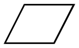
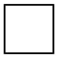
Chapter 3 – Symmetry and Group Theory

Symmetry Elements and Symmetry Observations

All of you have an idea of what is meant by the word *symmetry*. It conveys a sense of order. We will now discuss a way of quantifying symmetry. Consider the following two figures:  and . Both are fairly symmetrical, but is either more so? How can you tell?

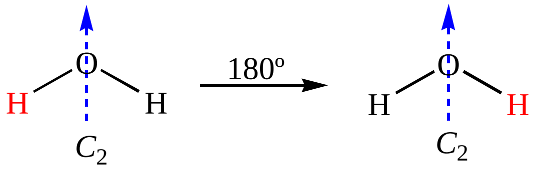
Before we go too far, we need to briefly address why this topic is important. A very simple consideration is melting points. Consider benzene and cyclohexane. Benzene melts at 4 ºC *vs*. -95° for cyclohexane. Why? The latter is a larger, heavier molecule, so using standard methods of prediction it should be easier to solidify (even taking into account the π-cloud). To answer this question first imagine the molecules in your mind's eye. Remember a crystal is a solid with ordered packing. Which will pack together most efficiently? (For this you have to decide, what does efficiently mean?) As you soon will be able to determine quantitatively, the benzene is significantly more symmetrical. This, along with differences in intermolecular forces, causes benzene to freeze at a much higher temperature.

A second and far more important use of group theory is in spectroscopy. You will be familiar with one aspect of this already. More symmetrical isomers tend to have simpler spectra. Consider the ^{1}H NMR spectra of *ortho*- vs. *para*-xylenes, for example. What would the spectra look like? Which molecule looks more symmetrical to you? Most importantly, group theory allows spectral prediction. We won't go into this in detail, but we'll go over an example later on.

The symmetry of a molecule can be described in total through the use of 5 operations. Each operation changes the molecule and the question is then asked as to whether the new orientation is indistinguishable from the old. I'll take the operations in a different order from the book. In the text that follows and in Experiment 2, I'll provide two dimensional images that I hope will help you visualize these operations. There is an excellent website linked on the course webpage to provide you with 3-D pictures that you may find helpful.

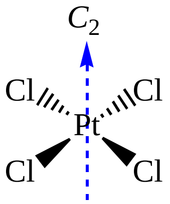
Identity, *E*- This operation does not change anything. All atoms remain in place. All molecules possess this symmetry element. This has mathematical significance and, so, must be included. Having it ensures that every molecule has a symmetry operation.

Rotational axes, C_n- an imaginary line is passed through the molecule and the molecule is rotated. If the molecule can be stopped in a position such that it is indistinguishable from the original molecule it has a rotation axis. For example, consider water (the hydrogen atoms have been labeled with different colors, but in reality are indistinguishable:



n = 360°/rotn = 360°/180° = 2 ⇒ C_2 axis (i.e. 2 rotations regenerate the original molecule)

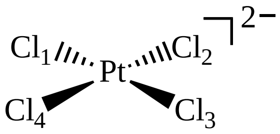
A C_2 is called a 2-fold rotational axis. Molecules may have more than 1 C_n axis. e.g. $PtCl_4^{2-}$



There are also coincident C_4 and C_2 axes perpendicular to the molecular plane, passing through the platinum atom.

The axis with largest n is called the principal rotation axis. In the case of $PtCl_4$ there are several other C_2 axes in the molecular plane. Also, it is important to note that the coincident axes are real. This will be discussed more later in the notes.

Mirror planes, σ - An imaginary plane is passed through a molecule and all atoms are shifted to a spot on the opposite side of the plane. If the result is indistinguishable from the original, the plane has a mirror plane.



There are 5 mirror planes in $PtCl_4^{2-}$

(i) passing through Pt and all four chlorine atoms,

(ii) through Pt, Cl_1, and Cl_3 (⊥ to the molecular plane) (also through Pt, Cl_2, and Cl_4)

(iii) through Pt and bisecting the angles made by Cl_1-Pt-Cl_2 and Cl_3-Pt-Cl_4 and ⊥ to the molecular plane (also Cl_1-Pt-Cl_4 and Cl_2-Pt-Cl_3)

A mirror plane including the principle axis is designated σ_v, those perpendicular are σ_h.

Inversion Center, *i* - This is a point in the center of the molecule. If all points x, y, z are inverted (i.e. go to -x, -y, -z) and the molecule retains its structure the molecule has an inversion center $PtCl_4^{2-}$ has an *i*, but H_2O doesn't.

Improper Rotation Axis, S_n - The first 4 symmetry elements are relatively easy to imagine, while the improper rotation axis is more difficult. Here the molecule is rotated by some angle then reflected through a σ_h plane. The book has a good illustration of a S_4 axis on page 52. Note S_1 and S_2 axes don't exist (σ & *i*, respectively) distinct entities.

If a molecule has a point that remains unchanged during all symmetry operations, the molecule is said to possess point symmetry. That point is the inversion center, if one exists, or the intersection of all elements if it does not. Molecules possess point symmetry, although collections of molecules in a crystal lattice may not.

Point Groups and Molecular Symmetry

It might seem that a very large number of combinations of the above symmetry elements would exist. In fact, while not very small, the number that actually occur in the chemical world is surprisingly small and most molecules fall into one of a small number of general classes, which makes keeping track of them less challenging.

Collectively, all the symmetry operations that describe a molecule are called its point group. For example, H_2O has 4 symmetry elements E, C_2, and 2 σ_v, as do CH_2Cl_2 and *cis*-$Cr(CO)_4(PH_3)_2$. While their spectra are not identical, many similarities exist. We will now look at different point groups.

1) Groups with very high symmetry – There are 3 of these: icosahedron, octahedron, and tetrahedron (I_h, O_h, and T_d, respectively). All are Platonic solids. All outer atoms must be the same.

2) Groups with very low symmetry - C_1 (only *E*), C_i (*E* and *i*), and C_s (*E* and σ).

3) Groups with an n-fold rotation axis - if the molecule has only *E* and C_n the group is C_n, if *E*, C_n, and σ_h, then C_{nh}, and if *E*, C_n, σ_v, then C_{nv}. The first 2 point groups are relatively uncommon, while C_{nv} is quite common. If a molecule is linear and has no inversion center, then its point group is $C_{\infty v}$.

4) Dihedral groups - Molecules with one or more C_2 axes perpendicular to the principle axis. Groups similar to C_n are present D_n (*E*, C_n, $C_2(\perp)$), D_{nd} (*E*, C_n, $C_2(\perp)$, σ_v), and D_{nh} (*E*, C_n, $C_2(\perp)$, σ_h) and $D_{\infty h}$ (linear molecule with inversion center). Of these, D_{nh} is most important.

You should be able to assign point groups by inspection. The flow chart on page 58 may help. Note: Most molecules have C_1, C_{nv}, or D_{nh} symmetry. Finally, it should be noted that a number of other point groups exist, but molecules possessing those symmetries are very rare.

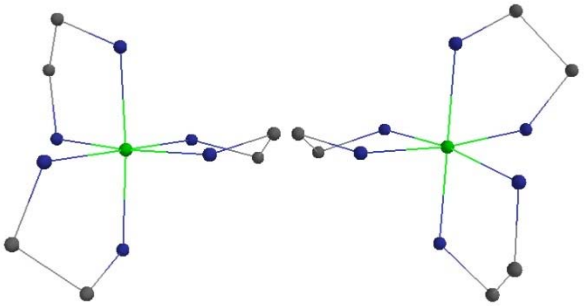
Irreducible Representations and Reducible Representations

A quick look back at Appendix D (p. A-13) shows that each point group has associated with it a Character Table. That character table has the symmetry elements listed across the top row with other information provided below. These tables are what make group theory useful to chemists. Each row is called an irreducible representation. We will discuss this in some detail in Experiment 2. The first two pages of this section in your book do a very nice job of explaining how certain irreducible representations are associated with certain molecular motions (e.g. rotation about the *z*-axis).

Uses of Point Group Symmetry

Optical Activity - You were taught in organic chemistry that a molecule is chiral if it is not superimposable on its mirror image. The vast majority of organic compounds use an asymmetric (chiral) carbon for this purpose, but chiral atoms are not required for a molecule to be chiral.

In contrast, relatively few inorganic compounds have chiral atoms. For example, consider $Co(en)_3^{2+}$ where en = ethylene diamine (see figure below, cobalt = green, nitrogen = blue, and carbon = black, hydrogen omitted for clarity). No atom in this complex is chiral, yet the whole is chiral.



Marion Cass has a website at Carlton College which shows similar complexes side-by-side in a way that makes visualizing the molecules easier. Chirality in these compounds is defined as the absence of an S_n axis. Note this includes a σ plane (S_1) or an inversion center (S_2).

Dipole moments - The book gives a definition of dipole moment. Another, more qualitative, one is the nonsymmetrical build-up of electron density on a molecule.

The book gives a complete listing of point groups that permit dipole moments. However, it may be easier to remember the two operations that exclude a molecule from having a dipole moment. They are *i* and σ_h.

Infrared and Raman Spectroscopy - Skip from here to end of chapter except as discussed when we go over "Experiment" 2 in the lab manual.

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