Topic I

Symmetry and Group Theory in Chemistry

I.1 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 counterclockwise 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 ${C_n}^n \equiv E$ 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* $\boldsymbol{{S_n}^m}$, **rotation-reflection operation**.

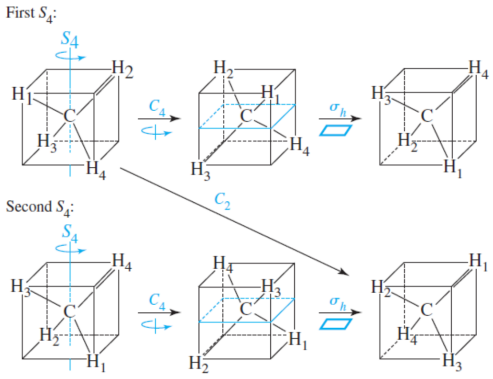
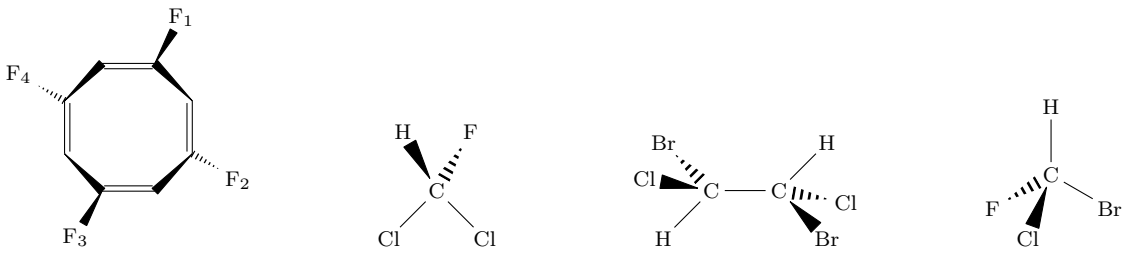


Figure I.1: Methane's S_4 symmetry.

  - Methane has S_4 symmetry.
  - Note that $S_1 \equiv \sigma_h$, $S_2 \equiv i$, and sometimes $S_{2n} \equiv C_n$. In methane, for example, ${S_4}^2 \equiv C_2$.
  - 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:
  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} and $B_{12}H_{12}{}^{2-}$.
- Low symmetry:



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

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 $Mn(CO)_3$, 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}).

I.3 Module 5: Group Theory 101

1/15:

- **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 off 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.

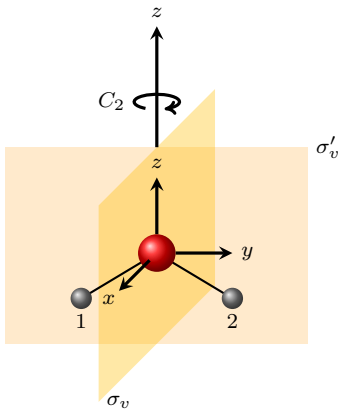


Figure I.3: Symmetry elements for H_2O.

  - H_2O 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**.
  - NH_3 is of the C_{2v} 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.
  - H_2O is of the C_{2v} point group (refer to Figure I.3).

$$\begin{aligned}\sigma'_v C_2 \sigma_v(1,2) &= \sigma'_v C_2(2,1) \\ &= \sigma'_v(1,2) \\ &= (1,2)\end{aligned} \qquad \begin{aligned}\sigma'_v(C_2\sigma_v)(1,2) &= \sigma'_v E(1,2) \\ &= \sigma'_v(1,2) \\ &= (1,2)\end{aligned} \qquad \begin{aligned}(\sigma'_v C_2)\sigma_v(1,2) &= \sigma_v\sigma_v(1,2) \\ &= \sigma_v(2,1) \\ &= (1,2)\end{aligned}$$

- Rule 3: Identity.
- Rule 4: Inverse.
  - For a C_{2v} point group:

$$E \cdot E = E \qquad C_2 \cdot C_2 = E \qquad \sigma_v \cdot \sigma_v = E \qquad \sigma'_v \cdot \sigma'_v = E$$

- Group multiplication tables.

C_{2h}	$\boldsymbol{E}$	$\boldsymbol{C_2}$	$\boldsymbol{\sigma_h}$	$\boldsymbol{i}$
$\boldsymbol{E}$	E	C_2	σ_h	i
$\boldsymbol{C_2}$	C_2	E	i	σ_h
$\boldsymbol{\sigma_h}$	σ_h	i	E	C_2
$\boldsymbol{i}$	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}	$\boldsymbol{E}$	$\boldsymbol{C_3}$	$\boldsymbol{{C_3}^2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v'}$	$\boldsymbol{\sigma_v''}$
$\boldsymbol{E}$	E	C_3	${C_3}^2$	σ_v	σ_v'	σ_v''
$\boldsymbol{C_3}$	C_3	${C_3}^2$	E	σ_v''	σ_v	σ_v'
$\boldsymbol{{C_3}^2}$	${C_3}^2$	E	C_3	σ_v'	σ_v''	σ_v
$\boldsymbol{\sigma_v}$	σ_v	σ_v'	σ_v''	E	C_3	${C_3}^2$
$\boldsymbol{\sigma_v'}$	σ_v''	σ_v	σ_v'	C_3	${C_3}^2$	E
$\boldsymbol{\sigma_v''}$	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 tabble 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?

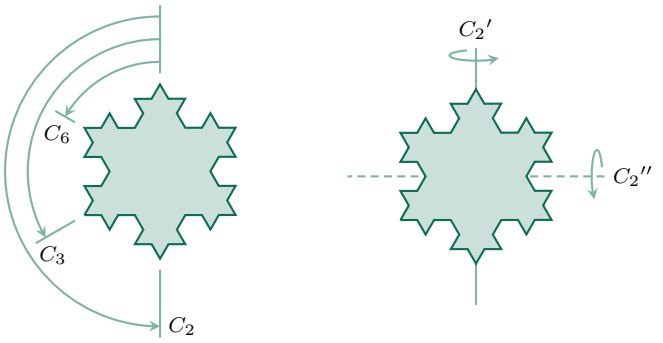
I.5 Chapter 4: Symmetry and Group Theory

From Miessler et al. (2014).

I.5.1 Notes

1/18:
- **Coincident** (axes): Two identical axes.
  - For example, the C_3 rotation axis of $CHCl_3$ is **coincident** with the C–H bond axis.
- Snowflakes, which are often planar and have hexagonal symmetry, have a twofold (C_2), threefold (C_3), and sixfold (C_6) axis through their center and perpendicular to their plane.
  - Rotations ${C_3}^2$ and ${C_6}^5$ are also symmetry operations.

1/19:



(a) About the principal axis. (b) About perpendicular axes.

Figure I.4: Rotations of a snowflake design.

1/18:

- "When necessary, the C_2 axes perpendicular to the principal axis are designated with primes; a single prime (C_2') indicates that the axis passes through several atoms of the molecule, whereas a double prime (C_2'') indicates that it passes between the outer atoms" (Miessler et al., 2014, p. 77).

1/19:

- Even though $S_2 \equiv i$ and $S_1 \equiv \sigma$, the i and σ notations are preferred because of the group theory requirement of maximizing the number of unique classes of symmetry operations associated with a molecule.
- **Point group**: A set of symmetry operations that describes a molecule's overall symmetry.
- Alternative steps for assigning point groups:
  1. Determine whether the molecule exhibits very low symmetry (C_1, C_s, C_i) or high symmetry (T_d, O_h, $C_{\infty v}$, $D_{\infty h}$, I_h).
  2. If not, find the highest order C_n axis for the molecule.
  3. Does the molecule have any C_2 axes perpendicular to the principal C_n axis? If it does, there will be n of such C_2 axes, and the molecule is in the D set of groups. If not, it is in the C or S set.
  4. Does the molecule have a mirror plane (σ_h) perpendicular to the principal C_n axis? If so, it is classified as C_{nh} or D_{nh}. If not, continue with Step 5.
  5. Does the molecule have any mirror planes that contain the principal C_n axis (σ_v or σ_d)? If so, it is classified as C_{nv} or D_{nd}. Iff not, but it is in the D set, it is classified as D_n. If the molecule is in the C or S set, continue with Step 6.
  6. Is there an S_{2n} axis collinear with the principal C_n axis? If so, it is classified as S_{2n}. If not, the molecule is classified as C_n.
- Groups of high symmetry:
  - $C_{\infty v}$ (linear): These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.
  - $D_{\infty h}$ (linear): These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular C_2 axes, a perpendicular reflection plane, and an inversion center.
  - T_d (tetrahedral): Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d planes. They have no C_4 axes.
    - Look for C_3 and C_2 axes.
  - O_h (octahedral): These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four C_3 rotations, three C_4 rotations, and an inversion.

    - Look for C_4, C_3, and C_2 axes.
- I_h (icosahedral): Icosahedral structures are best recognized by their six C_5 axes, as well as many other symmetry operations — 120 in all.
    - Look for C_5, C_3, and C_2 axes.
- T_h: Adds i to T_d. Example: $W[N(CH_3)_2]_6$.