Symmetry can help resolve many chemistry problems and usually the first step is to determine the symmetry. If we know how to determine the symmetry of small molecules, we can determine symmetry of other targets which we are interested in. Therefore, this module will introduce basic concepts of group theory and after reading this module, you will know how to determine the symmetries of small molecules.

Introduction

Symmetry is very important in chemistry researches and group theory is the tool that is used to determine symmetry. Usually, it is not only the symmetry of molecule but also the symmetries of some local atoms, molecular orbitals, rotations and vibrations of bonds, etc. that are important. For example, if the symmetries of molecular orbital wave functions are known, we can find out information about the binding. Also, by the selection rules that are associated with symmetries, we can explain whether the transition is forbidden or not and also we can predict and interpret the bands we can observe in Infrared or Raman spectrum.

Symmetry operations and symmetry elements are two basic and important concepts in group theory. When we perform an operation to a molecule, if we cannot tell any difference before and after we do the operation, we call this operation a symmetry operation. This means that the molecule seems unchanged before and after a symmetry operation. As Cotton defines it in his book, when we do a symmetry operation to a molecule, every point of the molecule will be in an equivalent position.

Symmetry Elements

For different molecules, there are different kinds of symmetry operations we can perform. To finish a symmetry operation, we may rotate a molecule on a line as an axis, reflect it on a mirror plane, or invert it through a point located in the center. These lines, planes, or points are called symmetry elements. There may be more then one symmetry operations associated with a particular symmetry

Identity E

The molecule does not move and all atoms of the molecule stay at the same place when we apply an identity operation, \( E \), on it. All molecules have the identity operation. Identity operation can also be a combination of different operations when the molecule returns to its original position after these operations are performed. This will be demonstrated later.
Proper Rotations and Cn axis

$C_n$ generates n operations, whose symbols are $C_n$, $C_n^2$, $C_n^3$, $C_n^4$, ..., $E (=C_n^n)$. However, we usually write them in another way. Table 1.2 shows the way we write the 6 operations generated by proper rotation $C_6$. From this table, we can see that the symbols of the 6 rotations generated by $C_6$ are $C_6$, $C_3$, $C_2$, $C_3^2$, $C_6^5$, $E$. One molecule can have many proper axes and the one with the largest n is called **principle axis**.

Table 1.2 $C_6$ axis and operations it generates

<table>
<thead>
<tr>
<th>Rotation Angle</th>
<th>Operations</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{2\pi}{6}$</td>
<td>$C_6$</td>
<td>$C_6$</td>
</tr>
<tr>
<td>$2\times \frac{2\pi}{6}$</td>
<td>$C_6^2 = C_3$</td>
<td>$C_3$</td>
</tr>
<tr>
<td>$3\times \frac{2\pi}{6}$</td>
<td>$C_6^3 = C_2$</td>
<td>$C_2$</td>
</tr>
<tr>
<td>$4\times \frac{2\pi}{6}$</td>
<td>$C_6^4 = C_1^2$</td>
<td>$C_1$</td>
</tr>
<tr>
<td>$5\times \frac{2\pi}{6}$</td>
<td>$C_6^5$</td>
<td>$C_5^2$</td>
</tr>
<tr>
<td>$6\times \frac{2\pi}{6}$</td>
<td>$C_6^6 = E$</td>
<td>$E$</td>
</tr>
</tbody>
</table>

Reflection and mirror plane $\sigma$

Take NH$_3$ for an example. There are 3 mirror planes in molecule NH$_3$. When we do a reflection through a mirror plane, molecule NH$_3$ dose not change (Figure 1.2).

Figure 1.2 A mirror plane of NH$_3$..bmp

Figure 1.2 A mirror plane of NH$_3$.

There are three different kinds of mirror plane, $\sigma_v$, $\sigma_h$, and $\sigma_d$. The mirror plane that contains the principle axis is called $\sigma_v$. The mirror plane that perpendicular to the principle axis is called $\sigma_h$. Figure 1.3 shows $\sigma_v$, $\sigma_h$, and $\sigma_d$ in PtCl$_4^{2-}$.
When mirror plane is operated n times, we have

\[
\sigma^n = \begin{cases} 
E \text{(when n is even)} \\
\sigma \text{(when n is odd)} 
\end{cases}
\]

**Inversion and inversion center i**

In a molecule, if we can find a point, on the straight line through which we can find a pair of same atoms on both side of this point, we call this molecule has an inversion center. The inversion center, i, is not necessarily on an atom of the molecule. Figure 1.4 shows the inversion center of \( \text{C}_2\text{H}_4\text{Cl}_2 \). When inversion is operated n times, we have

\[
i^n = \begin{cases} 
E \text{(when n is even)} \\
i \text{(when n is odd)} 
\end{cases}
\]

**Improper Rotations and S\text{n} axis**

Improper rotation is a combination of two operations, proper rotation C\text{n} and reflection ?. Figure 1.5 shows the improper rotation operation in CH4.

Table 1.3 and table 1.4 show the operations generated by S6 and S5 axes separately. The 6 operations generated by S6 axis are S6, C3, i, C3^2, S6^5 and E. And the 10 operations generated by S5 axis are S5, C5^2, S5^3, C5^4, ?, C5, S5^7, C5^3, S5^9 and E. Since S1= \( \text{\{\sigma \text{h}\}} \) and S2=\( \text{\sigma hC2=i} \), the order of improper rotation, n, must always be larger than 2. And generally, when n is even, there are n operations \( \{ S_n^1, S_n^2, ..., S_n^n \} \), while when n is odd, there are 2n operations \( \{ S_n^1, S_n^2, ..., S_n^{2n} \} \). And we have
For a molecule, all the symmetry operations that can be applied to the molecule have all the properties of a group.
Therefore, before we introduce the symmetry point groups, the concept and properties of a group will be introduced first.

When some elements have a certain kind of relationships and can be related to each other by these relationships, these elements can form a group.

**Closure**

If two elements A and B are in the group G, then the multiplicity of these two elements, C, is also in this group. It can be expressed as

**Associativity**

All the elements in the group must satisfy the law of associativity, which can be expressed as

\[(AB)C = A(BC)\]

**Identity**

The group must contain such an element E that

\[ER = RE = R\]

In group theory, it refers to the operation identity E. Because any molecule or substance must at least have the symmetry element E.

**Inverses**

If A is an element in group G, there must be another element \( A^{-1} \) in group G that satisfies \( AA^{-1} = A^{-1}A = E \). Usually we can write \( A^{-1} \) as B. It can be expressed as

If \( A \in G \) and \( AA^{-1} = A^{-1}A = E \) then \( A^{-1} = B \in G \)

**Group Multiplication Tables**

If there are n elements in a group G, and all of the possible \( n^2 \) multiplications of these elements are known, then this group G is unique and we can write all these \( n^2 \) multiplications in a table called group multiplication table. All the symmetry operations of a molecule can be written in the form of group multiplication table. There is a very important rule about group multiplication tables called *rearrangement theorem*, which is that every element will only appear once in each row or column.\(^1\)

In group theory, when the column element is A and row element is B, then the corresponding multiplication is AB, which means B operation is performed first, and then operation A follows.\(^1\)

<table>
<thead>
<tr>
<th>Table 2.1 Group multiplication table(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G6</td>
</tr>
<tr>
<td><strong>E</strong></td>
</tr>
</tbody>
</table>
Subgroups

From table 2.1 above, we can find several small groups in the group multiplication table. For example,

\[
\begin{array}{ccc}
G_2 & E & A \\
E & E & A \\
A & A & E \\
\end{array}
\]

In the same way, there are also many several small groups with orders 1, 2, 3 respectively. These small order groups that can be found in a higher order group are called subgroups. The number of elements in a group is called the order of a group, using a symbol \(h\). The number of elements consist a subgroup is called the order of a subgroup, using a symbol \(g\). From the previous two examples, we have\(^{1}\),

\[h/g=k \quad (k \text{ is a whole number})\]

Since the symmetry point group have all the properties of a group, there are also several subgroups that we can find in a particular symmetry point group. And sometimes we just use symmetry operations in one subgroup to apply to a system instead of using all the symmetry operations in the group, which can significantly simplify the calculations.

Classes

Class is another important concept in group theory which provides a way to simplify the expression of all the symmetry operations in a group. This means that we do not have to write down all the symmetry operations in a group but combine some related operations instead. The followin part will introduce the concept of classes and how to divide a group into classes.

Similarity transformation and conjugate:

A and B are two elements in a group, X is any elements in this group. If

\[X^{-1}AX=B\]
Then we can say the relationship of A and B is similarity transformation. A and B are conjugate. Conjugate elements have three properties:

a. As what mentioned above, all the symmetry operations of a molecule as a group can be written in the form of group multiplication table and they obey all the properties of a group. This group is called symmetry point group. It is called point group for two reasons. First reason is that this group have all the properties of a group. Second reason is that all the symmetry operations are related to a fixed point in the molecule, which is not necessarily to be an atom of the molecule. According to the symmetry of molecules, they can be classified as symmetry point groups. To determine the symmetry point group of a molecule is very important, because all symmetry related properties are dependent on the symmetry point group of the molecule. Symmetry point groups can be divided into 5 classes which are summarized below and the they are described in details here (symmetry point groups)

<table>
<thead>
<tr>
<th>Point groups</th>
<th>Symmetry Elements</th>
<th>Order</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonaxial</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>E</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C&lt;sub&gt;2H2F2Cl2.bmp&lt;/c&gt;</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;i&lt;/sub&gt;</td>
<td>E, i</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CH2BrCl.bmp</td>
</tr>
<tr>
<td></td>
<td>Cs</td>
<td>E, ?</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C2H4Cl2-1.bmp</td>
</tr>
<tr>
<td>Cyclic</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;</td>
<td>E, C&lt;sub&gt;n&lt;/sub&gt;</td>
<td>n</td>
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<td></td>
<td></td>
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<td>NH3.bmp</td>
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<tr>
<td></td>
<td>C&lt;sub&gt;nh&lt;/sub&gt;</td>
<td>E, C&lt;sub&gt;n&lt;/sub&gt;, n(\sigma_v)</td>
<td>2n</td>
</tr>
<tr>
<td>Point groups</td>
<td>Symmetry Elements</td>
<td>Order</td>
<td>Example</td>
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<td>--------------</td>
<td>-------------------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>Cnv</td>
<td>E, C_n, σ_h, S_n</td>
<td>2n</td>
<td>C2F2H2.bmp</td>
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<td>E, S_n</td>
<td>n</td>
<td>1,3,5,7-tetrafluoracyclooctatetraene</td>
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<td>2n</td>
<td>[Co(en)₃]³⁺</td>
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<tr>
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<td>E, C_n, σ_h, nC₂ (?C_n)</td>
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<td>Benzene.bmp</td>
</tr>
<tr>
<td>Dnd</td>
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<td>Benzene</td>
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<tr>
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<td>CCl₄</td>
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### Contributors and Attributions

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