Molecular Symmetry and Group Theory

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Introduction

Symmetry connects the world we see with 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 depend on symmetry, and an understanding of these concepts is rooted in algebra. We will take a interdisciplinary tour of this interface between chemistry and mathematics. Much of the presentation of point groups and character theory follows the treatments in [1–4].

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We will:

- Introduce some basic chemistry principles to aid understanding
- Look at molecular symmetry and how to categorize it via point groups
- Discuss groups, matrices, and characters
- Build character tables for point groups from scratch
- Look at the interplay of symmetry and molecular vibrations
- Look at a few applications of character theory in chemistry

Molecular bonding

Molecules are clusters of atoms that are bonded with one another by sharing pairs of electrons.

Two electrons shared between two atoms: Single bond (C−C).
Four electrons shared between two atoms: Double bond (C=C).
Six electrons shared between two atoms: Triple bond (C≡C).

Components of molecules can freely rotate along the axis of a single bond, but double and triple bonds are locked and cannot rotate.
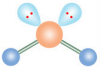
VSEPR theory
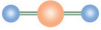
Molecular shape is determined by Valence Shell Electron Pair Repulsion theory (VSEPR). The name of the theory explains most of what you need to know:

- Valence shell (outermost shell) electrons participate in bonding
- Electrons tend to occur in pairs
- Like charges repel, so electron pairs tend to be as far away from each other as possible

Some electron pairs are bonding (shared with other atoms), and some will be nonbonding (not shared). A pair of nonbonding electrons is called a *lone pair*.

Molecular geometry

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.

Polarity

If the atoms have similar electronegativity, the electrons will be shared equally, forming a nonpolar bond.

If one atom has higher electronegativity, it will attract electrons 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 linear.

If the polar bonds do not cancel by symmetry, the molecule will be *polar*. This occurs in water (H_2O), which is bent.

Many of the interesting characteristics of water are a direct consequence of hydrogen bonds, due to polarity.

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!

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. The molecule will be indistinguishable before and after the symmetry operation.

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A proper rotation, C_n, is a rotation that can be achieved in 3D space. It is a rotation through $360°/n$ counterclockwise with respect to some axis. We have that $C_n^n \equiv E$, so $|C_n| = n$. If a molecule has more than one rotational axis, the one of highest order is called the *principal axis*.

Symmetry elements and operations

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.

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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.

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. [6]

There is a sequence of steps that can be followed to determine a point group.

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. To assist in the process, we will use a flowchart.

Point groups of low symmetry

Molecules in the C_1 group have no symmetry besides E. (Indeed, every point group contains E, but it will be implicit.) (wedge-dash)
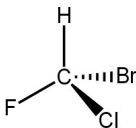
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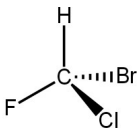
Molecules in the C_s group have only one mirror plane (in the following example, the mirror plane is the plane of the molecule).
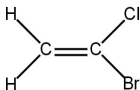
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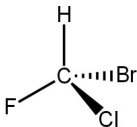
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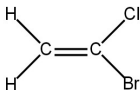
Molecules in the C_i group have only an inversion center.

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.

$$H \text{——} Cl$$

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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.

$$O \text{==} C \text{==} O$$

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$$O\!\!=\!\!=\!\!C\!\!=\!\!=\!\!O$$

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.
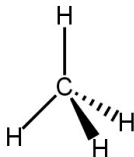
Point groups of high symmetry

Molecules in the O_h group are octahedral, with 48 symmetry operations in all. An example is sulfur hexafluoride.
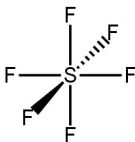
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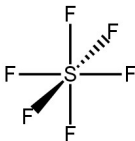
Molecules in the I_h group are icosahedral, with 120 symmetry operations in all. A fascinating example is buckminsterfullerene, a molecule with sixty carbon atoms in a soccer ball shape.
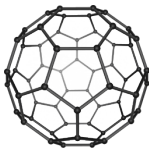
Other point groups
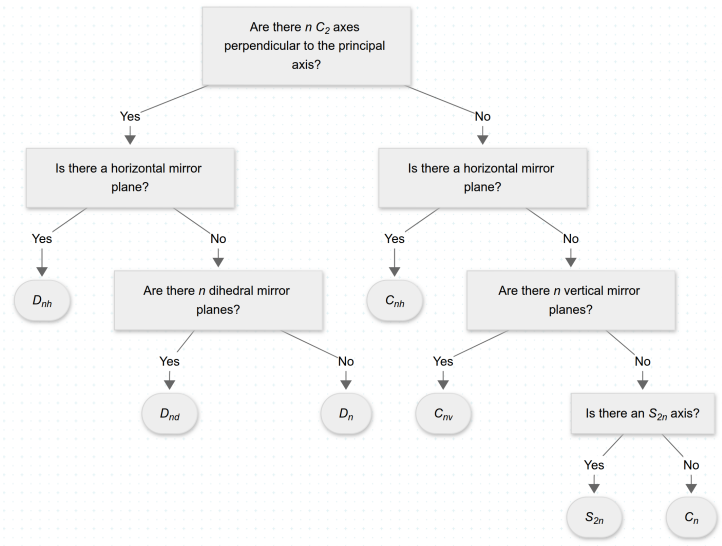
Other point groups

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:
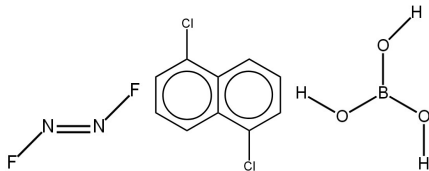
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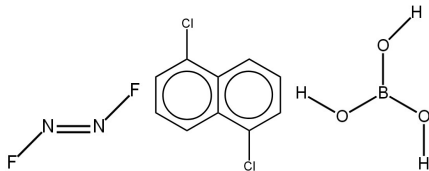
Molecules in the C_{nv} group contain a C_n rotation axis and n vertical mirror planes σ_v. The following examples are C_{2v}, C_{3v}, and C_{4v}, respectively:
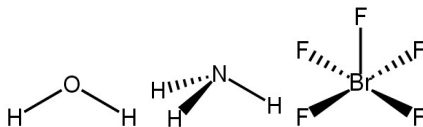
Other point groups

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.
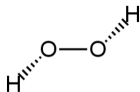
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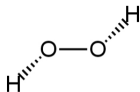
Molecules in the D_{nh} group contain a C_n rotation axis and n perpendicular C_2 rotation axes. They also have a horizontal mirror plane σ_h. The following examples are D_{3h}, and D_{3h}, and D_{4h}, and D_{6h}, respectively:
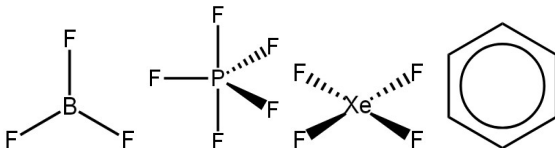
Other point groups

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.
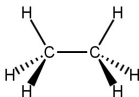
Other point groups

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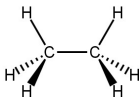
Other point groups are less common and will be skipped. The mathematical discussion that follows will focus on the point groups of water and ammonia, C_{2v} and C_{3v}, respectively.

Algebraic group structure of point groups

We will verify that C_{3v} satisfies the definition of a group by showing that it has an identity, inverses, closure, and associativity.

Clearly, C_{3v} has an identity element E. The C_3 rotation has the inverse C_3^2, and vice versa. 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 $C_{3v} \cong S_3$, 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. Closure can be verified from the Cayley table, and associativity follows from the associativity of function composition.

Algebraic group structure of point groups
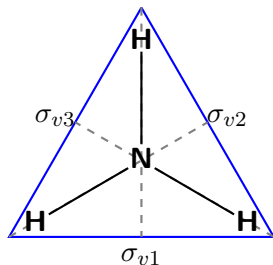
E: Identity

C_3: $120°$, CCW

C_3^2: $240°$, CCW

	$f \circ g$	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}
f	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

The top of the table is labeled g.

Algebraic group structure of point groups

We will do the same process with C_{2v}.

Clearly, C_{2v} has an identity element E. The elements C_2, σ_{v1}, and σ_{v2} are their own inverses. There are 4 symmetry operations in C_{2v}: $\{E, C_2, \sigma_{v1}, \sigma_{v2}\}$.

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 $C_{2v} \cong V_4$.

Algebraic group structure of point groups
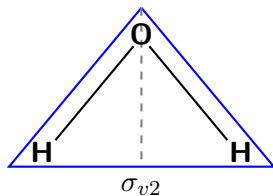
E: Identity

C_2: $180°$

σ_{v1}: Refl. over molecular plane

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

Representation of symmetry operations as matrices

Now we find matrix representations of E, C_n, σ, i, and S_n. We will define these operations as transformations of the coordinate vector $(x, y, z)^T$.

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

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 $\theta = \dfrac{360°}{n}$. Matrices for other axes can be constructed similarly.

Representation of symmetry operations as matrices

The reflection operations σ over the xy, yz, and xz planes are represented by the respective matrices

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

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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 is represented by a matrix like

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

We will look at the matrix representation for C_{2v} (H_2O) first. We use the notation previously established in the Cayley table. 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:
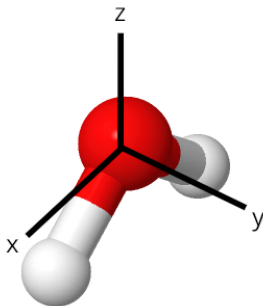
Matrix representation of C_{2v}

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 the Cayley table.

Now we will look at the matrix representation for C_{3v} (NH_3). We use the notation previous established in the Cayley table. 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:
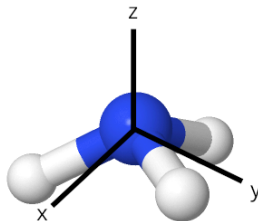
Matrix representation of C_{3v}

The matrices for the symmetry operations of C_{3v} are

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

$$M_{C_3^2} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, M_{\sigma_{v1}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

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

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Constructing those matrices 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.

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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.

Characters and reducible/irreducible representations

To simplify the representations, we will use characters instead of matrices. The characters 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 $\chi_{\sigma_{v3}} = 1$.

To simplify the representations, we will use characters instead of matrices. The characters 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 singletons $\{E\}$, $\{C_2\}$, $\{\sigma_{v1}\}$, and $\{\sigma_{v2}\}$, 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 operation in the same class has the same character, so they will be grouped together in the character tables.

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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*).

Irrep notation crash course

The irreps will be denoted using a standard notation system.

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 dimension. 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.

Character tables

Character tables provide all of the symmetry information in a given point group in a succinct way. In a sense, they prepackage the underlying group theory into an easily read table that is shared by every molecule in a given point group. We will look at the construction of some simple character tables, and then we will explore some of their applications.

We now construct the character table of C_{2v}. We block diagonalize the matrices we had before:

$$M_E = \begin{pmatrix} \boxed{1} & 0 & 0 \\ 0 & \boxed{1} & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix}, M_{C_2} = \begin{pmatrix} \boxed{-1} & 0 & 0 \\ 0 & \boxed{-1} & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix},$$

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

Character tables

We place 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 by the aforementioned rules. The last two columns and the empty row will be filled in later.

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

Character tables have several important 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.

Character tables

- 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. 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.

Character tables

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.

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}. Additional information has been added to the last two columns.

Character tables

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

R_x, R_y, and R_z indicate the rotational axes that are symmetric with respect to the irreps. For example, C_2 corresponds to R_z. We have that C_2 is symmetric with respect to A_2, so R_z is symmetric with respect to A_2. σ_{v1} 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 B_1, so R_y is symmetric with respect to B_1. Similarly, R_x is symmetric with respect to B_2.

Character tables

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

x^2, y^2, xy, etc. represent math functions that are symmetric with respect to the irreps. For instance, we know that xy is positive in quadrants I and III and negative in II and IV, 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 A_2. The functions x^2, y^2, and z^2 are always positive, so they are symmetric with respect to A_1.

Character tables

We now construct the character table for C_{3v}. We block diagonalize the matrices we had before:

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

$$M_{C_3^2} = \left(\begin{array}{cc|c} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array} \right), M_{\sigma_{v1}} = \left(\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & 1 \end{array} \right)$$

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

Character tables

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.

Following the above procedure established, we 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 and orthogonality relations hold. Also, notice that 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.

Expressing reducible representations in terms of irreps

The reducible representation Γ can be written as a linear combination of the 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.

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

Expressing reducible representations in terms of irreps

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. □

Molecular vibrations

Individual atoms can move around slightly within a molecule, producing molecular vibrations. To study these vibrations, we 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.

Molecular vibrations

As we will see, 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 $3N \times 3N$ 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 is tedious. Thankfully, the only thing we need from these matrices is their characters, and we can find the characters without explicitly constructing the matrices.

Molecular vibrations

We will use the vibrations of water as an example. For convenience, we stick with the same coordinate axes that were used earlier. 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, it has nine degrees of freedom.

Since water is nonlinear, it has $3N - 6 = 3$ vibrational modes. These are *symmetric stretch*, *antisymmetric stretch*, and *symmetric bend*. Each of these vibrational modes changes the *dipole moment* of water, causing its polarity to oscillate slightly.

Demo: `https://www.chem.purdue.edu/jmol/vibs/h2o.html`

Molecular vibrations

We could create a 9×9 matrix for each of the four symmetry classes in water. However, we can find the characters of each matrix without constructing the matrices. In E, every atom remains in the same position, so $\chi_E = 9$. In 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 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 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, $\chi_{\sigma_{v2}} = 1$.

Molecular vibrations

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		

Molecular vibrations

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

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

The three translational modes of C_{2v} correspond to the irreps that have x, y, or z listed on the right hand side of the character table, so the three translational modes correspond to 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 A_1 and one corresponds to B_1.

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.

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. Below, we see a labeled IR spectrum of water. [7]
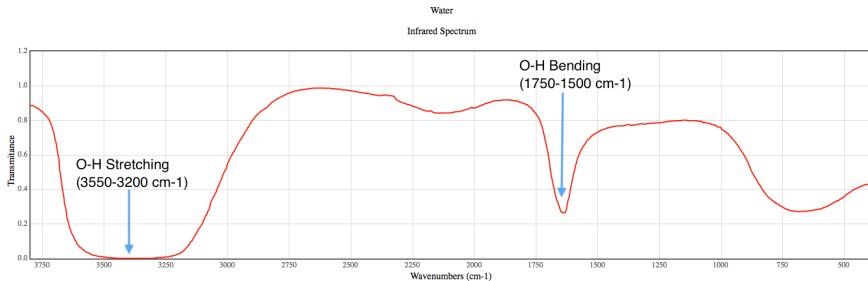
When a molecule absorbs IR light, vibrations that result in a change of dipole moment are affected. As we said earlier, the three vibrational modes of water all impact the dipole moment of water, so they appear in the IR spectrum. (The two stretch bands are so close together and broad that they merge into one large peak.)

Interestingly, even though carbon dioxide (CO_2) is nonpolar by linear symmetry, when it absorbs infrared 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. [8]

How do we know which vibrational modes are *IR active*? We 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.

Applications: Spectroscopy

With Raman spectroscopy, high energy light bombards molecules, putting them into an excited state. 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.
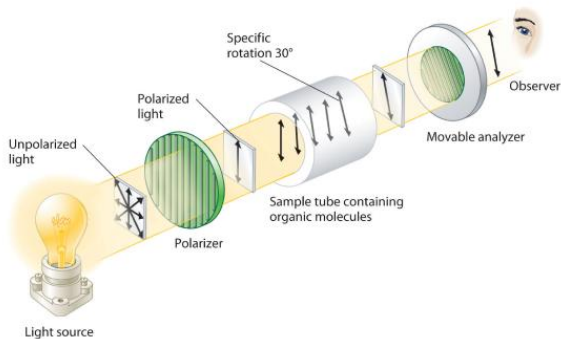
Our hands are mirror images of each other, but they are not superimposable. Likewise, *chiral* molecules are those that are non-superimposable over their mirror images. When an atom is bonded to four distinct atoms or clusters of atoms, the molecule is chiral. Each configuration is called an *enantiomer*. A non-chiral molecule is *achiral*.

Optical Isomerism

Imaginary Mirror
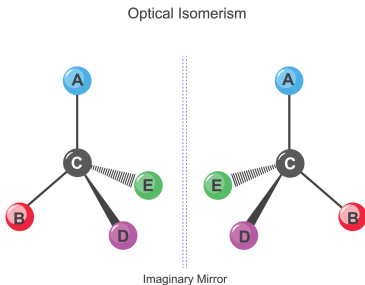
Notice that it is impossible to rotate the molecule on the left to look exactly like the molecule on the right.

Applications: Chirality [11]

Chiral compounds may occur in *racemic mixtures*, 50/50 mixtures of enantiomers. However, if plane polarized light is passed through a substance consisting of an unequal balance of the enantiomers, the direction of the light will rotate. This is called *optical activity*. The two enantiomers rotate light in opposite directions. This is the principle behind how liquid crystal displays (LCDs) work! [10]

Interestingly, 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. [12]

If a molecule contains any σ, S_n, or i symmetry elements, it is achiral. Hence, the only symmetries possible for a chiral compound are E ane 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.

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