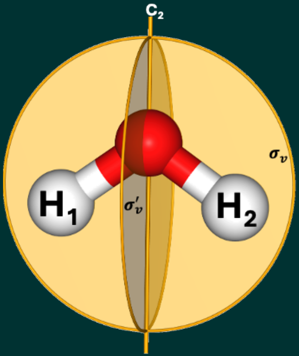

Molecular Symmetry

Prof. Adlane SAYEDE

Université d'Artois

adlane.sayede@univ-artois.fr

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Introduction to Symmetry in Chemistry

- Symmetry and its underlying mathematical theory play a crucial role in chemistry, as they allow us to solve many chemical problems.
- For example, they facilitate the classification of molecular and crystalline structures, the analysis of chemical bonding, the prediction of vibrational spectra, and the determination of the optical activity of compounds.
- We will explore the fundamental principles of molecular symmetry.

Definition of Symmetry

Larousse Dictionary

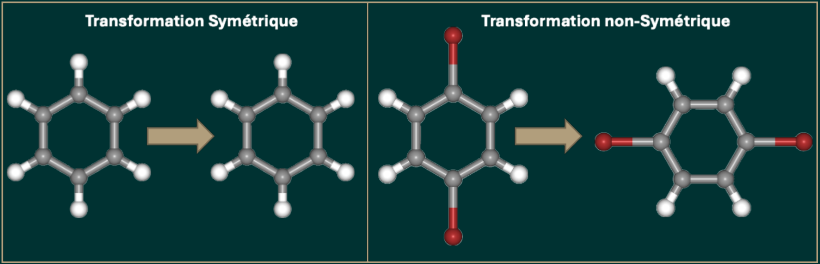
1. Correspondence in position of two or more elements with respect to a point or a median plane.
2. Harmonious aspect resulting from the regular, balanced arrangement of the elements of a set.
3. Repetition of organs or segments or parts of the body with respect to a line or plane.
4. Affine transformation that, to a point M, associates a point M', such that the midpoint of [MM'] is either a fixed point (central symmetry), or a point of a line or a plane H1, (MM') then being parallel to a line or a plane H2 intersecting H1.
5. Invariance of a figure under an orthogonal symmetry.

Definition of Symmetry

- A common definition is that symmetry is the self-similarity of an object. The more similar parts an object possesses, the more symmetric it is perceived.
- Take the example of a butterfly: if its two wings are identical, we consider it symmetric. Conversely, if the left wing differs significantly from the right, the butterfly loses symmetry.

Definition of Symmetry

- A geometric object possesses symmetry if, after undergoing a transformation, it remains indistinguishable from its initial form.



- We say that the object is invariant under certain operations if it is not altered by these transformations.

Symmetry Operation and Element

- To determine if an object possesses symmetry, it is necessary to apply various geometric transformations.
- Symmetry operations are performed with respect to what is called symmetry elements.
- A symmetry element can be a point, a line, or a plane about or through which a symmetry transformation is applied.

Symmetry Operation and Element

The symmetry element is the reference point or structure about which the symmetry operation is performed. The symmetry operation is the action or transformation that leaves the object unchanged.

Four Symmetry Elements

1. Center of inversion.
2. Axis of rotation.
3. Reflection plane.
4. Improper rotation.

Symmetry Operations

Symmetry Operations

1. Identity operation, denoted (E).
2. Inversion through a center of inversion, denoted (i).
3. Rotation of $(\frac{2\pi}{n})$ around a symmetry axis of order n, denoted C_n.
4. Reflection in a symmetry plane, denoted σ_h, σ_v, or σ_d.
5. Improper rotation S_n (rotation–reflection); rotation by $(\frac{2\pi}{n})$ followed by reflection in a plane perpendicular to the rotation axis.

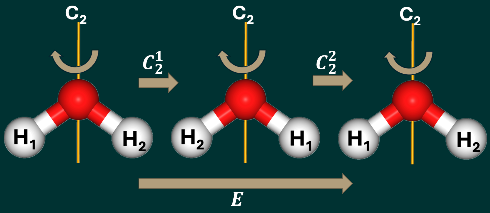
Identity (E)

- The identity indicates that each object is identical to itself when you do not move it in any way. It is present in every object.
- It can be designated by the Schoenflies symbol (E).
- This is a trivial statement, but necessary to complete the mathematical framework of symmetry and group theory.

Proper Rotation Axis (C_n)

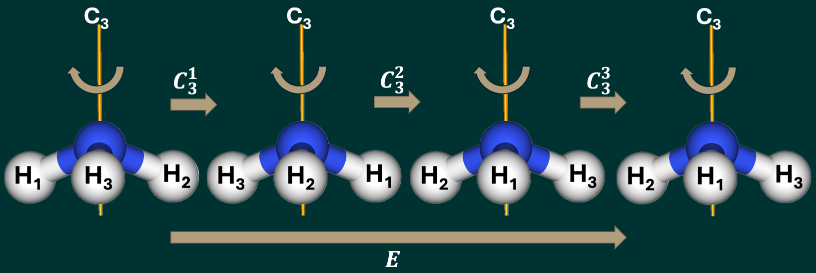
- A proper rotation is a simple rotation operation around an axis. It is denoted C_n^m, where n (=1,2,3,4,6) is the degree of rotation ($\frac{2\pi}{n}$) and m the number of times the operation is performed.
- C_n^n corresponds to the identity E operation.
- $C_n^{n+1} = C_n^1$.
- C_1 corresponds to the identity E operation.

Proper Rotation Axis (C_n)



- For example, a C_2 rotation represents a rotation by $\frac{2\pi}{2} = 180°$ around the C_2 axis.
- C_2^1 represents a rotation of $1 \times \frac{2\pi}{2} = 180°$, C_2^2 a rotation of $2 \times \frac{2\pi}{2} = 360° = E$.

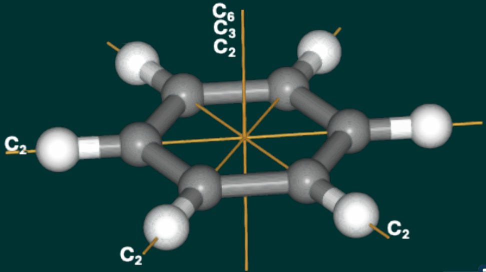
Proper Rotation Axis (C_n)



- C_3^1 represents a rotation of $1 \times \frac{2\pi}{3} = 120°$, C_3^2 a rotation of $2 \times \frac{2\pi}{3} = 240°$, C_3^3 a rotation of $3 \times \frac{2\pi}{3} = 360° = E$.

Proper Rotation Axis (C_n)

- If an object possesses several axes of different order n, the one with the highest order is called the principal axis and is oriented along the Z axis.
- The principal axis of benzene is the C_6 axis.
- By definition, it contains a C_3 and C_2 axis, which are coaxial with the C_6 axis: $C_6^2 = C_3^1$ and $C_6^3 = C_2^1$.

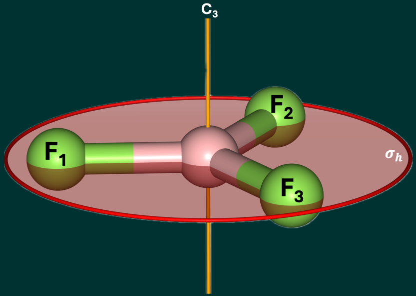


Reflection Planes (σ)

- A reflection plane, denoted σ, is a symmetry element that divides a molecule or object into two mirror-image halves.
- A horizontal reflection plane (σ_h) is perpendicular to the principal axis of the molecule.
- A vertical reflection plane (σ_v) contains the principal axis of the molecule.
- A dihedral reflection plane (σ_d) bisects the angle between two C_2 axes.

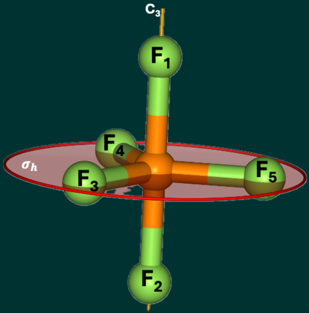
Horizontal Reflection Planes (σ_h)

- A horizontal reflection plane is always perpendicular to the principal axis.
- For the boron trifluoride molecule (BF_3), there is a horizontal mirror plane perpendicular to the principal axis C_3.



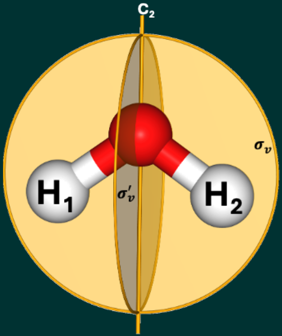
Horizontal Reflection Planes (σ_h)

- A horizontal reflection plane is always perpendicular to the principal axis.
- For phosphorus pentafluoride (PF_5), there is also a horizontal mirror plane perpendicular to the principal axis C_3.



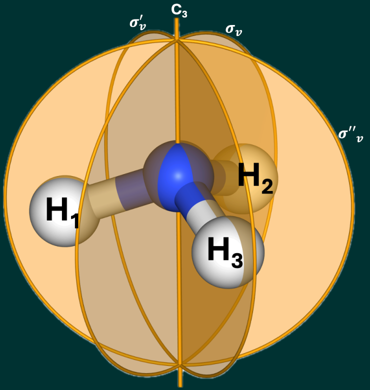
Vertical Reflection Planes (σ_v)

- A vertical reflection plane contains the principal axis.
- The water molecule has two vertical planes, denoted σ_v and σ_v'. Each contains the principal axis C_2.



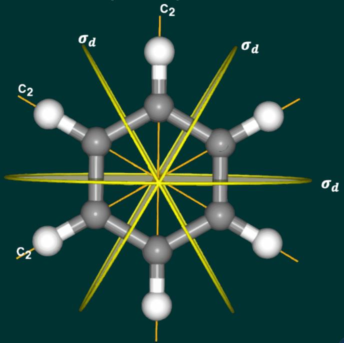
Vertical Reflection Planes (σ_v)

- The ammonia molecule (NH_3) has three vertical planes, denoted σ_v, σ_v', and σ_v'', passing through the three N-H bonds. Each contains the principal axis C_3.



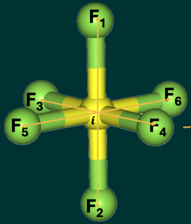
Dihedral Reflection Planes (σ_d)

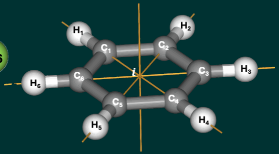
- A dihedral reflection plane is a symmetry element that bisects the angle between two C_2 rotation axes.
- For benzene, there are three dihedral reflection planes (σ_d) that pass through the bisectors of the angles formed by the C_2 axes perpendicular to the principal axis C_6.



Center of Inversion (i)

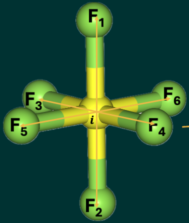
- A center of inversion is a symmetry element that divides a molecule into two symmetric parts with respect to a central point. Each coordinate (x,y,z) of an atom is inverted to coordinates (-x,-y,-z).
- The center of inversion may be located on an atom or not.
- For example, the center of inversion of sulfur hexafluoride SF_6 is located at the sulfur atom. F_1 is inverted to F_2, F_3 to F_4, etc.

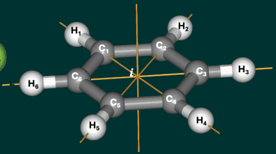




Center of Inversion (i)

- A center of inversion is a symmetry element that divides a molecule into two symmetric parts with respect to a central point. Each coordinate (x,y,z) of an atom is inverted to coordinates (-x,-y,-z).
- The center of inversion may be located on an atom or not.
- In benzene C_6H_6, which has a planar hexagonal geometry, the inversion center is at the center of the ring, where there is no atom. C_1 is inverted to C_4, H_1 to H_4, etc.



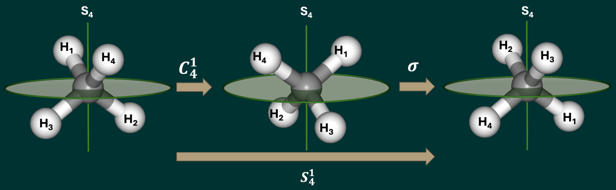


Rotation-Reflection Axis (S_n) - Improper Rotation

- A rotation-reflection S_n operation is a combination of a rotation by $(\frac{2\pi}{n})$ around a given axis, followed by a reflection through a plane perpendicular to that axis.
- This axis is called improper, because after the rotation alone, the molecule does not coincide with its initial configuration. Complete superposition requires a second step: reflection through a mirror plane perpendicular to the improper axis.
- The presence of a rotation-reflection does not require the existence of a proper rotation axis or a regular mirror plane (σ), but neither does it exclude their existence.
- S_1 is equivalent to a simple reflection (σ), and S_2 corresponds to an inversion (i).

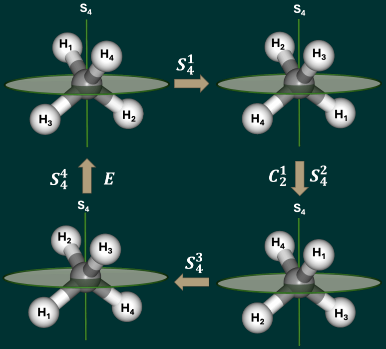
Rotation-Reflection Axis (S_n) - Improper Rotation

- For example, the S_4 operation consists of a $90°$ rotation about this axis, followed by a reflection through the plane perpendicular to this axis.
- Methane possesses several S_4 axes passing through the central carbon atom and aligned with the bisectors of the tetrahedral H-C-H angle.



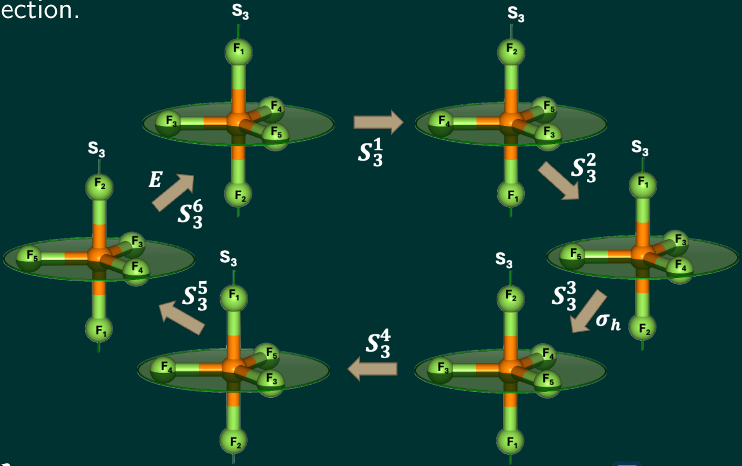
Rotation-Reflection Axis (S_n) - Improper Rotation

- For every S_n axis (S_4) of even order, there is a coaxial $C_{\frac{n}{2}}$ axis (C_2).
- If n is even, then $S_n^n = E$ (the identity), because the C_n^n rotation returns the molecule to its initial position.



Rotation-Reflection Axis (S_n) - Improper Rotation

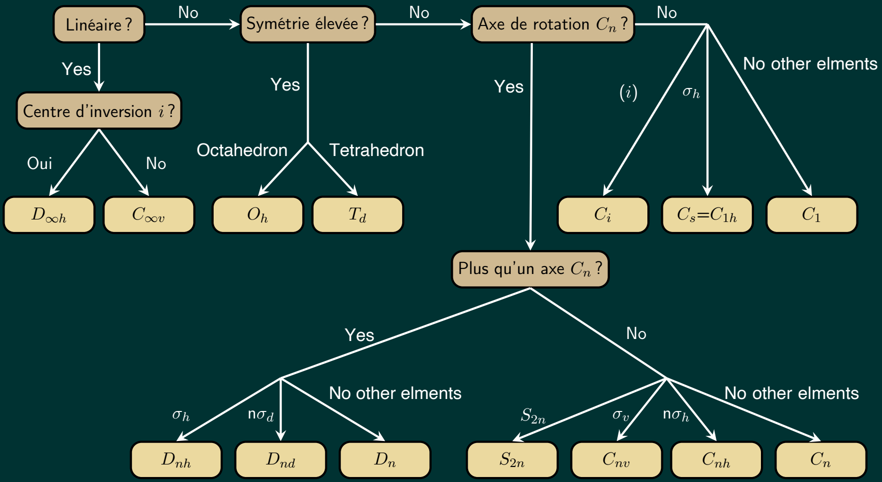
If n is odd, then $S_n^n = \sigma_h$, because after n operations, the molecule regains its initial position by rotation but undergoes an additional reflection.



Point Groups

- Each molecule is characterized by a set of symmetry operations that define its overall symmetry, i.e., its symmetry type. This set of operations is known as the molecule's point group.
- To determine the point group of a molecule, it is sufficient to identify a few characteristic symmetry elements using a flowchart.

Point Group Flowchart



Main Point Groups

In 1891, Arthur Moritz Schönflies classified and published the symmetry of 230 space groups. To group objects in order of increasing symmetry, he used the following symbols:

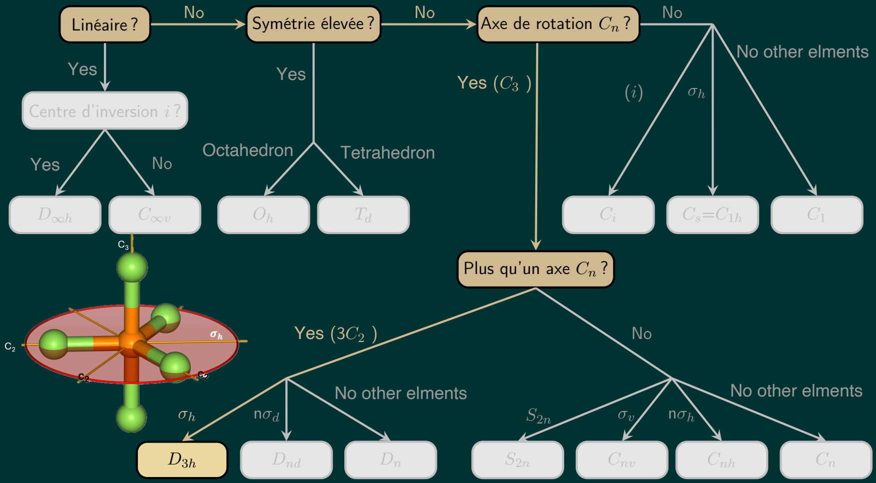
- C_n: only the C_n element
- C_{nv}: C_n and n vertical planes σ_v
- C_{nh}: C_n and one horizontal plane σ_h
- D_n: C_n and n C_2 axes $\perp$
- D_{nh}: D_n + horizontal plane σ_h
- D_{nd}: D_n + n bisector planes
- S_n: only the S_n element

Special Groups

In 1891, Arthur Moritz Schönflies classified and published the symmetry of 230 space groups. To group objects in order of increasing symmetry, he used the following symbols:

- T_d: Tetrahedron (3 S_4, 4 C_3, 6 σ_d)
- O_h: Octahedron (3 C_4, 4 C_3, 6 C_2, 3 σ_h, 6 σ_d)
- $C_{\infty v}$: Linear without inversion center
- $D_{\infty h}$: Linear with inversion center

Example: Phosphorus Pentafluoride (D3h)



Université d'Artois
adlane.sayede@univ-artois.fr

Your turn! Continue with the other modules to master symmetry.