Prediction of Reliable Heats of Formation and Bond Dissociation Energies

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Computational chemistry can be used to predict the properties of a wide range of compounds. New basis sets coupled with effective core potentials, improved theoretical methods implemented in high performance software, and access to high performance, massively parallel computers make it possible to calculate reliably the heats of formation of many compounds for the first time. This allows us to calculate a wide range of accurate bond dissociation energies which are not available from experiment due to difficulties in the measurements of heats of formation of radicals. We will describe issues in such calculations in terms of basis sets and the electrons that need to be correlated. We describe the prediction of the heats of formation of a range of compounds including main group and transition metal atoms. This allows for the reliable prediction of many bond energies for the first time and provides unique insights into chemical bonding. A key concept is the use of adiabatic vs. diabatic bond energies in correlating molecular properties. We will describe the application of our approach to rare gas compounds; transition metal oxides, hydrides, and fluorides; and to phosphorus and sulfur oxides and fluorides. A brief update on stratospheric ozone depletion chemistry based on new calculations on X_2O_2 isomers for X a halogen will also be provided.