Computational Studies

DOI: 10.1002/anie.200802500

No Important Suggestions

*Gernot Frenking**

When I read the names of three towering figures in theoretical chemistry as authors of the paper,[1] I expected something particularly valuable for the community. After reading the manuscript I felt like a guest who was invited to a gourmet restaurant where he was only served a thin soup. The authors comment about theoretical papers which predict new molecules that are suggested to be studied experimentally. They criticize statements which are sometimes made in such work on the predicted stability and the claims which are frequently found therein. In a rather colloquial style the authors make comments which are in reality neither helpful nor do they make realistic suggestions for an improvement. In fact, I find the suggestions to be more fuzzy and obscure than the criticized claims of stable molecules. The remarks about the technical aspects of theoretical studies are trivial and they do not need to be published in a prominent place. In detail I have the following comments on the paper.

1) In the first section entitled "Stable, Unstable" the authors remind the readers that there is a difference between thermodynamic and kinetic stability and that the strength of a bond does not mean that the molecule is stable in a condensed phase. So what? The information which is given here is usually taught in undergraduate chemistry courses and does not need to be repeated in a scientific publication.
2) The second part "Viable versus Fleeting" is particularly troublesome. Why should "viable" be restricted to molecules in particular laboratory environments? Cyclopropenylidene cannot be isolated under the suggested conditions, and yet it is the most abundant organic molecule having a nearly infinite lifetime that could be identified in interstellar space. Interstellar chemistry very interesting is from an academic viewpoint, and molecules that are very viable in outer space should not be discriminated because they do not survive in a "typical" chemical laboratory. The authors note themselves that some comments are biased towards organic molecules and ions. Many comments make no sense at all when it comes to inorganic molecules. For example, ionic molecules with higher charge than ±1 are easily isolated in a condensed phase. As a striking example, I cite the very recent publication of a homoleptic complex that contains an anion that carries a charge of -8.[2] The sentence that almost all dianions lose electrons spontaneously makes no sense at all, since numerous multiply charged anions can be stabilized in the presence of counterions. Some years ago, one of the authors published a bonding analysis of the dianion $[\mathrm{Ti}(\eta^5\text{-}\mathrm{P}_5)_2]^{2-}$, which is stable enough to perform an X-ray crystal structure analysis.[3] I wonder if, in light of the present manuscript, he would justify the publication of a theoretical paper which would predict such molecule as "viable".
Theoreticians are often criticized because they carry out calculations after experiments were done, and they are encouraged to make predictions and to guide experiment. The successful synthesis of a molecule that was thought to be too unstable to be isolated is often published as a spectacular achievement of experimental chemistry. Why should a theoretical prediction of such a species that may serve as a guideline for synthetic efforts not become published in a prominent place, provided that the molecule is interesting for the general community?
The suggestion that "realistic counterions should be included in the computations" makes no sense considering the actual situation in synthetic chemistry. What is a *realistic* counterion? Much progress has been made in recent years in synthesizing weakly coordinating anions that possess unprecedented power in stabilizing positively charged compounds. The question whether a molecule can be isolated and identified in a condensed phase is asking for the experimental skills of a synthetic chemist rather than the wording of the theoretician. I doubt if the skepticism of an experimentalist is allayed by calling a theoretically predicted molecule "fleeting" rather than "viable". The only meaningful contribution by a theoretician in this regard is the calculated activation barrier for rearrangement or fragmentation and the calculation of the lowest-lying vibrational frequencies. Nowadays, this is done in most theoretical papers. In short, the suggestion to distinguish between "fleeting" and "viable" molecules is eyewash. Equally unrealistic is the suggestion to distinguish between papers that are addressed to the organic/inorganic synthetic community and to the physical chemical/chemical physical community. I found the whole discussion to be heavily biased toward the viewpoint

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[*] Prof. Dr. G. Frenking
Fachbereich Chemie, Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35039 Marburg (Germany)
Fax: (+49) 6421-282-5566
E-mail: frenking@chemie.uni-marburg.de

of a synthetic chemist who deals with molecules in a condensed phase. Gas-phase chemistry, which reveals important information about the intrinsic stability of molecules, is largely ignored. For example, ozone depletion chemistry attracts the interest of inorganic and physical chemists alike. The theoretically predicted stability of the dication He_2^{2+}, which was later observed in the gas phase,[4] is certainly interesting for most chemists. And a molecule like HArF that was identified in a low-temperature matrix by comparing its experimentally observed vibrational spectrum with the quantum chemical values[5] is certainly also interesting for the inorganic community, because it was the first neutral argon molecule that could be synthesized in a condensed phase.

3) The third part of the paper, entitled "Accuracy and Precision in the Quantum Chemical World" makes some comments which are known to most theoreticians. There is nothing particularly important in this part of the paper except that the authors emphasize the large errors which are inherent in calculated total energies. Chemical research rarely deals with *absolute* energies while *relative* energies including bond dissociation energies can be given for medium-sized molecule by present-days standards with an accuracy that matches or even surpasses experimental values, particularly for inorganic molecules. There is no reason to request that "the terms 'accurate' or 'accuracy' be used only very rarely in descriptions of molecular electronic structure theory."
4) The final section "Significant Figures in Theoretical Calculations" makes some suggestions concerning the presentation of numbers, which are routinely followed by most theoreticians these days. Any reasonable computational or theoretical paper has supplementary material which gives the calculated data with high numerical precision that allows other workers in the field to repeat the calculations. The example about the distance between Ithaca to New York City is amusing, but that is all. Once in while there are papers from newcomers that give an unrealistically high number of decimals for numerical values. However, the vast majority of theoretical work follows the accepted standard, which agrees with the suggestion of the authors.

In summary, I think that the paper does not offer any new reasonable suggestions which would be helpful for theoretical or experimental chemists. Therefore, I do not recommend publication of this work in *Angewandte Chemie*.

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[2] S. Aldridge, *Angew. Chem.* **2008**, *120*, 2382; *Angew. Chem. Int. Ed.* **2008**, *47*, 2348.

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