Homeworks 13 and 14

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Molecular Symmetries- General Theory

The concept of symmetry is everywhere, and molecules are no exception. If we think about the structure of a molecule (like the one in the picture below), there are some symmetry operations that we can immediately see, such as the 120º rotations by the axis passing through the boron in the example below. And, for each existing symmetry operation in a certain molecule we associate a symmetry element, which may be an axis, a plane, a line or even a point. For example, rotations by the axis passing through the boron in the molecule below would have the same symmetry element. The possible types of symmetry elements a molecule may have are:

1. **Identity** (E): The identity operation leaves the molecule unchanged, thus the symmetry element is the entire molecule. All molecules have this element, which serves as the identity of the symmetry group.

2. **n-fold axis of rotation** (C_n): A molecule has rotational symmetry if it can be rotated by $\frac{360°}{n}$ around a symmetry axis and remain unchanged. Molecules may have more than one axis of rotation, and rotations, are, by convention, counterclockwise.

3. **Plane of Symmetry** (σ): A molecule possesses a plane of symmetry if it remains unchanged by a reflection on said plane. Reflection planes can be of the following types:

- Vertical planes (σ_v): Contain the axis of rotation.

- Horizontal planes (σ_h): Are perpendicular to the axis of rotation.

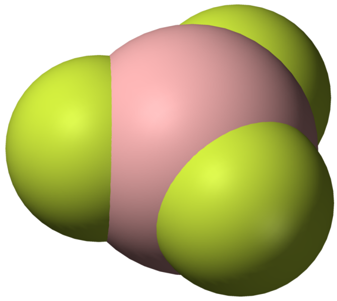
- Dihedral mirror planes (σ_d): Bisect the angles between two C_2 axes.

4. **Center of symmetry** (i): A molecule possesses a center of symmetry if when inverting by said center the molcule remains unchanged.

5. **n- fold improper rotation axis** (S_n): Consists of combining a rotation around an axis with a reflection through a plane perpendicular to the axis.

Molecules may be divided into different **molecular point groups**, based on which symmetry elements they possess. As a curiosity, there are 15 different molecular point groups, such as, for example, D_{nh} which contains all molecules with: identity, an n-fold axis of rotation, n 2-fold axis of rotation perpendicular to the principal one, n vertical mirror planes and an horizontal mirror plane.

Example: Boron Trifluoride (BF_3)



Boron trifluoride is a planar molecule, so it is fair to representing using just a plane. The symmetry elements of BF_3 are:

- A principal C_3 axis passing through the boron atom and perpendicular to the molecular plane.

- Three C_2 axes passing through the boron atom and bisecting the angles between the fluorine atoms.

- A horizontal plane of reflection (σ_h) coinciding with the molecular plane.

- Three vertical planes of reflection (σ_v), each containing the C_3 axis and one fluorine atom.

A visual clarification for this symmetries may be found on the end of the paper. Based on these elements, BF_3 belongs to the D_{3h} point group.

Applications

One may ask why this theory is relevant for chemistry. Well, studying the symmetries of molecules is, indeed, useful. I won't go into further detail, but here are some of the possible applications of this theory:

1. Predicting whether a molecule will be polar or chiral;
2. Visualization of molecular orbits;

3. Examination of chemical bonding;
4. Investigation of the vibrational motions of a given molecule.