MAT 541 001 Modern Algebra
Molecular Symmetry and Group Theory

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Contents

1 Introduction

Symmetry is a bridge that connects the world that we can see with the quantum mechanical realm that governs the laws of chemistry. The language that describes symmetry is that of mathematics, in particular group theory, representation theory, and character theory. Countless chemical processes are connected to the symmetry of molecules, and a deep understanding of these concepts is rooted in algebra. In this paper, we will take a interdisciplinary tour of this interface between chemistry and mathematics. First, we will introduce some basic chemistry principles that will aid in understanding. We will look at the symmetry that molecules possess and how to categorize it in a systematic fashion via point groups. Then we will switch to a mathematical discussion of groups, matrices, and characters, and learn how to build character tables for point groups from scratch. Then we will switch back to chemistry and discuss the interplay of symmetry and molecular vibrations. Finally, we will look at a few applications of character theory in chemistry. Much of the presentation of point groups and character theory follows the treatments in [1–4].

2 Brief review of chemical structures

At the submicroscopic level, all matter is composed of atoms, which are further broken into protons, neutrons, and electrons. Protons have positive charge, neutrons have no charge, and electrons have negative charge. Protons and neutrons are clustered together in the nucleus, a dense ball in the center of the atom. Electrons surround the nucleus in orbitals, which can be thought of as probabilistic "clouds" where the electrons are most likely to be at any given time. The identity of a particular atom (e.g., carbon, oxygen, etc.) is fully determined by the number of protons in its nucleus. Atoms can exist independently, but most of the matter we encounter on a daily basis is not made of individual atoms, but rather clusters of atoms in the form of molecules or ionic compounds.

Atoms *bond* together through interactions of their electrons. The driving force of the bonding process is stability; atoms are in their most stable state when their outermost orbital is completely filled with electrons. Atoms can either gain or lose electrons in order to achieve this stable state. When two atoms share electrons more or less equally with one another, we have a covalent bond. When one atom takes the electrons entirely from another atom, we have an ionic bond. Ionic bonds occur in table salt (NaCl), for example. We will be focusing instead on *molecules*, which are clusters of atoms that are covalently bonded with one another. Molecules exist in myriad fascinating ways, from simple molecules like H_2O to incredibly complicated molecules like DNA. Our main focus will be on characterizing the symmetry of simple molecules, although the process involved can be extended to more complicated cases.

When two electrons are shared between two atoms, we have a single bond, denoted as $C-C$, for example. When four electrons are shared, we have a double bond, denoted $C=C$. When six electrons are shared, we have a triple bond, denoted $C\equiv C$. Components of molecules can freely rotate along the axis of a single bond, but double and triple bonds are locked and cannot rotate.

To understand the shapes of molecules, it is essential to learn a little bit of VSEPR theory. VSEPR ("VES-per") stands for Valence Shell Electron Pair Repulsion. For this purpose, we will choose one atom in a molecule to be the central atom. (For the simple molecules we deal with, the central atom will be apparent

visually.) The name of VSEPR itself explains a lot of the theory. The valence shell is the outermost orbital of electrons, where bonding takes place; electrons tend to occur in pairs; like charges repel, so electron pairs tend to position themselves to be as far away from other electron pairs as possible. Now, some of the electron pairs on the central atom will be bonding (shared with other atoms), and some will be nonbonding (not shared). A pair of nonbonding electrons is called a *lone pair*.
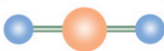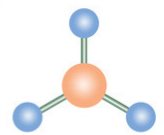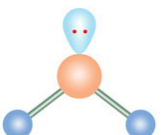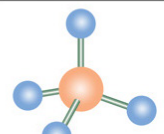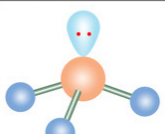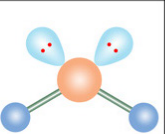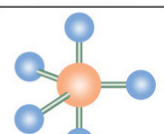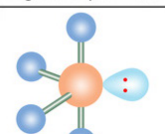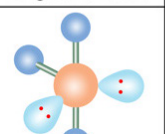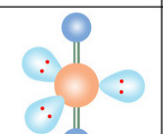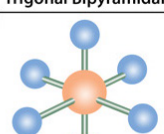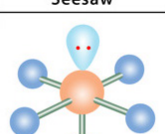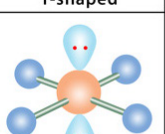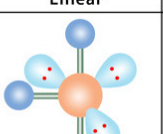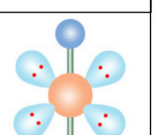
Number of Electron Groups	Lone Pairs = 0	Lone Pairs = 1	Lone Pairs = 2	Lone Pairs = 3	Lone Pairs = 4
2	Linear				
3	Trigonal Planar	Angular or Bent			
4	Tetrahedral	Trigonal Pyramidal	Angular or Bent		
5	Trigonal Bipyramidal	Seesaw	T-shaped	Linear	
6	Octahedral	Square Pyramidal	Square Planar	T-shaped	Linear

Figure 1: The most common molecular geometries based on VSEPR theory. [5]

The number of electron groups is the sum of the number of bonds and the number of lone pairs on the central atom. (For this purpose, single, double, and triple bonds are treated equally.) The number of electron groups and the number of lone pairs is all that is needed to determine the *molecular geometry*, as shown in Figure 1. In water (H_2O), the oxygen atom is bonded to two hydrogen atoms and has two lone pairs. Hence, water is a bent molecule. In ammonia (NH_3), the nitrogen atom is bonded to three hydrogen atoms and has one lone pair. Therefore, ammonia is a trigonal pyramidal molecule. In methane (CH_4), the carbon atom is bonded to four hydrogen atoms and has no lone pairs. Thus, methane is a tetrahedral molecule.

As mentioned above, the sharing of electrons between atoms in a covalent bond can be more or less equal. If the atoms are of similar "strength" (similar electronegativity), the electrons will be shared equally, forming a nonpolar bond. If one atom is "stronger" than another (higher electronegativity), it will attract electrons

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to it, causing the sharing to be unequal. This results in a polar bond. If the polar bonds are equal and in opposite directions, they cancel by *symmetry*, and the molecule will be *nonpolar*. This occurs in carbon dioxide (CO_2), which is a linear molecule (C has two double bonds, no lone pairs). By contrast, if the polar bonds do not cancel by symmetry, the molecule will be *polar*. This occurs in water. Many of the interesting characteristics of water (high boiling point, high surface tension, ice having a lower density that liquid water, etc.) are a direct consequence of the strong hydrogen bonds formed between different water molecules, and this is due to the polarity of the water molecule. If water were nonpolar, it would most likely be a gas at room temperature and behave more like carbon dioxide or methane. Life as we know it would be impossible if water was not a bent polar molecule!

2.1   Notes about notation

For the sake of representing three dimensional molecules on two dimensional paper, some bonds will be drawn as wedges and dashes. For example, consider the following molecule:
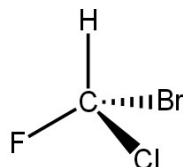
Here, the wedge bond implies that the chlorine (Cl) atom is facing towards the reader, while the dashed bond implies that the bromine (Br) atom is facing away from the reader. The normal (skinny) bonds should be interpreted as being in the plane of the paper.

One other convention that needs to be noted is the way benzene rings will be shown. Benzene is a ring of six carbons with alternating (conjugated) double and single bonds, with each carbon bound to a hydrogen, as follows:
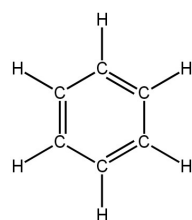
Due to the tedious nature of drawing this molecule and its frequency of occurrence, it will be shown in the following standard shorthand way:

3   Symmetry elements and operations

Many molecules contain *symmetry elements*, such as rotational axes, mirror planes, and inversion centers, upon which *symmetry operations* can be performed, such as rotation, reflection, or inversion. The molecule

will be indistinguishable before and after the symmetry operation.

The most basic symmetry operation is E, the identity operation. This is the act of doing nothing, and is required in order to express a collection of symmetries as a group.

A proper rotation, C_n, is a rotation that can actually be achieved in three-dimensional space. It is a rotation through $360°/n$ counterclockwise with respect to some axis. We have that $C_n^n \equiv E$, so that the order of the rotation C_n is n. If a molecule has more than one rotational axis, the one of highest order is called the *principal axis*. By convention, a C_2 axis will be denoted C_2' if it passes *through* outer atoms, and C_2'' if it passes *between* outer atoms.

A reflection over a mirror plane is denoted σ. In particular, a reflection plane that is perpendicular to the principal axis is called horizontal and denoted σ_h. A reflection plane that includes the principal axis is called vertical and denoted σ_v. A vertical reflection plane that bisects the angle between two C_2 axes is called dihedral and denoted σ_d.

The inversion operation, i, is where every point of the molecule is moved through the inversion center (the center of the molecule) to its opposite position the same distance from the center.

An improper rotation, S_n, also called a rotation-reflection, is a C_n rotation followed by a σ_h reflection through a plane perpendicular to the rotation axis. Two S_n operations together form a $C_{n/2}$ operation. An S_2 operation is equivalent to i. In some molecules, S_j axes are coincident with C_k axes.

4 Point groups

The collection of symmetry operations that a molecule possesses determines its *point group*. It is named such since every symmetry element shares a single point, and the symmetry elements and operations have an algebraic group structure. [6] Determining the point group of a molecule can be rather complicated, but there is a sequence of steps that can be followed to determine a point group without much trouble. To get started, we can classify molecules as being of *low symmetry*, *high symmetry*, or neither. We will list the point groups of the three categories and show example molecules that exhibit each group. To assist in determining the point groups for molecules of neither low nor high symmetry, we will use a flowchart.

4.1 Point groups of low symmetry

Molecules in the C_1 group have no symmetry besides the identity operation E. (Indeed, every point group contains E, but it will not be mentioned in the following groups.)
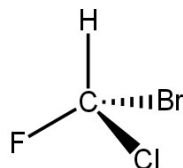
Molecules in the C_s group have only one mirror plane (in the following example, the mirror plane is the plane of the molecule).
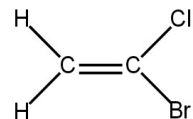
Molecules in the C_i group have only an inversion center.
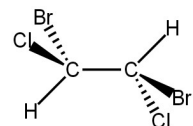
4.2 Point groups of high symmetry

Molecules in the $C_{\infty v}$ group are linear, with infinite rotation order and an infinite number of reflection planes containing the rotation axis. They contain no inversion center. An example is hydrogen chloride.

Molecules in the $D_{\infty h}$ group are like $C_{\infty v}$, but with perpendicular C_2 axes, a perpendicular mirror plane, and an inversion center. An example is carbon dioxide.

Molecules in the T_d group are tetrahedral, with four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d mirror planes. An example is methane.
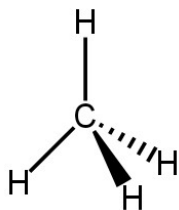
Molecules in the O_h group are octahedral, with 48 symmetry operations in all. An example is sulfur hexafluoride.
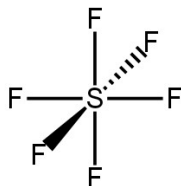
Molecules in the I_h group are icosahedral, with 120 symmetry operations in all. A fascinating example is buckminsterfullerene, a molecule with sixty carbon atoms in a soccer ball shape.
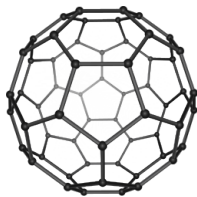
4.3   Other point groups

To help distinguish which molecules are in each of the remaining point groups, we can refer to the flowchart in Figure 2.

Are there n C_2 axes perpendicular to the principal axis?

Yes → Is there a horizontal mirror plane?

No → Is there a horizontal mirror plane?

Yes → D_{nh}

No → Are there n dihedral mirror planes?

Yes → C_{nh}

No → Are there n vertical mirror planes?

Yes → D_{nd}

No → D_n

Yes → C_{nv}

No → Is there an S_{2n} axis?

Yes → S_{2n}

No → C_n
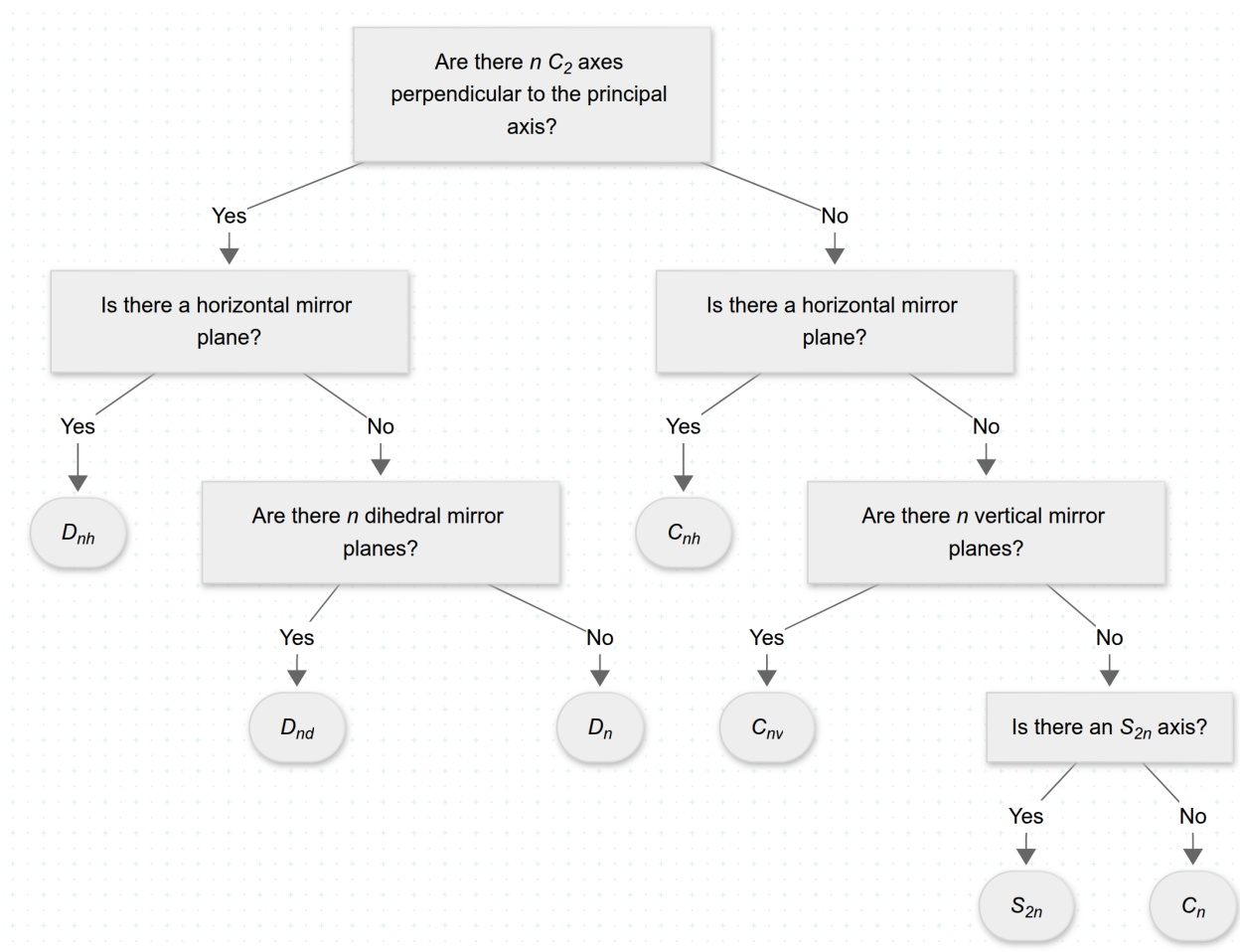
Figure 2: Flowchart to help determine point groups of molecules.

Molecules in the C_{nh} group contain a C_n rotation axis, a horizontal mirror plane σ_h, and an inversion center. The following examples are C_{2h}, C_{2h}, and C_{3h}, respectively:
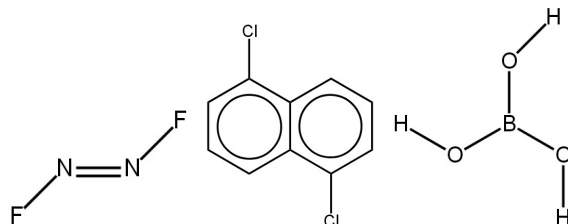
Molecules in the C_{nv} group contain a C_n rotation axis and n vertical mirror planes σ_v. The following examples are C_{2v}, C_{3v}, and C_{4v}, respectively:
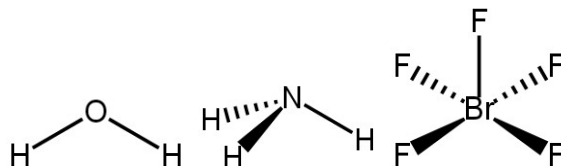
Due to the importance of water and ammonia, we will devote much of our mathematical study to the C_{2v} and C_{3v} point groups in the following sections.

Molecules in the C_n group contain a C_n rotation axis but no mirror planes. An example is hydrogen peroxide, which is in the C_2 point group.
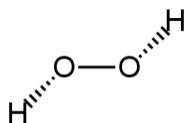
Molecules in the D_{nh} group contain a C_n rotation axis and n perpendicular C_2 rotation axes. They also have a horizontal mirror plane σ_h. The following examples are D_{3h}, D_{3h}, and D_{4h}, and D_{6h}, respectively:
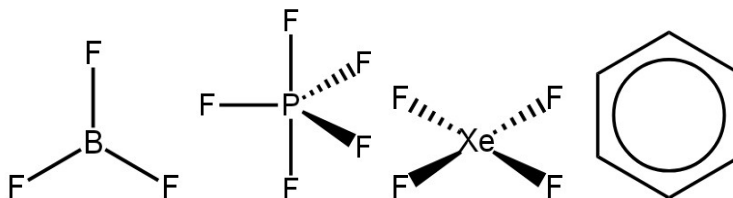
Molecules in the D_{nd} group contain a C_n rotation axis and n perpendicular C_2 rotation axes. They also have n dihedral mirror planes σ_d. An example is ethane, which is in the D_{3d} point group.
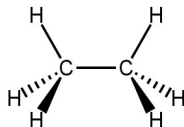
Molecules in the D_n group contain a C_n rotation axis and n perpendicular C_2 rotation axes, but no mirror planes. Only the skeletal structure is shown in the following example of a D_3 molecule in order to emphasize the shape.
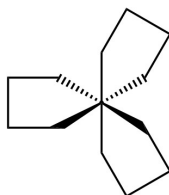
Molecules are in the S_{2n} group if they contain an S_{2n} rotation-reflection axis, one C_n rotation axis, and if they do not qualify to be in any of the C or D point groups. The following molecule is in the S_4 point group.
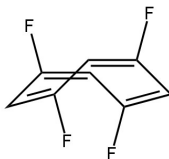
5   Algebraic group structure of point groups

To gain a deeper understanding of point groups, we need to look at them through an algebraic lens. The first thing that we need to do is to verify that point groups truly fit the algebraic definition of a group. To illustrate the group structure of the point groups, we will use the point groups of ammonia (NH_3), C_{3v}, and water (H_2O), C_{2v}, as examples. We will verify that C_{3v} satisfies the definition of a group by showing that it has an identity, inverses, closure, and associativity. Every point group, including C_{3v}, has a symmetry operation E which serves the role as the identity element of the group. The C_3 rotation has the inverse C_3^2, as $C_3 C_3^2 = C_3^3 = E$ and $C_3^2 C_3 = C_3^3 = E$. Likewise, C_3^2 has the inverse C_3. Each reflection σ_v is its own inverse. Note that C_{3v} does not have a perpendicular C_2 axis or a σ_h horizontal mirror plane (NH_3 is trigonal pyramidal, not trigonal planar). We have that the C_{3v} group is isomorphic to the S_3 permutation group, since the symmetries of NH_3 correspond to the permutations of the triangle of three hydrogen atoms. Thus there are $3! = 6$ symmetry operations in C_{3v}: $\{E, C_3, C_3^2, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}\}$. Note that C_{3v} is not abelian. The Cayley table for the C_{3v} group is shown in Table 1. Closure can be verified from the Cayley table, and associativity follows from the associativity of function composition.

We will do the same process with C_{2v}. Clearly, C_{2v} has the identity operation E. The C_2 rotation is its own inverse, as $C_2 C_2 = C_2^2 = E$. The reflections σ_{v1} and σ_{v2} are their own inverses. There are 4 symmetry operations in C_{2v}: $\{E, C_2, \sigma_{v1}, \sigma_{v2}\}$. The Cayley table for C_{2v} is shown in Table 2. Closure can be verified from the Cayley table, and associativity follows from the associativity of function composition. Furthermore, from the Cayley table, we can see that the C_{2v} is isomorphic to the Klein 4-group V_4.

Now that we know molecular symmetry can be expressed in terms of algebraic groups, it is natural to consider how group theory can help us to understand observable chemical processes. To gain understanding of the underlying mathematical structure, we will use representation theory to express the symmetry operations in

	g					
$f \circ g$	E	C_3	C_3^2	σ_{v1}	σ_{v2}	σ_{v3}
E	E	C_3	C_3^2	σ_{v1}	σ_{v2}	σ_{v3}
C_3	C_3	C_3^2	E	σ_{v3}	σ_{v1}	σ_{v2}
C_3^2	C_3^2	E	C_3	σ_{v2}	σ_{v3}	σ_{v1}
σ_{v1}	σ_{v1}	σ_{v2}	σ_{v3}	E	C_3	C_3^2
σ_{v2}	σ_{v2}	σ_{v3}	σ_{v1}	C_3^2	E	C_3
σ_{v3}	σ_{v3}	σ_{v1}	σ_{v2}	C_3	C_3^2	E

(f labels the row index.)
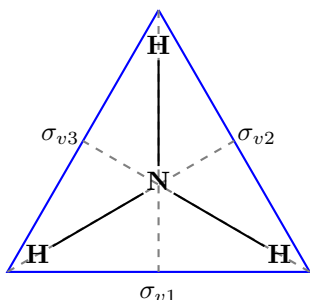
E: Identity

C_3: 120°, counterclockwise

C_3^2: 240°, counterclockwise

Table 1: The Cayley table for the C_{3v} point group, using ammonia (NH$_3$) as an example. The viewpoint of the molecule is with the nitrogen atom in the plane of the paper and the hydrogen atoms facing away from the reader.

	g			
$f \circ g$	E	C_2	σ_{v1}	σ_{v2}
E	E	C_2	σ_{v1}	σ_{v2}
C_2	C_2	E	σ_{v2}	σ_{v1}
σ_{v1}	σ_{v1}	σ_{v2}	E	C_2
σ_{v2}	σ_{v2}	σ_{v1}	C_2	E

(f labels the row index.)
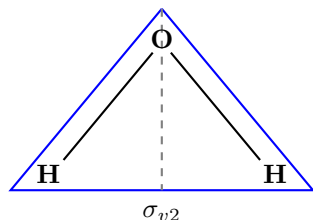
E: Identity

C_2: 180°

σ_{v1}: Reflection over molecular plane

Table 2: The Cayley table for the C_{2v} point group, using water (H$_2$O) as an example.

terms of matrices. Then we will use the principles of character theory to construct character tables, which are used by chemists to visualize the algebraic structure of various point groups in a concise and systematic way. We will use a standard system of notation to label the character tables, called *Mulliken symbols*. [7]

6   Representation of symmetry operations as matrices

Our next step in the mathematical analysis is to find matrix representations of the symmetry operations E, C_n, σ, i, and S_n. We will define these operations as transformations of the coordinate vector $(x, y, z)^T$. The identity operation E is represented by the identity matrix

$$M_E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The rotation operation C_n, where the rotation is about the z axis, is represented by the matrix

$$M_{C_n} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

where $\theta = \dfrac{360°}{n}$ (bond angles in chemistry are typically expressed in degrees). Matrices for other rotational axes can be constructed similarly. The reflection operations σ over the xy, yz, and xz planes are represented by the respective matrices

$$M_{\sigma_{xy}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, M_{\sigma_{yz}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \text{ and } M_{\sigma_{xz}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The inversion operation i is represented by the matrix

$$M_i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

Finally, the rotation-reflection operation S_n, where the rotation is about the z axis and the reflection is over the xy plane, is represented by the matrix

$$M_{S_n} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

where $\theta = \dfrac{360°}{n}$. Matrices for other rotational axes and reflection planes can be constructed similarly.

Now that we have a set of matrices for the symmetry operations, we can express the matrix representation of each of the point groups. To simplify the discussion, we will limit ourselves to the C_{2v} and C_{3v} point groups. We will look at the matrix representation for C_{2v} (H_2O) first. We use the notation established in Table 2. By convention, we define the z axis as the principal axis and the xz plane as the plane of the molecule, with the oxygen atom at the origin, as shown[1]:

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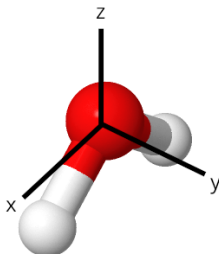
[1] The choice of axes is arbitrary. Mulliken [7] recommended using yz as the molecular plane for C_{2v}. However, in this paper, we are using the convention used in Miessler, Fischer, and Tarr [1].

Then the matrices for the symmetry operations of C_{2v} are

$$M_E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, M_{C_2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, M_{\sigma_{v1}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \text{ and } M_{\sigma_{v2}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Multiplying these matrices reveals the same group structure as shown in Table 2.

Now we will look at the matrix representation for C_{3v} (NH$_3$). We use the notation established in Table 1. By convention, we define the z axis as the principal axis, the xy plane as parallel to the hydrogen triangle, and the xz plane coinciding with one of the three σ_v mirror planes, with the nitrogen atom at the origin, as shown:
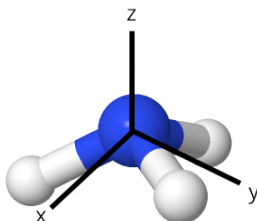
Then the matrices for the symmetry operations of C_{3v} are

$$M_E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, M_{C_3} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, M_{C_3^2} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$M_{\sigma_{v1}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, M_{\sigma_{v2}} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \text{ and } M_{\sigma_{v3}} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Multiplying these matrices reveals the same group structure as shown in Table 1.

7 Characters and reducible/irreducible representations

Constructing the matrices for the point groups above was challenging, especially in the case of C_{3v}, mainly because appropriate bases needed to be chosen, and the symmetries with respect to those bases needed to be computed with tedious hand calculations. Of course, different bases could have been used, which makes the matrix representations non-unique. These problems are disappointing, especially considering that C_{2v} and C_{3v} are two of the simplest and most common point groups in chemistry!

Thankfully, we have that the trace (character) of a matrix is conjugation invariant. Thus, if we change the basis, the characters remain the same. To simplify the representation of each point group, we will use characters instead of matrices. Quick calculations show that the characters of the symmetry operations in C_{2v} are $\chi_E = 3$, $\chi_{C_2} = -1$, $\chi_{\sigma_{v1}} = 1$, and $\chi_{\sigma_{v2}} = 1$. The characters in C_{3v} are $\chi_E = 3$, $\chi_{C_3} = 0$, $\chi_{C_3^2} = 0$, $\chi_{\sigma_{v1}} = 1$, $\chi_{\sigma_{v2}}1$, and $\chi_{\sigma_{v3}} = 1$.

The conjugacy classes in C_{2v} are the singleton sets $\{E\}, \{C_2\}, \{\sigma_{v1}\}, \{\sigma_{v2}\}$, which follows since $C_{2v} \cong V_4$ is an abelian group. The conjugacy classes in C_{3v} are the sets $\{E\}, \{C_3, C_3^2\}$, and $\{\sigma_{v1}, \sigma_{v2}, \sigma_{v3}\}$. Every symmetry operation in the same conjugacy class has the same character, and the operations in the same class will be grouped together when we create character tables.

The characters listed above for C_{2v} and C_{3v} are reducible representations. We will denote reducible representations by Γ. Our goal is to decompose these reducible representations into irreducible representations (irreps). The irreps will be denoted using a standard notation system, called Mulliken symbols. [7]

One dimensional irreps are denoted A if the representation is symmetric to the principal rotation (that is, $\chi_{C_n} = 1$) and B if the representation is antisymmetric to the principal rotation ($\chi_{C_n} = -1$). Two dimensional irreps are denoted E, and three dimensional irreps are denoted T. Furthermore, subscripts are used to distinguish irreps with the same letter label, and these subscripts are not arbitrary. Subscript 1 is used for an irrep that is symmetric to a perpendicular C_2 axis, and subscript 2 is used for an irrep that is antisymmetric to a perpendicular C_2. If there is no perpendicular C_2 axis, the subscript is determined based on the symmetry (1) or antisymmetry (2) with respect to the vertical mirror plane xz. Subscript g (*gerade*) is used for an irrep symmetric to inversion, and u (*ungerade*) is used in the antisymmetric case. For further distinction, $'$ is used for symmetry with respect to σ_h and $''$ is used for antisymmetry with respect to σ_h.

8 Character tables

Character tables are important in chemistry because they provide all of the symmetry information in a given point group in a succinct way. Group theory helps predict observable chemical behavior. In a sense, character tables package the underlying group theory into an easily read table that is shared by every molecule in a given point group. By reading a character table, a chemist can quickly determine which vibrational modes are IR- or Raman- active, the chirality of a molecule, or the way molecular orbitals can form, without needing to perform calculations. We will look at the construction of some simple character tables, and then we will explore some of their applications.

Now that we have found the matrices for the point groups C_{2v} and C_{3v}, we are ready to begin constructing the character table for those point groups, starting with C_{2v}. We now revisit the matrices for the C_{2v} symmetry operations, this time block diagonalized:

$$M_E = \begin{pmatrix} \boxed{1} & 0 & 0 \\ 0 & \boxed{1} & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix}, M_{C_2} = \begin{pmatrix} \boxed{-1} & 0 & 0 \\ 0 & \boxed{-1} & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix}, M_{\sigma_{v1}} = \begin{pmatrix} \boxed{1} & 0 & 0 \\ 0 & \boxed{-1} & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix}, \text{ and } M_{\sigma_{v2}} = \begin{pmatrix} \boxed{-1} & 0 & 0 \\ 0 & \boxed{1} & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix}.$$

We start building a character table by placing the elements from the first block in the first row (x), the elements from the second block in the second row (y), and the elements from the third block in the third row (z), and labeling the rows with Mulliken symbols. (Note that the xz plane of the water molecule drawn above corresponds to σ_{v1} in Table 2, which distinguishes B_1 and B_2.) The last two columns will be expanded upon later and their importance will become apparent. We will also fill in the empty row at the bottom.

C_{2v}	E	C_2	$\sigma_{v1}\ (xz)$	$\sigma_{v2}\ (yz)$		
B_1	1	-1	1	-1	x	
B_2	1	-1	-1	1	y	
A_1	1	1	1	1	z	
Γ	3	-1	1	1		

Character tables have several key properties. Let $\chi_i(C)$ represent the character of class C in the ith irrep.

- The number of symmetry operations is the order of the group, h.

- If symmetry operations are grouped by conjugacy class C, we show how many operations are in the class, n_C, in the top row. For example, if there are three rotations in the C_2 class, the top row will be labeled $3C_2$. We will call n_C the multiplicity of the class.

- The number of irreps equals the number of classes. That is, the character table needs to have the same number of rows and columns.

- Taking the sum over all of the irreps, we have

$$\sum_i \chi_i^2(E) = h,$$

  where E is the identity operation.

- For the ith irrep, we have

$$\sum_C n_C \chi_i^2(C) = h, \tag{1}$$

  where the sum is taken over all of the conjugacy classes.

- **Orthogonality Theorem.** Irreps are orthogonal. We have, for the ith and jth irreps,

$$\sum_C n_C \chi_i(C)\chi_j(C) = h\delta_{ij}, \tag{2}$$

  where δ_{ij} is the Kronecker delta. This form of the orthogonality formula is easily proven from the fact that every symmetry operation in a given conjugacy class has the same character. When $i = j$, (2) reduces to (1), and when $i \neq j$, we have

$$\sum_C n_C \chi_i(C)\chi_j(C) = 0.$$

- One irrep has characters that are all 1, which is labeled A_1.

- Each irrep must be distinct.

Applying these rules, we deduce that there is indeed a fourth irrep, and using the Orthogonality Theorem along with the other properties, we can find the characters of this fourth irrep, A_2.

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C_{2v}	E	C_2	$\sigma_{v1}\ (xz)$	$\sigma_{v2}\ (yz)$		
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

We now have a complete character table for C_{2v}. Notice that additional information has been added to the last two columns. The symbols R_x, R_y, and R_z indicate the rotational axes that are symmetric with respect to the irreps. For example, the C_2 operation corresponds to the R_z rotation. We have that C_2 is symmetric with respect to the A_2 irrep, so R_z is symmetric with respect to A_2. The σ_{v1} operation corresponds to a reflection over the xz plane, which is normal to the y axis. We have that σ_{v1} is symmetric with respect to the B_1 irrep, so R_y is symmetric with respect to B_1. Similarly, R_x is symmetric with respect to B_2.

The symbols x^2, y^2, xy, etc. represent mathematical functions that are symmetric with respect to the irreps. For instance, we know that the product function xy is positive in the first and third quadrants and negative in the second and fourth quadrants, and a 180° rotation about the z axis maintains these signs. However, a 180° rotation about the x or y axes reverses these signs. Hence, xy appears in the same row as R_z and is symmetric with respect to the A_2 irrep. The functions x^2, y^2, and z^2 are always positive, so they are symmetric with respect to the A_1 irrep.

At first, it may seem like these last two columns are only for curiosity's sake. However, as we will see, they have important applications in chemistry.

Now we will construct a character table for the C_{3v} point group. We now revisit the matrices for the C_{3v} symmetry operations, this time block diagonalized:

$$M_E = \left(\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right), M_{C_3} = \left(\begin{array}{cc|c} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right), M_{C_3^2} = \left(\begin{array}{cc|c} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right),$$

$$M_{\sigma_{v1}} = \left(\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right), M_{\sigma_{v2}} = \left(\begin{array}{cc|c} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right), \text{ and } M_{\sigma_{v3}} = \left(\begin{array}{cc|c} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right).$$

The C_3 and C_3^2 operations are in the same class, and likewise the three σ_v operations are in the same class, so they will be grouped together in the character table.

Following the procedure established above, we will go ahead and create the full character table for C_{3v}.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

We can verify that the order relations and orthogonality relations hold. For instance, $2^2 + 2(-1)^2 + 3(0)^2 = 6$, and $1 \cdot 2 + 2(1 \cdot -1) + 3(-1 \cdot 0) = 0$. Furthermore, notice that the label E was used for the two-dimensional irrep (2 in the E identity operation column). Confusingly, in chemistry, E is used to represent both the identity operation and 2D irreps. Also, notice that in the list of functions on the right, we group x and y together in parentheses. This is based on the block diagonalization, where x and y together form one block and z individually forms another block.

9 Expressing reducible representations in terms of irreps

The reducible representation Γ can be written as a linear combination of the irreducible representations (irreps). That is, for each class C, and for each character $\chi(C)$ in Γ, with corresponding character $\chi_i(C)$ in the ith irrep, there exist coefficients $n_1, n_2, \ldots$ such that

$$\chi_C = \sum_i n_i \chi_i(C). \tag{3}$$

Lemma 1. Each coefficient n_i in (3) is given by

$$n_i = \frac{1}{h} \sum_C n_C \chi(C) \chi_i(C),$$

where h is the order of the group.

Proof. From the Orthogonality Theorem, we have, for the ith and jth irreps,

$$\sum_C n_C \chi_i(C) \chi_j(C) = h \delta_{ij}.$$

Multiplying both sides by n_j, and taking the sum over all j irreps, we have

$$\sum_C n_C \sum_j n_j \chi_i(C) \chi_j(C) = h \sum_j n_j \delta_{ij} = h n_i. \tag{4}$$

We have by (3) that $\sum_j n_j \chi_j(C) = \chi(C)$. Substituting into (4), we get

$$\sum_C n_C \chi(C) \chi_i(C) = h n_i.$$

Divide both sides by h to complete the proof. $\qquad\square$

We can use Lemma 1 to find the number of times that an irrep contributes to Γ. We will look at an application of Lemma 1 in the next section, where we consider the vibrations of the water molecule.

10   Molecular vibrations

Not only do molecules as a whole move around, but also the individual atoms can move around slightly within the molecule, producing molecular vibrations. To mathematically study these vibrations, we need to first assign a separate 3D coordinate axis to each atom. For a molecule with N atoms, each atom can move independently in three dimensions, so there are $3N$ possible motions, called *degrees of freedom*.

In a nonlinear molecule, there are three translational *modes*, three rotational modes, and the remaining $3N - 6$ modes are vibrational. In a linear molecule, there are also three translational modes. However, a linear molecule only has two rotational modes, since a rotation along the axis of the molecule does not change the relative orientation of the atoms. Then the remaining $3N - 5$ modes are vibrational. As we will see in the next section, certain vibrational modes are represented by peaks in IR and Raman spectra. Counting and classifying vibrational modes is essential, as it lets chemists predict IR and Raman spectra from molecular structure. As we will see, character tables provide a systematic way to make these predictions.

If we create a $3N \times 3N$ transformation matrix to represent the effect of a symmetry operation on the position of each atom, an element in the diagonal of the matrix will be 1 if the atom remains in its original location, -1 if it reverses direction, and 0 if it moves. We can then take the character of the matrix for each symmetry operation. Since operations in the same class have the same character, we only need to construct one such matrix for each class. However, constructing these matrices explicitly can be tedious, especially for a molecule with many atoms. Thankfully, the only information we need from these matrices is their characters, and we can find the characters without explicitly constructing the matrices.

We will use the vibrations of the water molecule as an example. For convenience, we stick with the same coordinate axes that were used above, such that the z axis is the principal axis and the xz plane is the plane of the molecule. This time, however, each atom gets its own set of coordinate axes, and each atom is considered to be at its own origin. Since water has three atoms (one oxygen and two hydrogens), it has nine degrees of freedom.

Since water is a nonlinear molecule, it has $3N - 6 = 3$ vibrational modes. One of these is *symmetric stretch*, where the lengths of the O−H bonds lengthen and shorten in unison. One is *antisymmetric stretch*, where one O−H bond lengthens as the other one shortens. The last one is *symmetric bend*, where the bond angle increases and decreases, similar to a bird flapping its wings. Each of these vibrational modes changes the *dipole moment* of water, causing its polarity to oscillate slightly. If a picture is worth a thousand words, an animation is worth a million. The vibrational modes of water (and other molecules) can be seen at https://www.chem.purdue.edu/jmol/vibs/h2o.html.

We could create a 9×9 transformation matrix for each of the four symmetry classes in water. However, we can find the characters of each matrix without explicitly constructing the matrices. In the identity operation E, every atom remains in the same position, so the character $\chi_E = 9$. In the rotation C_2, the hydrogen atoms both move, so they contribute nothing to the character. The oxygen atom reverses direction with respect to x (-1) and y (-1), but not with respect to z (1). Thus, oxygen contributes a net of -1 to the character. Hence $\chi_{C_2} = -1$. In the reflection σ_{v1} (xz), in the plane of the molecule, the x and z directions stay the same for each atom, while the y direction flips for each atom. Then $\chi_{\sigma_{v1}} = 3 - 3 + 3 = 3$. In the reflection σ_{v2} (yz), the hydrogen atoms swap positions, so they contribute nothing to the character. The

oxygen atom reverses direction with respect to x (-1) but not with respect to y (1) or z (1). Therefore, $\chi_{\sigma_{v2}} = 1$. We are now ready to show the full C_{2v} character table again, this time with Γ included.

C_{2v}	E	C_2	σ_{v1}	σ_{v2}		
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
Γ	9	-1	3	1		

We can now use Lemma 1 to express Γ as a linear combination of the irreps A_1, A_2, B_1, and B_2. We have

$$n_{A_1} = \frac{1}{4}((9)(1) + (-1)(1) + (3)(1) + (1)(1)) = 3.$$

Similarly, we calculate $n_{A_2} = 1$, $n_{B_1} = 3$, and $n_{B_2} = 2$. We find that

$$\Gamma = 3A_1 + A_2 + 3B_1 + 2B_2. \tag{5}$$

Looking at the character table, the three translational modes of a C_{2v} molecule like water correspond to the irreps that have x, y, or z listed on the right hand side, so the three translational modes correspond to the irreps A_1, B_1, and B_2. The three rotational modes correspond to the irreps that have R_x, R_y and R_z listed, which are A_2, B_1, and B_2. Taking (5) and subtracting $A_1 + B_1 + B_2 + A_2 + B_1 + B_2$, for the translational and rotational modes, we have $2A_1 + B_1$ remaining, which are the three vibrational modes. Two correspond to the A_1 irrep and one corresponds to the B_1 irrep. This will be important in the next section.

For other molecules besides water, we do a similar process. We consider the effect of each symmetry operation on each atom in order to determine the characters of each class. Using Lemma 1, we express Γ as a linear combination of the irreps. From this linear combination, we subtract the irreps that correspond to translational or rotational modes (the ones that have x, y, z, R_x, R_y, or R_z listed) to find the number of vibrational modes that correspond to each irrep.

11   Applications: Spectroscopy

Much information can be determined about a molecule based on how it absorbs infrared light at various wavelengths. IR spectroscopy is a very common technique to "draw a picture" of a molecule in order to learn about the bonds and groups of atoms present. In Figure 3, we see a labeled IR spectrum of water.

When a molecule absorbs light in the infrared region of the spectrum, vibrations that result in a change of dipole moment are affected. As we said earlier, the three vibrational modes of water (symmetric stretch, antisymmetric stretch, and symmetric bend) all impact the dipole moment of water, so they appear in the IR spectrum. (The two stretch bands are so close together and broad that they merge into one large peak.) Interestingly, even though carbon dioxide (CO_2) is nonpolar by linear symmetry, when it absorbs infrared
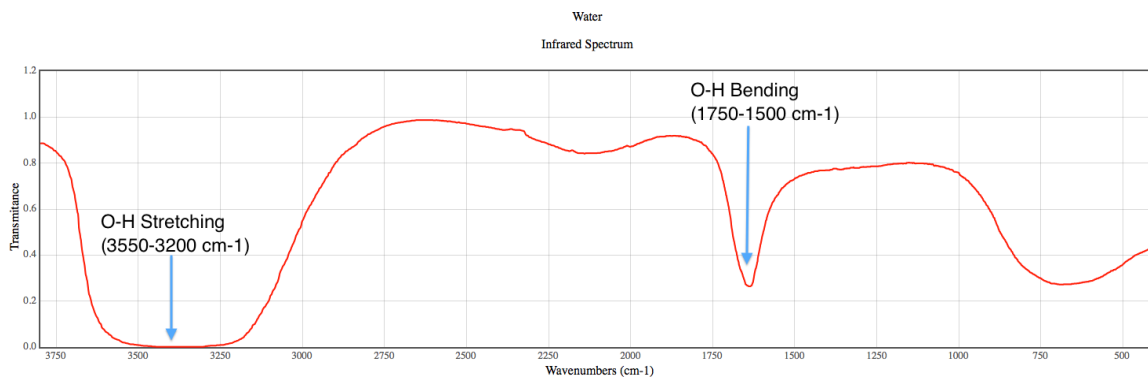
Figure 3: IR spectrum of water, showing the characteristic peaks of its IR active vibrational modes. [8]

light, it will vibrate in such a way as to momentarily break the linear symmetry and make CO_2 slightly polar! This is why CO_2 absorbs infrared light, making it a greenhouse gas. [9]

How do we know which vibrational modes affect the dipole moment and are thus represented by peaks in the IR spectrum? That is to say, which vibrations are *IR active*? Well, we just need to look at the character table and see which irreps have the same symmetry as x, y, or z. In the last section, we determined that water has two vibrational modes corresponding to the irrep A_1 and one corresponding to the irrep B_1. We see that A_1 has the same symmetry as z and B_1 has the same symmetry as x, so all three vibrational modes of water are IR active. This makes sense, since we said earlier that each of the vibrational modes of water changes the dipole moment! If there were a vibrational mode corresponding to, say, the A_2 irrep, then that mode would be *IR inactive* and not appear on an IR spectrum. But we have mathematically eliminated that possibility for water.

Raman spectroscopy is similar to IR spectroscopy, but using a different approach. High energy light bombards the molecules, putting them into an excited state temporarily. When they relax back to their various vibrational energy states, they release radiation that can be detected. A vibrational mode is *Raman active* if it exhibits a change of polarizability, which is the tendency to acquire a dipole moment from an electric field. To determine which vibrational modes are Raman active, we look for those irreps that have the same symmetry as x^2, y^2, z^2, xy, yz, or xz, or a linear combination of those. All of the vibrational modes of water are Raman active, which we can determine quickly from the C_{2v} character table.

12   Applications: Chirality

Our hands are mirror images of each other, but they are not superimposable. Likewise, *chiral* molecules are those that are non-superimposable over their mirror images, as in Figure 4. When an atom is bonded to four distinct atoms or clusters of atoms, the molecule is chiral. Each configuration is called an *enantiomer*. A molecule that is not chiral is *achiral*.

Chiral compounds may occur in *racemic mixtures* where 50% is in the one enantiomer and 50% is in the other. However, if plane-polarized light is passed through a sample of a chiral substance consisting of an unequal balance of the enantiomers, the direction of the light will rotate, as in Figure 5. This is called *optical*
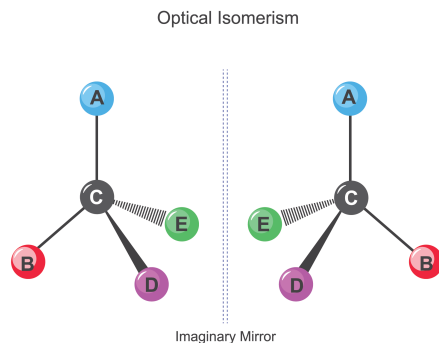
Optical Isomerism

Imaginary Mirror

Figure 4: Chiral molecules are non-superimposable over their mirror images. Notice that it is impossible to rotate the molecule on the left to look exactly like the molecule on the right. [10]

activity. The two enantiomers rotate light in opposite directions. This is the principle behind how liquid crystal displays (LCDs) work! [11]
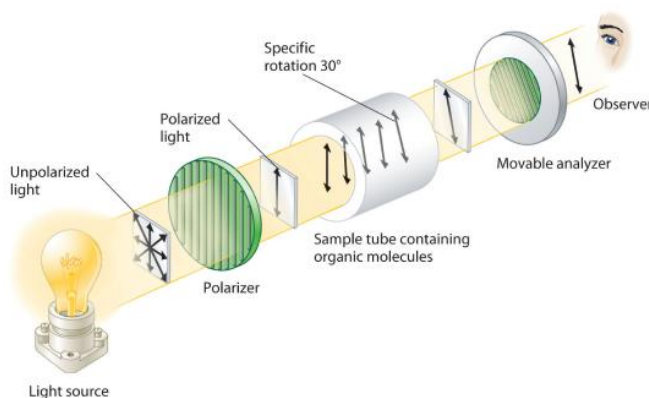

Figure 5: Chiral compounds that consist of an unequal mixture of enantiomers rotate plane-polarized light. [12]

Interestingly, the pain reliever ibuprofen is a chiral molecule. It is sold as a racemic mixture, although only one of its enantiomers is effective. Furthermore, the drug thalidomide is chiral. One of its enantiomers is a sedative, while the other causes extreme birth defects. [13]

If a molecule contains any $\sigma_h, \sigma_v, \sigma_d, S_n$, or i symmetry elements, it is achiral. Hence, the only symmetries possible for a chiral compound are the identity E and proper rotation axes C_n. A look at the character table of a molecule's point group will tell which symmetry elements are present, from which one can deduce that the molecule is chiral or achiral. For instance, by looking at the character tables for C_{2v} and C_{3v}, we see the presence of σ symmetry elements, precluding molecules that belong to these point groups from being chiral. Thus, water and ammonia are achiral molecules.

13 Conclusion

We have only begun to scratch the surface of the intricate links between symmetry and chemistry. A full development of molecular theory would not be possible without an algebraic treatment of symmetry. As we have seen, character tables provide a unique and readable "fingerprint" of point groups, eliminating the need to describe each molecule individually from a group-theoretic standpoint. From the table, much information can be quickly inferred, such as the numbers and types of symmetries present, IR/Raman activity, and chirality. This beautiful area of study ties together chemistry, geometry, group theory, representation theory, and linear algebra. I hope you have enjoyed reading this paper as much as I have enjoyed creating it!

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