Observation 1: Geometries of molecules

The geometry of a molecule includes a description of the arrangements of the atoms in the molecule. At a simple level, the molecular structure tells us which atoms are bonded to which. At a more detailed level, the geometry includes the lengths of all of these bonds, that is, the distances between the atoms which are bonded together, and the angles between pairs of bonds. For example, we find that in water, H2O, the two hydrogens are bonded to the oxygen and each O-H bond length is 95.72pm (where 1pm=10-12m). Furthermore, H2O

is a bent molecule, with the H-O-H angle equal to 104.5°. (The measurement of these geometric properties is difficult, involving the measurement of the frequencies at which the molecule rotates in the gas phase. In molecules in crystalline form, the geometry of the molecule is revealed by irradiating the crystal with x-rays and analyzing the patterns formed as the x-rays diffract off of the crystal.)

Not all triatomic molecules are bent, however. As a common example, CO2

is a linear molecule. Larger polyatomics can have a variety of shapes, as illustrated in Figure. Ammonia, NH3, is a pyramid-shaped molecule, with the hydrogens in an equilateral triangle, the nitrogen above the plane of this triangle, and a H-N-H angle equal to 107°. The geometry of CH4 is that of a tetrahedron, with all H-C-H angles equal to 109.5°. (See also Figure.) Ethane, C2H6, has a geometry related to that of methane. The two carbons are bonded together, and each is bonded to three hydrogens. Each H-C-H angle is 109.5° and each H-C-C angle is 109.5°. By contrast, in ethene, C2H4, each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7°. All six atoms of ethene lie in the same plane. Thus, ethene and ethane have very different geometries, despite the similarities in their molecular formulae.

We begin our analysis of these geometries by noting that, in the molecules listed above which do not contain double or triple bonds (H2O, NH3, CH4and C2H6

), the bond angles are very similar, each equal to or very close to the tetrahedral angle 109.5°. To account for the observed angle, we begin with our valence shell electron pair sharing model, and we note that, in the Lewis structures of these molecules, the central atom in each bond angle of these molecules contains four pairs of valence shell electrons. For methane and ethane, these four electron pairs are all shared with adjacent bonded atoms, whereas in

ammonia or water, one or two (respectively) of the electron pairs are not shared with any other atom. These unshared electron pairs are called lone pairs . Notice that, in the two molecules with no lone pairs, all bond angles are exactly equal to the tetrahedral angle, whereas the bond angles are only close in the molecules with lone pairs

One way to understand this result is based on the mutual repulsion of the negative charges on the valence shell electrons. Although the two electrons in each bonding pair must remain relatively close together in order to form the bond, different pairs of electrons should arrange themselves in such a way that the distances between the pairs are as large as possible. Focusing for the moment on methane, the four pairs of electrons must be equivalent to one another, since the four C-H bonds are equivalent, so we can assume that the electron pairs are all the same distance from the central carbon atom. How can we position four electron pairs at a fixed distance from the central atom but as far apart from one another as possible? A little reflection reveals that this question is equivalent to asking how to place four points on the surface of a sphere spread out from each other as far apart as possible. A bit of experimentation reveals that these four points must sit at the corners of a tetrahedron, an equilateral triangular pyramid, as may be seen in Figure. If the carbon atom is at the center of this tetrahedron and the four electron pairs at placed at the corners, then the hydrogen atoms also form a tetrahedron about the carbon. This is, as illustrated in Figure, the correct geometry of a methane molecule. The angle formed by any two corners of a tetrahedron and the central atom is 109.5°, exactly in agreement with the observed angle in methane. This model also works well in predicting the bond angles in ethane.

Tetrahedral Structure of Methane

The dotted lines illustrate that the hydrogens form a tetrahedron about the carbon atom.

The same tetrahedron is formed by placing four points on a sphere as far apart from one another as possible.

We conclude that molecular geometry is determined by minimizing the mutual repulsion of the valence shell electron pairs. As such, this model of molecular geometry is often referred to as the valence shell electron pair repulsion (VSEPR) theory . For reasons that will become clear, extension of this model implies that a better name is the Electron Domain (ED) Theory .

This model also accounts, at least approximately, for the bond angles of H2O

and NH3. These molecules are clearly not tetrahedral, like CH4, since neither contains the requisite five atoms to form the tetrahedron. However, each molecule does contain a central atom surrounded by four pairs of valence shell electrons. We expect from our Electron Domain model that those four pairs should be arrayed in a tetrahedron, without regard to whether they are bonding or lone-pair electrons. Then attaching the hydrogens (two for oxygen, three for nitrogen) produces a prediction of bond angles of 109.5°, very close indeed to the observed angles of 104.5° in H2O and 107° in NH3

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Note, however, that we do not describe the geometries of H2O

and NH3

as "tetrahedral," since the atoms of the molecules do not form tetrahedrons, even if the valence shell electron pairs do. (It is worth noting that these angles are not exactly equal to 109.5°, as in methane. These deviations will be discussed later.)

We have developed the Electron Domain model to this point only for geometries of molecules with four pairs of valence shell electrons. However, there are a great variety of molecules in which atoms from Period 3 and beyond can have more than an octet of valence electrons. We consider two such molecules illustrated in Figure.

First, PCl5 is a stable gaseous compound in which the five chlorine atoms are each bonded to the phosphorous atom. Experiments reveal that the geometry of PCl5 is that of a trigonal bipyramid : three of the chlorine atoms form an equilateral triangle with the P atom in the center, and the other two chlorine atoms are on top of and below the P atom. Thus there must be 10 valence shell electrons around the phosphorous atom. Hence, phosphorous exhibits what is called an expanded valence in PCl5. Applying our Electron Domain model, we expect the five valence shell electron pairs to spread out optimally to minimize their repulsions. The required geometry can again be found by trying to place five points on the surface of a sphere with maximum distances amongst these points. A little experimentation reveals that this can be achieved by placing the five points to form a trigonal bipyramid. Hence, Electron Domain theory accounts for the geometry of PCl5

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Second, SF6

is a fairly unreactive gaseous compound in which all six fluorine atoms are bonded to the central sulfur atom. Again, it is clear that the octet rule is violated by the sulfur atom, which must therefore have an expanded valence. The observed geometry of SF6

, as shown in Figure, is highly symmetric: all bond lengths are identical and all bond angles are 90°. The F atoms form an octahedron about the central S atom: four of the F atoms form a square with the S atom at the center, and the other two F atoms are above and below the S atom. To apply our Electron Domain model to understand this geometry, we must place six points, representing the six electron pairs about the central S atom, on the surface of a sphere with maximum distances between the points. The requisite geometry is found, in fact, to be that of an octahedron, in agreement with the observed geometry.

As an example of a molecule with an atom with less than an octet of valence shell electrons, we consider boron trichloride, BCl3

. The geometry of BCl3 is also given in Figure: it is trigonal planar , with all four atoms lying in the same plane, and all Cl-B-Cl bond angles equal to 120°. The three Cl atoms form an equilateral triangle. The Boron atom has only three pairs of valence shell electrons in BCl3

. In applying Electron Domain theory to understand this geometry, we must place three points on the surface of a sphere with maximum distance between points. We find that the three points form an equilateral triangle in a plane with the center of the sphere, so Electron Domain is again in accord with the observed geometry.

We conclude from these predictions and observations that the Electron Domain model is a reasonably accurate way to understand molecular geometries, even in molecules which violate the octet rule.