Symmetry helps us understand molecular structure, some chemical properties, and characteristics of physical properties (spectroscopy) – used with group theory to predict vibrational spectra for the identification of molecular shape, and as a tool for understanding electronic structure and bonding.

Symmetrical: implies the species possesses a number of indistinguishable configurations.
**Group Theory**: mathematical treatment of symmetry.

**symmetry operation** – an operation performed on an object which leaves it in a configuration that is indistinguishable from, and superimposable on, the original configuration.

**symmetry elements** – the points, lines, or planes to which a symmetry operation is carried out.

<table>
<thead>
<tr>
<th>Element</th>
<th>Operation</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Identity</strong></td>
<td>Identity</td>
<td>E</td>
</tr>
<tr>
<td><strong>Symmetry plane</strong></td>
<td>Reflection in the plane</td>
<td>σ</td>
</tr>
<tr>
<td><strong>Inversion center</strong></td>
<td>Inversion of a point $x,y,z$ to $-x,-y,-z$</td>
<td>$i$</td>
</tr>
<tr>
<td><strong>Proper axis</strong></td>
<td>Rotation by $(360/n)°$</td>
<td>$C_n$</td>
</tr>
<tr>
<td><strong>Improper axis</strong></td>
<td>1. Rotation by $(360/n)°$</td>
<td>$S_n$</td>
</tr>
<tr>
<td></td>
<td>2. Reflection in plane perpendicular to rotation axis</td>
<td></td>
</tr>
</tbody>
</table>

**Proper axes of rotation ($C_n$)**

Rotation with respect to a line (axis of rotation).

- $C_n$ is a rotation of $(360/n)°$.
  - $C_2 = 180°$ rotation, $C_3 = 120°$ rotation, $C_4 = 90°$ rotation, $C_5 = 72°$ rotation, $C_6 = 60°$ rotation...
- Each rotation brings you to an indistinguishable state from the original.

However, rotation by $90°$ about the same axis does not give back the identical molecule. Therefore $H_2O$ does NOT possess a $C_4$ symmetry axis.

XeF$_4$ is square planar.
It has four different $C_2$ axes.
A $C_4$ axis out of the page is called the **principle axis** because it has the largest $n$.
By convention, the principle axis is in the $z$-direction
If reflection of all parts of a molecule through a plane produced an indistinguishable configuration, the symmetry element is called a mirror plane or plane of symmetry.\(\sigma_v\) (vertical): plane colinear with principal axis

**Reflection through a planes of symmetry (mirror plane)**

\(\sigma_d\) (dihedral) Vertical, parallel to principal axis, \(\sigma\) parallel to \(C_n\) and bisecting two \(C_2\) axes
Reflection through a planes of symmetry (mirror plane)

$\sigma_h$(horizontal): plane perpendicular to principal axis

Inversion, Center of Inversion (i)

A center of symmetry: A point at the center of the molecule. $(x,y,z) \rightarrow (-x,-y,-z)$. It is not necessary to have an atom in the center (e.g. benzene).

Tetrahedrons, triangles, and pentagons don't have a center of inversion symmetry.

$C_2H_6$ \hspace{1cm} $Ru(CO)_6$ \hspace{1cm} $C_4H_4Cl_2F_2$
Rotation-reflection, Improper rotation ($S_n$)

This is a compound operation combining a rotation $360^\circ/n$ ($C_n$) with a reflection through a plane perpendicular to the $C_n$ axis $\sigma_h$ ($C_n$ followed by $\sigma_h$)

$$\sigma C_n = S_n$$

An improper rotation (or rotation–reflection), $S_n$, involves rotation about $360^\circ/n$ followed by reflection through a plane that is perpendicular to the rotation axis.
**Identity (E)**

Simplest symmetry operation. All molecules have this element. If the molecule does have no other elements, it is **asymmetric**.

The identity operation amounts to doing nothing to a molecule and so leaves any molecule completely unchanged.

![CHFCIBr and SOFCI molecules](image)

**Successive Operations**

![Successive rotations and symmetry elements](image)
Symmetry Point Groups

- Symmetry of a molecule located on symmetry axes, cut by planes of symmetry, or centered at an inversion center is known as **point symmetry**.

- Collections of symmetry operations constitute **mathematical groups**.

- Each symmetry **point group** has a particular designation.

<table>
<thead>
<tr>
<th>Point group</th>
<th>Characteristic symmetry elements</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁, C₂, C₃, C₄, C₅, C₆</td>
<td>E, one σ plane</td>
<td>-</td>
</tr>
<tr>
<td>Cᵥ</td>
<td>E, inversion centre</td>
<td>-</td>
</tr>
<tr>
<td>Cₙ</td>
<td>E, one (principal) n-fold axis</td>
<td>-</td>
</tr>
<tr>
<td>Cₙᵥ</td>
<td>E, one (principal) n-fold axis, n σᵥ planes</td>
<td>-</td>
</tr>
<tr>
<td>Cₙₐ</td>
<td>E, one (principal) n-fold axis, one σᵥ plane, one Sᵥ-fold axis which is coincident with the Cₙ axis</td>
<td>The Sᵥ axis necessarily follows from the Cₙ axis and σᵥ plane. For n = 2, 4 or 6, there is also an inversion centre.</td>
</tr>
<tr>
<td>Dₙₐ</td>
<td>E, one (principal) n-fold axis, n Cₙ axes, one σᵥ plane, n σᵥ planes, one Sᵥ-fold axis</td>
<td>The Sᵥ axis necessarily follows from the Cₙ axis and σᵥ plane. For n = 2, 4 or 6, there is also an inversion centre.</td>
</tr>
<tr>
<td>Dₙₐ</td>
<td>E, one (principal) n-fold axis, n Cₙ axes, n σᵥ planes, one Sᵥ-fold axis</td>
<td>For n = 3 or 5, there is also an inversion centre.</td>
</tr>
<tr>
<td>Tₐ</td>
<td>Tetrahedral</td>
<td>-</td>
</tr>
<tr>
<td>Oₐ</td>
<td>Octahedral</td>
<td>-</td>
</tr>
<tr>
<td>Iₐ</td>
<td>Icosahedral</td>
<td>-</td>
</tr>
</tbody>
</table>
Linear molecular species can be classified according to whether they possess a centre of symmetry (inversion centre) or not.
Tetrahedral Geometry

$P_4$  

$B_4Cl_4$

Octahedral Geometry

$Icosahedral Geometry$

$[W(CO)_6]$  

$[B_{12}H_{12}]^{2-}$
Identify the symmetry elements that are present in benzene.

Scheme for assigning point groups of molecules and molecular ions
**C<sub>n</sub> Point Groups**

\[ C^n = E \]

- **PBrClF**  
  - Point Group: **C<sub>1</sub>**

- **H<sub>2</sub>O<sub>2</sub>**  
  - Point Group: **C<sub>2</sub>**

- **As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>**  
  - Point Group: **C<sub>3</sub>**

- **Co(NH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>)<sub>3</sub>**  
  - Point Group: **C<sub>4</sub>**

**C<sub>nh</sub> Point Groups**

The direction of the C<sub>n</sub> axis is taken as vertical, so a symmetry plane perpendicular to it is a horizontal plane, σ<sub>h</sub>.

- **HOCl**  
  - Point Group: **C<sub>2h</sub>**

- **NH<sub>2</sub>F**  
  - Point Group: **C<sub>2h</sub>**

- **BBrClF**  
  - Point Group: **C<sub>2h</sub>**

- **N<sub>2</sub>F<sub>2</sub>**  
  - Point Group: **C<sub>2h</sub>**

- **B(OH)<sub>3</sub>**  
  - Point Group: **C<sub>3h</sub>**
**C\textsubscript{nv} Point Groups**

If a mirror plane contains the rotational axis, the group is called a C\textsubscript{nv} group.

- **H\textsubscript{2}O**
  - C\textsubscript{2v}

- **SF\textsubscript{4}**
  - C\textsubscript{2v}

- **NF\textsubscript{3}**
  - C\textsubscript{3v}

- **CHCl\textsubscript{3}**
  - C\textsubscript{3v}

- **SF\textsubscript{5}Cl**
  - C\textsubscript{4v}

---

**D\textsubscript{n} and D\textsubscript{nh} Point Groups**

Adding a C\textsubscript{2} axis perpendicular to a C\textsubscript{n} axis generates one of the dihedral groups.

- **D\textsubscript{2}**
  - Angle between rings not 0\(^\circ\) or 90\(^\circ\)

- **D\textsubscript{3}**
  - There must be \(n\) C\textsubscript{2} axes perpendicular to C\textsubscript{n}

Adding a \(\sigma\) to a D\textsubscript{n} group generates a D\textsubscript{nh} group.

- **C\textsubscript{2}H\textsubscript{4}**
  - D\textsubscript{2h}

- **[PtCl\textsubscript{4}]^{2-}**
  - D\textsubscript{4h}
Adding a vertical mirror plane to a $D_{n}$ group in such a fashion to bisect adjacent $C_2$ axes generates a $D_{nd}$ group.

Ferrocene
Fe(\(C_5H_5\)\(\_2\)

$D_{2d}$

\[
\begin{align*}
\text{dihedral angle of } 90^\circ
\end{align*}
\]
\[ S_n \text{ groups} \]

For odd \( n \), \((S_n)^n = \sigma_n\)

For even \( n \), \((S_n)^n = E\)

The \( S_n \) for odd \( n \) is the same as the \( C_{nh} \).

Absence of mirror planes distinguish \( S_n \) groups from \( D_{nh} \) groups.

---

**Linear Groups**

<table>
<thead>
<tr>
<th>( H-Cl )</th>
<th>( O=O )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{\infty v} )</td>
<td>( D_{\infty h} )</td>
</tr>
</tbody>
</table>

Has a \( \sigma_h \)

---

**High Symmetry Molecules**

- \( CCl_4 \) (\( T_d \))
- \( SF_6 \) (\( O_h \))
- \( C_{60} \) (\( I_h \))
The letter 'A'.

GeH$_3$F
SeH$_3$F
AsBr$_5$ (trigonal bipyramid)

trans rotamer of Si$_2$H$_6$
Crown-shaped S$_8$

GeH$_3$F
SeH$_3$F
AsBr$_5$ (trigonal bipyramid)

trans rotamer of Si$_2$H$_6$
Crown-shaped S$_8$
Characteristic symmetry elements of some important classes of point groups.

<table>
<thead>
<tr>
<th>Point group</th>
<th>Characteristic symmetry elements</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>$E$, one $\sigma$ plane</td>
<td></td>
</tr>
<tr>
<td>$C_i$</td>
<td>$E$, inversion centre</td>
<td></td>
</tr>
<tr>
<td>$C_n$</td>
<td>$E$, one (principal) $n$-fold axis</td>
<td></td>
</tr>
<tr>
<td>$C_{nv}$</td>
<td>$E$, one (principal) $n$-fold axis, $n$ $\sigma_v$ planes</td>
<td></td>
</tr>
<tr>
<td>$C_{nv}$</td>
<td>$E$, one (principal) $n$-fold axis, one $\sigma_h$ plane, one $S_n$-fold axis</td>
<td>The $S_n$ axis necessarily follows from the $C_n$ axis and $\sigma_h$ plane. For $n = 2, 4$ or $6$, there is also an inversion centre.</td>
</tr>
<tr>
<td>$D_{nk}$</td>
<td>$E$, one (principal) $n$-fold axis, $n$ $C_2$ axes, $n$ $\sigma_h$ plane, one $S_n$-fold axis</td>
<td>The $S_n$ axis necessarily follows from the $C_n$ axis and $\sigma_h$ plane. For $n = 2, 4$ or $6$, there is also an inversion centre.</td>
</tr>
<tr>
<td>$D_{nd}$</td>
<td>$E$, one (principal) $n$-fold axis, $n$ $C_2$ axes, $n$ $\sigma_v$ planes, one $S_n$-fold axis</td>
<td>For $n = 3$ or $5$, there is also an inversion centre.</td>
</tr>
<tr>
<td>$T_d$</td>
<td>Tetrahedral</td>
<td></td>
</tr>
<tr>
<td>$O_h$</td>
<td>Octahedral</td>
<td></td>
</tr>
<tr>
<td>$I_h$</td>
<td>Icosahedral</td>
<td></td>
</tr>
</tbody>
</table>
Character Tables

• Character tables contain, in a highly symbolic form, information about how something of interest (a bond, an orbital, etc.) is affected by the operations of a given point group.

• Each point group has a unique character table, which is organized into a matrix.

• Column headings are the symmetry operations, which are grouped into classes.

• Horizontal rows are called irreducible representations of the point group.

• The main body consists of characters (numbers), and a section on the right side of the table provides information about vectors and atomic orbitals.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

• Symmetry elements possessed by the point group are in the top row

• Left hand column gives a list of symmetry labels
  • Gives information about degeneracies (A and B indicate non-degenerate, E refers to doubly degenerate, T means triply degenerate)

• Main part of table contains characters (numbers) to label the symmetry properties (of MO's or modes of molecular vibrations)
To obtain from this total set the representations for vibration only, it is necessary to subtract the representations for the other two forms of motion: rotation and translation.

Vibrational Spectroscopy

"the study of the interaction of matter with energy (radiation in the electromagnetic spectrum)." A molecular vibration is a periodic distortion of a molecule from its equilibrium geometry. The energy required for a molecule to vibrate is quantized (not continuous) and is generally in the infrared region of the electromagnetic spectrum.

For a diatomic molecule (A-B), the bond between the two atoms can be approximated by a spring that restores the distance between A and B to its equilibrium value. The bond can be assigned a force constant, $k$ (in Nm$^{-1}$); the stronger the bond, the larger $k$) and the relationship between the frequency of the vibration, $\omega$, is given by the relationship:

$$\omega = \sqrt{\frac{k}{\mu}}$$

or, more typically

$$2\pi\nu = \sqrt{\frac{k}{\mu}}$$

where $c$ is the speed of light, $\nu$ is the frequency in "wave numbers" (cm$^{-1}$) and $\mu$ is the reduced mass (in amu) of A and B given by the equation:

$$\mu = \frac{m_A \times m_B}{m_A + m_B}$$

$r_e$ = equilibrium distance between A and B  \[D_{AB} = \text{energy required to dissociate into A and B atoms}\]

Translational Modes
A mode in which all atoms are moving in the same direction, equivalent to moving the molecule.

Rotational Modes
A mode in which atoms move to rotate (change the orientation of) the molecule. There are 3 rotational modes for nonlinear molecules, and 2 rotational modes for linear molecules.
Selection Rules: Infrared and Raman Spectroscopy

Infrared energy is absorbed for certain changes in vibrational energy levels of a molecule.

- for a vibration to be **infrared active**, there must be a change in the **molecular dipole moment** vector associated with the vibration.

For a vibration mode to be **Raman active**, there must be a change in the net **polarizability** tensor.

- polarizability is the ease in which the electron cloud associated with the molecule is distorted

For **centrosymmetric** molecules, the **rule of mutual exclusion** states that vibrations that are IR active are Raman inactive, and vice versa.

The transition from the vibrational ground state to the first excited state is the **fundamental transition**.

The two bending modes require the same amount of energy and are therefore **degenerate**.
If the symmetry label (e.g. $A_1$, $B_1$, $E$) of a normal mode of vibration is associated with $x$, $y$, or $z$ in the character table, then the mode is **IR active**.

If the symmetry label (e.g. $A_1$, $B_1$, $E$) of a normal mode of vibration is associated with a product term ($x^2$, $xy$) in the character table, then the mode is **Raman active**.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_z(xz)$</th>
<th>$\sigma_v(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$z$</td>
<td>$x^2, y^2, z^2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$R_z$</td>
<td>$xy$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$x, R_y$</td>
<td>$xz$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$y, R_x$</td>
<td>$yz$</td>
</tr>
<tr>
<td>( D_{3h} )</td>
<td>( E )</td>
<td>( 2C_3 )</td>
<td>( 3C_2 )</td>
<td>( \sigma_v )</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_2' )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>( E' )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>( A_1' )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( A_2' )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( E' )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>

120° rotation

\( C_3 \)

\( C_3 \)

\( C_3 \)

\( C_3 = E \)
The vibrational modes of CH\textsubscript{4} (T\textsubscript{d}), only two of which are IR active.
vibrational modes of $[\text{PtCl}_4]^{2-}$ ($D_{4h}$)
Point groups of octahedral metal carbonyl complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Point group</th>
<th>Symmetries of CO stretching modes</th>
<th>IR active modes</th>
<th>Number of absorptions observed in the IR spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(CO)$_6$</td>
<td>$O_h$</td>
<td>$A_{1g}, E_g, T_{2u}$</td>
<td>$T_{1u}$</td>
<td>1</td>
</tr>
<tr>
<td>M(CO)$_3$X</td>
<td>$C_{3v}$</td>
<td>$A_{1g}, A_{2g}, B_{1u}, E$</td>
<td>$A_{1g}, A_{2g}, E$</td>
<td>3</td>
</tr>
<tr>
<td>trans-M(CO)$_3$X$_2$</td>
<td>$D_{3h}$</td>
<td>$A_{1g}, B_{2g}, E_u$</td>
<td>$E_u$</td>
<td>1</td>
</tr>
<tr>
<td>cis-M(CO)$_3$X$_2$</td>
<td>$C_{2v}$</td>
<td>$A_{1g}, A_{2g}, B_{1u}, B_{2u}$</td>
<td>$A_{1u}, A_{2u}, B_{1u}, B_{2u}$</td>
<td>4</td>
</tr>
<tr>
<td>fac-M(CO)$_3$X$_3$</td>
<td>$C_{2v}$</td>
<td>$A_{1g}, E$</td>
<td>$A_{1g}, E$</td>
<td>2</td>
</tr>
<tr>
<td>mer-M(CO)$_3$X$_3$</td>
<td>$C_{2v}$</td>
<td>$A_{1g}, A_{2g}, B_{1u}$</td>
<td>$A_{1g}, A_{2g}, B_{1u}$</td>
<td>3</td>
</tr>
</tbody>
</table>
Enantiomers

A pair of enantiomers consists of two molecular species which are mirror images of each other and are nonsuperposable.
Up to this point, we have considered symmetry operations only insofar as they affect atoms occupying points in molecules.

Consider a water molecule (H\(_2\)O).

Coordinates are assigned according to the convention that the highest fold axis of rotation is aligned with the z-axis, and the x axis is perpendicular to the plane of the molecule.

Let the **translation of the molecule in the +y direction** be represented by unit vectors on the atoms, and consider how they change when undergoing the C\(_{2v}\) symmetry operations.

\[
\begin{align*}
B_2 &= \begin{pmatrix} +1 \\ -1 \\ -1 \\ +1 \end{pmatrix} 
\end{align*}
\]
The set of four labels (+1, -1, -1, +1) generated in the analysis constitutes one irreducible representation within the C$_{2v}$ point group. It is irreducible in the sense that it cannot be decomposed into a simpler or more fundamental form.

• Not only does it describe the effects on the $y$ translation but also on other 'y-vector functions' such as a p$_y$ orbital.

• Therefore, $y$ is understood to serve as a basis function for this irreducible representation within the C$_{2v}$ point group.

Effect of a symmetry rotation about the z-axis.

Translation of the molecule in the +x direction

Translation of the molecule in the +z direction
The resulting character table for $C_{2v}$ is shown above.

The column heading are classes of symmetry operations for the group, and each row depicts one irreducible representation.

The +1 and -1 numbers, which correspond to symmetric and antisymmetric behavior, are called characters.

Columns on the right are some of the basis functions which have the symmetry properties of a given irreducible representation.

$R_x$, $R_y$, $R_z$ stand for rotations about the specified axes.

Symbols in the column on the far left are Mulliken Labels.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_{(xz)}$</th>
<th>$\sigma_{(yz)}$</th>
<th>$x^2, y^2, z^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$z$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$R_z$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$x, R_y$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y, R_x$</td>
</tr>
</tbody>
</table>

Reducible Representations

When applying the methods of group theory to problems related to molecular structure or dynamics, the procedure that is followed usually involves deriving a reducible representation for the phenomenon of interest, such as a molecular vibration, and then decomposing it into its irreducible components.

A reducible representation will always be a sum of irreducible representations.

In some cases (simple molecules with few bonds) we can perform the decomposition by inspection, for the more general case (complicated molecule with many bonds), we can use the reduction formula.
Reducible Representations

The reduction can be achieved using the reduction formula. It is a mathematical way of reducing that will always work when the answer cannot be spotted by eye. It is particularly useful when there are large numbers of bonds involved.

The vibrational modes of the molecule are reduced to produce a reducible representation into the irreducible representations. This method uses the following formula reduction formula:

\[ N = \frac{1}{h} \sum_x \chi_i^x \chi_i^x n^x \]

\( N \) is the number of times a symmetry species occurs in the reducible representation,
\( h \) is the ‘order of the group’: simply the total number of symmetry operations in the group.
The summation is over all of the symmetry operations. For each symmetry operation, three numbers are multiplied together. These are:
\( \chi \), character of the reducible representation for the operations of the class
\( \chi_i \), character of the irreducible representation for the operations of the class
\( n \) is the number of symmetry operations in the class.

The characters of the reducible representation can be determined by considering the combined effect of each symmetry operation on the atomic vectors.

Atomic contributions, by symmetry operations, to the reducible representation for the 3N degrees of freedom for a molecule.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Contribution per atom*</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>3</td>
</tr>
<tr>
<td>C_2</td>
<td>-1</td>
</tr>
<tr>
<td>C_3</td>
<td>0</td>
</tr>
<tr>
<td>C_4</td>
<td>1</td>
</tr>
<tr>
<td>C_6</td>
<td>2</td>
</tr>
<tr>
<td>\sigma</td>
<td>1</td>
</tr>
<tr>
<td>i</td>
<td>-3</td>
</tr>
<tr>
<td>S_3</td>
<td>-2</td>
</tr>
<tr>
<td>S_4</td>
<td>-1</td>
</tr>
<tr>
<td>S_6</td>
<td>0</td>
</tr>
</tbody>
</table>

*\( C_n = 1 + 2\cos(360/n); S_n = -1 + 2\cos(360/n) \)
Obtain the reducible representation (for H$_2$O) by multiplying the number of unshifted atoms times the contribution per atom.
Reducible Representations

The reduction can be achieved using the reduction formula. It is a mathematical way of reducing that will always work when the answer cannot be spotted by inspection. It is particularly useful when there are large numbers of atoms and bonds involved.

The vibrational modes of the molecule are reduced to produce a reducible representation into the irreducible representations. This method uses the following formula reduction formula:

\[ N = \frac{1}{h} \sum \chi_r^x \chi_i^x n^x \]

\( N \) is the number of times a symmetry species occurs in the reducible representation,
\( h \) is the ‘order of the group’: simply the total number of symmetry operations in the group.

The summation is over all of the symmetry operations. For each symmetry operation, three numbers are multiplied together. These are:
\( \chi_r \) is the character for a particular class of operation in the reducible representation
\( \chi_i \) is the character of the irreducible representation
\( n \) is the number of symmetry operations in the class

Tabulate our known information.

### Reducible Representation (for \( \text{H}_2\text{O} \))

<table>
<thead>
<tr>
<th>( \Gamma_r )</th>
<th>( E )</th>
<th>( C_2 )</th>
<th>( \sigma_v(\text{zx}) )</th>
<th>( \sigma_v(\text{yz}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A_2</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>B_1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B_2</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>( E )</th>
<th>( C_2 )</th>
<th>( \sigma_v(\text{zx}) )</th>
<th>( \sigma_v(\text{yz}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A_2</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>B_1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B_2</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The vibrational modes of the molecule are reduced to produce a reducible representation into the irreducible representations. This method uses the following formula reduction formula:

\[ N = \frac{1}{h} \sum \chi_r^x \chi_i^x n^x \]

\( h = 4 \)

\[ A_1: (1/4)[(9)(1)(n^F) + (-1)(1)(n^C) + (1)(1)(n^\sigma_v(\text{zx})) + (3)(1)(n^\sigma_v(\text{yz}))] \]

\[ A_1: (1/4)[(9)(1)(n^F) + (-1)(1)(n^C) + (1)(1)(n^\sigma_v(\text{zx})) + (3)(1)(n^\sigma_v(\text{yz}))] = 3 \]
Calculate irreducible representation $A_2$

$$A_2: (1/h)[(\chi^E_r)^2(\chi^E_i)^2(n^E_r) + (\chi^E_r) (\chi^E_i)(n^E_r) + (\chi^E_r) \sigma_{v(xz)} (\chi^E_i) \sigma_{v(xz)} (n^E_r) + (\chi^E_r) \sigma_{v(yz)} (\chi^E_i) \sigma_{v(yz)} (n^E_r)]$$

$$A_2: (1/4)[(9)(1)(1) + (-1)(1)(1) + (1)(-1)(1) + (3)(-1)(1) = 1$$

Calculate irreducible representation $B_1$

$$B_1: (1/4)[(9)(1)(1) + (-1)(-1)(1) + (1)(1)(1) + (3)(-1)(1) = 2$$

Calculate irreducible representation $B_2$

$$B_2: (1/4)[(9)(1)(1) + (-1)(1)(1) + (1)(-1)(1) + (3)(1)(1) = 3$$

The reducible representation...

...is resolved into three $A_1$, one $A_2$, two $B_1$, and three $B_2$ species.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$\sigma_{v(xz)}$</th>
<th>$\sigma_{v(yz)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

$$\Gamma_{\text{tot}} = 3A_1 + A_2 + 2B_1 + 3B_2$$

$$-\Gamma_{\text{trans}} = A_1 + B_1 + B_2$$

$$-\Gamma_{\text{rot}} = A_2 + B_1 + B_2$$

$$\Gamma_{\text{vib}} = 2A_1 + B_2$$

Notice this is the same result we obtained by analyzing the symmetries of the vibrational modes.

-each mode is IR active
Consider only the OH stretches in H₂O
- consider the number of unchanged O-H bonds under the symmetry operations of the point group

\[
\begin{array}{cccc|c}
C_{2v} & E & C_2 & \sigma_v(xz) & \sigma_v(yz) \\
\hline
\text{Unchanged OH bonds} & 2 & 0 & 0 & 2 \\
\end{array}
\]

**Reducible Representation**

<table>
<thead>
<tr>
<th>(C_{2v})</th>
<th>(E)</th>
<th>(C_2)</th>
<th>(\sigma_v(xz))</th>
<th>(\sigma_v(yz))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(B_1)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(B_2)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Character Table**

By *inspection*, the reducible representation is composed of the \(A_1\) and \(B_2\) representation.

\[
\begin{array}{cccc|c}
\hline
\text{Sum of rows} & 2 & 0 & 0 & 2 \\
\end{array}
\]

**General Method:** Determine OH stretching in H₂O using reducible representations and reduction formula

\[
\begin{array}{cccc|c}
C_{2v} & E & C_2 & \sigma_v(xz) & \sigma_v(yz) \\
\hline
\text{Coefficient} & 1 & 1 & 1 & 1 \\
\text{Order of group} & 4 & & & \\
\text{Unchanged bonds (OH)} & 2 & 0 & 0 & 2 \\
\end{array}
\]

\[
\begin{array}{cccc|c}
\hline
\text{Coefficients} | E | C_2 & \sigma_v(xz) & \sigma_v(yz) \\
\hline
A_1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & -1 & 1 & -1 \\
B_1 & 1 & 1 & -1 & R_z \\
B_2 & 1 & -1 & -1 & y, R_y \\
\end{array}
\]

Using reducible representations and the reduction formula, one obtains \(A_1 + B_2\) modes.
Derive $\Gamma_{\text{tot}}$ for BCl$_3$ given the character table for D$_{3h}$.

Derive the number of vibrational modes and assign modes for BCl$_3$.

### Table: Unshifted atoms and Contribution per atom

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>2C$_3$</th>
<th>3C$_2$</th>
<th>$\sigma_h$</th>
<th>2S$_3$</th>
<th>3$\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unshifted atoms</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Contribution per atom</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-2</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_{\text{tot}}$</td>
<td>12</td>
<td>0</td>
<td>-2</td>
<td>4</td>
<td>-2</td>
<td>2</td>
</tr>
</tbody>
</table>

### Table: $D_{3h}$ representations

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>2C$_3$</th>
<th>3C$_2$</th>
<th>$\sigma_h$</th>
<th>2S$_3$</th>
<th>3$\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$x^2 + y^2, z^2$</td>
</tr>
<tr>
<td>$A_2'$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$R_z$</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$A_1'$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2''$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

### Results of using the reduction formula.

<table>
<thead>
<tr>
<th>$X_r^x X_i^x n^x$</th>
<th>1/h</th>
<th>Sum</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1'$</td>
<td>12</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$A_2'$</td>
<td>12</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>$E'$</td>
<td>24</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>$A_1'$</td>
<td>12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$A_2''$</td>
<td>12</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$E''$</td>
<td>24</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Therefore, we have determined

$$\Gamma_{\text{tot}} = A_1' + A_2' + 3E' + 2A_2'' + E''$$

but, subtract off the translational representations.

$$-\left[\Gamma_{\text{trans}} = E' + A_2'' \right]$$

and subtract off the rotational representations.

$$-\left[\Gamma_{\text{rot}} = A_2' + E'' \right]$$

$$\Gamma_{\text{vib}} = A_1' + 2E' + A_2''$$

$^{10}\text{BCl}_3$ 471 cm$^{-1}$  
$^{11}\text{BCl}_3$ 471 cm$^{-1}$  
$v_1$  

$^{10}\text{BCl}_3$ 480 cm$^{-1}$  
$^{11}\text{BCl}_3$ 460 cm$^{-1}$  
$v_2$  

$^{10}\text{BCl}_3$ 995 cm$^{-1}$  
$^{11}\text{BCl}_3$ 956 cm$^{-1}$  
$v_3$  

$^{10}\text{BCl}_3$ 244 cm$^{-1}$  
$^{11}\text{BCl}_3$ 243 cm$^{-1}$  
$v_4$


Raman active.  IR active.  Raman and IR active.

We can use isotopic substitution to interpret spectra, since the characteristic frequency of the mode will depend on the masses of the atoms moving in that mode.

**Review:** What do I do when I need to...?

**Assign symmetry labels to vibrational modes?**
- If the vibrational mode is known and illustrated, sketch the resulting vibrational mode before and after each symmetry operation of the point group. Using the character table, assign the symmetry label and identify if the mode is IR and/or Raman active.
- Determine the symmetries of all vibrational modes and if the modes are IR and/or Raman active?
  - Determine how many atoms are left unchanged by each symmetry operation. Find the reducible representation and reduce into the irreps. Subtract translational and rotational modes... Identify which modes are IR and/or Raman active....
- Determine the symmetries of only the stretching modes and if the modes are IR and/or Raman active?
  - Determine how many bonds are left unchanged by each symmetry operation. Find the reducible representation and reduce into the irreps. Identify which are IR and/or Raman active....
- Develop a character table?
  - Determine the effect of each symmetry operation on the $x$, $y$, $z$ translation and the rotation $R_x$, $R_y$, and $R_z$. The resulting set of characters correspond to an irrep in the character table.
Determine the number of and assign the vibrational modes of the following:
How many peaks in the (1) IR spectra and (2) Raman spectra

1. NH₃
2. CH₄
3. [PtCl₄]²⁻
4. SF₆
5. SF₅Cl

Determine the symmetries and number of vibrational modes, and number IR and Raman peaks for a) CO stretching modes b) all vibrational modes:

1. Mn(CO)₆
2. Mn(CO)₅Cl
3. trans-Mn(CO)₄Cl₂
4. cis-Mn(CO)₄Cl₂
5. fac-Mn(CO)₃Cl₃
6. mer-Mn(CO)₃Cl₃