physical and chemical properties division

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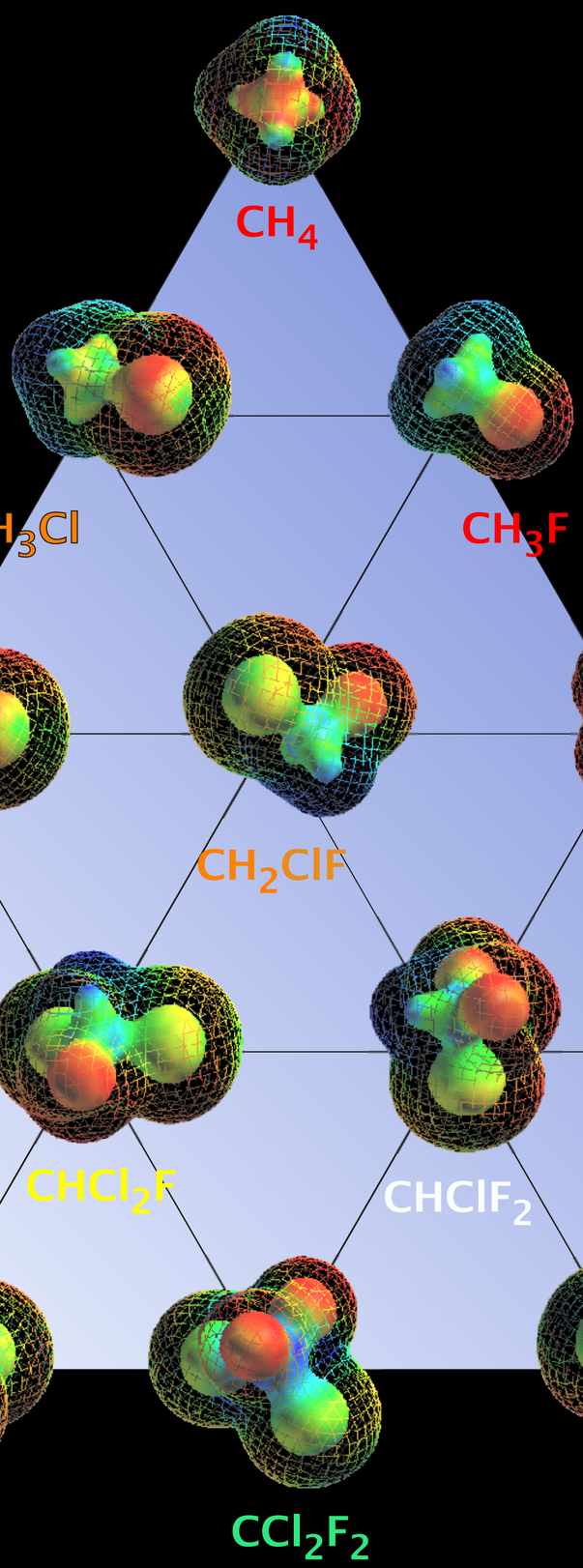
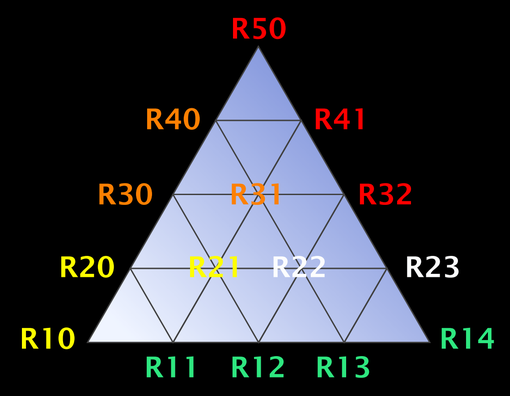
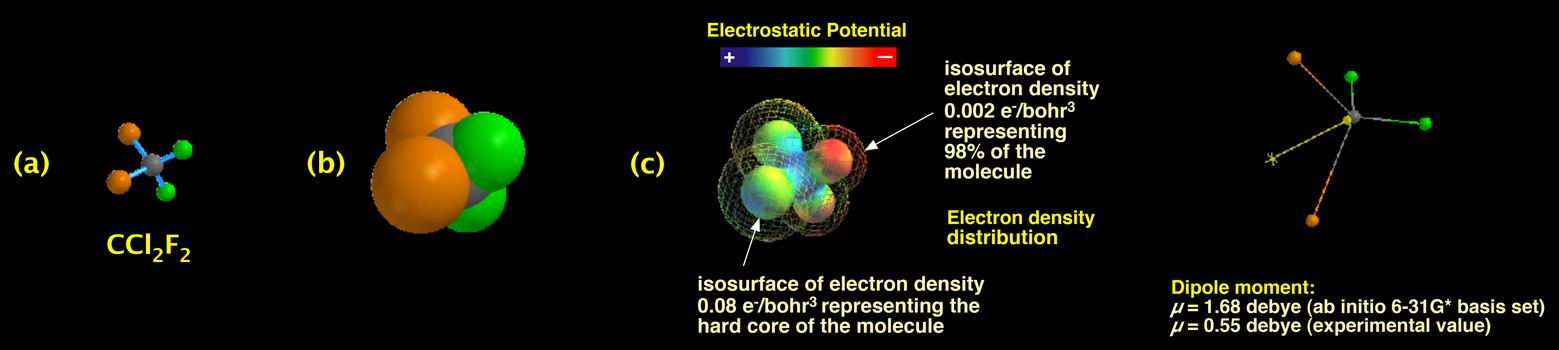
Halocarbons I: Methane Derivatives





Our Evolving View of Molecular Structure



Nobel Prize in Chemistry 1998

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John Pople

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Walter Kohn

The molecular structure (size and shape) of a compound determines its macroscopic physical and chemical properties. Simple representations of molecules as *balls and sticks* (a) reflect only their shape in terms of bond lengths and angles but not their size.

Space-filling representations (b) show the individual atoms as spheres with their respective diameters. This structural picture is more realistic than *ball and stick models* (a) because it reflects also the size and shape of a molecule. However, the atomic spheres are assumed to be rigid ("hard") instead of soft.

Bond lengths, angles, and atomic radii used to be measured experimentally. In theory, they can be determined with great accuracy by solving Schrödinger's equation. This quantum mechanical equation accounts for the motions of nuclei and electrons in atoms or molecules. However, for anything more complicated than the hydrogen atom, there are no exact solutions to this equation.

Quantum mechanical chemistry dates back to the late 1920's when the hydrogen bond was interpreted by Heitler and London using valence bond theory. Hückel's molecular orbital approach followed a few years later. But the real breakthrough came in the 1960's when semi-empirical programs became available and *ab initio* calculations of molecular and intermolecular properties could be carried out with quantitative accuracy.

Three advances catalyzed this progress:

- the development of computational methods by John Pople and many others in the 1950's,
- the development of *density functional theory* by Walter Kohn and others, and
- the increasing availability and speed of computers.

These methods were employed here to elucidate the molecular structures of the methane derived halocarbons in fine detail. Schrödinger's equation was solved for each of the 15 molecules by approximating the atomic orbitals with the 6-31G* basis set of Gaussian functions. The results are shown in terms of two surfaces of constant electron density (c). The electron density gives the number of electrons per unit volume at each point in space. Summed over all space this gives the total number of electrons in a molecule.

The outer mesh of each molecule represents the isosurface of 0.002 e^-/ $bohr^3$ electron density which comprises about 98% of a molecule. Electron density increases toward the nuclei of a molecule. To illustrate this, a second isosurface of electron density 0.08 $e^-/bohr^3$ is rendered solid for each molecule. As seen in Figure (c), the distance between the inner and the outer electron density isosurface differs for different atoms. It is larger for the chlorine atoms and smaller for the fluorine atoms. Fluorine binds its electrons more tightly so that it has a "harder" electron cloud than chlorine. Therefore, collisions with fluorine atoms are more repulsive than with the softer chlorine atoms. These differences on the atomistic level cause profound variations in the bulk properties of matter.

Another important result of ab initio calculations is the charge distribution in a molecule. The electrostatic potential describes the interaction energy of a positive probe at each point around a molecule. This is color-mapped on the electron density isosurfaces. Blue marks electron-poor regions while red indicates electron-rich regions. Fluorine atoms are centers of negative charge. Non-uniform charge distribution creates dipolar, quadrupolar, or higher-order polar species whose interactions are orientation dependent. It induces long range attractions which result in molecular associations via hydrogen bonds. Such electrostatic effects contribute significantly to the macroscopic properties of matter.

Arno.Laesecke@Boulder.NIST.Gov
National Institute of Standards and Technology
Physical and Chemical Properties Division
Experimental Properties of Fluids Group
325 Broadway, MC 838.07
Boulder, CO 80305, U.S.A.

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