Symmetry elements, operations and point groups (‘in the molecular world’)

Symmetry concept is extremely useful in chemistry in that it can help to predict infra-red spectra (vibrational spectroscopy) and optical activity. It can also help in describing orbitals involved in bonding, and in interpreting electronic spectra of molecules.

The five fundamental symmetry elements (operators) or operations:

The following symbols (Schoenflies) are used to describe both symmetry elements as well as the symmetry operations (application of the symmetry element)

E (Identity) – all molecules have E (or C₁); causes no change in the molecule

$C_n$ (Rotation axis, clockwise by definition) – $360°$ (or $2\pi$)/n rotation about a rotation axis
‘Highest order’ or ‘principal’ rotation axis: the axis with the highest n value
e.g. C₃ (in CHCl₃), C₆ (snowflake, benzene); C$_\infty$ (linear molecules)

σ (Reflection plane) – mirror plane (exchange of ‘left and right’)
four different types of reflections: $\sigma_v$, $\sigma_h$, $\sigma_d$, $\sigma$
$\sigma_v$: vertical mirror plane (contains principal rotation axis)
example: BF₃ (planar)

$\sigma_h$: horizontal mirror plane (plane perpendicular to principal axis)
example: BF₃ (trivial because its planar)

$\sigma_d$: dihedral mirror plane (planes that cut the angle between 2 C₂ axes in half)
example: allene
σ: Mirror plane, but no rotational axis
   ex: aniline (because the 2 hydrogen atoms on NH₂ are out of plane)

\[
\begin{array}{c}
\sigma \\
\hline \\
\end{array}
\]

i (Inversion centre) – position of all atoms remains unchanged after their reflection through the inversion centre
   ex: [PtCl₄]²⁻

\[
\begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{Cl} \quad \text{Cl} \\
\end{array}
\]

Sₙ (Mirror-rotation or rotation-reflection axis or improper axis) – 360° /n rotation followed by a reflection through a plane perpendicular to the rotation axis
   Ex: staggered ethane – S₆

Note: S₁ ≡ σ; S₂ ≡ i
Multiplication of symmetry operations

One of the important features of symmetry operations is that they can be performed multiple times and they can also be combined:

1. Repetition of symmetry operations:

Example 1: $C_2^2 \equiv E$ (the superscript indicates how many times $C_2$ is performed)

   Obviously $C_2^2$ does not lead to a new symmetry operation

   Another example of this: $\sigma_h^2 \equiv E$

Example 2: $C_3^2$ is a new symmetry operation (whereas $C_3^3 \equiv E$)

   $\Rightarrow$ the symmetry element $C_3$ creates the symmetry operations $C_3$ and $C_3^2$

2. Combination of different sym. operations:

   B x A (A first, B second)

Example 1: CH$_2$Cl$_2$

Example 3: $C_6$ (benzene): only $C_6$ and $C_6^5$ are symmetry operations of $C_6$

   $C_6^2 = C_3$, $C_6^3 = C_2$, $C_6^4 = C_3^2$, $C_6^5$, $C_6^6 = E$

Example 2: $S_n = \sigma_h \times C_n$
3. Inverse operation:
For each operation there is one that brings the molecule back into its original position.

Example 1: $C_2^{-1}$ (counterclockwise rotation by 180 deg), $C_2^{-1} = C_2$ and $C_2 \times C_2^{-1} = E$
Generally: $C_n^{-1} = C_n^{n-1}$

Example 2: $C_3^{-1} = C_3^2$

Example 3: $\sigma^{-1} = \sigma; i^{-1} = i$
**Point Groups**

Each molecule has at least one point which is unique and which remains unchanged, no matter how many or what type of symmetry operations are performed. Such point is termed *singular point.* (e.g. centre of the benzene molecule)

- **Point group** = The complete set of symmetry operations that characterize a molecule’s overall symmetry.

- **Space groups** = Symmetry classes characterizing entities with translational symmetry. [Space groups don’t have singular points!]

Because there is a limited number of symmetry elements (at least in the molecular world, because n is usually <10) and their combinations, there must be a limited number of point groups! Therefore, so many different molecules belong to the same point group:

Example: H₂O and CH₂Cl₂ both C₂ᵥ (E, C₂, σᵥ, σᵥ’)

**Three point groups of low symmetry:**

<table>
<thead>
<tr>
<th>Point group</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>asymmetry</td>
<td>CHFClBr</td>
</tr>
<tr>
<td>Cₘ</td>
<td>only 1 symmetry (mirror) plane</td>
<td>C₂H₂ClBr</td>
</tr>
<tr>
<td>Cᵢ</td>
<td>only 1 inversion centre (very rare)</td>
<td>1,2-dibromo-1,2-dichloroethane (staggered)</td>
</tr>
<tr>
<td>Point group</td>
<td>Description</td>
<td>Example</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------</td>
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</tbody>
</table>
| $C_{\infty v}$ | linear  
infinite number of rotations  
infinite number of reflection planes containing the principal axis  
*easy criterion: linear but no i* | H-F              |
| $D_{\infty h}$ | linear (like $C_{\infty v}$ but with additional $\sigma_h$, $C_2$, and i)  
*easy criterion: linear + i* | CO$_2$           |
| $T_d$      | tetrahedral symmetry  
Contains 24 symmetry operations  
(E, $4C_3$, $4C_3^2$, $3S_4$, $3S_4^3$, $3C_2$, $6\sigma_d$) | CH$_4$           |
| $O_h$      | octahedral symmetry  
(48 symmetry operations) | SF$_6$           |
| $I_h$      | icosahedral symmetry (120 symmetry operations) | B$_{12}$H$_{12}^{2-}$ |

![Diagram of tetrahedral symmetry](image)

![Diagram of icosahedral symmetry](image)
Groups of high symmetry

<table>
<thead>
<tr>
<th>Group</th>
<th>Description</th>
<th>Examples</th>
</tr>
</thead>
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<tr>
<td>$C_{\infty}$</td>
<td>These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.</td>
<td>$\text{C}_=\text{H}--\text{Cl}$</td>
</tr>
<tr>
<td>$D_{\infty h}$</td>
<td>These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular $C_2$ axes, a perpendicular reflection plane, and an inversion center.</td>
<td>$\text{C}--\text{O}=\text{C}=\text{O}$</td>
</tr>
<tr>
<td>$T_d$</td>
<td>Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four $C_3$ axes, three $C_2$ axes, three $S_4$ axes, and six $\sigma_d$ planes. They have no $C_4$ axes.</td>
<td>$\text{H}--\text{C}=\text{H}$</td>
</tr>
<tr>
<td>$O_h$</td>
<td>These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four $C_3$ rotations, three $C_4$ rotations, and an inversion.</td>
<td>$\text{F}--\text{S}--\text{F}$</td>
</tr>
</tbody>
</table>

Icosahedral structures are best recognized by their six $C_5$ axes (as well as many other symmetry operations—120 total).

$\text{B}_3\text{H}_6\text{S}^2$ with BH at each vertex of an icosahedron

Symmetry operations for high symmetry point groups and their rotational subgroups

<table>
<thead>
<tr>
<th>Point Group</th>
<th>Symmetry Operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_h$</td>
<td>$E$, 12$C_3$, 12$C_3^2$, 20$C_3$, 15$C_2$, $i$, 12$S_{10}$, 12$S_{10}'$, 20$S_6$, 15$S$</td>
</tr>
<tr>
<td>$I$</td>
<td>$E$, 12$C_3$, 12$C_3^2$, 20$C_3$, 15$C_2$, $i$, 12$S_{10}$, 12$S_{10}'$, 20$S_6$, 15$S$</td>
</tr>
<tr>
<td>$O_h$</td>
<td>$E$, 8$C_3$, 6$C_2$, 6$C_4$, 3$C_3$ ($= C_2^3$), $i$, 6$S_4$, 8$S_6$, 3$S_{4u}$, 6$S_{4d}$</td>
</tr>
<tr>
<td>$O$</td>
<td>$E$, 8$C_3$, 6$C_2$, 6$C_4$, 3$C_3$ ($= C_2^3$), $i$, 6$S_4$, 8$S_6$, 3$S_{4u}$, 6$S_{4d}$</td>
</tr>
<tr>
<td>$T_d$</td>
<td>$E$, 8$C_3$, 3$C_2$, 6$S_4$, 6$S_d$</td>
</tr>
<tr>
<td>$T$</td>
<td>$E$, 4$C_3$, 4$C_3^2$, 3$C_2$</td>
</tr>
<tr>
<td>$T_h$</td>
<td>$E$, 4$C_3$, 4$C_3^2$, 3$C_2$, $i$, 4$S_6$, 4$S_6$, 3$S_{4u}$</td>
</tr>
</tbody>
</table>
Diagram of the Point Group Assignment Method

1. Group of low symmetry?
   - Yes: $C_1, C_s, C_i$
   - No: Group of high symmetry?
     - Yes: $T_d, O_h, C_{m, v}, D_{m, v}, l_h$
     - No: Highest-order rotation axis $C_n$

2. Perpendicular $C_2$ axes?
   - Yes: $D$ groups
     - 4. $\sigma_h$?
       - Yes: $D_{nh}$
       - No: $D_{md}$
   - No: $C$ or $S_{2n}$ groups
     - 4. $\sigma_h$?
       - Yes: $C_{nh}$
       - No: $S_{2n}$

3. $\sigma_d$?
   - Yes: $D_n$
   - No: $C_n$
C<sub>n</sub> and S<sub>n</sub> point groups

**Point groups without any mirror planes:**

**C<sub>n</sub>**
the only symmetry element is C<sub>n</sub>;
symmetry operations: C<sub>n</sub>, C<sup>2</sup><sub>n</sub>, C<sup>3</sup><sub>n</sub>, C<sup>n-1</sup><sub>n</sub>

C<sub>1</sub> complete asymmetry
C<sub>2</sub>, C<sub>3</sub>, … are (extremely) rare and difficult to visualize

Example of C<sub>2</sub>: H<sub>2</sub>O<sub>2</sub> (C<sub>2</sub> cuts angle between the two OOH planes, 94 deg, in half)

![C<sub>2</sub> diagram](image)

**S<sub>n</sub>**
(only possible with n = 2, 4, 6, …)
symmetry operations: S<sub>n</sub>, S<sup>2</sup><sub>n</sub>, S<sup>3</sup><sub>n</sub>, S<sup>n-1</sup><sub>n</sub>

S<sub>2</sub> ≡ C<sub>i</sub>  example: staggered 1,2-dibromo-1,2-dichloroethane

S<sub>4</sub>: Rare! Contains symmetry operations S<sub>4</sub>, S<sup>2</sup><sub>4</sub> (≡ C<sub>2</sub>), S<sup>3</sup><sub>4</sub>
Example: 1,3,5,7-tetrafluorocyclooctatetraene

![S<sub>4</sub> diagram](image)

**Point groups with mirror planes:**

**C<sub>nv</sub>**
symmetry operations: C<sub>n</sub>, ..., C<sup>n-1</sup><sub>n</sub>, n x σ<sub>v</sub>

C<sub>1v</sub> ≡ C<sub>s</sub>
$C_{2v}$ (very common): $\text{H}_2\text{O}$, 1,2-dichlorobenzene

\[\text{Cl Cl} \quad \sigma_v' \quad \sigma_v \quad \text{Cl Cl} \]

$C_{3v}$ (very common): trigonal-pyramidal molecules ($\text{NH}_3$, $\text{CH}_3\text{Cl}$)

\[\text{H} - \text{N} - \text{H} \quad \text{Cl} - \text{Br} - \text{F} - \text{F} - \text{F} \]

$C_{4v}$: square-pyramidal molecules ($\text{BrF}_5$)

\[\text{F} - \text{Br} - \text{F} - \text{F} - \text{F} \]

$C_{5,6,\ldots v}$: very rare

$C_{\infty v}$: all linear molecules without inversion centre ($\text{HF}$, $\text{HCl}$)

\[\text{symmetry elements: } C_n, \sigma_h, \text{ if } n \text{ even, } S_n \]

$C_{nh}$ symmetry elements: $C_n$, $\sigma_h$, $i$ if $n$ even, $S_n$

$C_{2h}$ has $C_2$, $\sigma_n$ and $i$

example: difluorodiazene (planar)

\[\text{N} - \text{N} - \text{F} - \text{F} \]
C₃₇: B(OH)₃ boric acid (planar)

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{B} \\
\text{O} \\
\text{H}
\end{array}
\]

C₄₅₆₇₈₉: extremely rare

D point groups

Criterion: in contrast to Cₙ groups, D groups have n C₂ axes perpendicular to Cₙ!

Dₙ: symmetry operations: Cₙ, ..., Cₙ⁻¹, n x C₂ (rare point group!)

D₂: one of the excited states of ethylene (slight deviation from planarity!)

fragmentation method: D₂ can be regarded as consisting of 2 identical C₂v fragments joined back to back, so that one half is rotated (with respect to other) by any degree (except m x π/n with m = 2,4,6,...; n = order of C)

D₃: [Co(en)₃]³⁺ en = ethylenediamine
$D_{nd}$: symmetry elements: $C_n$, $n \times C_2$, $S_{2n}$, $n \times \sigma_d$

$D_{2d}$: allene

$D_{3d}$: symmetry operations: $C_3$, $C_3^2$, $3 C_2$, $S_6$, $S_6^3 = i$, $S_6^5$, $3 \sigma_d$
example: staggered ethane (2 $C_{3v}$ fragments: $H_3C$, rotation by 60 deg)

$D_{4d}$: $S_8$

$D_{5d}$: Ferrocene
D_{nh}:
symmetry elements: C_n, n x C_2, \sigma_h, S_n, n \times \sigma, i \text{ if } n \text{ is even}

**Note:** the horizontal mirror plane is usually easily identifiable!

D_{2h}: e.g. C_2H_4 (has 3 equivalent C_2 axes; therefore: assigning a \_v or \_h subscript to \sigma is redundant)

D_{3h}: PF_5 (trigonal-bipyramidal), BF_3 (planar)

D_{4h}: molecules with the geometry of a square (XeF_4)

D_{5h}: planar with 5-fold rotational symmetry (e.g. cyclopentadienyl anion)

D_{6h}: planar with 6-fold rotational symmetry (benzene)

D_{\infty h}: linear symmetrical molecules (N_2, C_2H_2)

**Three tips for assigning point groups**

1. Most of the low and high symmetry point groups are relatively easy to assign.
2. When it comes to D vs. C or S: look for n C_2 axes perpendicular to C_n.
3. Then look for \sigma_h.

**Chirality**

**Group-theoretical criterion for chirality: Absence of S_n!**

T_d, O_h, C_{nh}, D_{nd}, D_{nh} possess S_n. Molecules belonging to these point groups can therefore not be chiral!

Note: Molecules are usually chiral when neither i (S_2) nor \sigma_h is present (\sigma_h ≡ S_1)