Summary

Title: Development and application of accurate thermochemical methods
Author: Ádám Ganyecz

5 most important publications:
Á. Ganyecz, J. Csontos, B. Nagy, and M. Kállay, *J. Phys. Chem. A*, **2015**, 119:1164
Á. Ganyecz, M. Kállay, and J. Csontos, *J. Phys. Chem. A*, 2017, 121:1153
Á. Ganyecz, M. Kállay, and J. Csontos,*J. Chem. Theory Comput.*, **2017**, 13:4193
Á. Ganyecz, M. Kállay, and J. Csontos, *J. Phys. Chem. A*, **2018**, 122:5993
Á. Ganyecz, M. Kállay, and J. Csontos, *J. Phys. Chem. A*, **2019**, 123:4057

During my PhD work I have had two goals kept in my mind. On the one hand, I wanted to develop an accurate thermochemical protocol, as well as apply previously defined ones, to obtain reliable theoretical data for the aforementioned species. On the other hand, I also wanted to combine my theoretical results with critically evaluated literature data in various thermochemical networks (TN), thereby providing the best possible thermochemical values based on our current knowledge.

At first, fluoroethyl radicals were studied with the diet-HEAT model chemistry, which provided the most reliable theoretical values at the time for the 8 species studied. The importance of the excitations beyond the perturbative triples and relativistic effects were noteworthy. The contribution to the heats of formation obtained from CCSDT(Q) and scalar-relativistic calculations increased with the size of the radical, i.e., with the number of fluorine atoms, and it was as large as 5 kJ/mol for CF_3-CF_2. Therefore, they seem to be unavoidable in thermochemical protocols seeking chemical accuracy.

The next work introduced an *ab initio* parameter composite model chemistry with moderate-cost, baptized as diet-HEAT-F12. It was developed to calculate accurate thermochemical data for species containing first- and second-row atoms, and was designed to be parameter free. The model proposed has a 0.5 kcal/mol 95% confidence interval for the benchmark HEAT values. It was also shown by using a test set of accurate TAEs that the diet-HEAT-F12 protocol yielded the most accurate data among the conceptually similar model chemistries, W3-F12, W3X, and W3X-L, investigated.

In the next study, diet-HEAT-F12 and thermochemical network approach were applied to get the heat of formation values for 50 atmospherically relevant species including various fluorinated and chlorinated methanes and ethanes. In 28 out of the 50 cases, this method presented the most reliable estimates for the heats of formation. For the other species, the results agreed well with the most accurate data from ATcT or JPL, while according to statistical measures for six species further investigation is still needed to collect more established heats of formation. This study also showed that conventional CCSD(T) calculations, even with the 5Z basis sets, could suffer from BSSE, while explicitly correlated methods are hardly affected by this error. Therefore, the usage of the diet-HEAT-F12 model chemistry generally is recommended over the conventional diet-HEAT. Furthermore, the work highlighted the importance of the quality and reliability of the data provided by the theoretical model and supplied into the TN. It was observed that, low-quality theoretical results undermine the benefits of the thermochemical networks.

During the last part of my PhD work, reliable and consistent heats of formation and sublimation enthalpies had been established for uracil, thymine, cytosine, and adenine. On the one hand, the diet-HEAT-F12 protocol was utilized to provide accurate theoretical gas-phase heats of formation data. On the other hand, the available combustion and sublimation data along with my diet-HEAT-F12 results were arranged into a TN. The solution of the TN yielded the best estimates for the studied thermochemical quantities in case of uracil, thymine, and cytosine. In the case of adenine, the available data was not consistent with my results. This could be attributed to the fact that different preparations of the sample lead to different degree of crystallinity.