148a Accurate Ab Initio Thermochemistry Via Various Reaction Schemes

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Accurate thermochemistry for molecular species is of crucial importance in many areas. It is in especially high demand in the area of kinetic simulations of complex physico-chemical systems, such as combustion, atmospheric processes, chemical vapor deposition, etc. As computer processing capabilities continue to increase, the use of computational chemistry in this area becomes a much more important tool. Techniques such as ab initio are useful because they calculate species properties "from first principles" or, without empirical data of any kind. It is important, however, to compare the theoretically calculated values with those generated from experimentation in order to evaluate the accuracy of the theoretical model. Additionally, it has been recognized that, while the total enthalpy values generated from ab initio calculations are extremely accurate, the conversion to conventional thermochemical data (i.e. enthalpies of formation) remains an obstacle in the final accuracy of ab initio methods. Not only must a set of references species with accurate experimental thermochemical data be selected, but a particular reaction scheme, such as atomization, isodesmic etc., must also be adopted. However, both requirements are difficult to meet in that accurate experimental thermochemical data for the reference species are often absent while the reaction schemes are selected arbitrarily. This work will report the effect of reaction scheme selection on the accuracy of the formation enthalpies derived from the ab initio calculations. A set of 47 chemical species comprising four elements C, N, O and H and whose experimental enthalpies of formation are known with high accuracy were selected. The theoretical enthalpies of formation of these species were determined at the G2 and G3 level employing an optimization procedure similar to that of least squares method. The reaction sets chosen were: conventional (number and type of atoms conserved), isostoichiometric (conventional reactions where sum of stoichiometric coefficients is zero), isodesmic (number and type of bonds conserved). Thus far, the highest accuracy has been observed under the isodesmic reaction scheme although the accuracy of the other methods is not significantly inferior leading us to conclude that the effect of stoichiometry in converting the total ab inito energies into enthalpies of formation is less important than previously thought.