Chapter 6. Molecular Symmetry
An introduction to symmetry analysis.

M.C. Escher and Symmetry Drawings
M.C. Escher has uncommon visions and intuitions. Many of Escher's
drawings contain mathematical ideas never seen elsewhere. One of the things
that he did touched me deeply - the interlocking shapes of people, birds and
fish which repeat over a flat surface with no gaps.

Symmetry
M.C. Escher

Fish and Boats
Symmetry

Symmetry Butterflies
Symmetry elements and operations

A symmetry operation is the process of doing something to a shape or an object so that the result is indistinguishable from the initial state

- Identity \( (E) \)
- Proper rotation axis of order \( n \) \( (C_n) \)
- Plane of symmetry \( (\sigma) \)
- Improper axis (rotation + reflection) of order \( n \) \( (S_n) \), an inversion center is \( S_2 \)

\[ E - \text{the identity element} \]

The symmetry operation corresponds to doing nothing to the molecule. The \( E \) element is possessed by all molecules, regardless of their shape. \( C_1 \) is the most common element leading to \( E \), but other combination of symmetry operation are also possible for \( E \).

\( i^{2n} = E, \; n = \text{integer} \)

\( i^n = i \) for odd \( n \)

\[ C_n - \text{a proper rotation axis of order } n \]

- The symmetry operation \( C_n \) corresponds to rotation about an axis by \( (360/n)^0 \).
- \( H_2O \) possesses a \( C_2 \) since rotation by \( 360/2^0 = 180^0 \) about an axis bisecting the two bonds sends the molecule into an indistinguishable form:
Proper rotations, $C$

$C_n$ is a rotation about the axis by $\frac{2\pi}{n}$

Thus, $C_2$ is a rotation by $180^\circ$, while $C_3$ is a rotation by $120^\circ$. If a molecule contains a $C_n$ axis, we call this the "principle axis" of the molecule and it is defined as the $z$ axis.

$c_n^m$ is a rotation about the axis by $m\frac{2\pi}{n}$

Note: $c_n^1 = E = c_n^{2n} = c_n^{3n}$ etc.

A $C_n$ axis generates $n$ operations:

$C_n, c_n^2, c_n^3, ..., c_n^n (= E)$

$\sigma$ - a plane of reflection

The symmetry operation corresponds to reflection in a plane. $H_2O$ possesses two reflection planes. Labels: $\sigma_h, \sigma_d$ and $\sigma_v$. 
\[ \sigma \]

in a plane which contains the principle axis

\[ v \]

in a plane ⊥ principle axis

\[ h \]

in a plane containing principle axis and bisecting lower order axes

e.g. \((xy)\): \((x,y,z) \rightarrow (x,y,-z)\)

Note: \(2n = E, n = \text{integer}\)

**i - an inversion center**

The symmetry operation corresponds to inversion through the center. The coordinates \((x,y,z)\) of every atom are changed into \((-x,-y,-z)\):

\[ i \text{ (x,y,z) } \rightarrow (-x,-y,-z) \]
\[ i^n (x,y,z) \rightarrow ((-1)^n x, (-1)^n y, (-1)^n z) \]

\[ S_n = \perp \cdot C_n = C_n \cdot \perp (C_n \text{ and } \perp \text{ always commute}). \]

(Note that in general, \( R_1 \cdot R_2 \) does not equal \( R_2 \cdot R_1 \))

e.g.

\begin{align*}
\text{invert through} & \quad \text{centre} \\
\text{invert through} & \quad \text{centre}
\end{align*}
A collection of symmetry elements which are interrelated according to certain rules as shown above is called a "point group". For example, the $C_{2v}$ point group contains the $E$, $C_2$, $v(xz)$ and $v(yz)$ symmetry elements.

**Point groups**

It is convenient to classify molecules with the same set of symmetry elements by a label. This label summarizes the symmetry properties. Molecules with the same label belong to the same point group. For example, all square molecules belong to the $D_{4h}$ point group irrespective of their chemical formula.

**Point Group Assignment**

There is a systematic way of naming most point groups C, S or D for the principal symmetry axis. A number for the order of the principal axis (subscript) $n$. A subscript $h$, $d$, or $v$ for symmetry planes $\sigma$: $\sigma_h$, $\sigma_d$, or $\sigma_v$
Special Point Groups

- Linear molecules have a $C_\infty$ axis - there are an infinite number of rotations that will leave a linear molecule unchanged.
- If there is also a plane of symmetry perpendicular to the $C_\infty$ axis, the point group is $D_{\infty h}$.
- If there is no plane of symmetry, the point group is $C_\infty v$.
- Tetrahedral molecules have a point group $T_d$.
- Octahedral molecules have a point group $O_h$.
- Icosahedral molecules have a point group $I_h$.

Character tables

Always remember - character tables are our friends! They make life easy for us by showing us how to assign atomic and molecular orbitals to various "irreducible representations" (IR's). Each table shows for an orbital in a particular IR, the "character" (1 or -1, i.e. symmetric or anti-symmetric) of the orbital under each symmetry operation.
Character tables summarize a considerable amount of information and contain almost all the data that is needed to begin chemical applications of molecule. 

**Symmetry Classes**

The symmetry classes for each point group and are labeled in the character table

**Label Symmetry Class**

- **A** Singly-degenerate class, symmetric with respect to the principal axis
- **B** Singly-degenerate class, asymmetric with respect to the principal axis
- **E** Doubly-degenerate class
- **T** Triply-degenerate class

For example: H$_2$O molecule belongs to C$_{2v}$ point group:

For example, in the C$_{2v}$ point group an orbital which is symmetric with respect to (w.r.t.) rotation around the principle axis (C$_2$) will be designated a. If in addition it is symmetric w.r.t. reflection in the vertical plane containing the C$_2$ axis, it is designated a$_1$. An orbital which is antisymmetric w.r.t. rotation about the C$_2$ axis (the z axis), antisymmetric w.r.t. reflection in the xz plane, and symmetric w.r.t. reflection in the yz plane is designated b$_2$. (Normally we use lower case letters to refer to the reducible representations of individual orbitals.)

**Information on Character Table**
The order of the group is the total number of symmetry elements and is given the symbol \( h \). For \( C_{2v} \), \( h \) (order) = 4.

First Column has labels for the irreducible representations. \( A_1 \), \( A_2 \), \( B_1 \), \( B_2 \).

The rows of numbers are the characters \((1, -1)\) of the irreducible representations.

\( p_x \), \( p_y \) and \( p_z \) orbitals are given by the symbols \( x \), \( y \) and \( z \) respectively.

\( d_{z^2} \), \( d_{x^2-y^2} \), \( d_{xy} \), \( d_{xz} \) and \( d_{yz} \) orbitals are given by the symbols \( z^2 \), \( x^2-y^2 \), \( xy \), \( xz \) and \( yz \) respectively.

Character Table \( T_d \)

<table>
<thead>
<tr>
<th>( T_d )</th>
<th>( E )</th>
<th>( 8C_3 )</th>
<th>( 3C_2 )</th>
<th>( 6S_4 )</th>
<th>( 6\sigma_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_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>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( T_1 )</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

In the top row, the point group label is given followed by the symmetry elements. The **order** of the group is the total number of symmetry elements and is given the symbol \( h \). For \( C_{2v} \), there are four symmetry elements so \( h = 4 \). For \( T_d \), there are \( 1 + 8 + 3 + 6 + 6 \) symmetry elements so \( h = 24 \).

The rows of numbers in the **purple central area** are the characters of the irreducible representations. The symbols in the **blue left area** are the labels for the irreducible representations.

The symbols in **orange right area** show which IRs some important and commonly used objects and properties belong to (so saving the user the effort of working them out).

For example, they show how the atomic orbitals on a **central** atom
behave. (All of the symmetry elements pass through a central atom. Examples include the oxygen atom in water and the carbon atom in methane. There is no central atom in benzene).

The IRs spanned the central atom's $p_x$, $p_y$ and $p_z$ orbitals are given by the symbols $x$, $y$ and $z$ respectively. Hence in water, $p_x$ transforms as $b_1$, $p_y$ transforms as $b_2$ and $p_z$ transforms as $a_1$ as can be readily checked by comparing the characters with those generated previously. In methane ($T_d$), the carbon $p$-orbitals transform as $t_2$; as the symbols are all inside brackets, $(x, y, z)$, they are degenerate.

The IRs spanned by the central atom's $d_{2z}$, $d_{x^2-y^2}$, $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals are given by the symbols $z^2$, $x^2-y^2$, $xy$, $xz$ and $yz$ respectively. (Sometimes the $x^2$, $y^2$ and $y^2$ symbols are given separately or in sums. If given separately then sums such as $x^2-y^2$ transform in the same way. $x^2+y^2$ is a circle and $x^2+y^2+z^2$ is a sphere. $2z^2-x^2-y^2$ is a more complicated way of indicating $d_{2z}$).

In a tetrahedral complex like $\text{FeCl}_4^{2-}$, the iron $d$-orbitals transform as $e + t_2$ and so are predicted to be split into a set of two and a set of three (as described by crystal-field theory).

The IR spanned by the central atom's $s$-orbital is always the totally symmetric representation; that is, the one with a full set of $+1$ characters. This is always the first row of the character table.

- Other properties are also assigned in the orange right area. The IRs spanned by the molecule's rotations (useful for working out selection rules for microwave spectroscopy) are given by the symbols $R_x$, $R_y$ and $R_z$. The IRs spanned by the molecule's translations are given by the symbols $x$, $y$ and $z$. These symbols also give the IRs spanned by the
electric dipole operator (useful for working out selection rules in infrared and electronic spectroscopy). The symbols $x^2$, $y^2$, $z^2$, $xy$, $xz$ and $yz$ (and their sums) give the IRs spanned by the polarizability tensor (useful for working out selection rules for Raman spectroscopy).

**Rules for naming IR's.**

i. Singly-degenerate IR's are designated as A or B; doubly-degenerate as E; triply-degenerate as T or F.

ii. Singly-degenerate IR's are A if symmetric with respect to rotation about principle axis $C_n$ (i.e. character $= 1$), B if antisymmetric.

iii. Subscripts 1 and 2 are usually attached to A and B to designate symmetric or antisymmetric, respectively, with respect to a $C_2$ axis perpendicular to the principal axis, or if such an axis does not exist with respect to a vertical plane containing the principle axis.

iv. Prime or double prime on letters indicate symmetric or antisymmetric with respect to $h$.

v. Subscripts g and u designate symmetric or antisymmetric with respect to i (centre of inversion).

**Molecular Polarity and Chirality**

**Polarity**

Only molecules belonging to the point groups $C_n$, $C_{nv}$ and $C_s$ are polar. The dipole moment lies along the symmetry axis for molecules belonging to the point groups $C_n$ and $C_{nv}$. 

**Chirality**
Only molecules lacking a $S_n$ axis can be chiral. This includes mirror planes and a centre of inversion as $S_2 = s$ and $S_1 = i$.

![Molecular Orbital Diagrams of a Molecule](http://138.47.34.166/chem481/Chem481c4.html)

Molecular Orbital Diagrams of a Molecule
Symmetry allowed combinations
• Find symmetry species spanned by a set of orbitals
• Next find combinations of the atomic orbitals on central atom which have these symmetries.
• Combining these are known as symmetry adapted linear combinations (or SALCs).
• The characters show their behavior of the combination under each of the symmetry operations. Several methods for finding the combinations.

Example: Valence MOs of Water

• $\text{H}_2\text{O}$ has $C_{2v}$ symmetry.
• The symmetry operators of the $C_{2v}$ group all commute with each other (each is in its own class).
• Molecular orbitals should have symmetry operators $E$, $C_2$, $\sigma_{v1}$, and $\sigma_{v2}$.

Building a MO diagram for $\text{H}_2\text{O}$

Symmetry of $a_1$ orbital of $\text{H}_2\text{O}$

$E \phi(1a_1) \longrightarrow (+1) \phi(1a_1)$
$C_2 \phi(1a_1) \longrightarrow (+1) \phi(1a_1)$
$\sigma_{v1} \phi(1a_1) \longrightarrow (+1) \phi(1a_1)$
$\sigma_{v2} \phi(1a_1) \longrightarrow (+1) \phi(1a_1)$
Symmetry of $b_1$ orbital of $H_2O$

\[ \sigma_{v2} \]

\[ E\phi(1b_1) \quad \rightarrow \quad (+1)\phi(1b_1) \]

\[ \sigma_{v2}\phi(1b_1) \quad \rightarrow \quad (+1)\phi(1b_1) \]

Symmetry of $b_1$ orbital of $H_2O$, cont.

\[ C_2 \]

\[ \sigma_{v1} \]

\[ C_2\phi(1b_1) \quad \rightarrow \quad (-1)\phi(1b_1) \]

\[ \sigma_{v1}\phi(1b_1) \quad \rightarrow \quad (-1)\phi(1b_1) \]

Symmetry of $b_2$ orbital of $H_2O$

\[ \sigma_{v1} \]

\[ E\phi(1b_2) \quad \rightarrow \quad (+1)\phi(1b_2) \]

\[ \sigma_{v1}\phi(1b_2) \quad \rightarrow \quad (+1)\phi(1b_2) \]

Symmetry of $b_2$ orbital of $H_2O$, cont.
MO diagram for H$_2$O

C$_2\phi(1b_2)$
\sigma_v\phi(1b_2)

\rightarrow\quad (-1)\phi(1b_2)
\rightarrow\quad (-1)\phi(1b_2)
Group Theory and Vibrational Spectroscopy

- When a molecule vibrates, the symmetry of the molecule is either preserved (symmetric vibrations) or broken (asymmetric vibrations).
- The manner in which the vibrations preserve or break symmetry can be matched to one of the symmetry classes of the point group of the molecule.
- Linear molecules: $3N - 5$ vibrations
  Non-linear molecules: $3N - 6$ vibrations ($N$ is the number of atoms)

**Normal Modes of Vibration**

The complex vibrations of a molecule are the superposition of relatively simple vibrations called the *normal modes of vibration*. Each normal mode of vibration has a fixed frequency. It is easy to calculate the expected number of normal modes for a molecule made up of $N$ atoms.

**Determining Normal Mode Symmetries of $\text{H}_2\text{O}$**
The symmetries of the normal modes can be classified by group theory. As an example, water has a symmetrical bent structure of $C_{2v}$ symmetry. It has three atoms and three normal modes of vibration ($3 \times 3 - 6 = 3$). Pictures of the three normal modes are shown here along with their symmetry types.

Find reducible rep. for all nuclear motions. Eliminate translations and rotations (6 for nonlinear molecules, 5 for linear molecules). This guarantees that normal modes involve no net translation or rotation of center of mass. $\text{H}_2\text{O}$ has three atoms and three normal modes of vibration ($3 \times 3 - 6 = 3$).

Can be symbolised as $\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3$.

If we carry out the symmetry operations of $C_{2v}$ on this set, we will obtain a transformation matrix for each operation. E.g. $C_2$ effects the following transformations:

$x_1 \rightarrow -x_2, \ y_1 \rightarrow -y_2, \ z_1 \rightarrow z_2, \ x_2 \rightarrow -x_1, \ y_2 \rightarrow -y_1, \ z_2 \rightarrow z_1, \ x_3 \rightarrow -x_3, \ y_3 \rightarrow -y_3, \ z_3 \rightarrow z_3$.

This, and the effects of the other symmetry operations, are summarised by a set of four $9 \times 9$ transformation matrices.
The resulting characters can be summarised as follows

\[
\begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
\end{bmatrix}
\]

\[\chi(E) = 9\]

\[
\begin{bmatrix}
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
\end{bmatrix}
\]

\[\chi(C_2) = -1\]

\[
\begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\]

\[\chi(\sigma_{xz}) = 1\]

\[\chi(\sigma_{yz}) = 3\]

These constitute the representation \(\Gamma_{3N'}\):

\[
\Gamma_{3N'} = 9 \quad -1 \quad 1 \quad 3
\]

Use reduction formula:

The reduction can always be achieved using the reduction formula.

The number of times an irrep occurs in the reducible representation is given by:

\[
n_i = \frac{1}{h} \sum_c g_c \chi_i \chi_r
\]

\[h = \text{the order of the group}\]

\[\chi_r = \text{character of reducible representation}\]

\[\chi_i = \text{character of irreducible representation}\]

\[g_c = \text{no. of symmetry operations in the class}\]

(i.e. the number of equivalent operations, e.g. for \(C_2\) \(g_c = 1\))

\[
\begin{align*}
C_{2v} & \quad 1 \quad E \quad 1C_2 \quad 1\sigma_v \quad 1\sigma_{v'} \\
A_1 & \quad 1 \quad 1 \quad 1
\end{align*}
\]
For example, in the $C_{2v}$ point group an orbital which is symmetric with respect to (w.r.t.) rotation around

$$\Gamma_{3N} = 9 \quad -1 \quad 1 \quad 3$$

$$A_1 = 1/4 \left[ (9 \times 1 \times 1) + (-1 \times 1 \times 1) + (1 \times 1 \times 1) + (3 \times 1 \times 1) \right] = 3$$

$$A_2 = 1/4 \left[ (9 \times 1 \times 1) + (-1 \times 1 \times 1) + (1 \times -1 \times 1) + (3 \times -1 \times 1) \right] = 1$$

$$B_1 = 1/4 \left[ (9 \times 1 \times 1) + (-1 \times -1 \times 1) + (1 \times 1 \times 1) + (3 \times -1 \times 1) \right] = 2$$

$$B_2 = 1/4 \left[ (9 \times 1 \times 1) + (-1 \times -1 \times 1) + (1 \times -1 \times 1) + (3 \times -1 \times 1) \right] = 3$$

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

The number should come out as zero or as a positive integer: if it does not then either the formula has been used incorrectly or the reducible representation has been generated incorrectly...or both.

It sounds complicated but, as the examples below show, it is actually just tedious to use.

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

This was obtained using $3N$ cartesian coordinate vectors. Using $3N$ (translation + rotation + vibration) vectors would have given the same answer.

But we are only interested in the $3N-6$ vibrations.

The irreducible representations for the rotation and translation vectors are listed in the character tables,

**e.g. for $C_{2v}$,**

$$\Gamma_T = A_1 + B_1 + B_2$$

$$\Gamma_R = A_2 + B_1 + B_2$$

i.e. $$\Gamma_T + \Gamma_R = A_1 + A_2 + 2B_1 + 2B_2$$
But $\Gamma_{\text{vib}} = \Gamma_{3N} + \Gamma_{T+R}$

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

i.e. of the 3 (= 3N-6) vibrations for a molecule like H$_2$O, two have $A_1$ and one has $B_2$ symmetry

The irreducible representations for the rotation and translation vectors are listed in the character tables, e.g. for $C_{2v}$,

$2A_1 + B_2$

Vibrational Spectroscopy

There are two types of spectroscopy that involve vibrational transitions. You should be very familiar with one of these from your Organic Chemistry course - infrared spectroscopy. During infrared spectroscopy experiments we observe transitions between vibrational energy levels of a molecule induced by the absorption of infrared (IR) radiation. The second type of vibrational spectroscopy is Raman spectroscopy. In Raman spectroscopy, vibrational transitions occur during the scattering of light by molecules.

At room temperature almost all molecules are in their lowest vibrational energy levels with quantum number $n = 0$. For each normal mode, the most
probable vibrational transition is from this level to the next highest level \((n = 0 \rightarrow 1)\). The strong IR or Raman bands resulting from these transitions are called **fundamental bands**. Other transitions to higher excited states \((n = 0 \rightarrow 2, \text{ for instance})\) result in **overtone bands**. Overtone bands are much weaker than fundamental bands.

Not all fundamental vibrational transitions can be studied by both IR and Raman spectroscopy because they have different **selection rules**. Selection rules tell us if a transition is allowed or forbidden. An allowed transition has a high probability of occurring and will result in a strong band. Conversely a forbidden transition's probability is so low that the transition will not be observed. If a normal mode has an allowed IR transition, we say that it is **IR active**. Similarly if a normal mode has an allowed Raman transition, we say that it is **Raman active**.

If you know the point group of the molecule and the symmetry labels for the normal modes, then group theory makes it easy to predict which normal modes will be IR and/or Raman active. Look at the character table for the point group of the molecule.

**If the symmetry label of a normal mode corresponds to** \(x, y, \text{ or } z\), **then the fundamental transition for this normal mode will be IR active.**

**If the symmetry label of a normal mode corresponds to** products of \(x, y, \text{ or } z\) (such as \(x^2, yz\)) **then the fundamental transition for this normal mode will be Raman active.**

Consider the character table for the \(C_{2v}\) group shown at the right. We see that if a normal mode has \(A_1, B_1, \text{ or } B_2\) symmetry...
then it will be both IR and Raman active. If a normal mode has $A_2$ symmetry then it will be only Raman active.

In the example above, water has three normal modes: two of $A_1$ symmetry and one of $B_2$ symmetry. All of these are IR and Raman active. We would expect water to have three peaks corresponding to fundamental vibrations in the IR spectrum. There also would be three peaks in its Raman spectrum at the same frequencies as in the IR.

**Polarized and Depolarized Raman Bands**

The assignment of Raman lines may be aided by measuring their intensity with a polarizing filter, first parallel and the perpendicular to the polarization of the incident radiation. If the polarization of the scattered beam is the same as that of the incident beam (intense only in the parallel direction), then the Raman line is said to be *polarized*. If the scattered light is intense in both the parallel and perpendicular direction, then the Raman line is *depolarized*.

Only totally symmetric vibrations (a normal mode with all characters $= 1$ in the character table) give rise to polarized lines.

In the water example above, two of the Raman lines correspond to a totally symmetric vibration ($A_1$) and would be polarized. One would be depolarized.

**Example: The Geometry of the Sulfur Dioxide Molecule**

Consider three possible
geometries for the SO₂ molecule, linear and bent, shown at the right with their point groups.

The symmetry types for the normal modes of the three structures are shown here. For the C₃ form 3 A' means that there are three different normal modes, all having the same symmetry (A'). Similarly, for the C₂ᵥ form two of the three normal modes have the same symmetry (A₁). These modes are not identical and do not have the same energy - they just happen to have the same symmetry.

Now we need to look at the character tables to see which normal modes one would expect to be observed in the IR and Raman for each structure. The character tables for the three point groups are shown below.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Normal Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃</td>
<td>3 A'</td>
</tr>
<tr>
<td>C₂ᵥ</td>
<td>2 A₁, B₂</td>
</tr>
<tr>
<td>D₃oh</td>
<td>Σ⁺ₑ, Σ⁺ₐ, Πₐ</td>
</tr>
</tbody>
</table>

**C₃ structure:** 3 normal modes, all having A' symmetry

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>σₖ</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Raman A'</td>
<td>1</td>
<td>x, y, R₂</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>x², y², z², xy</td>
</tr>
<tr>
<td>A''</td>
<td>1</td>
<td>z, Rₓ, Rᵧ</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>yz, xz</td>
</tr>
</tbody>
</table>

The C₃ structure should have 3 IR active fundamental transitions. These three fundamental transitions also should be Raman active. We would expect to observe three strong peaks in the IR and three strong peaks in the Raman at the same frequency as in the IR.
All of the Raman lines would be polarized because they are totally symmetric (A'symmetry).

C\textsubscript{2v} structure: 3 normal modes, two with A\textsubscript{1} symmetry, one with B\textsubscript{2}.

<table>
<thead>
<tr>
<th>C\textsubscript{2v}</th>
<th>E</th>
<th>C\textsubscript{2}</th>
<th>(\sigma\textsubscript{v}(xx))</th>
<th>(\sigma\textsubscript{1'}(yz))</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{1}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z</td>
<td>(x^2, y^2, z^2)</td>
</tr>
<tr>
<td>A\textsubscript{2}</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>R\textsubscript{z}</td>
<td>xy</td>
</tr>
<tr>
<td>B\textsubscript{1}</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>x, R\textsubscript{y}</td>
<td>xz</td>
</tr>
<tr>
<td>IR</td>
<td>Raman</td>
<td>B\textsubscript{2}</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

The C\textsubscript{2v} structure should have 3 IR active fundamental transitions. These three fundamental transitions also should be Raman active. We would expect to observe three strong peaks in the IR and three strong peaks in the Raman at the same frequency as in the IR.

Two of the Raman lines are totally symmetric (A\textsubscript{1} symmetry) and would be polarized. One Raman line would be depolarized.

D\textsubscript{0oh} structure: 3 normal modes with \(\Sigma\textsubscript{g}^+, \Sigma\textsubscript{u}^+, \Pi\textsubscript{u}\) symmetries.

The D\textsubscript{0oh} structure should have two IR active fundamental transitions.
The experimental infrared and Raman bands of liquid and gaseous sulfur dioxide have been reported in a book by Herzberg. Only the strong bands corresponding to fundamental transitions are shown below. The polarized Raman bands are in red.

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$2C_{\infty}^\Phi$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman $\Sigma_g^+$</td>
<td>1</td>
<td>1</td>
<td>$x^2 + y^2, z^2$</td>
</tr>
<tr>
<td>$\Sigma_g^-$</td>
<td>1</td>
<td>1</td>
<td>$R_z$</td>
</tr>
<tr>
<td>$\Pi_g^+$</td>
<td>2</td>
<td>$2 \cos \Phi$</td>
<td>($R_x, R_y$)</td>
</tr>
<tr>
<td>$\Delta_g$</td>
<td>2</td>
<td>$2 \cos 2\Phi$</td>
<td>($x^2 - y^2, xy$)</td>
</tr>
<tr>
<td>IR $\Sigma_u^+$</td>
<td>1</td>
<td>1</td>
<td>$z$</td>
</tr>
<tr>
<td>$\Sigma_u^-$</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>IR $\Pi_u$</td>
<td>2</td>
<td>$2 \cos \Phi$</td>
<td>($x,y$)</td>
</tr>
<tr>
<td>$\Delta_u$</td>
<td>2</td>
<td>$2 \cos 2\Phi$</td>
<td></td>
</tr>
</tbody>
</table>

The experimental infrared and Raman bands of liquid and gaseous sulfur dioxide have been reported in a book by Herzberg. Only the strong bands corresponding to fundamental transitions are shown below. The polarized Raman bands are in red.

<table>
<thead>
<tr>
<th>Fundamental</th>
<th>2</th>
<th>1</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR (cm$^{-1}$)</td>
<td>519</td>
<td>1151</td>
<td>1336</td>
</tr>
<tr>
<td>Raman (cm$^{-1}$)</td>
<td>524</td>
<td>1151</td>
<td>1336</td>
</tr>
</tbody>
</table>

**Conclusion:**

The existence of three experimental bands in the IR and Raman corresponding to fundamental transitions weighs strongly against the symmetrical linear ($D_{\text{ooh}}$) structure. We usually do not expect more strong bands to exist than are predicted by symmetry.

Group theory predicts that both bent structures would have three fundamental transitions that are active in both the IR and Raman. However all three of the
Raman lines would be polarized if the structure were unsymmetrical ($C_s$ symmetry). The fact that one Raman line is depolarized indicates that the structure must be bent and symmetrical ($C_{2v}$ symmetry).

**The sulfur dioxide molecule has $C_{2v}$ symmetry.**

Reducing

Once a set of orbitals have been used to generate a representation, the next task is to break down (or reduce) the representation down into its component parts. This gives the symmetry species spanned by the orbitals. The orbitals can only contribute to molecular orbitals of these symmetries. There are two ways of doing the reduction. The simplest and quickest, at least for small representations, is to try to reduce by eye. There is also a foolproof, but more time consuming, method using the reduction formula. You should be able to reduce a representation: test.

Symmetry allowed combinations

After finding the symmetry species spanned by a set of orbitals, the next task is to find the combinations of the orbitals which have these symmetries. These combinations are known as symmetry adapted linear combinations (or SALCs). The characters of the irreducible representation show the behaviour of the combination under each of the symmetry operations. There are several methods for finding the combinations. The quickest is to match the symmetry of an atomic orbital on the central atom. There is also a foolproof, but more time-consuming, method using projection operators which is needed for cases where there is no atomic orbital on the central atom of the desired symmetry. It is also useful for dealing with 2D and 3D representations. You should be able to construct SALCs:
Symmetry

1 Elements of symmetry - definition of point group - group criteria - show that symmetry operations satisfy group membership criteria. Introduction to matrix representation of symmetry operations.

2 Show that matrices obey group membership criteria - similarity transformations - character of the matrix - direct sum rule.

3 Reduction of matrices. Irreducible representations - nomenclature of point groups.

4 Application of Group Theory to Molecular Vibrations $\text{SO}_2$, as example, removal of non genuine vibrations (translations and rotations) Direct Product Rule.

5 Orthogonality Theorem - Determination of allowed bonds in Infrared and Raman. Apply to molecule with centre of symmetry.

6 Classification of atomic orbitals in molecules - Assignment of symmetry to $\pi$ molecular orbitals - symmetry of $\pi$ excited states. Determination of allowed/non-allowed $\pi \rightarrow \pi$ transitions. vibronic coupling.

7 Bonding in simple molecules e.g. $\text{H}_2\text{O}$, $\text{BH}_3$ - correlation energy diagram.

8 Conservation of orbital symmetry, conversion of buta-1,3-diene to cyclobutene, energy diagrams for conrotatory and disrotatory mode of ring closure.

9 Crystal field theory - applied to octahedral complexes low spin high spin cases. Variation of ionic radii of dipositive ions of first transition series. Crystal field stabilisation energy - lattice energy of chlorides of transition metal ions.

10 Molecular orbital treatment of octahedral complexes - treatment of ligands with $\sigma$ bonding orbital only - ligand field stabilisation energy. Role of 4$s$ and 4$p$ metal orbitals - 18 electron rule.

11 Introduction of ligands containing $\pi$ orbitals, (a) case of filled $\pi$ orbitals (b) case of empty $\pi$ orbitals. Excited states in transition metal compounds. Revision of terms L, S, and J. Russell Saunders coupling scheme for inequivalent electrons. Coupling scheme for equivalent electrons e.g. $2p^2$, $3d^2$ microstates and atomic states.
12 Splitting of Levels and Terms in octahedral environment for \(d^1 \rightarrow d^{10}\) configuration - ground states of \(d_n\) configurations and excited states of \(d_n\) configuration. Extend to tetrahedral situation.

**Spectroscopy**

13 Vibrational spectroscopy, basic concept of vibrational and infrared spectroscopy. Units rotation of diatomic molecules, classical treatment of the interaction of electromagnetic field rotating molecule, general selection rules, classical argument based on \(\hbar \omega^2/2 = kT\) to show that absorption will be in microwave energy region.


15 Vibration of diatomics: Review of harmonic oscillator model: energy levels and selection rules. Potential energy curves for diatomic molecules and their interpretation, the parabolic approximation, transitions, population of levels.

16 Deviations from the HO model, anharmonicity, overtones, hot bands, extrapolation to the dissociation limit, etc. The vibration-rotation bands of diatomic molecules, rotational fine structure of the vibrational transitions, energy level diagram for combined vib-rot. states, selection rules, transitions, P and R branches, population of levels and intensity distribution in the absorption band.

17 Normal modes - \(CO_2\) used as an example with simple model worked out in detail, selection rules, rotational structure of bending and stretching modes in linear molecules, the Q branch. The aman Effect - physical explanation as photon scattering process with change of frequency, Rayleigh and Raman scattering. Example of deduction of vibrational energy jump in molecule from change in wavelength of scattered visible light.

18 Raman Spectroscopy - mutual complementarity of IR and Raman transitions in molecules with centre of symmetry. Analysis of Raman spectra of small molecules. Extension to normal modes of large molecules; symmetric and asymmetric vibrations, use of polarisation to establish symmetry, examples \(CCl_4\) and \(AuCl_4\), comparison with IR, use of mutual exclusion rule to determine cis and trans isomers.
Symmetry Tutorial - Introduction

Welcome to the world of symmetry! Symmetry plays an central role in the analysis of the structure, bonding, and spectroscopy of molecules. In this tutorial, we will explore the basic symmetry elements and operations and their use in determining the symmetry classification (point group) of different molecules.

The symmetry properties of objects (and molecules) may be described in terms of the presence of certain symmetry elements and their associated symmetry operations. The various symmetry elements and operations are described in the table below.

Symmetry Elements and Operations


Fluorescence, internal conversion, radiative lifetime, resonance fluorescence. Intersystem crossing. Phosphorescence.

Resonance Raman spectroscopy - basic concept, use of Raman spectroscopy to obtain electronic as well as vibrational information, advantages of enhanced sensitivity, applications in solution and on surfaces - surface enhanced Raman spectroscopy, the basic concept.

Fourier Transform methods in modern vibrational spectroscopy. Use of an interferometer to collect spectra, the Fourier Transform - advantages and disadvantages.
4.2 The point groups of molecules

http://www.emory.edu/CHEMISTRY/pointgrp/

Applications of symmetry

http://chemistry.umeche.maine.edu/Modeling/symmetry.html


**Basic symmetry tutorial**
(Adapted from some notes by Brenda Thiess.)

It is clear that some molecules are more symmetric than others. Highly symmetric molecules contain a number of "symmetry elements" and these give rise to various "symmetry operations" in a molecule. These two ideas are described below, followed by an outline of how to assign a molecule to a particular "point group", and finally how to summarise all this information in a "character table".

1. A *symmetry element* is a geometrical entity (a line, plane or point) with respect to which one or more symmetry operations may be carried out.
2. Types of symmetry operation (see table above)

(a) Inversion,
\[ i (x,y,z) \rightarrow (-x,-y,-z) \]
\[ i^n (x,y,z) \rightarrow ((-1)^n x, (-1)^n y, (-1)^n z) \]
(b) Identity, E, no change at all
\[ i^{2n} = E, n \text{ integer} \]
\[ i^n = i \text{ for odd } n \]
(c) Proper rotations, C
\[ C_n \text{ is a rotation about the axis by } \frac{2\pi}{n} \]
Thus, \( C_2 \) is a rotation by 180°, while \( C_3 \) is a rotation by 120°. If a molecule contains a \( C_n \) axis, we call this the "principle axis" of the molecule and it is defined as the z axis.
\[ c_n^m \text{ is a rotation about the axis by } m*\frac{2\pi}{n} \]
Note: \( c_n^m = E = c_n^{\frac{2\pi}{n}} = c_n^{\frac{\pi}{n}} \) etc.

A \( C_n \) axis generates \( n \) operations:
$C_n, C_{n}^2, C_{n}^3, ... C_{n}^h (= E)$

(d) Reflections,
- $v$: in a plane which contains the principle axis
- $h$: in a plane $\perp$ principle axis
- $d$: in a plane containing principle axis and bisecting lower order axes

e.g. $(xy): (x,y,z) \rightarrow (x,y,-z)$

Note: $2n = E, n = integer$

(e) Improper rotations, $S$

$S_n = \perp C_n = C_n \& C_n^{-1}$ (Note that in general, $R_1 \& R_2$ does not equal $R_2 \& R_1$)

e.g.

A collection of symmetry elements which are interrelated according to certain rules as shown above is called a "point group". For example, the
\(C_{2v}\) point group contains the \(E\), \(C_2\), \(v(xz)\) and \(v(yz)\) symmetry elements.

3. **How to assign a molecule to a particular point group.**

After identifying the symmetry elements in a molecule, use the flowchart below (taken from FA Cotton "Chemical applications of group theory") to obtain the molecular point group.

4. **Character tables**

Always remember - character tables are our friends! They make life easy for us by showing us how to assign atomic and molecular orbitals to various "irreducible representations" (IR's). Each table shows for an orbital in a particular IR, the "character" (1 or -1, i.e. symmetric or antisymmetric) of the orbital under each symmetry operation.

Rules for naming IR's.
i. Singly-degenerate IR's are designated as A or B;

doubly-degenerate as E;
triply-degenerate as T or F.

ii. Singly-degenerate IR's are A if symmetric with respect to rotation about principle axis $C_n$ (i.e. character = 1), B if antisymmetric.

iii. Subscripts 1 and 2 are usually attached to A and B to designate symmetric or antisymmetric, respectively, with respect to a $C_2$ axis perpendicular to the principal axis, or if such an axis does not exist with respect to a vertical plane containing the principle axis.

iv. Prime or double prime on letters indicate symmetric or antisymmetric with respect to $h$.

v. Subscripts g and u designate symmetric or antisymmetric with respect to $i$ (centre of inversion).

For example, in the $C_{2v}$ point group an orbital which is symmetric with respect to (w.r.t.) rotation around the principle axis ($C_2$) will be designated $a$. If in addition it is symmetric w.r.t. reflection in the vertical plane containing the $C_2$ axis, it is designated $a_1$. An orbital which is
antisymmetric w.r.t. rotation about the $C_2$ axis (the z axis), antisymmetric w.r.t. reflection in the xz plane, and symmetric w.r.t. reflection in the yz plane is designated $b_2$. (Normally we use lower case letters to refer to the irreducible representations of individual orbitals.)

For more details and many beautiful examples, see the classic book by F. Albert Cotton, "Chemical applications of group theory" (Wiley, 1971).

4.3 Polar molecules
4.4 Chiral molecules
The symmetries of orbitals
4.5 Character tables and symmetry labels

http://truth.wofford.edu/~whisnantdm/shortcl2o4/CharTables.htm
http://www.hull.ac.uk/php/chsajb/symmetry/char_tables.html

Character tables

Character tables are divided into three main areas. The examples given below show the $C_{2v}$ and $T_d$ tables with the three areas distinguished by colours.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$s_v$</th>
<th>$s'_v$</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>

| $T_d$  | E | 8$C_3$ | 3$C_2$ | 6$S_4$ | 6$s_d$ |

http://138.47.34.166/chem481/Chem481c4.html 4/2/2003
In the top row, the point group label is given followed by the symmetry elements. The order of the group is the total number of symmetry elements and is given the symbol $h$. For $C_{2v}$, there are four symmetry elements so $h = 4$. For $T_d$, there are $1 + 8 + 3 + 6 + 6$ symmetry elements so $h = 24$.

The rows of numbers in the purple central area are the characters of the irreducible representations. The symbols in the blue left area are the labels for the irreducible representations.

The symbols in orange right area show which IRs some important and commonly used objects and properties belong to (so saving the user the effort of working them out).

For example, they show how the atomic orbitals on a central atom behave. (All of the symmetry elements pass through a central atom. Examples include the oxygen atom in water and the carbon atom in methane. There is no central atom in benzene).

The IRs spanned the central atom's $p_x$, $p_y$ and $p_z$ orbitals are given by the symbols $x$, $y$ and $z$ respectively.

Hence in water, $p_x$ transforms as $b_1$, $p_y$ transforms as $b_2$ and $p_z$ transforms as $a_1$ as can be readily checked by comparing the characters with those generated previously. In methane ($T_d$), the carbon $p$-orbitals transform as $t_2$; as the symbols are all inside brackets, $(x, y, z)$, they are degenerate.

The IRs spanned by the central atom's $d_{x^2}$, $d_{y^2}$, $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals are given by the symbols $z^2$, $x^2-y^2$, $xy$, $xz$ and $yz$ respectively.

<table>
<thead>
<tr>
<th>IR</th>
<th>Characters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$1$ $1$ $1$ $1$ $1$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$1$ $1$ $1$ $-1$ $-1$</td>
</tr>
<tr>
<td>$E$</td>
<td>$2$ $-1$ $2$ $0$ $0$</td>
</tr>
<tr>
<td>$T_1$</td>
<td>$3$ $0$ $-1$ $1$ $-1$</td>
</tr>
<tr>
<td>$T_2$</td>
<td>$3$ $0$ $-1$ $-1$ $1$</td>
</tr>
</tbody>
</table>
Sometimes the $x^2$, $y^2$ and $y^2$ symbols are given separately or in sums. If given separately then sums such as $x^2-y^2$ transform in the same way. $x^2+y^2$ is a circle and $x^2+y^2z^2$ is a sphere. $2z^2-x^2-y^2$ is a more complicated way of indicating $d_{x^2}$. 

In a tetrahedral complex like $\text{FeCl}_4^{2-}$, the iron d-orbitals transform as $e + t_2$ and so are predicted to be split into a set of two and a set of three (as described by crystal-field theory).

The IR spanned by the central atom's s-orbital is always the totally symmetric representation; that is, the one with a full set of +1 characters. This is always the first row of the character table.

Other properties are also assigned in the orange right area. The IRs spanned by the molecule's rotations (useful for working out selection rules for microwave spectroscopy) are given by the symbols $R_x$, $R_y$ and $R_z$. The IRs spanned by the molecule's translations are given by the symbols $x$, $y$ and $z$. These symbols also give the IRs spanned by the electric dipole operator (useful for working out selection rules in infrared and electronic spectroscopy). The symbols $x^2$, $y^2$, $z^2$, $xy$, $xz$ and $yz$ (and their sums) give the IRs spanned by the polarizability tensor (useful for working out selection rules for Raman spectroscopy).

4.6 The interpretation of character tables
4.7 The construction of molecular orbitals

The symmetries of molecular vibrations

Group Theory Basics

A. symmetry elements

1. E - the identity operation, all molecules possess this operation.

2. $C_n^-$ - n-fold rotation of $(360/n)^0$. $\text{H}_2\text{O}$ has a two-fold rotation, $\text{NH}_3$ has a $C_3^\prime$, $\text{CH}_4$ has a $C_4^\prime$, and $\text{C}_6\text{H}_6$ has a $C_6^\prime$. Molecules can have additional rotation axes that are perpendicular to the primary rotation axis (the one with the biggest n), benzene, for example, has
6 $C_2$ axes that are perpendicular to the $C_6$. Also, rotation of 1/6 of the way around the benzene ring is a $C_6$, going 2/6 is considered a $C_3$, and 3/6 is a $C_2$, you always reduce your fractions.

3. $\sigma_v$ - vertical plane of symmetry, contains the primary rotation axis. There will always be $n-\sigma_v$'s for a molecule with a $C_n$ rotational axis.

4. $\sigma_h$ - horizontal plane of symmetry, is perpendicular to the primary axis. Only planar species have these.

5. $i$ - inversion center, reflection of all atoms through the inversion point results in the same molecule. For an octahedral metal complex, the inflection point is the center of the octahedron (the metal). For $C_2H_4$, it is a point in the center of the double bond.

6. $S_n$ - improper rotation, rotation of $(360/n)$ followed by reflection through a horizontal mirror plane. These are hard to see, the best example of this is staggered ethane, $C_2H_6$, if you rotate $60^\circ$ then reflect, the methyl hydrogens with be transmuted to each other.

In a rigorous treatment of group theory, you would be expected to examine a molecule, determine the symmetry elements that are present, and assign the molecule to one of the available point groups. The beauty of point groups is that they can be used to predict chemistry purely on symmetrical arguments. All molecules that have $C_{2v}$ symmetry, for example, $H_2O$, will have the same symmetry properties.

For this class you need to know the following:

1) Each non-linear molecule has $3N-6$ molecular vibrations. (the individual atom motions will be given to you)
2) Each of these vibrations can be assigned a symmetry (you
may be asked to do this).
3) From group theory, you can determine which of these vibrations will be IR and Raman active purely from symmetry arguments. For example, H\textsubscript{2}O and CH\textsubscript{2} are triatomics with very different chemical properties, but the number of peaks (not their location) in their IR and Raman spectra will be identical. In addition, a molecule like ketene, CH\textsubscript{2}C=\text{C}=O, also belongs to the C\textsubscript{2V} point group, it will have more vibrations than H\textsubscript{2}O (12 vs. 3) but all of them will fall into the same categories as the water vibrations. We will discuss these categories next.

B. Symmetries of Vibrations

Assigning the symmetries of molecular vibrations can be an arduous process. You may be asked to do this for simple molecules, but most of the time I will provide you with the symmetries of the vibrations. The process goes as follows: let’s look at H\textsubscript{2}O, there are three vibrations, the symmetric stretch (\(\nu_1\)), the asymmetric stretch (\(\nu_2\)), and the symmetric bend (\(\nu_3\)).

To assign a symmetry to a vibration, you must look at the vectors and ask how they transform under the symmetry elements of the appropriate group. Water is in the C\textsubscript{2V} point group, which has the identity element (E), a C\textsubscript{2} axis, and two \(\sigma\textsubscript{V}\) planes (one contains the whole molecule, the other bisects the hydrogens). Let’s look at each of the three vibrations.

1. Performing the identity operation on this molecule produces no
changes in the positions of the vectors of \( \nu_1 \). Rotating through the \( C_2 \) axis also produces no change. Neither do the two mirror planes. This vibration is totally symmetric.

2. The \( \nu_2 \) vibration is also totally symmetric with respect to the identity operator. But now when you perform a \( C_2 \) operation, the vector that was pointing left and down is pointing right and down, and vice versa. From the point of view of the hydrogen on the left, it was moving away from the oxygen, after the rotation it will be moving towards the oxygen, we say that this vibration is antisymmetric with respect to rotation about the primary axis. This vibration is symmetric w.r.t. one of the planes (the one that contains the molecule) and is antisymmetric w.r.t the other one.

3. The \( \nu_3 \) bend is symmetric w.r.t. the identity, the rotation, and reflection through both planes.

Now let's look at the group table.

<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>

Now, we can see under the heading \( C_{2V} \), several symmetry designators, \( A_1, B_2 \), etc., called representations. In this table we see \( A \) and \( B \) type representations, the \( A \) or \( B \) designate that that representation is symmetric (A) or antisymmetric (B) w.r.t rotation.
about the primary axis. The 1 and 2 indicate representations that are symmetric (1) and antisymmetric (2) w.r.t the first mirror plane. Other groups that contain a horizontal plane will have representations bearing single primes (') or double primes ("), indicating a representation that is symmetric and a.s. to reflection through the horizontal plane. Finally if the point group contains an inversion center, the subscripts g and u (for gerade and ungerade (german for even and odd)) are used to designate those representations that are symmetric and a.s. w.r.t to inversion. Some groups also have representations that are double and triply degenerate, these are designated E and T to which the usual hosts of subscripts and superscripts are appended, e.g. \( T_{2g} \), \( E'' \), etc.

We can compare how these symmetry designations respond to the four symmetry elements. The \( A_1 \) state in \( C_{2v} \) is totally symmetric w.r.t. all four elements. Thus, by comparison, the \( \nu_1 \) and \( \nu_3 \) vibrations in water are totally symmetric and have the symmetry designation \( A_1 \). Depending on how you set up your coordinate system, the asymmetric stretch (\( \nu_2 \)) is either \( B_1 \) or \( B_2 \): symmetric w.r.t E, anti-symmetric w.r.t \( C_2 \), and depending on whether you put the molecule in the yz or the xz plane, symmetric to one mirror plane and a.s. to the other. By convention, the z direction is defined to contain the primary rotation axis. As far as the x and y axes go, pick a coordinate system and stick to it for the duration of the problem.

Please notice that the x, y and z axes transform as certain symmetries under \( C_{2v} \), they will be different for other point groups. Also see that rotation about the x, y and z axes (\( R_x \), \( R_y \), \( R_z \)) transform as \( B_2 \), \( B_1 \), and \( A_2 \), and that the combination of Cartesian coordinates \( x^2 \), \( xy \), \( xz \), etc. are also assigned symmetries. These are what are important for understanding IR, Raman, and microwave spectroscopies.

C. Multiplying Symmetry Representations.
To multiply two symmetry representations together, you go to the point group table and multiply the individual numbers for each symmetry element for the two states.

example: $A_2 \times B_2$:

- for $E$, $1 \times 1 = 1$
- for $C_2$, $1 \times -1 = -1$
- for $\sigma_{xz}$, $-1 \times -1 = 1$
- for $\sigma_{yz}$, $-1 \times 1 = -1$

this is $B_1$.

Some general rules:

a. the product of any two representations must be another representation.
b. the product of any representation $i$ and the totally symmetric representation is $i$.
c. the product of any representation with itself is the totally symmetric representation.

D. The symmetry selection rules:

For a vibrational transition to be allowed by quantum mechanics, the following integral must be non-zero.

$$\text{integral } [(\text{symmetry of ground state})(\text{symmetry of photon}) (\text{symmetry of final state})]$$

Now, the ground state of a molecule is always totally symmetric, ($A_1$ in $C_{2v}$). The symmetry of the photon is the same symmetry as $x$, $y$, or $z$. Finally, the symmetry of the final state is the symmetry of the vibration itself.
Here is the important part:

within a group, all representations are orthogonal, i.e., the integral of $R_i \ast R_j$, where $R_i$ and $R_j$ are any individual representation, is equal to:

1, if $i = j$
0, if not.

for example in $C_{2v}$, the integral of $A_1 \ast A_2 = 0$; the product of these representations is not zero, but the integral of the product is. Now we also know that the product of $A_1$ and $A_2 = A_2$.

Thus, the integral of $A_2$ is zero. We can also show that the integral of $B_1$ and $B_2$ are also zero by the same argument. The only representation whose integral is non-zero is the totally symmetric one ($A_1$ in $C_{2v}$) since it can be thought of as the square of any individual representation $R_i$.

so.......we need the product of [(symmetry of ground state) (symmetry of photon) (symmetry of final state)] to be totally symmetric.

Remember that the ground state is always totally symmetric and that it will multiply the product of the other two symmetries to give that product back. So, we need the product of the (symmetry of the photon) and (the symmetry of the vibration) to be totally symmetric. Since the photon can transform as x, y, or z only, the only vibrations that will be allowed are those that transform the same as x, y, and z. In $C_{2v}$, only $A_1$, $B_1$ and $B_2$ vibrations are allowed.

a sample problem:

The molecule BF$_3$ has symmetry $D_{3h}$. It has 6 vibrations of
symmetry, $A_1^\prime$, $E^\prime$, $E^\prime$, and $A_2^\prime$ (remember that E vibrations are doubly degenerate and count as two vibrations). Which ones are IR active? There are group tables in the back of your P-chem book.

4.8 Vibrating molecules: the modes of vibration
4.9 Symmetry considerations

http://www.wpi.edu/Academics/Depts/Chemistry/Courses/CH4420/symme

Molecular Symmetry and Group Theory

Molecular Symmetry

Two molecules are shown Figure SYM-1. A chemist would say that FeF$_6^{3-}$ is more symmetrical than H$_2$O. What does this mean? Although we are used to the concept of symmetry in an informal context, symmetry can also be discussed formally in terms of specific geometrical entities, called symmetry elements, and specific maneuvers about these elements, called symmetry operations.

Definition: A symmetry element is a geometrical entity (point, line, or plane) with respect to which one or more symmetry operations (SOs) may be performed.

Definition: A symmetry operation (SO) is a movement of a body that takes the body into an equivalent configuration (or orientation) where an "equivalent configuration" is a configuration that is indistinguishable from (but not necessarily identical with) the original.

There are 4 types of symmetry element and associated SOs.

<table>
<thead>
<tr>
<th>Element</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane $\sigma$</td>
<td>reflection, $\sigma$</td>
</tr>
<tr>
<td>Point (center of symmetry), $i$</td>
<td>inversion, $i$</td>
</tr>
<tr>
<td>Proper axis, $C_n$</td>
<td>rotation(s)</td>
</tr>
<tr>
<td>Rotation-reflection (improper)</td>
<td>One or more repetitions of the</td>
</tr>
</tbody>
</table>
Symmetry planes and reflection. Here the symmetry element is a plane that passes through the center of the molecule. This plane is symbolized \( \sigma \). The symmetry operation associated with the plane is reflection in the plane. This reflection operation is also symbolized \( \sigma \).

Ex: \( \text{H}_2\text{O} \). It is recommended that you build a MODEL in order to see things clearly in 3 dimensions. See Figure SYM-1.

In Figure SYM-1, the final orientation is equivalent to but not identical with the original. If the numbers were not there, it would not be possible to tell that the operation of reflection had been done. If the \( \sigma \) operation is applied a second time in the same plane, a configuration identical to the original is obtained. See Figure SYM-1.

Definition: any operation or combination of operations that gives a configuration identical to the original is the identity operation. The identity operation is symbolized \( E \).

It follows from what was said above that \( \sigma \sigma = \sigma^2 = E \). Generally, \( \sigma^n = E \) if \( n \) even, \( \sigma \) if \( n \) odd.

Definition: the inverse of a SO, say SO A, is the operation that undoes the effect of A. The inverse of A is symbolized \( A^{-1} \). \( A^{-1}A = AA^{-1} = E \)

Because \( \sigma \sigma = E \), it follows that \( \sigma^{-1} = \sigma \); the reflection operation is its own inverse.

The Inversion center (center of symmetry) and the inversion operation. Here the symmetry element is a point at the center of the molecule called the center of symmetry. This point is symbolized \( i \). The symmetry operation associated with the point is inversion of the molecule through the point. This operation is also symbolized \( i \).

Ex: Octahedral \( \text{AB}_6 \). See Figure SYM-2 for an illustration of the inversion operation.

Inversion produces an orientation indistinguishable from the original. Thus \( i \) is a SO for
Application of \( i \) twice in succession produces an orientation identical with the original: \( ii = i^2 = E \). Thus \( i \) is its own inverse: \( i^{-1} = i \). In general, \( i^n = E \) if \( n \) even; \( i \) if \( n \) odd.

Exercise: does the chair form of cyclohexane have \( i \)?

*Proper rotation axis and the proper rotations.* This is illustrated best by a specific example. Consider placing an axis (a straight line) through the center of an equilateral triangle, perpendicular to the plane of the triangle. Then rotate the triangle \( 120^\circ \), clockwise (cw), about the axis. This is illustrated in Figure SYM-3. Because clockwise \( 120^\circ \) rotation produces an orientation equivalent to the original, this rotation is a SO for the triangle. It is possible to perform 3 successive cw rotations by \( 120^\circ \) before getting back to the original orientation. Thus the equilateral triangle has a 3-fold proper rotation axis. The axis is symbolized as \( C_3 \). The subscript 3 is called the order of the axis. In this case, the axis is the symmetry element, and the symmetry operations are the possible rotations (3 in this example) about the axis. The operation of cw rotation by \( 120^\circ \) is also symbolized \( C_3 \). Clockwise rotation by \( 240^\circ \) is clearly also a SO (see Figure SYM-3). But this is just 2 successive cw \( 120^\circ \) rotations-- two successive \( C_3 \) operations. Clockwise rotation by \( 240^\circ \) is therefore symbolized \( C_3^2 \). Similarly, cw rotation by \( 360^\circ \) is \( C_3^3 \). Clearly \( C_3^3 = E \).

In general, an \( n \)-fold proper rotation axis is symbolized \( C_n \). This axis generates \( n \) SOs:

\[
\begin{array}{|c|c|}
\hline
C_n = \text{rotation cw by} & 360/n \text{ (basic rotation)} \\
\hline
C_n^2 & 2(360)/n \\
\hline
C_n^m & m(360)/n \\
\hline
\ldots & \ldots \\
\hline
n(360)/n = 360 & \\
\hline
\end{array}
\]
It may seem that further operations, rotations by angles larger than $360^\circ$, are possible, for example $C_n^{n+1}$. However, $C_n^{n+1} = C_n^1 C_n^1 = EC_n^1 = C_n^1$, so nothing new is encountered in rotations larger than $360^\circ$. In this discussion, we have implicitly assumed that

\begin{itemize}
  \item a) $C_n^p C_n^q = C_n^{p+q}$. This is obvious from the geometry of angles;
  \item b) $E C_n^p = C_n^p$. But this is obvious since $E$ does nothing!
\end{itemize}

Just as $C_n^m$ means cw rotation by $m(360/n)$ $C_n^{-m}$ means counterclockwise (ccw) rotation by $m(360/n)$. But $C_n^{-m} = C_n^n C_n^{-m} = C_n^{n-m}$, so all cw rotations duplicate ccw rotations and are therefore not new operations. Also, since $C_n^m C_n^{n-m} = C_n^n = E$, $C_n^{n-m}$ is the inverse of $C_n^m$. Thus $(C_n^m)^{-1} = C_n^{n-m} = C_n^{-m}$.

As an additional example, consider benzene, which has a $C_6$ axis perpendicular to the plane of the molecule. Benzene is shown with its $C_6$ axis in Figure SYM-4. Six SOs are generated by the $C_6$ axis:

\begin{center}
\begin{tabular}{cccccc}
  $C_6$ & $C_6^2$ & $C_6^3$ & $C_6^4$ & $C_6^5$ & $C_6^6$ (=E) \\
  \downarrow & \downarrow & \downarrow & & & \\
  $C_3$ & $C_2$ & $C_3^2$ & & & \\
\end{tabular}
\end{center}

By convention, SOs are written in "lowest terms". So rather than write $C_6^2$, we instead write $C_3$.

In order to have a $C_n$ axis, a molecule must satisfy a number of restrictions.

http://138.47.34.166/chem481/Chem481c4.html
4/2/2003
1) There may be any number of any species of atom lying on an axis, because rotation does not shift these; however.

2) If one atom of a certain type lies off $C_n$, there must be $n-1$ more such atoms placed at equal intervals about the axis, for a total of $n$.

We state without proof two theorems about certain molecules having $C_n$.

Theorem: The presence of a $C_n$ axis and a $C_2$ axis $\perp$ to $C_n$ in a molecule requires $n-1$ more $\perp C_2$'s.

**Example:** The equilateral triangle. Suppose you see the $C_3$ and one $C_2$.

This theorem says there MUST be 2 more $C_2$'s. See Figure SYM-5.

Suppose the circled $C_2$ is the one we first notice. Clearly the other 2 must exist because they can be generated from the first $C_2$ by rotations about $C_3$.

**Example:** Examine $C_5H_5^-$ (a planar aromatic anion) in terms of this theorem.

Theorem: The presence of a $C_n$ axis and a $\sigma$ containing the $C_n$ axis requires $n-1$ more $\sigma$ containing $C_n$.

**Example:** NH$_3$. **Build a Model.** See Figure SYM-6.

The figure shows that $\sigma_2$ and $\sigma_3$ are generated from $\sigma_1$ by SOs about C3.

As the first theorem indicates, there are many molecules with more than one proper axis.

Which is most important? This question is addressed by the following definition.

**Definition:** The highest-fold proper rotation axis in a molecule is called the principal axis, $C_n$. When there are two or more highest-order axes, the one passing thru the greatest number of atoms is principal.
Planes of symmetry containing \( C_n \) are called vertical planes (\( \sigma_v \)). Examples are the planes in NH3. A symmetry plane \( \perp \) to \( C_n \) is called a horizontal plane (\( \sigma_h \)). An example is the molecular plane of benzene.

Examine the following molecules for proper rotation axes and planes of symmetry.

a) \( \text{C}_2\text{H}_4 \) (3 \( C_2 \))

b) \( \text{CH}_4 \) (4\( C_3 \), 3\( C_2 \))

c) \( \text{C}_6\text{H}_6 \) (6\( C_2 \))

d) \( \text{SOCl}_2 \) (only \( C_1 = E \))

*The Improper Rotation (rotation-reflection) Axis.* This is the most difficult symmetry element to find in a molecule, and probably the most difficult to understand. First, it is necessary to understand what is meant by an improper rotation. An improper rotation takes place in 2 steps:

1) A proper rotation about an axis.

2) Reflection in a plane perpendicular to the rotation axis.

The improper rotation axis is symbolized \( S_n \), where \( n \) is the order of the axis. The SO of rotation by \( 360/n \), followed by reflection, is also denoted \( S_n \). Based on the definition, \( S_n = C_n \sigma = \sigma C_n \), where \( \sigma \) must be in the plane perpendicular to the axis of rotation.

*Example: Staggered ethane,* shown in Figure SYM-7. **Build a Model.**

Perform \( C_6 \) about the C-C bond, followed by \( \sigma \) in the plane \( \perp \) to this bond. See Figure SYM-7.

The figure shows that:

1) the last and first structures are equivalent. Thus \( \sigma C_6 \) is a SO for staggered ethane.

2) the central structure is distinguishable from the other two. Thus neither \( C_6 \) nor \( \sigma \) is by itself a SO.
We get the same result when we reflect first, then rotate. Thus $\sigma C_6 = C_6 \sigma = S_6$. We conclude that staggered ethane possesses an $S_6$ axis, coincident with C-C bond.

As for the other symmetry elements, we consider SOs generated by the $S_n$ axis. We must look at 2 cases:

a. Even order axis, say $S_6$ (ex: staggered ethane)

$$S_6 = C_6 \sigma$$
$$S_6^2 = C_6C_6^2 = C_6^2 = C_3$$
$$S_6^3 = C_6^3 \sigma = C_2 \sigma = i$$
$$S_6^4 = C_6^2$$
$$S_6^5$$
$$S_6^6 = C_6 \sigma^6 = C_6^6 = E$$

From this we conclude that

1) When n is even, $S_n$ generates n SOs
2) The presence of $S_n$, n even, requires the presence of $C_{n/2}$ (in this case, $C_3$, $C_3^2$, $C_3^3 = E$). Staggered ethane has $C_3$, required by the $S_6$ axis.
3) $S_6^3 = C_2 \sigma = i$. This is not obvious, but can be proven in general by operating on a general point $[xyz]$:

Assume $C_2 = z$ axis, $\sigma = xy$ plane

$$C_2[xyz] = [-x-yz]$$

$$\sigma[xyz] = [xy-z]$$

Thus $C_2 \sigma[xyz] = C_2[xy-z] = [-x-y-z]$. Since by definition $i[xyz] = [-x-y-z]$, it follows that $C_2 \sigma = i$. 

http://138.47.34.166/chem481/Chem481c4.html 4/2/2003
b. Odd-order axis, say $S_5$ (ex: eclipsed ferrocene)

\[
\begin{align*}
S_5^1 &= C_5^1 \\
S_5^2 &= C_5^2 \sigma^2 = C_5^2 \\
S_5^3 &= C_5^3 \sigma \\
S_5^4 &= C_5^4 \\
S_5^5 &= \sigma \\
S_5^6 &= C_5^6 = C_5 \\
S_5^7 &= C_5^2 \sigma \\
S_5^8 &= C_5^3 \\
S_5^9 &= C_5^4 \sigma \\
S_5^{10} &= E
\end{align*}
\]

From this we conclude that

1) When $n$ is odd, $S_n$ generates $2n$ SOs

2) $S_5$ requires presence of $C_5 \sigma$. In general, $S_n$, $n$ odd, requires $C_n \sigma$.

We now consider the inverses of the $S_n^m$ SOs. It is easy to show that

\[
(S_n^m)^{-1} = S_n^{n-m} \text{ when } n \text{ is even and } S_n^{2n-m} \text{ when } n \text{ is odd}
\]

Thus $(S_4^1)^{-1} = S_4^3$ consistent with $S_4^3 S_4^1 = C_4^3 \sigma^3 C_4^4 \sigma = C_4^4 \sigma^4 = E$, and $(S_5^2)^{-1} = S_5^{8}$, consistent with $S_5^8 S_5^2 = C_5^8 \sigma^8 C_5^2 \sigma^2 = C_5^{10} \sigma^{10} = C_5^5 C_5^5 \sigma^{10} = E$.

Finally, $S_2 = C_2 \sigma = i$; $S_1 = C_1 \sigma = E \sigma = \sigma$. Thus $i$ and $\sigma$ are special cases of $S_n$.

Examine the following molecules for the presence of improper axes.
Mathematical Groups

Suppose we have a complete list of all SOs of a molecule. We want to show that this collection satisfies all requirements of a mathematical group.

Definition: A group is a collection of elements (i.e., members) that are interrelated according to certain rules. The number of members in the group is the order of the group, $h$.

The rules governing a group are as follows:

1) The product of any two members must also be a member. By "product" we mean a combination according to some law. If $A$ and $B$ are 2 members, we can write the product as $AB$ or $BA$. In general these are not the same; i.e., the commutative law of combination does not necessarily hold.

   If $AB \neq BA$, $A$ and $B$ do not commute
   If $AB = BA$, $A$ and $B$ commute.
   If $AB = C$ and $BA = D$, $C$ and $D$ must also be in the group.

2) One member of the group must commute with all others and leave them unchanged. This is the identity element, $E$. If $X$ is a member of the group, $EX = XE = X$.

3) The associative law of combination must hold.

   $A(BC) = (AB)C = ABC$

4) Every member of the group must have a reciprocal, or inverse, which is also a member of the group.

   B is the reciprocal of A if $AB = BA = E$.
   If we denote the reciprocal of A as $A^{-1}$, then $A^{-1} = B$.

A collection of entities satisfying these 4 rules constitutes a mathematical group. An example of a group is the collection of integers (+, -, 0), which is a group of infinite order. The Law of Combination is addition.
1) Any integer = sum of other integers. Rule 1 holds.
2) The identity is 0. \( n + 0 = 0 + n = n \)
3) Combination is associative: \( 2 + [3 + (-7)] = [2 + 3] + (-7) = -2 \)
4) Every member has an inverse, which is its negative: \( n + (-n) = 0 \)

Now we will show that a complete collection of SOs is a group. In doing this, we must agree on the ground rules. First, we define product as successive application of. The successive application of SOs A and B is AB or BA. If \( C = AB \), C is the product of A and B, whereas if \( D = BA \), D is the product of B and A. Second, when the product is written AB, it means "first apply SO B, then apply SO A to the result." SOs are applied in order as written from right to left. This parallels the application of operators in quantum mechanics.

Example: Consider \( \text{NH}_2 \). We first list the symmetry elements and SOs.

<table>
<thead>
<tr>
<th>Element</th>
<th>SO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_3 )</td>
<td>( C_3, C_3^2, C_3^3 = E )</td>
</tr>
<tr>
<td>( 3\sigma_v )</td>
<td>( \sigma_v1 \sigma_v2 \sigma_v3 )</td>
</tr>
</tbody>
</table>

We only include E once in the list of symmetry operations, and it is considered to be generated from the principal axis. To demonstrate that this set of SOs is a group, we work with the picture in Figure SYM-8a.

1) First, we must show that all products of SOs are SOs. Two examples will suffice. We examine the products, \( C_3 \sigma_v1 \) and \( \sigma_v1C3 \). The net effect of \( C_3 \sigma_v1 \) is to interchange H1 and H3. We could do this in one step by applying the \( \sigma_v2 \) operation. Thus

\[
C_3 \sigma_v1 = \sigma_v2
\]

The net effect of \( \sigma_v1C3 \) is to interchange H1 and H2. Thus \( \sigma_v1C3 = \sigma_v3 \), which is also in the SO collection. Note that \( \sigma_v1C3 \) NOT = \( C_3 \sigma_v1 \). These two SOs are not commutative.

2) Second, we must find one SO that commutes with all others and leaves them unchanged. This, of course, is E. In fact, this is why the identity SO is defined and

http://138.47.34.166/chem481/Chem481c4.html 4/2/2003
included in the collection of SOs.

3) Next, we must demonstrate that the Associative Law of Combination holds. Consider the ternary product ABC, assuming that $A = C_3$, $B = \sigma_{v1}$, and $C = \sigma_{v3}$.

$$(AB)C = (C_3 \sigma_{v1}) \sigma_{v3}$$

Since $C_3 \sigma_{v1} = \sigma_{v2}$, we must evaluate $\sigma_{v2} \sigma_{v3}$, which is done in Figure SYM-8b. From the figure, it follows that $(C_3 \sigma_{v1}) \sigma_{v3} = C_3^2$. You show that $A(BC) = C_3(\sigma_{v1} \sigma_{v3}) = C_3C_3 = C_3^2$, and thus that the associative rule is obeyed for this set of 3 SOs.

4) Finally, we must show that every SO has an inverse which is also an SO of the collection. But in fact, we have shown this during our development of the symmetry elements and operations. Therefore, rule 4 is obeyed.

Thus a complete collection of SOs for a molecule is a mathematical group. We refer to complete collections of SOs as symmetry groups, or point groups. The binary products of the SOs of a symmetry group are summed up in a so-called Multiplication Table. For the group of SOs of NH$_3$ (group label $C_{3v}$), the binary products are given in Table SYM-1.

**Table SYM-1**

<table>
<thead>
<tr>
<th></th>
<th>$C_{3v}$</th>
<th>E</th>
<th>$C_3$</th>
<th>$C_3^2$</th>
<th>$\sigma_{v1}$</th>
<th>$\sigma_{v2}$</th>
<th>$\sigma_{v3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>E</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$\sigma_{v1}$</td>
<td>$\sigma_{v2}$</td>
<td>$\sigma_{v3}$</td>
<td></td>
</tr>
<tr>
<td>$C_3$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>E</td>
<td>$\sigma_{v3}$</td>
<td>$\sigma_{v1}$</td>
<td>$\sigma_{v2}$</td>
<td></td>
</tr>
<tr>
<td>$C_3^2$</td>
<td>$C_3^2$</td>
<td>E</td>
<td>$C_3$</td>
<td>$\sigma_{v1}$</td>
<td>$\sigma_{v2}$</td>
<td>$\sigma_{v3}$</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{v1}$</td>
<td>$\sigma_{v1}$</td>
<td>$\sigma_{v2}$</td>
<td>$\sigma_{v3}$</td>
<td>$\sigma_{v2}$</td>
<td>$\sigma_{v3}$</td>
<td>$\sigma_{v3}$</td>
<td></td>
</tr>
</tbody>
</table>
By convention, the entry at the juncture of column S and row R is the combination SR (not RS). We find $\sigma_{v2}$ at the juncture of column C3 and row $\sigma_{v1}$, so $\sigma_{v2} = C3 \sigma_{v1}$. The multiplication table can be used to divide members of a group into classes, which are subgroups of equivalent SOs.

**Classes of SOs.** Classes are subsets of groups that contain equivalent symmetry operations. The concept of equivalent symmetry operations is intuitively simple but mathematically somewhat obscure. The intuitive view is that equivalent SOs accomplish similar transformations of the molecule. Thus $C_3$ and $C_3^2$ are equivalent, because they both involve rotation by $120^0$. The three vertical reflections are also equivalent, because they all involve reflection in a plane that contains the $C_3$ axis. The identity operation ($C_3^3$) is in a class by itself, because no other operation leaves the molecule in an identical orientation. It is also true that equivalent SOs can be generated from each other by other SOs of the group. Thus $\sigma_{v2}$ and $\sigma_{v3}$ in NH3 can be generated from $\sigma_{v1}$ by application of $C3$, meaning that the 3 SOs are in same class. Similarly, $C_3^{-1}$ ($= C_3^2$) can be generated from $C_3$ by reflection in any of the planes. See Figure SYM-9.

The mathematical development of classes requires the introduction of an operation called the similarity transformation.

**Definition:** The similarity transform of the SO A by the SO X, where X is a member of the group to which A belongs, is defined as

$$X^{-1}AX$$

If $B = X^{-1}AX$, A and B are said to be conjugate.

A collection of conjugate SOs in a group constitutes a class of the group. To find the classes formally, we must find all possible transforms of each element in the group. The Multiplication Table can be used for this.
Example: Find transforms of $C_3$ in $C_{3v}$.

$$E^{-1}C_3E = C_3$$
$$C_3^{-1}C_3C_3 = C_3$$
$$C_3^{-2}C_3C_3 = C_3$$
$$\sigma_{v1}^{-1}C_3\sigma_{v1} = C_3^2$$
$$\sigma_{v2}^{-1}C_3\sigma_{v2} = C_3^2$$
$$\sigma_{v3}^{-1}C_3\sigma_{v3} = C_3^2$$

The first 3 were done by inspection; the last 3 were obtained by application of the multiplication table. It is clear that all transforms of $C_3$ are either $C_3$ or $C_3^2$. $C_3$ and $C_3^2$ are therefore conjugate. Similarly, all transforms of $C_3^2$ are either $C_3$ or $C_3^2$. Thus $C_3$, $C_3^2$ constitute a class. You should try to complete the assignment of the $C_{3v}$ SOs to classes. You should find the following 3 classes in this group:

$$E$$
$$C_3, C_3^2$$
$$\sigma_{v1}\sigma_{v2}\sigma_{v3}$$

As we have noted above, $E$ is in a class by itself, which is true in every group. The example shows that the orders of the classes are integral multiples of the order of the group.

**Symmetry Point Groups**

Having established that a complete list of SOs for a molecule constitutes a mathematical group, we ask, how many such groups are there? All small molecules can be assigned to one of 15 groups, called the Symmetry Point Groups. These are labelled to indicate the symmetry elements present in the member molecules.

These groups, their symmetry elements and SOs, and an example of each are in Table
From the table, we extract some generalizations:

1) There are three simple groups

- $C_1$ (no symmetry)
- $C_s$ (a plane of symmetry only)
- $C_i$ (a center of symmetry only)

Then there are the $C_n$ type groups ($C_n +$ planes); the $D_n$ type groups ($C_n + nC_2 \perp C_n$, plus planes); and the special groups.

2) Only the symmetry elements necessary to uniquely define a group are listed. In some cases, there are additional symmetry elements, but in all cases these are required to be present by SOs generated from the listed elements.

- **Ex:** $D_{nh}$ has $C_n + nC_2 + \sigma_h$ listed. It also has $\sigma_v$ but these are required because they are products of SOs generated by $C_2$ and $\sigma_h$. We show this by one example.

  Let $C_n$ lie along z, let $C_2$ lie along x. $\sigma_h$ is the xy plane. Then

  $C_2(x)[x\ y\ z] \Rightarrow [x\ -y\ -z]$

  $\sigma_h[x\ -y\ -z] \Rightarrow [x\ -y\ z]$

  This is equivalent to performing $\sigma_{xz}$ directly to the original set of coordinates.

3) The notation $\sigma_d$ is used, which we have not seen. d stands for dihedral. A dihedral plane, $\sigma_d$, is a vertical plane that bisects the angle between C2 axes.

- **Ex:** allene. See Figure SYM-10. Build a Model. Find the axes and the planes. The principal axis lies along the CCC line.

4) There are two groups for linear molecules. $C_{\psi\psi\psi\psi}$, $D_{\psi\psi\psi\psi}$. The $\psi\psi\psi\psi$-fold rotation axis coincides with the molecular axis. In $C_{\psi\psi\psi\psi}$, there is an $\psi\psi\psi\psi$; number of
\[ \sigma_v \text{. In } D_{\psi v;h}, \text{ there is an } C_2 \text{ axes perpendicular to } C_{\psi v;\cdot}. \]

A systematic procedure for the classification of molecules into point groups is given below. Figures SYM-11 and SYM-12 are flow charts for group classification.

Systematic Procedure for Point Group Classification:

1) Determine whether the molecule is in a "special" group: \( C_{\psi v;v}, D_{\psi v;h}, Td, Oh, \) or \( Ih \). If so, classify accordingly.

2) If the molecule does not belong to a special group, look for a proper rotation axis. If any are found, proceed to step 3). If none, look for a center of symmetry, \( i \), or a mirror plane, \( \sigma \). If only \( i \) is present, the group is \( C_i \) (rare). If only \( \sigma \) is present, the group is \( C_s \). If no symmetry elements are present, \( E \) is the only SO and the group is \( C_1 \).

3) Locate the principal axis \( C_n \). Does a rotation-reflection axis \( S_{2n} \) exist coincident with \( C_n \)? If so and there are no other symmetry elements except \( i \), the molecule belongs to one of the \( S_n \) point groups, \( n \) even (rare). If other symmetry elements are present or if \( S_{2n} \) is absent, go to 4).

4) Look for a set of \( n \) two-fold axes \( \perp \) to \( C_n \). If found, the molecule is in one of the groups \( D_n, D_{nh}, \) or \( D_{nd} \). Proceed to 5). If not, the molecule must belong either to \( C_n, C_{nh}, \) or \( C_{nv} \). Skip 5) and go to 6).

5) If you have arrived at this step, the molecule must be assigned to \( D_n, D_{nh}, \) or \( D_{nd} \). If the molecule possesses \( \sigma_h \), the group is \( Dnh \). If there is no \( \sigma_h \), look for a set of \( n \) \( \sigma_d \) bisecting angles between \( C2s \). If these are found, the group is \( Dnd \). If \( \sigma_d \) and \( \sigma_h \) are both absent, the molecule is in \( Dn \).

6) The molecule must be assigned to \( C_n, C_{nh}, \) or \( C_{nv} \). If the molecule possesses \( \sigma_h \), the group is \( Cnh \). If there are \( n \) \( \sigma_v \) vs, the molecule is in \( Cnv \). If neither \( \sigma_v \) nor \( \sigma_h \) is present,
We now look at a few examples.

1) H₂O

Step 1. Not a special group
Step 2. Proper axis? Yes, a C₂.
Step 3. S₄ coincident with C₂? NO.
Step 4. Are there 2 C₂ axes \perp C₂ found in step 2? NO. Thus is a C-type group.
Step 6. Is there a σᵥ? YES. Point group = C₂v

2) NH₃. Build a model.

Step 1. Not a special group.
Step 2. Proper axis? YES, a C₃.
Step 3. S₆ coincident with C₃? NO.
Step 4. Are there 3 C₂s \perp to C₃? NO. Thus is a C-type group.
Step 6. Is there a σᵥ? YES. Point group = C₃v.

3) PF₅. Build a model!

Step 1. Not a special group
Step 2. Proper axis? YES, a C₃.
Step 3. S₆ coincident with C₃? NO.
Step 4. Are there 3 C₂s \perp C₃? YES. Thus a D-type group.
Step 5. σᵥ? YES. Point group = D₃h

4) Cyclooctatetraene.

Step 1. Not a special group.
Step 2. Proper axis? YES, a C₂.
Step 3. S₄ coincident with C₂? YES. But there are other symmetry elements, namely planes and other C₂ axes, so group is not S₄.
Step 4. Are there 2 $C_2 \perp C_2$? YES. Thus a D-type group.

Step 5. $\sigma_h$? NO. $\sigma_d$? YES. (Note how $\sigma_{ds}$ bisect angles between C2s.) Point group = D2d.

Reasoning by analogy:

\[
\begin{align*}
PH_3 &= NH_3 = CHCl_3 \\
CH_2Cl_2 &= H_2O \\
cis-Co(NH_3)_4Cl_2^+ &= H_2O
\end{align*}
\]

10) Construction of LCAO-MOs for molecules.

Symmetry elements and operations: test

List all of the symmetry elements possessed by the following molecules:

(a) $H_2O$, (b) benzene, (c) phenol, (d) trans-1,2-dichloroethene,

(e) ferrocene, (f) PCl$_3$, (g) SF$_4$, (h) O$_3$, (i) ($^6$C$_6$H$_6$)Cr(CO)$_3$ and (j) PtCl$_4^{2-}$

Answers

Symmetry elements and operations: answers to test

If you didn't spot some of the elements, go back and see if you can find them. Click on the molecule name to reveal the elements.

(a) $H_2O$: E, C$_2$, $s_v$ and $s_v'$

(b) benzene: E, 2C$_6$, 2C$_3$, C$_2$, 3C'$\prime$, 3C''$, i, 2S$_3$, 2S$_6$, $s_h$, 3$s_d$ and 3$s_v$

(c) phenol: E, and $s$.

(d) trans-1,2-dichloroethene: E, C$_2$, i and $s_h$
(e) ferrocene: E, 2C$_5$, 2C$_5^2$, 5C$_2$, s$_h$, 2S$_5$, 2S$_5^2$ and 5s$_v$

(f) PCl$_3$: E, 2C$_3$ and 3s$_v$

(g) SF$_4$: E, C$_2$, s$_v$ and s$_v'$

(h) O$_3$: E, C$_2$, s$_v$ and s$_v'$

(i) ($h^6$-C$_6$H$_6$)Cr(CO)$_3$: E, 2C$_3$ and 3s$_v$

(j) PtCl$_4$-$: E, 2C$_4$', C$_2$, 2C$_2'$, 2C$_2''$, i, 2S$_4$, s$_h$, 2s$_d$ and 2s$_v$

**Point groups: answers**

If you didn't get some of the point groups, go back and see if you can find them.
Click on the molecule name to reveal the flowchart path.

(a) H$_2$O: C$_{2v}$

(b) benzene: D$_{6h}$

(c) phenol: C$_s$

(d) trans-1,2-dichloroethene: C$_{2h}$

(e) ferrocene: D$_{5h}$

(f) PCl$_3$: C$_{3v}$

(g) SF$_4$: C$_{2v}$
(h) $O_3^-$: $C_{2v}$

(i) $(\text{h}^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3$: $C_{3v}$

(j) $\text{PtCl}_4^{2-}$: $D_{4h}$

**Generating representations:**

Generate the representations for the following sets of orbitals:

(a) the H 1s orbitals in methane ($T_d$),
(b) the C $p_p$ orbitals in benzene ($D_{6h}$),
(c) F hybrids directed at the S in SF$_4$ ($C_{2v}$),
(d) N donor orbitals in $[\text{Ni(en)}_3]^{2+}$ ($D_3$)

(Click on the point group symbol for a list of the symmetry elements in a new window)

**Answers**

**Generating representations: answers**

If you didn't get some of the characters, go back and see if you can find them. Click on the molecule name to reveal the method.

(a) the H 1s orbitals in methane ($T_d$)

$$
\begin{array}{cccccc}
E & 8C_3 & 3C_2 & 6S_4 & 6s_d \\
G^H & 4 & 1 & 0 & 0 & 2 \\
\end{array}
$$

(b) the C $p_p$ orbitals in benzene ($D_{6h}$)

$$
\begin{array}{cccccccc}
E & 2C_6 & 2C_3 & C_2 & 3C_2' & 3C_2'' & i & 2S_3 & 2S_6 & s_h & 3s_d & 3s_v \\
\end{array}
$$
(c) F hybrids directed at the S in SF$_4$ ($C_{2v}$)

The F hybrids may be divided into two sets, \{F$_{\text{axial}}$\} and \{F$_{\text{equatorial}}$\}, or kept as a set of four.

\[
\begin{align*}
\begin{array}{cccc}
\text{E} & \text{C}_2 & s_v & s'_v \\
G_{\text{Faxial}} & 2 & 0 & 0 & 2 \\
G_{\text{Fequatorial}} & 2 & 0 & 2 & 0 \\
G_{\text{Fboth}} & 4 & 0 & 2 & 2 \\
\end{array}
\end{align*}
\]

(d) N donor orbitals in [Ni(en)$_3$]$^{2+}$ ($D_3$)

\[
\begin{align*}
\begin{array}{cccc}
\text{E} & \text{2C}_3 & \text{3C}_2 \\
G_{\text{N}_\text{s}} & 6 & 0 & 0 \\
\end{array}
\end{align*}
\]

**Reducing representations: test**

Reduce the following representations for the following sets of orbitals (generated in the test above):

(a) the H 1s orbitals in methane (T$_d$),
(b) the C$_p$ orbitals in benzene (D$_{6h}$),
(c) F hybrids directed at the S in SF$_4$ ($C_{2v}$),
(d) N donor orbitals in [Ni(en)$_3$]$^{2+}$ ($D_3$)

(Click on the point group symbol for the appropriate character table in a new window)

**Answers**
Reducing representations: answers

If you didn't reduce them correctly, go back and see if you can find them. Click on the molecule name to show the reduction formula method.

(a) the H 1s orbitals in methane (Tₐ)

\[ G_H = A_1 + T_2 \]

(b) the C p orbitals in benzene (D₆h)

\[ G_{pp} = B_{2g} + E_{1g} + A_{2u} + E_{2u} \]

(c) F hybrids directed at the S in SF₄ (C₂ᵥ)
The axial representation reduces to $A_1$ and $B_2$ and the equatorial representation reduces to $A_1$ and $B_1$:

$$G_{\text{Faxial}} = A_1 + B_2$$

$$G_{\text{Fequatorial}} = A_1 \text{ and } B_1$$

(or $G_{\text{both}} = 2A_1 + B_1 + B_2$)

(d) N donor orbitals in $[\text{Ni(en)}_2]^{2+} (D_3)$

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_2$</th>
<th>$s_v$</th>
<th>$s_v'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</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>
<tr>
<td>$G_{\text{Faxial}}$</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_3$</th>
<th>$s_v$</th>
<th>$s_v'$</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>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The table above summarizes the character table for the symmetries $C_2$, $s_v$, and $s_v'$ for the axial and equatorial representations, along with the overall representation for both orientations.
The representation reduces to $A_1, A_2$ and two lots of $E$:

$$G_{Ns} = A_1 + A_2 + 2E$$

**Generating SALCs: test**

Generate the SALCs of the following sets of orbitals:

(a) F hybrids directed at the S in SF₄ ($C_{2v}$), (b) The H 1s orbitals in BH₃ ($D_{3h}$), (c) Cl s-donor orbitals in [PtCl₄]²⁻ ($D_{4h}$) and (d) the C p orbitals in benzene ($D_{6h}$)

(Check on the point group symbol for the appropriate character table in a new window)

**Answers**

**Generating SALCs: answers**

If you didn't generate them correctly, go back and see if you can find them. Matching with the orbitals of the central atom is the quickest method and is used here. Click on the molecule name to show the projection operator method.

(a) F hybrids directed at the S in SF₄ ($C_{2v}$),

The axial orbitals span $A_1$ and $B_2$ and the equatorial orbitals have $A_1$ and $B_1$.

Inspection of the character table shows that the sulfur s and $p_z$ orbitals have $A_1$ symmetry, $p_x$ has $B_1$ symmetry and $p_y$ has $B_2$ symmetry. The required combinations for the axial and equatorial hybrids are then:
Axial

(b) the H 1s orbitals in $\text{BH}_3$ ($D_{3h}$)

The representation generated by the set of three equivalent H 1s orbitals is

$$
\begin{align*}
D_{3h} & \quad E & \quad 2C_3 & \quad 3C_2 & \quad s_h & \quad 2S_3 & \quad 3S_v \\
G_{3H} & \quad 3 & \quad 0 & \quad 1 & \quad 3 & \quad 0 & \quad 1
\end{align*}
$$

which reduces to

$$
G_{3H} = A_1' + E'
$$

Inspection of the character table shows the boron s-orbital has $A_1$' symmetry and the $p_x$ and $p_y$ together have $E'$ symmetry.
Notice that one of the hydrogens makes no contribution to the lower ("p_y") E' combination. It makes twice as large contribution to the upper ("p_x") E' combination as the other hydrogens. This is required in order to match the nodal plane of the p-orbital in the two cases. Overall, the three hydrogens make the same contribution to the pair.

(c) Cl s-donor orbitals in $[\text{PtCl}_4]^{2-}$ (D$_{4h}$)

With the x and y axes lying along the Pt-Cl bonds, the representation generated by the 4 Cl s-donor orbitals is

$$
\begin{array}{cccccccc}
D_{4h} & E & 2C_4 & C_2 & 2C'_2 & 2C''_2 & i & 2S_4 & s_h & 2s_v & 2s_d \\
G_{4\text{Cl}_s} & 4 & 0 & 0 & 2 & 0 & 0 & 0 & 4 & 2 & 0 \\
\end{array}
$$

which reduces to

$$
G_{4\text{Cl}_s} = A_{1g} + B_{1g} + E_u
$$

Inspection of the character table shows that the platinum s-orbital has $A_{1g}$, the d$_x$ - d$_y$ orbital has $B_{1g}$ and the p$_x$ and p$_y$ orbitals together have E$_u$ symmetry:
(d) the C \( p_p \) orbitals in benzene \( (D_{6h}) \)

The \( p_p \) orbitals transform as

\[
G_{p_p} = B_{2g} + E_{1g} + A_{2u} + E_{2u}
\]

Inspection of the character table shows that the \( p_z \) orbital on the (imaginary) central atom has \( A_{2u} \) symmetry whilst \( d_{xz} \) and \( d_{yz} \) together have \( E_{1g} \) symmetry. There are no s, p or d-orbitals to match with the \( B_{2g} \) and \( E_{2u} \) combinations. The \( A_{2u} \) combination is then

The \( E_{1g} \) combinations are
Notice how the nodal planes of the two SALCs match those of the d-orbitals. The lower combination has no contribution from two of the carbons. To compensate, the upper combination has twice as large a contribution from these two atoms as from the others.

Although this is as far as one can get by matching with orbitals on the central atom, the other combinations can be obtained by a little guesswork. The $A_{2u}$ orbital drawn above has a continuous ring of in-phase orbitals: it has zero nodes. Both of the $E_{1g}$ combinations have one node (there is a change of phase as the dotted line is crossed). The other combinations have two and three nodes. There is only one way of having three nodes (three dotted lines so that the orbital changes phase):

Whilst there are two ways of having two nodes:
and these are the $B_{2g}$ and $E_{2u}$ SALCs respectively.

Please return to the referring document and note the hypertext link that led you here.