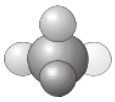
1.3: Symmetry Classification of Molecules- Point Groups

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 labeling 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 for the remainder of the course[1].

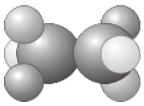
> *Some of the **point groups** share their names with symmetry **operations**, so be careful you do not mix up the two. It is usually clear from the context which one is being referred to.*

Molecular Point Groups

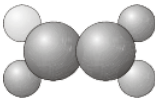
1. C_1 - contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation E) e.g. CHDFCl.



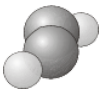
2. C_i - contains the identity E and a center of inversion i.



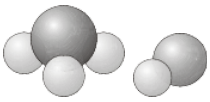
3. C_S - contains the identity E and a plane of reflection σ.



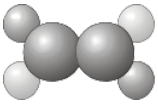
4. C_n - contains the identity and an n-fold axis of rotation.



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



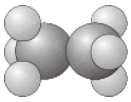
6. C_{nh} - contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a center of inversion).



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.

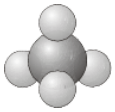
9. D_{nd} - contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



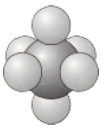
10. S_n - contains the identity and *one* S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).

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. CH_4.



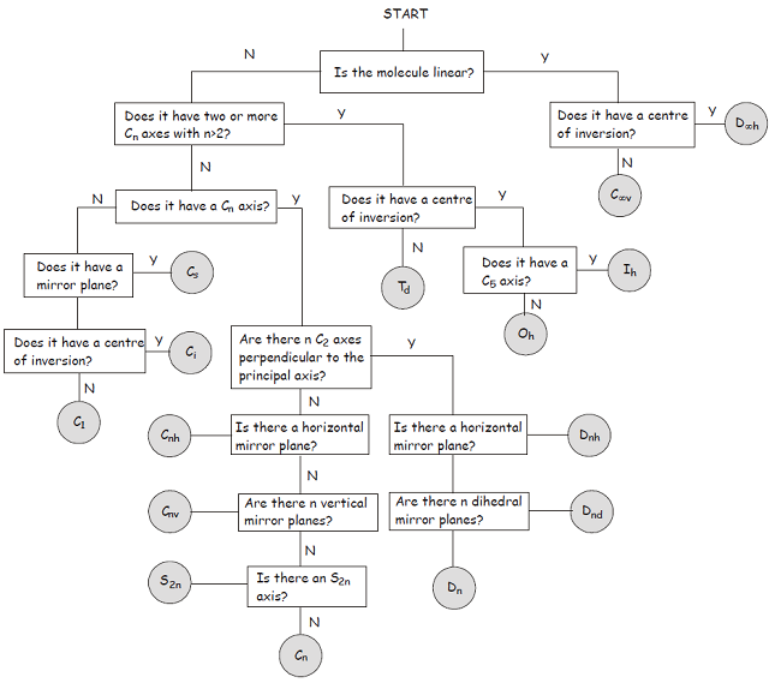
12. T - as for T_d but no planes of reflection.
13. T_h - as for T but contains a center of inversion.
14. O_h - the group of the regular octahedron e.g. SF_6.



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

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics. However, we won't be treating it any further here.

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.



[1]Though the Hermann-Mauguin system can be used to label point groups, it is usually used in the discussion of crystal symmetry. In crystals, in addition to the symmetry elements described above, translational symmetry elements are very important. Translational symmetry operations leave no point unchanged, with the consequence that crystal symmetry is described in terms of *space groups* rather than *point groups*.
