

Topic I

Symmetry and Group Theory in Chemistry

I.1 Module 3: Symmetry Elements and Operations

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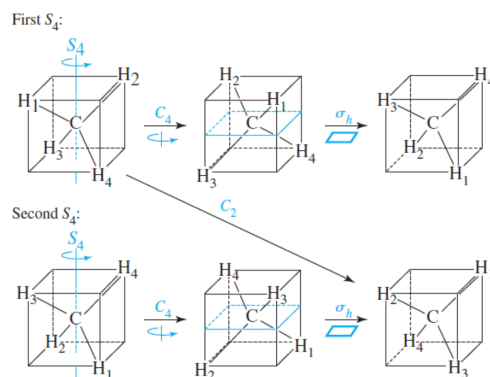
- He will upload lecture slides in advance in the future.
- An object is symmetric if one part is the same as other parts.
- The symmetry of discrete objects is described using **Point Symmetry**.
- **Point groups** (~ 32 for molecules) provide us with a way to indicate the symmetry unambiguously.
- 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 counterclockwise direction.

¹Not 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 σ_v .*
- **Horizontal mirror plane:** A mirror plane that is perpendicular to the principal axis. *Also known as σ_h .*
- **Dihedral mirror planes:** A special type of σ_v that is between sides or planes. *Also known as σ_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 $360^\circ/n$ 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 S_n^m .*

Figure I.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.

I.2 Module 4: Symmetry Point Groups

- Identifying the point groups:
 - Determine if the symmetry is special (e.g., octahedral).
 - Determine if there is a principal rotation axis.
 - Determine if there are rotation axes perpendicular to the principal axis.
 - Determine if there are mirror planes.
 - 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:

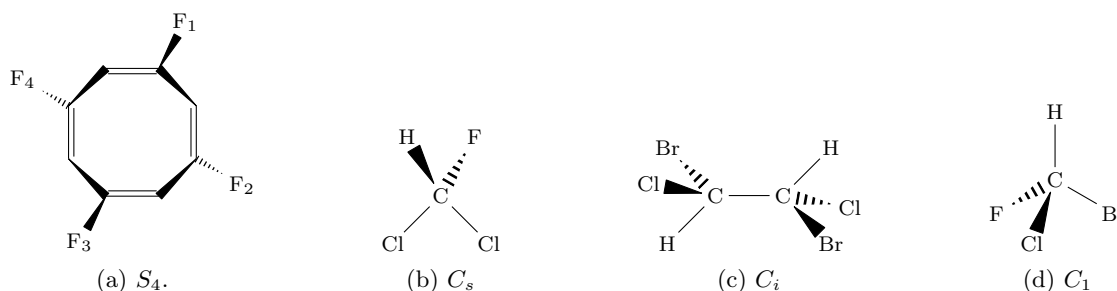


Figure I.2: Low symmetry point groups.

- 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.

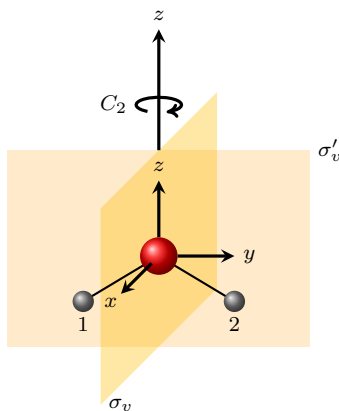
- A square prism has D_{4h} symmetry.
- CO_2 has $D_{\infty h}$ symmetry.
- D_n groups: A C_n axis, n perpendicular C_2 axes, and no mirror planes.
 - A 3-bladed propeller has D_3 symmetry.
- D_{nd} groups: A C_n axis, n perpendicular C_2 axes, and a σ_d .
 - Ethane in the staggered conformation has 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 $\text{Mn}(\text{CO})_3$, this molecule has only C_s symmetry.
 - However, spectroscopically, there is fast rotation about the Mn–Cp bond. This means that the $\text{Mn}(\text{CO})_3$ 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 $\text{P}(\text{Et})_3$ 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}).

I.3 Module 5: Group Theory 101

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- **Group:** A set of elements together with an operation that combines any two of its elements to form a third element satisfying four conditions called the group axioms.
- **Closure:** All binary products must be members of the group.
- **Associativity:** Associative law of multiplication must hold.
- **Identity:** A group must contain the identity operator.
- **Inverse:** Every operator must have an inverse.
- The integers with the addition operation form a group, for example.
- History:
 - Early group theory was driven by the quest for solutions of polynomial equations of degree 5 and above.
 - Early 1800s: Évariste Galois realized that the algebraic solution to a polynomial equation is related to the structure of a group of permutations associated with the roots of the polynomial, the Galois group of the polynomial.
 - [Link to Galois video here.](#)
 - 1920s: Group theory was applied to physics and chemistry.
 - 1931: It is often hard or even impossible to obtain a solution of the Schrödinger equation — however, a large part of qualitative results can be obtained by group theory. Almost all the rules of spectroscopy follow from the symmetry of a problem.
- We will use group theory for describing symmetry of molecules. We will use group theory to understand the bonding and spectroscopic features of molecules.

- For us, a group consists of a set of symmetry elements (and associated symmetry operations) that completely describes the symmetry of a molecule.
- **Order** (of a group): The total number of elements (i.e., symmetry operations) in the group. *Also known as h .*
- Rule 1: Closure.

Figure I.3: Symmetry elements for H₂O.

- H₂O is of the C_{2v} point group (refer to Figure I.3).
 - Symmetry operations: E , C_2 , $\sigma_{v(xz)}$, and $\sigma'_{v(yz)}$.
 - $\sigma_v \cdot C_2 = \sigma'_v = C_2 \cdot \sigma_v$.
 - The above property (order *does not* matter) shows that C_{2v} is an **Abelian group**.
- NH₃ is of the C_{3v} point group.
 - Symmetry operations: E , C_3^+ , C_3^- , σ_v , σ'_v , and σ''_v .
 - $\sigma''_v \cdot C_3 = \sigma_v$, but $C_3 \cdot \sigma''_v = C_3^- = C_3^2$.
 - The above property (order *does* matter) shows that C_{3v} is a **non-Abelian group**.
- Rule 2: Associativity.
 - H₂O is of the C_{2v} point group (refer to Figure I.3).

$\sigma'_v C_2 \sigma_v(1, 2) = \sigma'_v C_2(2, 1)$	$\sigma'_v(C_2 \sigma_v)(1, 2) = \sigma'_v E(1, 2)$	$(\sigma'_v C_2) \sigma_v(1, 2) = \sigma_v \sigma_v(1, 2)$
$= \sigma'_v(1, 2)$	$= \sigma'_v(1, 2)$	$= \sigma_v(2, 1)$
$= (1, 2)$	$= (1, 2)$	$= (1, 2)$
- Rule 3: Identity.
- Rule 4: Inverse.
 - For a C_{2v} point group:

$E \cdot E = E$	$C_2 \cdot C_2 = E$	$\sigma_v \cdot \sigma_v = E$	$\sigma'_v \cdot \sigma'_v = E$
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- Group multiplication tables.

C_{2h}	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E

Table I.1: Group multiplication table for the C_{2h} point group.

- Table I.1 corresponds to the C_{2h} point group, which has E , C_2 , σ_h , and i operations.
- Note that the operation in the top row is the one that's applied first, while the one in the left column will be applied second.

- **Subgroup:** Fractional parts of groups that are groups, too.

C_{2v}	E	C_3	C_3^2	σ_v	σ'_v	σ''_v
E	E	C_3	C_3^2	σ_v	σ'_v	σ''_v
C_3	C_3	C_3^2	E	σ''_v	σ_v	σ'_v
C_3^2	C_3^2	E	C_3	σ'_v	σ''_v	σ_v
σ_v	σ_v	σ'_v	σ''_v	E	C_3	C_3^2
σ'_v	σ''_v	σ_v	σ'_v	C_3	C_3^2	E
σ''_v	σ'_v	σ''_v	σ_v	C_3^2	E	C_3

Table I.2: Group multiplication table for the C_{2v} point group.

- If $h = 6$ (as in the C_{3v} group), subgroup order can be $h = 3, 2, 1$. Why only these?
- The order 1 and 3 charts are subgroups.
- The order 2 chart is not a subgroup because C_3^2 is not an operation in the group (therefore, the “subgroup” is not closed).
- We use subgroups because they can make complex problems simpler.
 - For example, calculating the vibrational modes of CO_2 .
 - As another example, D_{2h} is a subgroup of $D_{\infty h}$.

I.4 Module 6: Representations

- Items of the same point group have the same vibration modes.
- **Representation** (of a group): Any collection of quantities (or symbols) which obey the multiplication table of a group. *Also known as* Γ .
- For our purposes, these quantities are the matrices that show how certain characteristic of a molecule behave under the symmetry operations of the group.
- Operations (on a point (x, y, z) in Cartesian coordinates):
 - $E(x, y, z) = (x, y, z)$.
 - $\sigma_{xz}(x, y, z) = (x, -y, z)$.
 - $i(x, y, z) = (-x, -y, -z)$.
 - C_n : Convention is a counterclockwise rotation of the point by $\theta = \frac{2\pi}{n}$ radians.
 - S_n : Convention is a clockwise rotation of the point C_n followed by a σ through a plane perpendicular to C .

- Matrix forms of operations:

- Identity: $E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$.

- One example of a reflection (there are two more): $\sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$.

- Inversion: $i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$.

- Rotation: Counterclockwise is $C_n(\theta) = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$ and clockwise is $C_n(\theta) = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$.

- A derivation of this matrix can be found in the slides.

- Improper rotation: $S_n(\theta) = \sigma_h C_n(\theta)$.

- Reducible representations:

- A representation of a symmetry operation of a group.
 - Can be expressed in terms of a representation of lower dimension.
 - Can be broken down into a simpler form.
 - Characters can be further diagonalized.
 - Are composed of the direct sum of irreducible representations.
 - Infinite possibilities.

- Irreducible representations:

- A fundamental representation of a symmetry operation of a group.
 - Cannot be expressed in terms of a representation of lower dimension.
 - Cannot be broken down into a simpler form.
 - Characters cannot be further diagonalized.
 - Small finite number dictated by point group.

- Good example of reducible/irreducible representations?