

## Topic II

# Symmetry and Group Theory in Chemistry

## II.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** ( $\sim 32$  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**<sup>[1]</sup> (230 total).
- Reading: Miessler et al. (2014) Chapter 4 and [https://en.wikipedia.org/wiki/Molecular\\_symmetry](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.

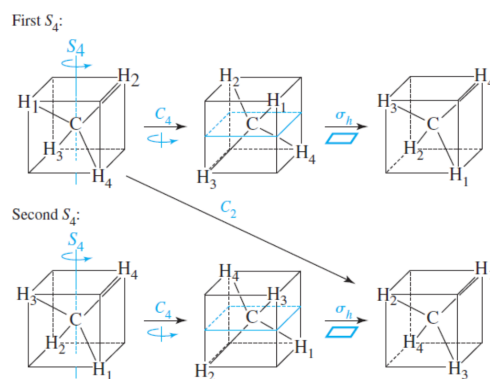
Element	Operation
Identity, $E$	nothing
Rotation axis, $C_n$	$n$ -fold rotation
Improper rotation axis, $S_n$	$n$ -fold improper rotation
Plane of symmetry, $\sigma$	Reflection
Center of symmetry, $i$	Inversion

- **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  $\text{H}_2\text{O}$ , there is a  $C_2$  axis, so we can perform a 2-fold ( $180^\circ$ ) rotation to get the same molecule.
    - Remember, because of quantum mechanical properties, the hydrogens are indistinguishable so when we rotate it  $180^\circ$ , we cannot tell it apart from the unrotated molecule.
  - Rotations are considered positive in the counterclockwise direction.

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<sup>1</sup>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  $C_\infty$  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  $\sigma_v$ .*
- **Horizontal mirror plane:** A mirror plane that is perpendicular to the principal axis. *Also known as  $\sigma_h$ .*
- **Dihedral mirror planes:** A special type of  $\sigma_v$  that is between sides or planes. *Also known as  $\sigma_d$ .*
  - 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  $360^\circ/n$  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  $S_n^m$ , rotation-reflection operation.*

Figure II.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  $\sigma_h$ .
- 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.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.,  $C_{60}$  and  $B_{12}H_{12}^{2-}$ .

- Low symmetry:

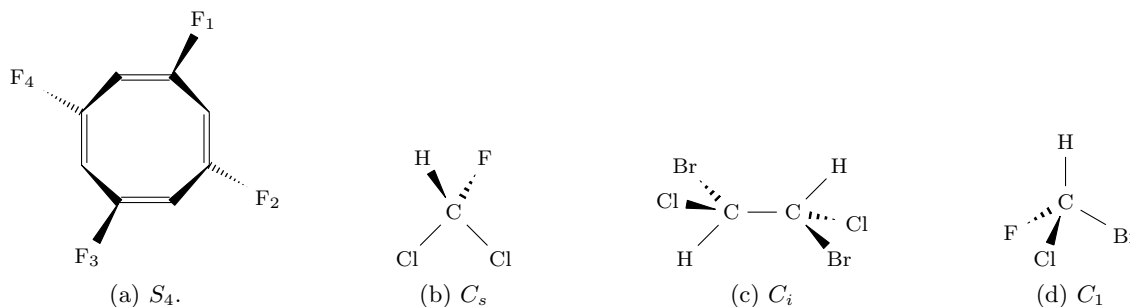


Figure II.2: Low symmetry point groups.

- 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  $\sigma_h$  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  $\sigma_v$  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  $\sigma_v$  mirror planes.
- $D_{nh}$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and a  $\sigma_h$  reflection plane.

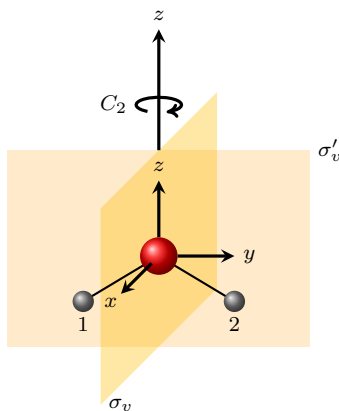
- $\text{BH}_3$  has  $D_{3h}$  symmetry.
- A square prism has  $D_{4h}$  symmetry.
- $\text{CO}_2$  has  $D_{\infty h}$  symmetry.
- $D_n$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and no mirror planes.
  - A 3-bladed propeller has  $D_3$  symmetry.
- $D_{nd}$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and a  $\sigma_d$ .
  - 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  $\text{C}_5\text{H}_5$  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 ( $D_{2h}$ ).

## II.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 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 II.3: Symmetry elements for H<sub>2</sub>O.

- H<sub>2</sub>O is of the  $C_{2v}$  point group (refer to Figure II.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<sub>3</sub> is of the  $C_{3v}$  point group.
  - Symmetry operations:  $E$ ,  $C_3^+$ ,  $C_3^-$ ,  $\sigma_v$ ,  $\sigma'_v$ , and  $\sigma''_v$ .
  - $\sigma''_v \cdot C_3 = \sigma_v$ , 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<sub>2</sub>O is of the  $C_{2v}$  point group (refer to Figure II.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.

$C_{2h}$	$E$	$C_2$	$\sigma_h$	$i$
$E$	$E$	$C_2$	$\sigma_h$	$i$
$C_2$	$C_2$	$E$	$i$	$\sigma_h$
$\sigma_h$	$\sigma_h$	$i$	$E$	$C_2$
$i$	$i$	$\sigma_h$	$C_2$	$E$

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

- Table II.1 corresponds to the  $C_{2h}$  point group, which has  $E$ ,  $C_2$ ,  $\sigma_h$ , 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.

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$
$E$	$E$	$C_3$	$C_3^2$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$
$C_3$	$C_3$	$C_3^2$	$E$	$\sigma''_v$	$\sigma_v$	$\sigma'_v$
$C_3^2$	$C_3^2$	$E$	$C_3$	$\sigma'_v$	$\sigma''_v$	$\sigma_v$
$\sigma_v$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$	$E$	$C_3$	$C_3^2$
$\sigma'_v$	$\sigma''_v$	$\sigma_v$	$\sigma'_v$	$C_3$	$C_3^2$	$E$
$\sigma''_v$	$\sigma'_v$	$\sigma''_v$	$\sigma_v$	$C_3^2$	$E$	$C_3$

Table II.2: Group multiplication table for the  $C_{3v}$  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  $\text{CO}_2$ .
  - As another example,  $D_{2h}$  is a subgroup of  $D_{\infty h}$ .

## II.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*  $\Gamma$ .
- 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  $\sigma$  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** ( $\Gamma$ ):

- 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** ( $\Gamma_i$ ):

- 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?

- A representation shows how certain characteristics of an object (a basis) behave under the symmetry operation of the group.

- **Conjugate elements:** Two elements  $X$  and  $Y$  for which there exists an element  $Z$  in the group such that

$$Z^{-1} \cdot X \cdot Z = Y$$

- Every element is conjugated with itself (let  $Z = E$ ).
- If  $X$  is conjugated with  $Y$ , then  $Y$  is conjugated with  $X$ .
- If  $X$  is conjugated with  $Y$  and  $W$ , then  $Y$  and  $W$  are also conjugate.

- **Class:** A complete set of elements of a group that are conjugate to one another.

- Geometric meaning: operations in the same class can be converted into one another by changing the axis system through application of some symmetry operation of the group.

- Find the conjugates to  $C_3$  in the  $C_{3v}$  point group (refer to Table II.2 throughout the following discussion).

- Let  $X = C_3$ , let  $Z$  iterate through the six symmetry elements ( $E, C_3, C_3^2, \sigma_v, \sigma'_v, \sigma''_v$ ), and let  $Z^{-1}$  iterate through the corresponding inverses ( $E, C_3^2, C_3, \sigma_v, \sigma'_v, \sigma''_v$ ).
- Thus, we have

$$\begin{aligned} E \cdot C_3 \cdot E &= C_3 \\ C_3^2 \cdot C_3 \cdot C_3 &= C_3 \\ C_3 \cdot C_3 \cdot C_3^2 &= C_3 \\ \sigma_v \cdot C_3 \cdot \sigma_v &= C_3^2 \\ \sigma'_v \cdot C_3 \cdot \sigma'_v &= C_3^2 \\ \sigma''_v \cdot C_3 \cdot \sigma''_v &= C_3^2 \end{aligned}$$

- It follows from the above that  $C_3$  and  $C_3^2$  are conjugates, and  $C_3$  and  $C_3^2$  are conjugates.
- Thus,  $C_3$  and  $C_3^2$  are in the same class.
- We can use a similar method to prove that  $\sigma_v, \sigma'_v$ , and  $\sigma''_v$  are all in the same class within the  $C_{3v}$  point group.
- Likewise  $E$  is in a class by itself.
- Thus, for the  $C_{3v}$  point group,  $E$  forms a class of order 1,  $C_3, C_3^2$  form a class of order 2, and  $\sigma_v, \sigma'_v, \sigma''_v$  form a class of order 3.

- **Similarity transformation:** The transformation

$$v^{-1} \cdot A \cdot v = A'$$

- $A$  is a representation for some type of symmetry operation.
- $v$  is a similarity transform operator.
- $v^{-1}$  is the inverse of the similarity transform operator.
- $A'$  is the product.
- $A$  and  $A'$  are conjugates, and we say that  $A'$  is the similarity transform of  $A$  by  $v$ .
- **Block-diagonal (matrix):** A matrix with nonzero values only in square blocks along the diagonal from the top left to the bottom right.

$$\begin{bmatrix} 2 & 3 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{bmatrix}$$

- The above matrix is an example of a block-diagonal matrix.
- Irreducible representations are the ones where the matrices have the most block-diagonalized form that they can.

## II.5 Module 7: Characters and Character Tables

1/19:

- Nocera Lecture 3 notes (on Canvas) explain how reducible and irreducible transformations are related to each other through the similarity transformations.
- For  $H_2O$ , each atom has 3 Cartesian coordinates, so our transformation matrix<sup>[2]</sup> is 9-square.

<sup>2</sup>Some values in it are negative because of the cosine/sine definition of a rotation matrix for  $\theta = 180^\circ$ .



- However, we can also apply a smaller matrix to the molecule as a whole and invoke symmetry to find the position of the individual atoms.
- **Characters** (of a representation): The traces (i.e., sums of the diagonal matrix elements) of the representation matrices for each operation. *Also known as  $\chi$ .*
  - The character is an invariant for each type of symmetry operation (e.g., regardless of the axis about which a  $C_n$  operation is performed, the trace of the corresponding matrix will be the same).
- Common characters:
  - $C_n$  character:  $\chi = 2 \cos \theta + 1$ .
  - $\sigma_v, \sigma_d$  character:  $\chi = 1$ .
  - $S_2 \equiv i$  character:  $\chi = -3$ .
  - $S_n$  character:  $\chi = 2 \cos \theta - 1$ .
  - $\perp C_2$  axes character:  $\chi = -1$ .
- **Character table:** The collection of characters for a given irreducible representation, under the operations of a group. *Also known as  $\chi$  table.*

Irreducible Representations	Group Symbol	Symmetry Elements				linear	quadratic
	$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
	$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
	$A_2$	1	1	-1	-1	$R_z$	$xy$
	$B_1$	1	-1	1	-1	$x, R_y$	$xz$
	$B_2$	1	-1	-1	1	$y, R_x$	$yz$
Characters						Basis Functions	

Figure II.4: A character table.

- Character tables for all point groups are listed in Appendix C of Miessler et al. (2014).
- **Mulliken symbols** are used to classify irreducible representations based on degeneracy and symmetry.
  - A or B: singly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is  $1 \times 1$ ).
  - E: Doubly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is  $2 \times 2$ ).
  - T: Triply degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is  $3 \times 3$ ).
  - A: symmetric (+) with respect to  $C_n$ .
  - B: anti-symmetric (–) with respect to  $C_n$ .
  - Subscript g: symmetric (+) with respect to  $i$ . *Etymology* short for gerade (German for symmetric).
  - Subscript u: anti-symmetric (–) with respect to  $i$ . *Etymology* short for ungerade (German for unsymmetric).
  - If the molecule has a center of inversion, we label irreducible representations with  $g$  or  $u$ .
  - Subscript 1: symmetric (+) with respect to  $\perp C_2$  or  $\sigma_v$ .
  - Subscript 2: anti-symmetric (–) with respect to  $\perp C_2$  or  $\sigma_v$ .
  - Superscript ': symmetric (+) under  $\sigma_h$  (if no  $i$ ).
  - Superscript ": anti-symmetric (–) under  $\sigma_h$  (if no  $i$ ).

- Don't mistake the operation  $E$  for the Mulliken symbol  $E$ !
- To assign Mulliken symbols, use the character table.
  - Assigning the main letter:
    - If  $E$ -character = 1 and  $C_n$ -character = 1:  $A$ .
    - If  $E$ -character = 1 and  $C_n$ -character =  $-1$ :  $B$ .
    - If  $E$ -character = 2:  $E$ .
    - If  $E$ -character = 3:  $T$ .
  - Assigning a subscript  $g$  or  $u$ :
    - If  $i$ -character = 1:  $g$ .
    - If  $i$ -character =  $-1$ :  $u$ .
    - This subscript can be assigned to  $A, B, E, T$  representations.
  - Assigning a superscript  $'$  or  $''$ :
    - If  $\sigma_h$ -character = 1:  $'$ .
    - If  $\sigma_h$ -character =  $-1$ :  $''$ .
    - This subscript can be assigned to  $A, B$  representations.
  - Assigning a subscript 1 or 2:
    - If  $\perp C_2$  or  $\sigma_v$ -character = 1: 1.
    - If  $\perp C_2$  or  $\sigma_v$ -character =  $-1$ : 2.
    - This subscript can be assigned to  $A, B$  representations.
- $\sigma$ ,  $\pi$ , and  $\delta$  bonds come from the Mulliken symbols!
  - Infinity tables use Greek rather than Latin letters.

$D_3$	$E$	$2C_3(z)$	$3C'_2$	linear	quadratic
$A_1$	1	1	1		$x^2 + y^2, z^2$
$A_2$	1	1	$-1$	$z, R_z$	
$E$	2	$-1$	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$ .

Table II.3: Character table for the  $D_3$  point group.

- In character tables, we need to multiply each symmetry operation by the number of types there are (see Table II.3).
- Basis functions show us how different functions transform under different symmetry operations.
- In the  $C_{2v}$  point group:
  - The  $p_x$  orbital has  $B_1$  symmetry.
  - $p_x$  transforms as  $B_1$ .
  - $p_x$  has the same symmetry as  $B_1$ .
  - $p_x$  forms a basis for the  $B_1$  irreducible representation.
  - $p_x$  is  $B_1$  because (see Table 0.2 and Figure II.4) it does not change under  $E$ , it inverts under  $C_2$ , it does not change under  $\sigma_v(xz)$ , and it inverts under  $\sigma'_v(yz)$ .
- We can apply the same procedure to other more complex functions.
  - For example, in the  $C_{2v}$  point group, we know that (with respect to orbitals):
    - $p_y$  is  $B_2$ .

- $p_z$  is  $A_1$ .
  - $d_{z^2}$  is  $A_1$ .
  - $d_{x^2-y^2}$  is  $A_1$ .
  - $d_{yz}$  is  $B_2$ .
  - $d_{xy}$  is  $A_2$ .
  - $d_{xz}$  is  $B_1$ .
  - We can even go into the cubic functions describing the  $f$  orbitals and assign them Mulliken symbols.
- Essentially, the right hand side of a character table tells you how atomic orbitals will transform under certain symmetry operations.
- Properties of a character table:
  1. The characters of all matrices belonging to the operations in the same class are identical in a given irreducible representation.
    - As such, we form **classes** of operations.
    - We most commonly form a **rotational class** and a **reflection class**.
  2. The number of irreducible representations in a group is equal to the number of classes of that group.
  3. There is always a totally symmetric representation for any group.
    - I.e., a representation where every character is 1.
  4. The sum of the squares of the **dimensionality** of all the irreducible representations is equal to the order of the group. Mathematically,

$$h = \sum_i [\chi_i(E)]^2$$

- For example, the dimensionalities of the  $D_3$  point group (see Table II.3) are 1, 1, and 2, and the order is, indeed,  $6 = 1^2 + 1^2 + 2^2$ .
- 5. The sum of the squares of the characters multiplied by the number of operations in the class equals the order of the group. Mathematically,

$$h = \sum_{R_c} g_c [\chi_i(R_c)]^2$$

- For example, with respect to the  $D_3$  point group (see Table II.3),
 
$$\begin{aligned} 6 &= (1)(1)^2 + (2)(1)^2 + (3)(1)^2 \\ &= (1)(1)^2 + (2)(1)^2 + (3)(-1)^2 \\ &= (1)(2)^2 + (2)(-1)^2 + (3)(0)^2 \end{aligned}$$
- 6. The sum of the products of the corresponding characters of any two different irreducible representations of the same group is zero. Mathematically,

$$\sum_{R_c} g_c \chi_i(R_c) \chi_f(R_c) = 0$$

- Basically, this means that if we treat irreducible representations as vectors in  $h$ -space, they are orthogonal.
  - For example, with respect to the  $D_3$  point group (see Table II.3),
 
$$\begin{aligned} 0 &= 1(1)(1) + 2(1)(1) + 3(1)(-1) \\ &= 1(1)(2) + 2(1)(-1) + 3(1)(0) \\ &= 1(1)(2) + 2(1)(-1) + 3(-1)(0) \end{aligned}$$
- **Dimensionality:** The character of the identity operation  $E$ . Also known as **dimension**.

## II.6 Module 8: Using Character Tables

- A reducible representation of a group is any representation  $\Gamma$  of the form

$$\Gamma = \sum_i a_i \Gamma_i$$

where each  $\Gamma_i$  is an irreducible representation of the group and  $a_i$  is a real scalar.

- Basically, a reducible representation is any nontrivial linear combination of irreducible representations.
- For example, with respect to the  $C_{2v}$  point group (see Figure II.4),  $\Gamma = (7, 1, 5, 3) = 4A_1 + 2B_1 + B_2$  is a reducible representation.
- We may “factor” reducible representations by inspection, or by the...
- Decomposition/reduction formula for a reducible representation:

$$a_i = \frac{1}{h} \sum_Q N \cdot \chi(R)_Q \cdot \chi_i(R)_Q$$

- $a_i$  is the number of times the irreducible representation appears in  $\Gamma_1$ .
- $h$  is the order of the group.
- $N$  is the number of operations in class  $Q$ .
- $\chi(R)_Q$  is the character of the reducible representation.
- $\chi_i(R)_Q$  is the character of the irreducible representation.
- This formula cannot be applied to  $D_{\infty h}$  and  $C_{\infty v}$ .
- Let's look at decomposing  $\Gamma = (7, 1, 5, 3)$  into its component irreducible point groups using the above formula.

$$\begin{aligned} a_{A_1} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot 1 + 1 \cdot 5 \cdot 1 + 1 \cdot 3 \cdot 1) = 4 \\ a_{A_2} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot 1 + 1 \cdot 5 \cdot -1 + 1 \cdot 3 \cdot -1) = 0 \\ a_{B_1} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot -1 + 1 \cdot 5 \cdot 1 + 1 \cdot 3 \cdot -1) = 2 \\ a_{B_2} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot -1 + 1 \cdot 5 \cdot -1 + 1 \cdot 3 \cdot 1) = 1 \end{aligned}$$

- You can also find websites that will apply the formula for you.
- Basis  $\rightarrow$  reducible representation  $\rightarrow$  irreducible representations workflow:
  1. Assign a point group.
  2. Choose a basis function (bond, vibration, orbital, angle, etc.).
  3. Apply operations.
    - The following shortcuts allow us to skip matrix math in certain situations.
      - If the basis stays the same: +1.
      - If the basis is reversed: -1.
      - If it is a more complicated change: 0.
  4. Generate a reducible representation.
  5. Reduce to irreducible representation.

- We now look at an example of applying the above method to  $\text{H}_2\text{O}$ .
  - $\text{H}_2\text{O}$  is of the  $C_{2v}$  point group.
  - The  $9 \times 9$  identity matrix represents the identity operation on the 3 atoms in  $\text{H}_2\text{O}$ , each described by 3 Cartesian coordinates. Thus,  $\chi(E) = 9$ .
  - The following matrix represents the  $C_2$  symmetry operation. Thus,  $\chi(C_2) = -1$ .

$$\begin{array}{c} \text{O} \\ \text{H}_a \\ \text{H}_b \end{array} \begin{array}{c} \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \\ \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \\ \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \end{array} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \begin{array}{c} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \\ \begin{bmatrix} x \\ y \\ z \end{bmatrix} \\ \begin{bmatrix} x \\ y \\ z \end{bmatrix} \end{array} \begin{array}{c} \text{O} \\ \text{H}_a \\ \text{H}_b \end{array}$$

- Note that atoms moved during the transformation do not contribute to the character of the transformation matrix.
- Since under  $\sigma_v(xz)$  only O is unshifted, we need only consider its part of the transformation matrix (as follows) when looking for the character. Thus,  $\chi(\sigma_v(xz)) = 1^{[3]}$ .

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

- Since under  $\sigma_v(yz)$  no atom is shifted, we need to consider each (identical) part of the transformation matrix (as follows) when looking for the character. Thus,  $\chi(\sigma_v(yz)) = 3$ .

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

- Thus, the characters of our final reducible representation is  $\Gamma_{3N} = (9, -1, 1, 3)$ .

■ This representation represents fully unrestricted motion of all 3 ambiguities of freedom.

- Another example:  $\text{XeOF}_4$ .

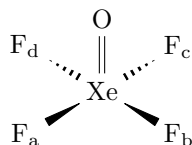


Figure II.5:  $\text{XeOF}_4$ .

- Point group:  $C_{4v}$ .
- Basis function: F atoms.
- Let's see what happens to the fluorine atoms under the  $C_{4v}$  operations (remember that if a basis element (a fluorine atom) stays the same, it contributes +1 to the character of an operation, and if it moves, it contributes 0 to the character).

<sup>3</sup>Note also that  $a_{11} = 1$  since the  $x$ -vector (a basis) is unchanged under  $\sigma_v(xz)$ ,  $a_{22} = -1$  since the  $y$ -vector is reversed under  $\sigma_v(xz)$ , and  $a_{33} = 1$  since the  $z$  vector is unchanged under  $\sigma_v(xz)$ .

$E$	all unchanged	4
$C_4$	all move	0
$C_2$	all move	0
$2\sigma_v$	2 move, 2 unchanged	2
$2\sigma_d$	all move	0

Table II.4: Changes in the fluorine atoms of  $\text{XeOF}_4$  under the  $C_{4v}$  symmetry operations.

- Thus,  $\Gamma = (4, 0, 0, 2, 0)$ .
- With the  $C_{4v}$  character table and the decomposition formula, we can discover that  $\Gamma = A_1 + B_1 + E$ .

## II.7 TA Review Session 1

1/22:

- We also don't need to show the equatorial electron pair in the shape picture.
- For  $\text{SeCl}_4$ , we need to show that the axial bonds are longer and are not straight up and down.
- For  $\text{I}_3^-$ , it's trigonal bipyramidal EPA and linear molecular geometry — there's an extra electron pair around the central iodine atom. This makes it  $D_{\infty h}$  point group.
- For  $\text{SeOCl}_4$ , we should also make the axials longer and bent away from the oxygen atom.
  - This molecule is  $sp^3d$  hybridized, not  $sp^2d^2$ , as it would be if the oxygen were axial.
- For  $\text{IO}(\text{OH})_5$ , we should show the equatorial OH's pushed away from the oxygen atom. The oxygen bond should also be a bit shorter.
- In the exam, they will specify whether we need to consider the hydrogens or not when calculating symmetry.
- For  $\text{ClOF}_4^-$ , one or the other of the lone pair/oxygen will push the equatorial fluorines a bit. You don't have to know which, just show bent.
- For  $\text{XeO}_2\text{F}_2$ , show the lone pair pushing the axial fluorines away.
- For  $\text{IF}_3^{2-}$ , show that this is a *distorted* T.
- A tennis ball belongs to the  $D_{2d}$  point group since you have perpendicular  $C_2$  axes punching through the seam and mirror planes at  $45^\circ$  angles to the  $C_2$  axes (i.e., dihedral).
- $\text{FeF}_6^{3-}$  also loses 4  $C_2$  axes.
- There are three possible isomers of  $\text{IF}_3\text{O}_2$  (see Figure I.1), but the one with equatorial oxygens is the most stable.
  - The structure analogous to Figure I.1a has  $C_{2v}$  symmetry.
  - The structure analogous to Figure I.1b has  $D_{3h}$  symmetry.
  - The structure analogous to Figure I.1c has  $C_s$  symmetry.
- Determine the point group of  $\text{NO}_3^{2-}$ ,  $\text{HFC}=\text{C}=\text{CHF}$ ,  $\text{H}_2\text{C}=\text{CF}_2$ , and  $\text{C}_2\text{H}_6$  (consider three possible conformers).
  - $\text{NO}_3^{2-}$  is of the  $D_{3h}$  point group.
  - $\text{HFC}=\text{C}=\text{CHF}$  is of the  $C_2$  point group.
  - $\text{H}_2\text{C}=\text{CF}_2$  is of the  $C_{2v}$  point group.
  - $\text{C}_2\text{H}_6$  eclipsed has  $D_{3h}$  symmetry, staggered has  $D_{3d}$  symmetry, and others have  $D_3$  symmetry.

## II.8 Module 9: Molecular Vibrations

1/25:

- If you have a nonlinear triatomic molecule (like  $\text{H}_2\text{O}$ ), we have  $3 \text{ atoms} \times 3 \text{ DOF} = 9 \text{ DOF}$ .
  - This accounts for any possible perturbations of our molecules.
- We can break this down into three types of motion:
  - Translational motion along the  $x$ -,  $y$ -, and  $z$ -axes (3 DOFs).
  - Rotational motion about the  $x$ -,  $y$ -, and  $z$ -axes (3 more DOFs).
  - The remaining degrees of freedom are vibrational.
- Every *nonlinear* molecule has 3 translational and 3 rotational DOFs.
  - The number of vibrations is  $3N - 6$ , where  $N$  is the number of atoms.
- Every *linear* molecule has 3 translational and 2 rotational DOFs.
  - The number of vibrations is  $3N - 5$ , where  $N$  is the number of atoms.
- **Vibrational mode:** A perturbation of molecular structure that keeps the center of mass of the molecule in one place.
- For  $\text{H}_2\text{O}$ , there are three vibrational modes: antisymmetric stretch (one H moves away from the O as the other moves in, and then the process reverses), symmetric stretch (both H's move away from the O and then move back in), and scissoring bend (the bond angle changes).
- For molecules in general, there are these three and an additional three: wagging (in  $\text{H}_2\text{O}$ , the H's rotate out of the plane of the molecule and then back), twisting (in  $\text{H}_2\text{O}$ , both H's rotate out of the plane of the molecule, but one in one direction and one in the other), and rocking (in  $\text{H}_2\text{O}$ , both H's rotate about the O within the plane of the molecule preserving the bond angle, and then go back).
- What vibrational modes a molecule can and cannot have is governed by its point group and group theory.
- Each normal mode of vibration forms a basis for an irreducible representation of the point group of the molecule.
- Workflow to identify the vibrational properties of a molecule:
  1. Find number/symmetry of vibrational modes.
  2. Assign the symmetry of known vibrations.
  3. What does the vibration look like?
  4. Find if a vibrational mode is IR or Raman Active.
- To find vibrational modes, follow the 5-step Basis  $\rightarrow$  reducible representation  $\rightarrow$  irreducible representation workflow and then subtract translational and rotational motion.
  - For example, with  $\text{H}_2\text{O}$ , as before, we have  $C_{2v}$  point group,  $3N$  basis,  $\Gamma_{3N} = (9, -1, 1, 3)$ , and  $\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$ .
  - We now need to use the basis functions in the  $C_{2v}$  character table to determine the translational and rotational degrees of freedom. From Figure II.4, the  $x, y, z$ -translational modes come from the  $B_1, B_2$ , and  $A_1$   $\Gamma_i$ 's, respectively. Thus, the total translational mode, sufficient to describe all possible translations in 3 DOFs, is  $\text{trans} = A_1 + B_1 + B_2$ . Similarly, we can determine that the total rotational mode is  $\text{rot} = A_2 + B_1 + B_2$ .
  - Thus, we can determine that the total vibrational mode is  $\Gamma_{3N} - \text{trans} - \text{rot} = 2A_1 + B_2$ .

- When H<sub>2</sub>O scissors or symmetrically stretches, it maintains its  $C_{2v}$  symmetry. Thus, both of these vibrations are represented by the totally symmetric irreducible representation  $A_1$  (hence the  $2A_1$  component).
- As to asymmetric stretch, there exist points in time where H<sub>2</sub>O lowers its symmetry from  $C_{2v}$  to  $C_s$ , losing its  $C_2$  and  $\sigma_v(xz)$  symmetry elements but maintaining  $E$  and  $\sigma_v(yz)$ . This shift is encapsulated by the  $B_2$  irreducible representation.
- We can see all of these modes in H<sub>2</sub>O's infrared absorption spectrum.
  - Note that this spectrum does not tell us the energy of vibrations (we can model this with quantum mechanics), or if it is IR or Raman active (which modes will appear in the respective spectrum).
- Determine the number and symmetry types for the translations, vibrations, and rotations of PF<sub>5</sub>.

- Point group:  $D_{3h}$ .

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_6$	$3\sigma_v$	linear	quadratic
$A'_1$	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A'_2$	1	1	-1	1	1	-1	$R_z$	
$E'$	2	-1	0	2	-1	0	$(x, y)$	$(x^2 - y^2, xy)$
$A''_1$	1	1	1	-1	-1	-1		
$A''_2$	1	1	-1	-1	-1	1	$z$	
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$	$(xz, yz)$

Table II.5: Character table for the  $D_{3h}$  point group.

- We could write out all 18  $x, y, z$ -vectors, or we can use a shortcut: To construct  $\Gamma_{3N}$ , we can, for each symmetry element, multiply the number of atoms atoms unmoved under the operation by the corresponding character the representation that accounts for  $x, y, z$ -movements.

$$\Gamma_{3N} = (\Gamma_{x,y,z}) \cdot (\# \text{ unmoved atoms})$$

Applying this shortcut, we have  $\Gamma_{x,y,z} = E' + A''_2 = (3, 0, -1, 1, -2, 1)$ . We also have  $\#$  unmoved atoms =  $(6, 3, 2, 4, 1, 4)$ . Thus,  $\Gamma_{3N} = (18, 0, -2, 4, -2, 4)$ .

- We can now reduce it into  $\Gamma_{3N} = 2A'_1 + A'_2 + 4E' + 3A''_2 + 2E''$ .
  - Note that we still have our 18 degrees of freedom because each  $E$  is double degenerate, meaning that  $4E'$  counts for 8 degrees of freedom and  $2E''$  counts for 4 degrees of freedom.
- This combined with the fact that  $\Gamma_{\text{trans}} = \Gamma_{x,y,z} = E' + A''_2$  and  $\Gamma_{\text{rot}} = A'_2 + E''$  implies that  $\Gamma_{\text{vibs}} = 2A'_1 + 3E' + 2A''_2 + E''$ .
  - For a similar reason to the note above, we can count  $12 = 3N - 6$  degrees of freedom (vibrational modes) in  $\Gamma_{\text{vibs}}$ .
- Although degenerate modes count for multiple DOFs, the multiple modes they count for are of the same type.
  - In an ideal world, those modes corresponding to  $E$  would be twice as intense as the others.
  - From the definition of  $\Gamma_{\text{vibs}}$  and the above discussion, we know that PF<sub>5</sub> has  $2 + 3 + 2 + 1 = 8$  distinct vibrational modes.
- There are (broadly) two types of vibrations: **stretches** ( $\nu$ ) and **bends** ( $\delta$ ).
  - These two types appear in different energies in IR and Raman spectra.
- To differentiate between stretching and bending modes: Look at how the stretching modes transform. Each stretch happens along a single vector from central atom to ligand. Thus, if we let these vectors be our basis and look at how many vectors stay the same (+1) or change (-1) under each operation, we will have a reducible representation that can be decomposed. Its components will be the stretching modes and  $\Gamma_{\text{vibs}} - \Gamma_{\nu}$  will equal  $\Gamma_{\delta}$ .



- Applied to  $\text{PF}_5$ , we have  $\Gamma_\nu = (5, 2, 1, 3, 0, 3) = 2A'_1 + E' + A'_2$ .
- Thus, both  $A'_1$  representations, one  $E'$  representation, and one  $A'_2$  representation correspond to stretching modes. Consequently, the other two  $E'$  representations, the other  $A'_2$  representation, and the  $E''$  representation correspond to bending modes.

## II.9 Module 10: IR and Raman Active Vibrations

- Today, we will learn what we need to know for PSet 2. Tomorrow, we will introduce a more rigorous, quantum mechanical foundation.
- Molecular vibrations can be experimentally observed by **infrared spectroscopy** or **Raman spectroscopy**.
- **Infrared spectroscopy**: A method of measuring the change in dipole moment during a vibration<sup>[4]</sup>. *Also known as IR spectroscopy*.
- **Raman spectroscopy**: A method of measuring the change in the polarizability during a vibration. We impinge upon a sample of a substance with an incident light (a powerful laser). Most of the light that scatters will be a **Raleigh scatter**, but some will be a **Raman scatter** (a new wavelength).
- **Raleigh scatter**: The same wavelength is emitted as was impinged by the incident light because the laser was elastically scattered. The electrons fell the same number of energy levels that they rose after absorbing the light.
- **Raman scatter**: A new wavelength is emitted, different than the one impinged by the incident light. The electrons fell fewer (**Stokes Raman scattering**) or more (**Anti-Stokes Raman scattering**) energy levels than they rose after absorbing the light.
- **IR active** (vibration): A vibration that transforms with the same symmetry as the  $\vec{x}$ ,  $\vec{y}$ , and  $\vec{z}$  vectors (see the  $\chi$  tables).
- **Raman active** (vibration): A vibration having the same symmetry as the quadratic  $x, y, z$  terms, i.e.,  $x^2, z^2, yz$ , etc.
- For molecules possessing inversion centers, IR and Raman activity will be mutually exclusive.
- Activity data comes from character tables.
  - All vibration representations that have a linear term are IR active, while those that have a quadratic term are Raman active.
- Continuing with the  $\text{PF}_5$  example...
  - Table II.5 tells us that  $E'$  and  $A'_2$  vibrations are IR active, and  $A'_1$ ,  $E'$ , and  $E''$  are Raman active.
  - Thus, since  $\Gamma_{\text{vibs}} = 2A'_1 + 3E' + 2A'_2 + E''$ , there are  $3 + 2 = 5$  IR active bonds (corresponding to  $3 \cdot 2 + 2 = 8$  vibrations) and  $2 + 3 + 1 = 6$  Raman active bonds (corresponding to  $2 + 3 \cdot 2 + 1 \cdot 2 = 10$  vibrations).

## II.10 Chapter 4: Symmetry and Group Theory

From Miessler et al. (2014).

- 1/18: • **Coincident** (axes): Two identical axes.
- For example, the  $C_3$  rotation axis of  $\text{CHCl}_3$  is **coincident** with the C–H bond axis.

<sup>4</sup>Refer to Labalme (2020), specifically the discussion of spectroscopy in Chapter 13.

- 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:

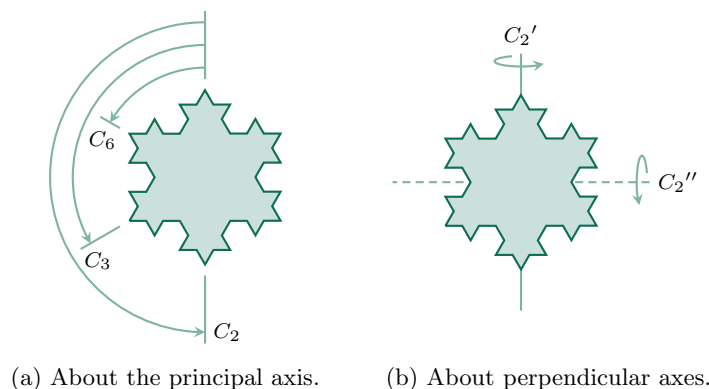


Figure II.6: Rotations of a snowflake design.

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  $\sigma$  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 ( $\sigma_h$ ) 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 ( $\sigma_v$  or  $\sigma_d$ )? If so, it is classified as  $C_{nv}$  or  $D_{nd}$ . If 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  $\sigma_d$  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:  $\text{W}[\text{N}(\text{CH}_3)_2]_6$ .

1/24:

- When we have a block-diagonalized reducible representation, the irreducible representations can be obtained from the individual blocks.
- This is because we will find that an analogous set of blocks satisfies the multiplication table for the group.
- For the  $C_{2v}$  point group, we have the following reducible representation that can be applied to each coordinate.

$$E : \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2 : \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(xz) : \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v(yz) : \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- The above matrices are block diagonalized. Thus, the sets of  $a_{11}$ ,  $a_{22}$  and  $a_{33}$  form three irreducible representations (and we can confirm that these obey the  $C_{2v}$  group multiplication table).

$$\begin{array}{llll} E : [1] & C_2 : [-1] & \sigma_v(xz) : [1] & \sigma_v(yz) : [-1] \\ E : [1] & C_2 : [-1] & \sigma_v(xz) : [-1] & \sigma_v(yz) : [1] \\ E : [1] & C_2 : [1] & \sigma_v(xz) : [1] & \sigma_v(yz) : [1] \end{array}$$

- Three of the  $C_{2v}$  irreducible representations can be found in this way. The fourth can be found w/ linear algebra and the character table properties (or by inspection).
- If one matrix in the reducible representation cannot be blocked past having a  $2 \times 2$  chunk, per se, then the others must also have that  $2 \times 2$  chunk (so that we have an irreducible  $2 \times 2$  representation).
- “Matching the symmetry operations of a molecule with those listed in the top row of the character table will confirm any point group assignment” (Miessler et al., 2014, p. 99).
- **Symmetric:** Character of 1.
- **Antisymmetric:** Character of  $-1$ .
- Mulliken symbol rules:
  1. “Letters are assigned according to the dimension of the irreducible representation” (Miessler et al., 2014, p. 99).
    - Assign  $A$  if the dimension is 1 and the representation is symmetric to the principal rotation operation ( $\chi(C_n) = 1$ ).
    - Assign  $B$  if the dimension is 1 and the representation is antisymmetric to the principal rotation operation ( $\chi(C_n) = -1$ ), or if  $\chi(S_{2n}) = -1$  even if  $\chi(C_n) = 1$ .
    - Assign  $E$  if the dimension is 2.
    - Assign  $T$  if the dimension is 3.

2. “Subscript 1 designates a representation symmetric to a  $C_2$  rotation perpendicular to the principal axis, and subscript 2 designates a representation antisymmetric to the  $C_2$ . If there are no perpendicular  $C_2$  axes, 1 designates a representation symmetric to a vertical plane, and 2 designates a representation antisymmetric to a vertical plane” (Miessler et al., 2014, p. 100).
3. “Subscript  $g$  designates representations symmetric to inversion, and subscript  $u$  designates representations antisymmetric to inversion” (Miessler et al., 2014, p. 100).
4. “Single primes are symmetric to  $\sigma_h$  and double primes are antisymmetric to  $\sigma_h$  when a distinction between representations is needed ( $C_{3h}$ ,  $C_{5h}$ ,  $D_{3h}$ ,  $D_{5h}$ )” (Miessler et al., 2014, p. 100).

## II.11 Nocera Lecture 3

From Nocera (2008).

- 1/25:
- Corresponding blocks within block-diagonalized matrices obey the same multiplication properties as the block-diagonalized matrices, themselves.
  - One basis may not uncover all irreducible representations.
    - For example, we can use a Cartesian basis to uncover the  $A_1$  and  $E$  irreducible representations of the  $D_3$  point group (see Table II.3) and the basis function  $R_z$  ( $E : R_z \rightarrow R_z$ ,  $C_3 : R_z \rightarrow R_z$ ,  $\sigma_v : R_z \rightarrow \bar{R}_z$ ) to uncover the  $A_2$  irreducible representation.
  - We can also construct a character table algebraically. Continuing with the  $D_3$  example...
    - There is one totally symmetric representation  $\Gamma_i = (1, 1, 1)$ .
    - $h = 6 = \sum_i [\chi_i(E)]^2$ . Since each  $\chi_i(E)$  can only be 1, 2, or 3, we know that  $\chi_1(E) = \chi_2(E) = 1$  and  $\chi_3(E) = 2$ .
    - This combines with orthogonality to reveal that

$$\begin{aligned}
 0 &= \sum_{R_c} g_c \chi_1(R_c) \chi_2(R_c) \\
 &= 1 \cdot 1 \cdot 1 + 2 \cdot 1 \cdot \chi_2(C_3) + 3 \cdot 1 \cdot \chi_2(\sigma_v) \\
 &= 1 + 2\chi_2(C_3) + 3\chi_2(\sigma_v)
 \end{aligned}$$

i.e.,  $\Gamma_i = (1, 1, -1)$ .

- To determine the last representation, we can use two rules and solve as a system of equations.

$$\begin{aligned}
 0 &= \sum_{R_c} g_c \chi_1(R_c) \chi_3(R_c) & 6 &= \sum_{R_c} g_c [\chi_3(R_c)]^2 \\
 &= 2 + 2\chi_3(C_3) + 3\chi_3(\sigma_v) & &= 4 + 2[\chi_3(C_3)]^2 + 3[\chi_3(\sigma_v)]^2
 \end{aligned}$$

From this, we can determine that  $\chi_3(C_3) = -1$  and  $\chi_3(\sigma_v) = 0$ . Therefore,  $\Gamma_i = (2, -1, 0)$ .