

## SYNERGIES BETWEEN CALORIMETRY AND COMPUTATIONAL CHEMISTRY IN MODERN THERMOCHEMISTRY

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Calorimetric techniques, such as reaction-solution, combustion, and Calvet calorimetry provide a variety of thermochemical data, which reflect the bonding energetics of molecules and their intermolecular interactions in the solid and liquid states. Enthalpies of formation in the ideal gas phase, for example, can be analyzed in terms of bond enthalpy contributions,  $E(X-Y)$ , and bond dissociation enthalpies,  $DH^{\circ}(X-Y)$ , two concepts that are central to discuss the relationship between the energy of a molecule and its structure or chemical reactivity. The interpretation of these parameters can be considerably enriched by quantum chemistry studies. These studies give insights into the nature of the chemical bonds and are more general than purely empirical approaches; they can also be used to predict new data and assist in identifying experimental results which are likely to be wrong. There is, however, a synergistic relation between the information obtained from the experimental and theoretical investigations since, on the other hand, reliable experimental results are always needed to assess the predictions of the theoretical methods and therefore help in the refinement of the underlying models. This is also true when intermolecular interactions are considered. Experimental enthalpies of sublimation are, for example, important to define the intermolecular potential functions used to analyze the interactions that determine crystal structures, via molecular dynamics simulations.

In our laboratory calorimetric and computational chemistry methods have been used in recent years, to study a variety of problems involving the relationship between molecular energetics, structure, and reactivity. The synergistic role of the experimental and computational approaches will be illustrated for organic and organometallic systems.