Topic II

Symmetry and Group Theory in Chemistry

II.3 Module 3: Symmetry Elements and Operations

1/13:

- He will upload lecture slides in advance in the future.
- An object is symmetric if one part is the same as other parts.
- The symmetry of discrete objects is described using **Point Symmetry**.
- **Point groups** (~ 32 for molecules) provide us with a way to indicate the symmetry unambiguously.
- Point groups have symmetry about a single point at the center of mass of the system.
- Extended objects (e.g., crystals) have **translational symmetry** described by **Space groups**[1] (230 total).
- Reading: Miessler et al. (2014) Chapter 4 and https://en.wikipedia.org/wiki/Molecular_symmetry.
- **Symmetry elements**: Geometric entities about which a **symmetry operation** can be performed. In a point group, all symmetry elements must pass through the center of mass (the point).
- **Symmetry operation**: The action that produces an object identical to the initial object.

Element	Operation
Identity, E	nothing
Rotation axis, C_n	n-fold rotation
Improper rotation axis, S_n	n-fold improper rotation
Plane of symmetry, σ	Reflection
Center of symmetry, i	Inversion

- **Identity**: Does nothing to the object, but is necessary for mathematical completeness.
- ***n*-fold rotation**: A rotation of $360^\circ/n$ about the C_n axis ($n \in [1, \infty)$).
  - In H_2O, there is a C_2 axis, so we can perform a 2-fold (180°) rotation to get the same molecule.
    - Remember, because of quantum mechanical properties, the hydrogens are indistinguishable so when we rotate it 180°, we cannot tell it apart from the unrotated molecule.
  - Rotations are considered positive in the counter-clockwise direction.

[1] Not covered in this course.

  - Each possible rotation operation is assigned using a superscript integer m of the form ${C_n}^m$. m is the number of sequential applications.
  - The rotation ${C_n}^n = E$ is equivalent to the identity operation (nothing is moved).
  - Linear molecules have an infinite number of rotational options C_∞ because any rotation on the molecular axis will give the same arrangement.
- **Principal axis**: The highest order rotation axis.
  - By convention, the principal axis is assigned to the z-axis if we are using Cartesian coordinates.
- **Reflection**: Exchanges one half of the object with the reflection of the other half.
- **Vertical mirror plane**: A mirror plane that contains the principal axis. *Also known as* $\boldsymbol{\sigma_v}$.
- **Horizontal mirror plane**: A mirror plane that is perpendicular to the principal axis. *Also known as* $\boldsymbol{\sigma_h}$.
- **Dihedral mirror planes**: A special type of σ_v that is between sides or planes. *Also known as* $\boldsymbol{\sigma_d}$.
  - For example, we might have vertical mirror planes in the xz- or yz-planes. In this case, the dihedral planes would contain the lines $y = \pm x$.
- Two successive reflections are equivalent to the identity operation.
- **Inversion**: Every part of the object is reflected through the inversion center, which must be at the center of mass of the object.
  - $(x, y, z) \xrightarrow{i} (-x, -y, -z)$.
- ***n*-fold improper rotation**: This operation involves a rotation of $360°/n$ followed by a reflection perpendicular to the axis. It is a single operation and is labeled in the same manner as "proper" rotations. *Also known as* $\boldsymbol{{S_n}^m}$.

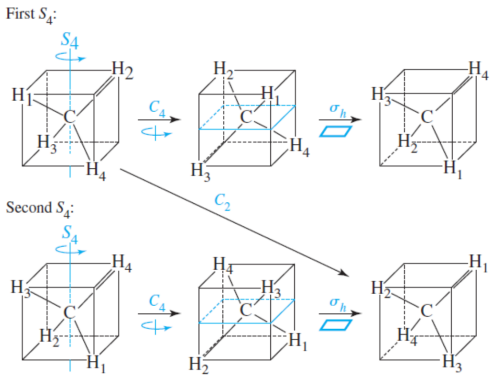
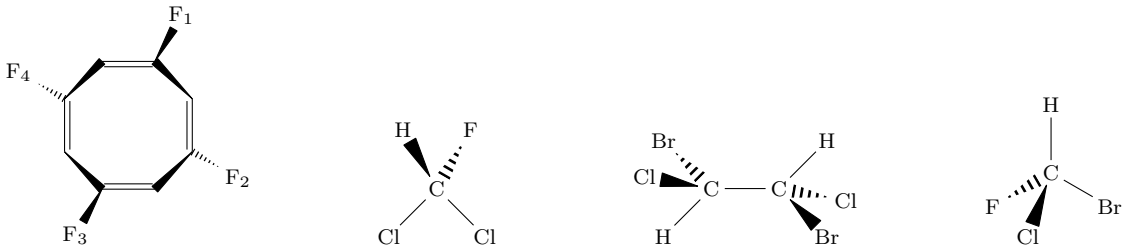


Figure II.1: Methane's S_4 symmetry.

  - Methane has S_4 symmetry.
  - Note that $S_1 = \sigma_h$, $S_2 = i$, and sometimes $S_{2n} = C_n$. In methane, for example, ${S_4}^2 = C_2$.
  - Applied to a triangular prism, is a good example.
  - If n is even, we have n unique operations. There should be $C_{n/2}$.
  - If n is odd, we have $2n$ unique operations. There should be C_n and σ_h.
- The absence of an S_n axis is the defining symmetry property of **chiral** molecules.
  - Formerly, we learned that chiral molecules should not have mirror planes and inversion centers.
  - Rigorously, chiral molecules must not have any improper rotation axes.

II.4 Module 4: Symmetry Point Groups

- Identifying the point groups:
  1. Determine if the symmetry is special (e.g., octahedral).
  2. Determine if there is a principal rotation axis.
  3. Determine if there are rotation axes perpendicular to the principal axis.
  4. Determine if there are mirror planes.
  5. Assign point groups.
- High symmetry and low symmetry groups are the most difficult to identify.
- High symmetry:
  - Perfect tetrahedral (T_d), e.g., P_4 and CH_4.
  - Perfect octahedral (O_h), e.g., SF_6.
  - Perfect icosahedral (I_h), e.g., C_{60}.
- Low symmetry:



(a) S_4. (b) C_s (c) C_i (d) C_1

Figure II.2: Low symmetry point groups.

  - Only an improper axis: S_n.
  - Only a mirror plane: C_s.
  - Only an inversion center: C_i.
  - No symmetry: C_1.
- C_n groups:
  - Only a C_n axis. Note that conformation is important.
- C_{nh} groups have a C_n axis and a σ_h reflection plane (such as $B(OH)_3$).
  - H_2O_2 has C_{2h} symmetry.
- All symmetry elements are listed in the top row of the corresponding characters table (Appendix C in Miessler et al. (2014)).
- C_{nv} groups have a C_n axis and a σ_v reflection plane.
  - NH_3 has C_{3v} symmetry.
  - CO has $C_{\infty v}$ symmetry since there are an infinite number of both C_n axes and σ_v mirror planes.
- D_{nh} groups: A C_n axis, n perpendicular C_2 axes, and a σ_h reflection plane.
  - BH_3 has D_{3h} symmetry.

  - A square prism has D_{4h} symmetry.
  - CO_2 has $D_{\infty h}$ symmetry.
- D_n groups: A C_n axis, n perpendicular C_2 axes, and no mirror planes.
  - A 3-bladed propeller has D_3 symmetry.
- D_{nd} groups: A C_n axis, n perpendicular C_2 axes, and a σ_d.
  - Ethane in the staggered conformation has D_{3d} symmetry.
- Local symmetry:
  - Sometimes, rigorous math analysis needs to be adjusted to physical reality.
  - If a cyclopentane ring is bonded through the center to $Mn(CO)_3$, this molecule has only C_s symmetry.
  - However, spectroscopically, there is fast rotation about the Mn−Cp bond. This means that the $Mn(CO)_3$ fragment exhibits pseudo-C_{3v} symmetry while the C_5H_5 ligand exhibits pseudo-C_{5v} symmetry.
  - Often, the absolute symmetry of a molecule is very low, but the interactions are far away from the centers of interest, and do not perturb them significantly.
  - If we have platinum as a central atom bonded to two chlorines and two $P(Et)_3$ groups, this molecule technically has C_1 symmetry due to the orientations of atoms within R groups (staggered), but IR spectroscopy is characteristic of highly symmetric species (D_{2h}).