Symmetry and Point Groups

Chapter 4

Monday, September 28, 2015
So far we can say staggered ethane has three operations: $E$, $C_3$, and $C_3^2$. 
So we add three more operations: $C_2$, $C_2'$, and $C_2''$
Now we’ve added three reflections: $\sigma_d$, $\sigma_d'$, and $\sigma_d''$

Note that there is no $\sigma_h$ for staggered ethane!
Ethane also has an inversion center that lies at the midpoint of the C-C bond (the center of the molecule).
Symmetry in Molecules: Staggered Ethane

Finally, staggered ethane also has an improper rotation axis. It is an $S_6$ ($S_{2n}$) axis that is coincident with the $C_3$ axis.

An $S_6$ rotation is a combination of a $C_6$ followed by a perpendicular reflection (i.e., a $\sigma_h$).
Finally, staggered ethane also has an improper rotation axis. It is an $S_6$ ($S_{2n}$) axis that is coincident with the $C_3$ axis.
Symmetry in Molecules: Staggered Ethane

It turns out that there are several redundancies when counting up the unique improper rotations:

So the improper rotations add only two unique operations.
Symmetry in Molecules: Staggered Ethane

Let’s sum up the symmetry operations for staggered ethane:

<table>
<thead>
<tr>
<th>Operation type</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity</td>
<td>1</td>
</tr>
<tr>
<td>Rotations</td>
<td>5 ((2C_3 + 3C_2))</td>
</tr>
<tr>
<td>Reflections</td>
<td>3 ((3\sigma_d))</td>
</tr>
<tr>
<td>Inversion</td>
<td>1</td>
</tr>
<tr>
<td>Improper Rotations</td>
<td>2 ((S_6 + S_6^5))</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>12</strong></td>
</tr>
</tbody>
</table>

- These 12 symmetry operations describe completely and without redundancy the symmetry properties of the staggered ethane molecule.

- The complete set of symmetry operations possessed by an object defines its **point group**. For example, the point group of staggered ethane is \(D_{3d}\).

- The total number of operations is called the **order** \(h\) of a point group. The order is always an integer multiple of \(n\) of the principal axis. For staggered ethane, \(h = 4n \ (4 \times 3 = 12)\).
Symmetry Elements and Operations

- elements are imaginary points, lines, or planes within the object.
- operations are movements that take an object between equivalent configurations – indistinguishable from the original configuration, although not necessarily identical to it.
- for molecules we use “point” symmetry operations, which include rotations, reflections, inversion, improper rotations, and the identity. At least one point remains stationary in a point operation.
- some symmetry operations are redundant (e.g., $S_6^2 \equiv C_3$); in these cases, the convention is to list the simpler operation.
Low-Symmetry Point Groups

These point groups only contain one or two symmetry operations.

- $C_1$: \{E\}
- $C_s$: \{E, \sigma_h\}
- $C_i$: \{E, i\}
High-Symmetry Point Groups

These point groups are high-symmetry groups derived from Platonic solids.

- **$T_d$**
  \[ \{E, 8C_3, 3C_2, 6S_4, 6\sigma_d\} = 24 \]

- **$O_h$**
  \[ \{E, 8C_3, 6C_2, 6C_4, 3C_2, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d\} = 48 \]

- **$I_h$**
  \[ \{E, 12C_5, 12C_5^2, 20C_3, 15C_2, i, 12S_{10}, 12S_{10}^3, 20S_6, 15\sigma\} = 120 \]

The five regular Platonic solids are the tetrahedron \( (T_d) \), octahedron \( (O_h) \), cube \( (O_h) \), dodecahedron \( (I_h) \), and icosahedron \( (I_h) \) respectively.
High-Symmetry Point Groups

In addition to $T_d$, $O_h$, and $I_h$, there are corresponding point groups that lack the mirror planes ($T$, $O$, and $I$).

Adding an inversion center to the $T$ point group gives the $T_h$ point group.

**TABLE 4.5 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>$E$ \hspace{1cm} $12C_5$ \hspace{1cm} $12C_5^2$ \hspace{1cm} $20C_3$ \hspace{1cm} $15C_2$ \hspace{1cm} $i$ \hspace{1cm} $12S_{10}$ \hspace{1cm} $12S_{10}^3$ \hspace{1cm} $20S_6$ \hspace{1cm} $15\sigma$</td>
</tr>
<tr>
<td>$I$</td>
<td>$E$ \hspace{1cm} $12C_5$ \hspace{1cm} $12C_5^2$ \hspace{1cm} $20C_3$ \hspace{1cm} $15C_2$</td>
</tr>
<tr>
<td>$O_h$</td>
<td>$E$ \hspace{1cm} $8C_3$ \hspace{1cm} $6C_2$ \hspace{1cm} $6C_4$ \hspace{1cm} $3C_2(=C_4^2)$ \hspace{1cm} $i$ \hspace{1cm} $6S_4$ \hspace{1cm} $8S_6$ \hspace{1cm} $3\sigma_h$ \hspace{1cm} $6\sigma_d$</td>
</tr>
<tr>
<td>$O$</td>
<td>$E$ \hspace{1cm} $8C_3$ \hspace{1cm} $6C_2$ \hspace{1cm} $6C_4$ \hspace{1cm} $3C_2(=C_4^2)$</td>
</tr>
<tr>
<td>$T_d$</td>
<td>$E$ \hspace{1cm} $8C_3$ \hspace{1cm} $3C_2$ \hspace{1cm} \hspace{1cm} $6S_4$ \hspace{1cm} \hspace{1cm} $6\sigma_d$</td>
</tr>
<tr>
<td>$T$</td>
<td>$E$ \hspace{1cm} $4C_3$ \hspace{1cm} $4C_3^2$ \hspace{1cm} $3C_2$</td>
</tr>
<tr>
<td>$T_h$</td>
<td>$E$ \hspace{1cm} $4C_3$ \hspace{1cm} $4C_3^2$ \hspace{1cm} $3C_2$ \hspace{1cm} $i$ \hspace{1cm} $4S_6$ \hspace{1cm} $4S_6^5$ \hspace{1cm} $3\sigma_h$</td>
</tr>
</tbody>
</table>

$T_h$ example:
Linear Point Groups

These point groups have a $C_\infty$ axis as the principal rotation axis

$C_{\infty v}$
\{E, $2C_\infty$, $\cdots$, $\infty \sigma_v$\}

$D_{\infty h}$
\{E, $2C_\infty$, $\cdots$, $\infty C_2$, $i$, $2S_\infty$, $\infty \sigma_v$\}

\[\text{H} \equiv \text{C} \equiv \text{N} \quad \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{H}\]
**$D$ Point Groups**

These point groups have $nC_2$ axes perpendicular to a principal axis ($C_n$)

$D_n$

{E, (n-1)C_n, $n \perp C_2$}

$D_{nh}$

{depends on $n$, with $h = 4n$}

$D_{nd}$

{depends on $n$, with $h = 4n$}

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$$D_3$$

{E, 2C_3, 3C_2, $\sigma_h$, 2$S_3$, 3$\sigma_v$}

$$D_{3h}$$

$$D_{2d}$$

{E, 2$S_4$, $C_2$, 2$C_2'$, 2$\sigma_d$}

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**allene (propadiene)**
C Point Groups

These point groups have a principal axis ($C_n$) but no $\perp C_2$ axes

$C_n$

$\{E, (n-1)C_n\}$

$C_{nv}$

$\{E, (n-1)C_n, n\sigma_v\}$

$C_{nh}$

$\{\text{depends on } n, \text{ with } h = 2n\}$

$C_2$

$\{E, C_2\}$

$C_{3v}$

$\{E, 2C_3, 3\sigma_v\}$

$C_{2h}$

$\{E, C_2, i, \sigma_h\}$
S Point Groups

If an object has a principal axis ($C_n$) and an $S_{2n}$ axis but no $\perp C_2$ axes and no mirror planes, it falls into an $S_{2n}$ group.

$S_{2n}$

{depends on $n$, with $h = 2n$}

$cyclopentadienyl (Cp)$ ring =

$Co_4Cp_4$

$S_4$

{E, $S_4$, $C_2$, $S_4^3$}