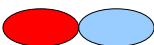

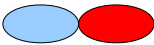
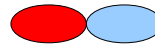
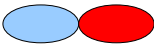
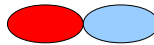
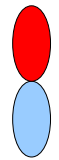
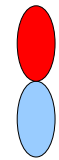
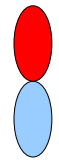
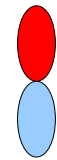
$$B2: \frac{1}{4} (3 \cdot 1 + (-1) \cdot (-1) + 1 \cdot (-1) + 1 \cdot 1) = 1$$

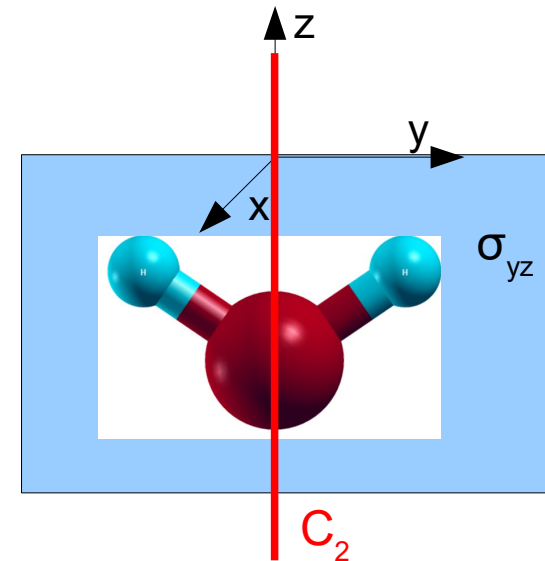
$$\Rightarrow \Gamma = A1 + B1 + B2$$

C_{2v} (water): oxygen orbitals

The relevant oxygen orbitals are $2s$, $2p_x$, $2p_y$ and $2p_z$.

$2s$ is spherically symmetric and does not change under any of the symmetry operations (A1). Note, that the $2p$ -orbitals have a phase.

	E	C2	σ_{xz}	σ_{yz}	
$2p_y$					= B2
	1	-1	-1	1	
$2p_x$					= B1
	1	-1	1	-1	
$2p_z$					= A1
	1	1	1	1	



C_{2v} (water): overlap integrals

Overlap integral: $\langle \phi | \psi \rangle = \int dV \phi * \psi$

Any nonzero integral must contain the totally symmetric representation A.

- 1) apply symmetry operations to each orbital, ϕ , ψ
- 2) multiply characters of the orbitals
- 3) find irreducible representation
- 4) if the irreducible representation does not contain a totally symmetric representation, then the integral will be zero otherwise we have to calculate the integral.

Overlap integral of $|1s\rangle$ and $|2p_z\rangle$ orbital in a C_{2v} molecule: possibly nonzero

$$\Gamma(1s) = 1 \ 1 \ 1 \ 1 = A1$$

$$\Gamma(2p_z) = 1 \ 1 \ 1 \ 1 = A1$$

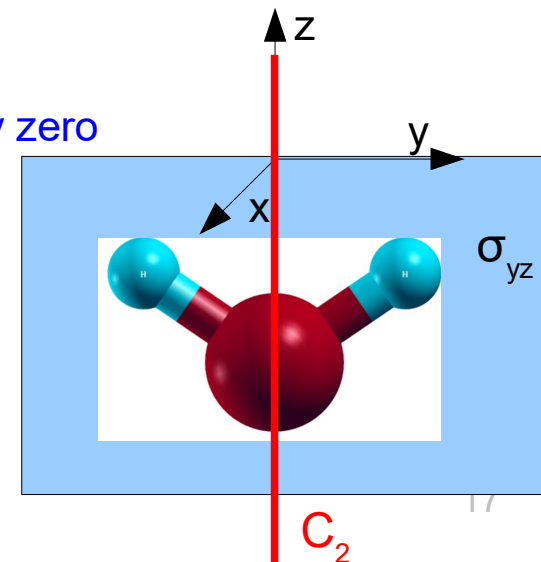
$$\Gamma(1s) * \Gamma(2p_z) = 1 \ 1 \ 1 \ 1 = A1$$

Overlap integral of $|1s\rangle$ and $|2p_x\rangle$ orbital in a C_{2v} molecule: definitely zero

$$\Gamma(1s) = 1 \ 1 \ 1 \ 1 = A1$$

$$\Gamma(2p_x) = 1 \ -1 \ 1 \ -1 = B1$$

$$\Gamma(1s) * \Gamma(2p_x) = 1 \ -1 \ 1 \ -1 = B1$$



C_{2v} (water): dipole matrix elements

Dipole matrix element:
$$\vec{p} = \langle \phi | e \vec{r} | \psi \rangle = e \int dV \phi^* \vec{r} \psi$$

- 1) find symmetry of each orbital, ϕ , ψ
- 2) character of the components of the dipole operator (character of x , y , z),
- 3) multiply characters of the orbitals and character of component of dipole operator
- 4) find irreducible representation
- 5) if the irreducible representation does contain the totally symmetric representation (A_1), then the dipole transition will be allowed between these states

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

$$\langle A_1 | x | A_1 \rangle = 0 \text{ forbidden}$$

$$\langle A_1 | z | A_1 \rangle \neq 0 \text{ allowed}$$

$$\langle A_1 | y | B_2 \rangle \neq 0 \text{ allowed}$$

$$\langle A_2 | x | B_2 \rangle \neq 0 \text{ allowed}$$

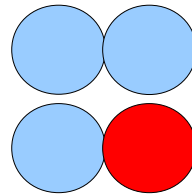
This can be generalized to any operator C , where one can ask for which symmetry of the operator a transition will be allowed.

Molecular orbitals: LCAO

Molecular orbitals can be formed from linear combinations of atomic orbitals (LCAO). For example the two H-atoms in H₂O provide each a 1s-orbital giving two possible LCAO.

$$\Phi_+ = c_1 \psi_{1s}^{H1} + c_2 \psi_{1s}^{H2}$$

$$\Phi_- = c_1 \psi_{1s}^{H1} - c_2 \psi_{1s}^{H2}$$



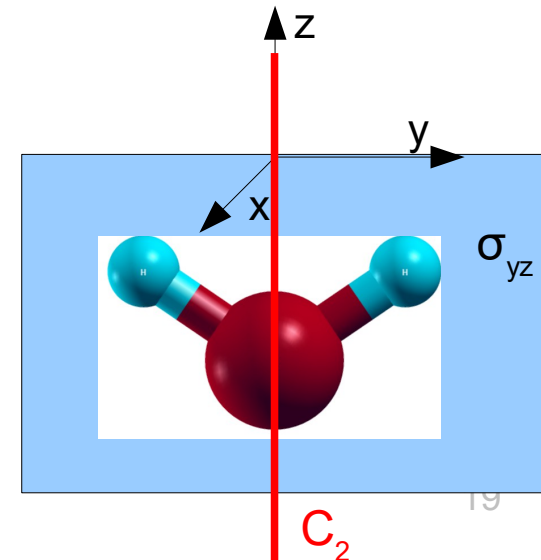
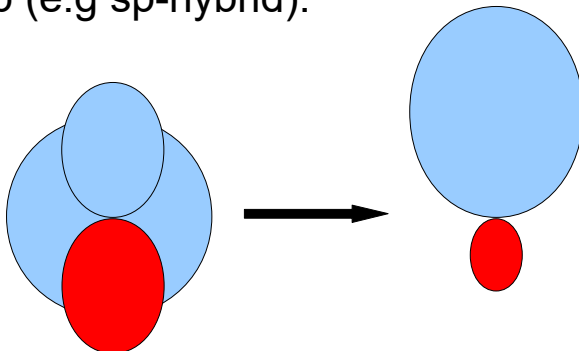
A1

B2

Together with the oxygen orbitals H₂O has 3 A₁ (2s, 2p_z, Φ₊), 2 B₂ (2p_y, Φ₊) and 1 B₁ (2p_x) molecular orbitals, which can be filled with 2 electrons (Pauli principle) starting from lowest one. Using only symmetry adapted linear combinations (SALC) the lowest bonding MO would be:

$$MO = c_1 \psi_{2s}^O + c_2 \psi_{2p_z}^O + c_3 \Phi_+$$

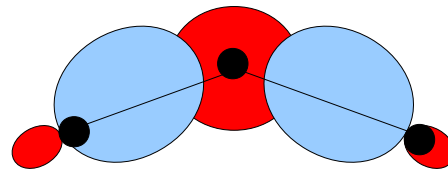
The MO correspond to a delocalized view of the orbitals and are used to construct hybrid orbitals due to constructive/destructive overlap (e.g sp-hybrid).



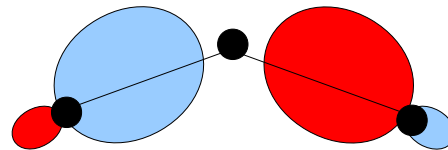
MO for systems with central atom (AB_n)

- start from symmetry of molecule AB_n
- find symmetry of relevant orbitals of central atom (A) and the SALC for B_n
- Molecular orbitals are constructed from orbitals of same symmetry
- depending on overlap of the orbitals and energies the resulting MO can be classified as **bonding, nonbonding, or antibonding orbitals**

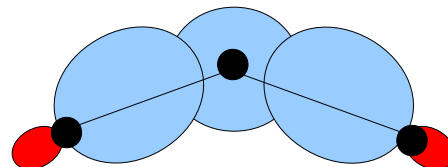
Antibonding



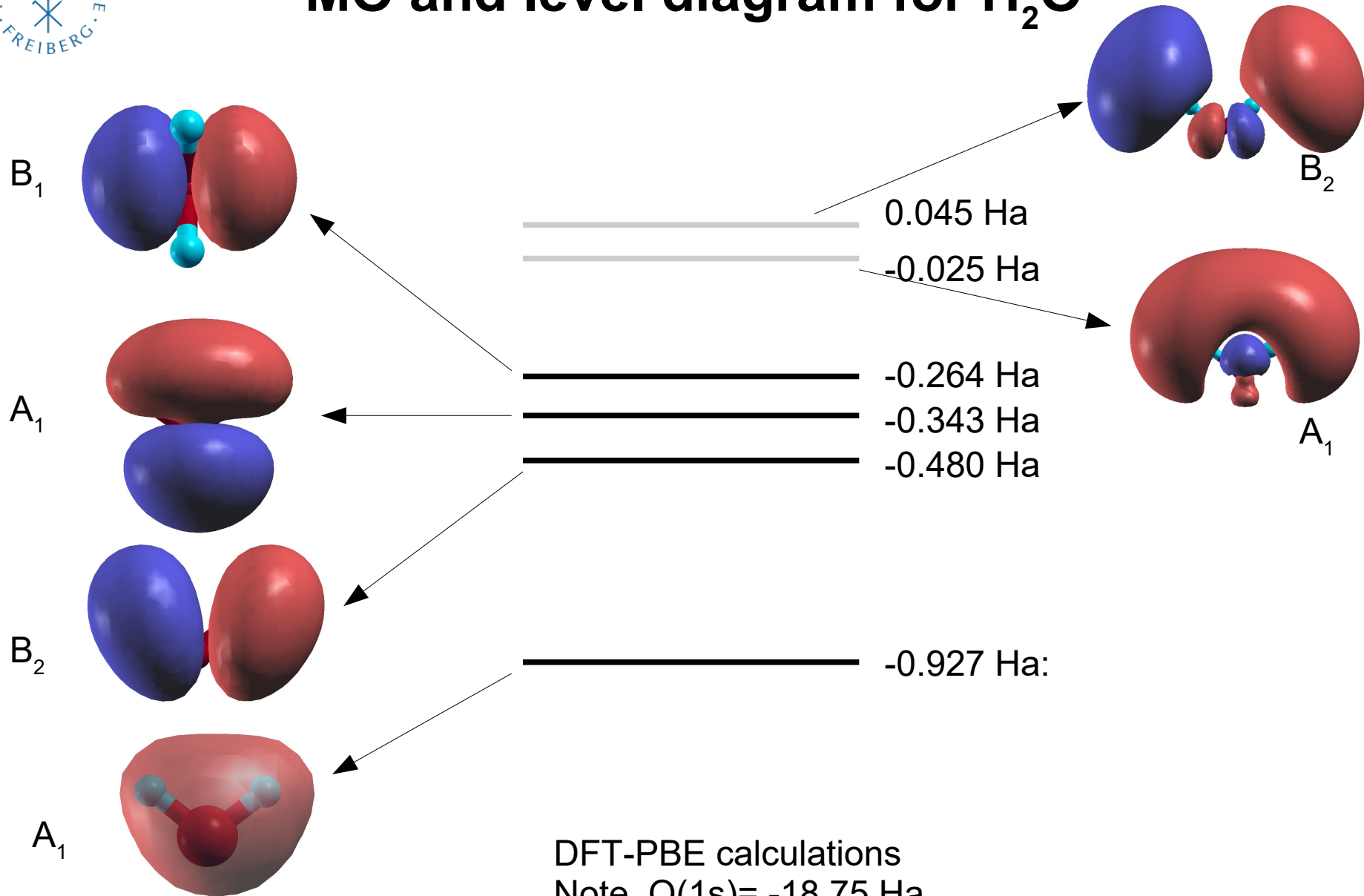
Non-bonding



Bonding



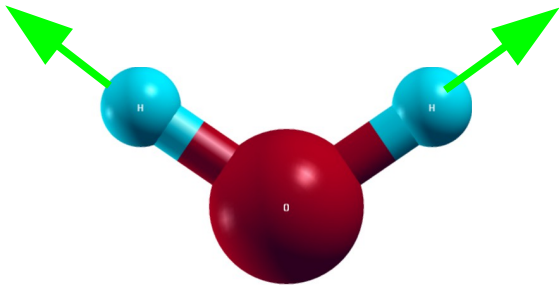
MO and level diagram for H₂O



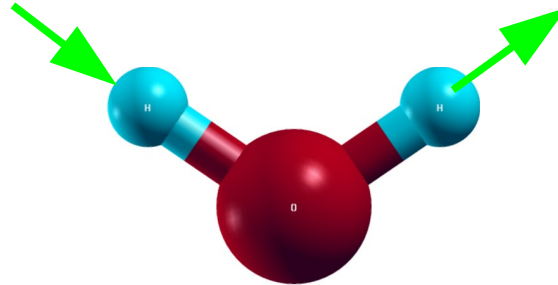
C_{2v} (water): vibrational modes

Any non-linear molecule has $3N-6$ vibrational modes. In case of H_2O we expect therefore only 3 vibrational modes.

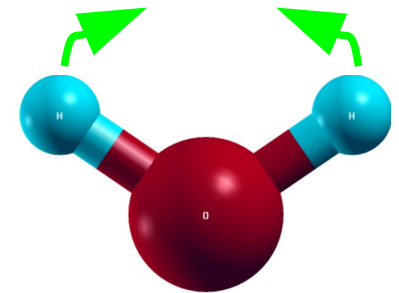
The displacement vectors of the normal modes will transform according to the irreducible representations.



Symmetric stretch (ν_1)



anti-symmetric stretch (ν_2)



bending (ν_3)

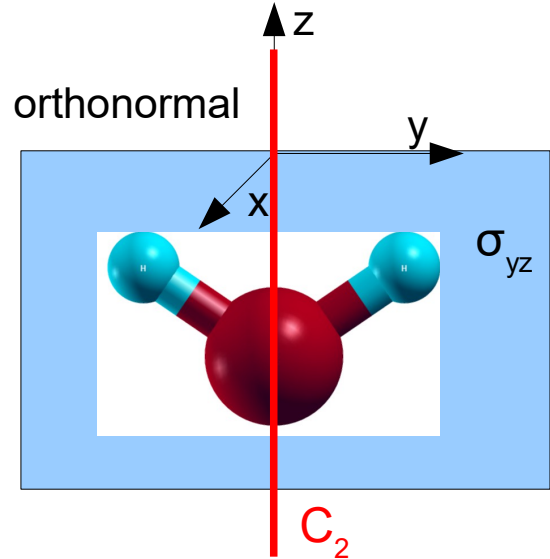
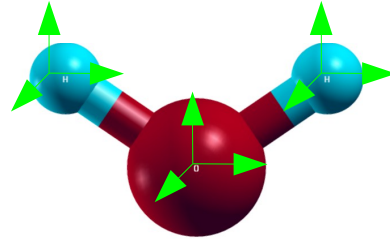
C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
ν_1	1	1	1	1	
ν_2	1	-1	-1	1	
ν_3	1	1	1	1	

$$\Gamma_{\text{vib}} = 2A_1 + B_2$$

C_{2v} (water): normal modes

The displacement of the atoms can be described by vectors in an orthonormal coordinate system attached to each atom of the molecule.



We need the transformation behavior under the symmetry operations of the molecule.

E:	$(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3) \rightarrow (x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3)$	$\chi(E) = 9$
C_2 :	$(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3) \rightarrow (x_3, y_3, z_3, -x_2, -y_2, z_2, x_1, y_1, z_1)$	$\chi(C_2) = -1$
σ_{xz} :	$(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3) \rightarrow (x_3, -y_3, z_3, x_2, -y_2, z_2, x_1, -y_1, z_1)$	$\chi(\sigma_{xz}) = 1$
σ_{yz} :	$(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3) \rightarrow (-x_1, y_1, z_1, -x_2, y_2, z_2, -x_3, y_3, z_3)$	$\chi(\sigma_{yz}) = 3$

The reducible representation for vibrations is then $\Gamma_{3N} = \{9, -1, 1, 3\}$.

C_{2v} (water): normal modes

With help of the reduction formula we find the irreducible representation in $\Gamma_{3N} = \{9, -1, 1, 3\}$.

$$a_i = \frac{1}{h} \sum_R \chi_{\Gamma}(R) * \chi_{\Gamma_i}(R) N_R$$

$$A_1: \frac{1}{4} (9 \cdot 1 + (-1) \cdot 1 + 1 \cdot 1 + 3 \cdot 1) = 3$$

$$A_2: \frac{1}{4} (9 \cdot 1 + (-1) \cdot 1 + 1 \cdot (-1) + 3 \cdot (-1)) = 1$$

$$B_1: \frac{1}{4} (9 \cdot 1 + (-1) \cdot (-1) + 1 \cdot 1 + 3 \cdot (-1)) = 2$$

$$B_2: \frac{1}{4} (9 \cdot 1 + (-1) \cdot (-1) + 1 \cdot (-1) + 3 \cdot 1) = 3$$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy, Rz
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

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

Γ_{3N} contains translational, rotational and vibrational degrees of freedom.

The translations correspond to irreducible representations x, y and z (A_1, B_1, B_2)

The rotations are given by rotation around the axes R_x , R_y and R_z .

$$\Gamma_{\text{vib}}(\text{H}_2\text{O}) = (3A_1 + A_2 + 2B_1 + 3B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2) = 2A_1 + B_2$$

C_{2v} (water): IR and Raman activity

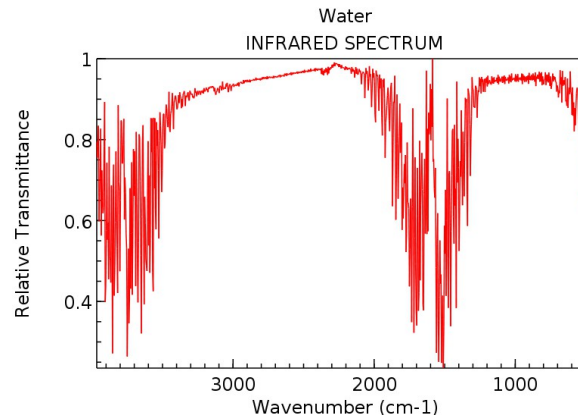
If Γ_{vib} contains irreducible representations corresponding to x, y, and z (dipole matrix element) then the mode will be IR active.

For H_2O the modes A_1 and B_2 are IR active since Γ_{vib} contains $2A_1 + B_2$.

Raman activity is proportional to a change of the polarizability. Raman active modes must contain irreducible representations corresponding to z^2 , x^2-y^2 , xy , xz or yz in Γ_{vib} .

For H_2O , z^2 and x^2-y^2 transform as A_1 , xy as A_2 , xz as B_1 and yz as B_2 , therefore the modes A_1 and B_2 maybe also Raman active.

The IR spectrum of H_2O shows three bands. The two stretch modes ν_1 and ν_2 occur at 3756 and 3657 cm^{-1} whereas the bending ν_3 mode occurs at 1595 cm^{-1} . (NIST reference gas phase data)



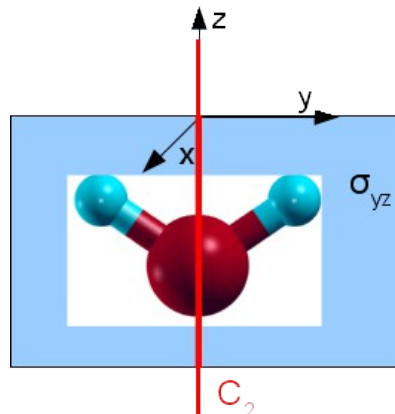
Summary

Group theory is a very powerful tool to investigate vibrational or electronic properties of molecular systems!

Electronic or vibronic wavefunctions can be classified using irreducible representations. The symmetry then decides on possible interactions which will result in splittings of levels or transition matrix elements.

Group theory is therefore often used to understand:

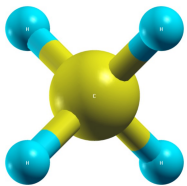
- vibrational IR and Raman spectra (normal modes, selection rules)
- electronic wavefunctions (MO levels, LCAO method, Hückel-theory, π -electron approximation, Valence Shell Electron Pair Repulsion Theory = VSEPR, ...)



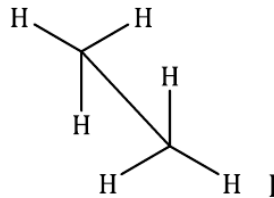


1) Find the point group of the following molecules and list the symmetry elements of the group.

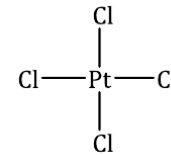
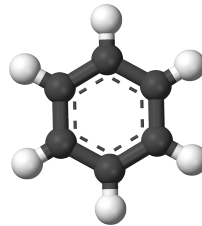
Methene



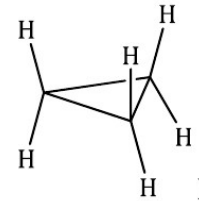
Ethane (staggered)



Benzene



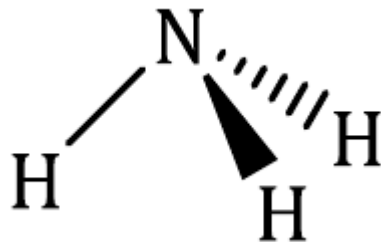
Cyclopropane



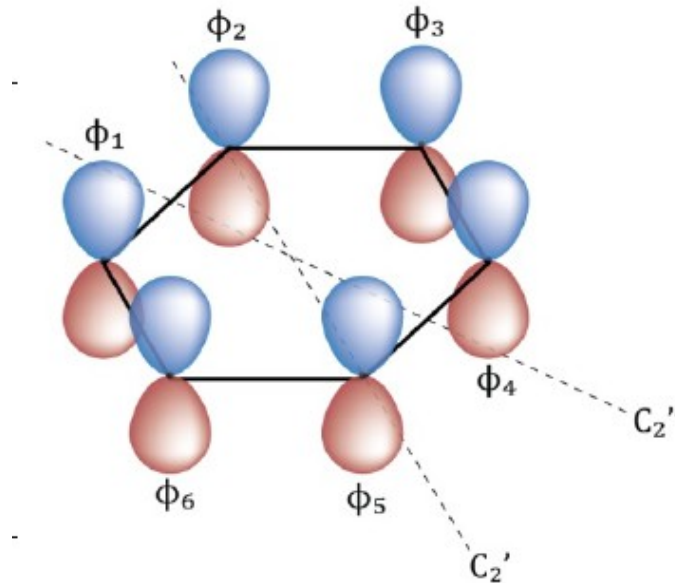
2) If a molecule has an improper rotation (S_n), then it is optically inactive.

Which of the following molecules may have a dipole moment or is optically inactive?
 Methene, benzene, ethane, CO_2 , H_2O , NH_3 , PtCl_4

3) Find the normal modes of ammonia NH_3 and discuss IR/Raman activity of the modes!

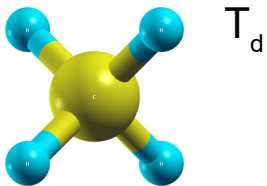


4) Use the subgroup D_6 and sketch possible molecular orbitals for benzene considering only p_z -orbitals! (Construction of benzene π -states)

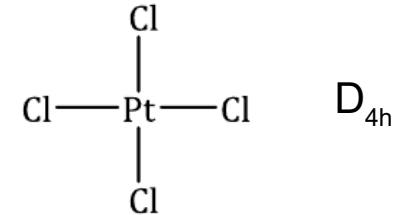
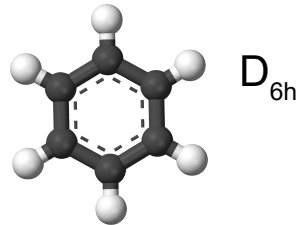


1) Find the point group of the following molecules and list the symmetry elements of the group.

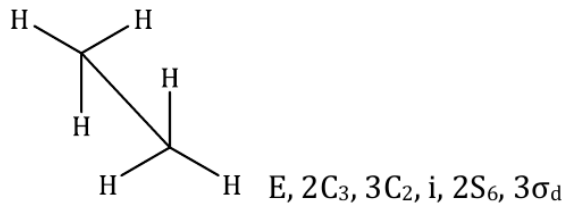
Methene



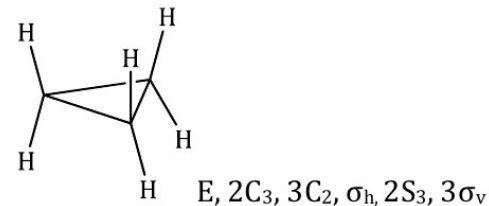
Benzene



Ethane (staggered) - D_{3d}



Cyclopropane - D_{3h}



2) If a molecule has an improper rotation (S_n), then it is optically inactive.

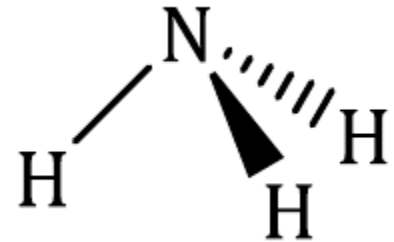
Which of the following molecules may have a dipole moment or is optically active?

Methene, benzene, ethane, CO_2 , H_2O , NH_3 , $PtCl_4$

Dipole: H_2O , NH_3

3) Find the normal modes of ammonia NH_3 and discuss IR/Raman activity of the modes!

C_{3v}	E	$2 C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ^{3N}	12	0	2



$$\Gamma_{\text{vib}}(\text{H}_2\text{O}) = (3A_1 + A_2 + 4E) - (A_1 + E) - (A_2 + E) = 2A_1 + 2E$$

Modes are IR and Raman active.

- i) Add 1 to the character if the basis function is unchanged by the symmetry operation
- ii) Add -1 to the character if the basis function changes sign under the symmetry operation;
- iii) Add 0 to the character if the basis function moves when the symmetry operation is applied.

Using a character table:

The character for the $3N$ Cartesian basis is simply the sum of the characters for the x , y and z functions listed in the character table.

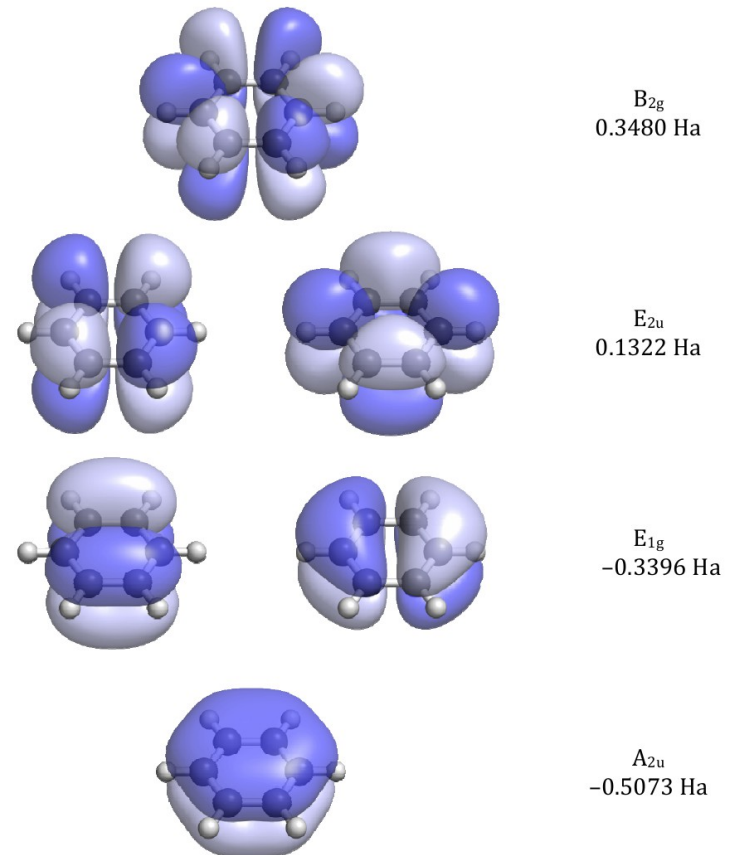
Just multiply this by the number of atoms in the molecule that are not changed by the symmetry operation.

(x,y) transforms like E and z transforms like A1:

E	C3	σ	
3	0	1	sum of characters x,y,z
4	1	2	atoms unchanged by symmetry operation
12	0	2	product of above lines

4) Use the subgroup D_6 and sketch the possible molecular orbitals for benzene considering only p_z -orbitals! (Construction of benzene π -states)

D_6	E	$2 C_6$	$2 C_3$	C_2	$3 C_2'$	$3 C_2''$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0



4) Use the subgroup D_6 and sketch the possible molecular orbitals for benzene considering only p_z -orbitals! (Construction of benzene π -states)

D_6	E	$2 C_6$	$2 C_3$	C_2	$3 C_2'$	$3 C_2''$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0

