3.2: Group Theory in Chemistry

In Chemistry, group theory is useful in understanding the ramifications of symmetry within chemical bonding, quantum mechanics and spectroscopy. The group elements we are concerned with are **symmetry operations**.

Symbol	Operation	Description	Element	Mathematical example
E	identity	This is the “don’t do anything to it” operation	E.	$E(x, y, z) = (x, y, z)$
C_n	Proper rotation	This is an operation in which the object is rotated about an axis by an angle of $\frac{2\pi}{n}$ radians. The axis will be referred to as the “C_n axis”.	C_n. The axis with the largest value of n is designated the “principle rotation axis” and the z-axis is always assigned as lying along the **principle rotation axis**.	$C_4(x, y, z) = (y, -x, z)$ $C_2(x, y, z) = (-x, -y, z)$ Etc.
σ	Reflection plane	This operation involves reflection of the object through a mirror plane.	σ_v, σ_d or σ_h. σ_v and σ_d contain the principle rotation axis, whereas σ_h planes are perpendicular to the principle rotation axis.	$\sigma_v(x, y, z) = (-x, y, z)$ (for reflection through the yz plane) $\sigma_h(x, y, z) = (x, y, -z)$ $\sigma_d(x, y, z) = (y, x, z)$
i	Inversion center	This operation involves reflection trough a point.	i. The inversion center (if it exists) will always be located at the center of mass of a molecule.	$i(x, y, z) = (-x, -y, -z)$
S_n	Improper rotation	This operation involves a rotation through a C_n axis followed by reflection by a σ_h plane.	S_n.	

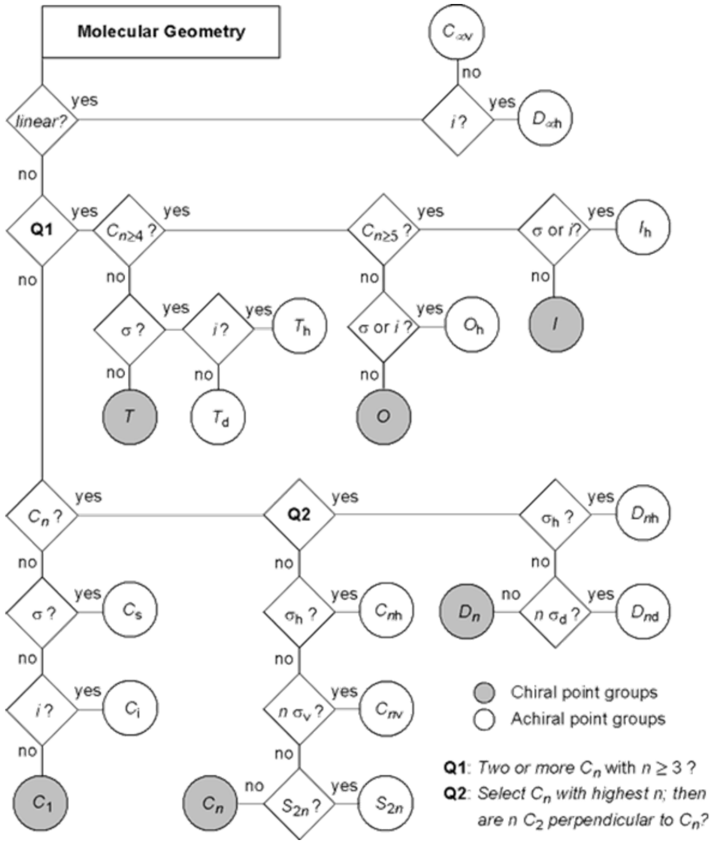

Figure 3.2.1

A symmetry operation is a geometrical manipulation that leaves an object in a geometry that is indistinguishable from that which it had before the manipulation. There are five important types of symmetry operations with which we are concerned. Each type of operation has an associated **symmetry element**. Using standardized notation, these operations and elements can be summarized as follows.

A given molecule may have several of the above symmetry elements. The particular combination will define a group, and that group can be given a named based on the type of symmetry elements it contains. Further, all of the convenient wavefunctions that describe the vibrations, rotations and molecular orbitals of the molecule will be eigenfunctions of the symmetry elements, forcing some very useful mathematical properties upon the wavefunctions.

A case study: the symmetry of a tennis racket

A tennis racquet has all of the same symmetry elements as a water molecule or a formaldehyde molecule. Let's identify these symmetry elements and write out a group multiplication table for the group to which that particular set belongs.

The most obvious symmetry element is always the identity element (E). Every object possesses this symmetry element. Some objects are so asymmetrical that this is the only symmetry element they possess. Certainly, a tennis racquet possesses the symmetry element **E**.

The next most useful element to examine is the reflection plane. An object may or may not possess this type of symmetry. A tennis racquet has two vertical (σ_v) reflection planes. One is in the plane of the strings and the other is perpendicular to the face of the racquet. This happens often that an object has more than one of a given type of symmetry element. For our purposes, we will designate the plane that is perpendicular to the face of the racquet as σ_v and the one that is parallel to the face of the racquet as σ_v'.

A tennis racquet possesses neither an inversion center (i) nor an improper rotation axis (S_n).

The set of symmetry elements that the object does possess (E, C_2, σ_v and σ_v') define a group that goes by the label C_{2v}. Any object that has these and only these symmetry elements is said to have C_{2v} symmetry. It is easy to demonstrate that the set of symmetry elements that define C_{2v} define a group.