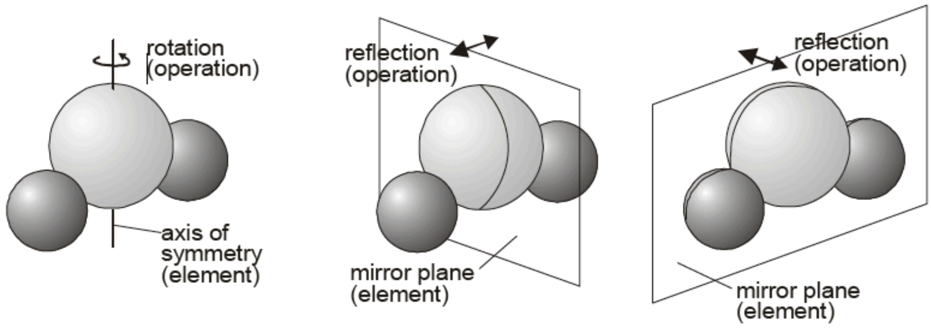
SYMMETRY CONSIDERATIONS AND MOLECULAR COORDINATES

1. Introduction

You will already be familiar with the concept of symmetry in an everyday sense. If we say something is ‘symmetrical’, we usually mean it has mirror symmetry, or ‘left-right’ symmetry, and would look the same if viewed in a mirror. Symmetry is also very important in chemistry, providing a considerable insight into many of chemical and physical properties molecular systems.

A **symmetry operation** is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. It will also look the same if we reflect it through either of two mirror planes, as shown in the figure below.



Each symmetry operation has a corresponding **symmetry element**, which is the axis, plane, line or point with respect to which the symmetry operation is carried out. The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a symmetry axis; in a reflection the points that remain unchanged make up a plane of symmetry.

The symmetry elements that a molecule may possess are:

1. E - the identity. The identity operation consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule has at least this element.

2. C_n - an n-fold axis of rotation. Rotation by 360°/n leaves the molecule unchanged. The H_2O molecule above has a C_2 axis. Some molecules have more than one C_n axis, in which case the one with the highest value of n is called the principal axis. Note that by convention rotations are counterclockwise about the axis.

3. σ - a plane of symmetry. Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a **vertical mirror plane** and is labelled σ_v, while one perpendicular to the axis is called a **horizontal mirror plane** and is labelled σ_h. A vertical mirror plane that bisects the angle between two C_2 axes is called a **dihedral mirror plane**,

σ_d.

4. i - a centre of symmetry. Inversion through the centre of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the centre of inversion and out to the same distance on the other side of the molecule.

5. S_n - an n-fold improper rotation axis (also called a rotary-reflection axis). The rotary reflection operation consists of rotating through an angle 360°/n about the axis, followed by reflecting in a plane perpendicular to the axis. Note that *S_1 is the same as reflection and S_2 is the same as inversion.*

The identity E and rotations C_n are symmetry operations that could actually be carried out on a molecule. For this reason they are called **proper symmetry operations**. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed **improper symmetry operations.**

A note on axis definitions: Conventionally, when imposing a set of Cartesian axes on a molecule, the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

3. Symmetry classification of molecules – point groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called point groups (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labelling symmetry groups, called the Schoenflies and Hermann-Mauguin (or International) systems. The symmetry of individual molecules is usually described using the Schoenflies notation, and we shall be using this notation. The molecular point groups are listed below:

TABLE OF THE MOLECULAR POINT GROUPS

1. C_1 – contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation E).

2. C_i - contains the identity E and a centre of inversion i.

3. C_S - contains the identity E and a plane of reflection σ.

4. C_n – contains the identity and an n-fold axis of rotation.

5. C_{nv} – contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_V.

6. C_{nh} - contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a centre of inversion).

7. D_n - contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.

8. D_{nh} - contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.

9. D_{nd} - contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.

10. S_n - contains the identity and one S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).

The following groups are the cubic groups, which contain more than one principal axis. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h). The icosahedral group also exists but is not included below.

11. T_d – contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes (e.g. CH4).

12. T - as for T_d but no planes of reflection.

13. T_h – as for T but contains a centre of inversion.

14. O_h – the group of the regular octahedron e.g. SF_6.

15. O - as for O_h but with no planes of reflection