### High Symmetry Groups

It is usually easy to recognize objects that belong to high symmetry groups. They have multiple higher-order rotation axes, all meeting at the center of the body. The highest symmetry finite 3D object is a sphere, this having an infinite number of rotation axes of infinite order. The point group of the Sphere is given the label K, and this is the point group used for free atoms in the gas phase.

We are usually dealing with molecules, and these can be very high in symmetry. The five Platonic solids are shapes of high symmetry belonging to point groups we encounter for many molecules.

Three of the Platonic solids are polyhedra having all regular triangles for faces. The one with the smallest number of faces is the tetrahedron:



Threefold axes of symmetry pass through each vertex of the tetrahedron, while two-fold axes of symmetry pass through the center of each edge. There are also mirror planes of symmetry that contain each edge. The point group label for tetrahedral symmetry is  $T_d$ . Examples of molecules belonging to the  $T_d$  point group are P<sub>4</sub> (white phosphorus) and methane, CH<sub>4</sub>.

The next Platonic solid with all regular triangles as faces is the octahedron:



Here we have six vertices. Through each vertex passes a four-fold axis of symmetry. Through each face of the octahedron passes a three-fold axis of symmetry. Through the center of each edge passes a two-fold axis of symmetry, while in addition, there are mirror planes that contain four edges each. There are also mirror planes that contain two vertices each and bisect a pair of edges. There is also an inversion center. This octahedron has a lot of symmetry! The label given to the point group representing octahedral symmetry is  $O_h$ .

Examples of molecules having octahedral symmetry are  $SF_6$ , a compound of the *p*-block elements, and tungsten hexacarbonyl,  $W(CO)_6$ , a transition-metal organometallic species. In addition, also belonging to the  $O_h$  point group is the polyhedral borane  $(BH)_6^{2-}$ , a hollow molecular ion with octahedral symmetry and no atom at its center!

Even higher in symmetry is the icosahedron, the Platonic solid with twenty triangular faces and twelve vertices. When you draw the icosahedron, it is helpful to first put down on paper the twelve vertices as nested hexagons, and then to connect the dots using broken lines for the edges that are in back. Practice drawing the icosahedron this way; this approach works nicely also for the other Platonic solids.



What is the order of the rotation axes that pass through the vertices of the icosahedron? Find a model of buckminsterfullerene,  $C_{60}$ , and determine the number of the highest-order rotation axes. Is it the same as for the icosahedron? Of course, the icosahedron has twenty three-fold rotation axes, one passing through the center of each face of this polyhedron. The  $B_{12}H_{12}^{2-}$  ion (dodecaborane dianion) is a nice example of a molecule having  $I_h$  point group symmetry.

The other two Platonic solids are the cube (square faces) and the pentagonal dodecahedron (twelve regular pentagons as faces). Can you explain the relationship of these solids to the octahedron and the icosahedron, respectively? Focus on the number of rotation axes of orders ranging from two to five. To what point groups do the square and the pentagonal dodecahedron belong?

Organic chemists have synthesized wonderful molecules shaped like a cube or like a dodecahedron, including "cubane",  $(CH)_8$ , and "dodecahedrane",  $(CH)_{20}$ .

#### Low Symmetry Groups

When inspecting a molecule to determine its point group, it is also easy to recognize molecules that have low symmetry. The lowest symmetry of all is the case where there is not any of the following: a mirror plane, an axis of proper or improper rotation, an inversion center. To this point group we give the label  $C_1$ , thus indicating that there is a one-fold proper axis of rotation, this being only the identity operation as possessed by all molecules.

If in addition to the identity operation, there is present for the system a single mirror plane and nothing else, then the molecule belongs to the  $C_s$  point group. The subscript "s" here will remind you of the  $\sigma$  symbol representing a mirror plane. Belonging to this point group are the butterfly (bilaterial symmetry) and a molecule such as CH<sub>2</sub>ClBr. Draw the latter molecule and verify that only a mirror plane is present.

If there is only present a center of inversion, then the molecule belongs to the  $C_i$  point group. An example is  $(CHFCl)_2$  when drawn in the right conformation. Draw this using a Newman projection and it should be easy to see that the inversion center is present, but not any proper axes of rotation or mirror planes.

# Linear Molecules

Some of the molecules in Earth's atmosphere are linear (CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O), and therefore easy to classify in symmetry terms. Linear molecules have an infinite number of proper rotation axes and mirror planes coincident with their long axis, and there is either present or absent an additional mirror plane perpendicular to the molecule's long axis. So, there are only two point groups for linear molecules:  $D_{\infty h}$  and  $C_{\infty v}$ . The  $D_{\infty h}$  point group label has an "h" subscript to remind you that there is a "horizontal" mirror plane perpendicular to the long axis of the molecule. On the other hand, the  $C_{\infty v}$  point group label has a "v" subscript to remind you that all the mirror planes are "vertical", meaning that they are coincident with the highest-order principal rotation axis of the molecule, which in this case is infinite.

## C Groups

Typical point group labels for the C groups are as follows:  $C_{3v}$ ,  $C_{2h}$ ,  $C_2$ . The key thing to recognize about these labels is that the number in the subscript indicates the order of the highestorder principal axis of rotation, of which (in contrast to the high symmetry groups) there is only one. Then, the "v" and "h" subscripts have the same meaning as in the case of linear molecules. If there is only a number for a subscript, then the molecule has present no mirror planes at all. If the molecule belongs to a C group and its point group label has only a number subscript, then the molecule has only the operations generated by the  $C_n$  axis.

Here are some examples: the ammonia molecule  $(NH_3)$  is  $C_{3v}$ , trans-dichloroethylene is  $C_{2h}$ .



In the graphic above, we have an example of  $C_2$  point group symmetry. This is a so-called "ansa-metallocene" molecule that is actually used as an olefin polymerization pre-catalyst. Isotactic polypropylene is made using catalysts derived from  $C_2$ -symmetric zirconium complexes of this type. Hydrogen atoms are omitted from the drawing for purposes of clarity; the five-membered carbon rings have all  $sp^2$  carbon atoms, while the other carbon atoms all are  $sp^3$  hybridized and have two

hydrogens each. With reference to the page on which the ansa-metallocene is drawn, where is the  $C_2$  axis?

## **D** Groups

Like the C groups, the D groups have a single higher-order principal rotation axis. In addition to that, however, the D groups have  $n C_2$  axes perpendicular to their principal  $C_n$  axis. Common D point groups have labels such as  $D_{4h}$ ,  $D_3$ , and  $D_{5d}$ . An example of  $D_{4h}$  symmetry is the square-planar  $PtCl_4^{2-}$  ion, while the cation  $Fe(bipy)_3^{2+}$  belongs to the  $D_3$  point group. If a molecule belongs to a D group and its point group label has only a number for a subscript, then the molecule has the shape of an *n*-bladed propellor.

In terms of the subscripts encountered for the D point groups, one we haven't seen before is "d", which stands for "dihedral". It means that the  $n C_2$  axes *bisect* the vertical mirror planes, rather than being coincident with them. A good example is given by the  $D_{5d}$  conformation of ferrocene:

