

## ***Interactive comment on “Electrical charging changes the composition of sulfuric acid-ammonia/dimethylamine clusters” by I. K. Ortega et al.***

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The topic of the manuscript is important. The paper's nicely written and easy to follow. However, the manuscript in the present form is unlikely to meet the high ACP standards and should be revised before it can be further considered for publication. A number of issues, some of them are quite serious, should be addressed in order to transform this manuscript into a high-quality paper that meets the ACP standards.

The paper is largely focused on computations of the evaporation rates using the previously obtained formation free energies using formulas (1) and (2). However, equation

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(2) (Su and Bowers, 1972) has been chosen out of a number ion- molecule collision models (Tammet and Kulmala, J. Aerosol Sci. 3 (2), 173, 2005) at no explanation.

The benchmarks performed and conclusions made in the present paper could be useful. However, the benchmarking methodology is questionable, no analysis of uncertainties and their propagation were carried out and some of the conclusions made based on the benchmarks are not fully justified.

Specific comments:

1. The methodology of benchmarking is far from perfect, while the quality of the data analysis may be affected by a number of methodological issues.

I agree with the Reviewer 1 that the authors should pay more attention to hydration, which strongly affects the thermochemical properties of the nucleating clusters, and move the focus of their study closer to neutral clusters/complexes. However, there exist other important issues to be addressed.

In particular, the data of Lovejoy and Froyd (2003), on which the comparison of computed evaporation rates of negatively charge sulfuric acid clusters (Table 1) are based, are denoted in the present study as “experimental data”. However, they all, except for the hydration free energies not considered in the present paper, are the semi-experimental estimates made based on experimental reaction enthalpies combined the theoretical, low level HF/6-31+G\*, reaction entropies. This means that the comparison of theoretical and computed evaporation rates shown in Fig.1 is not fully legitimate.

The authors should add a thorough comparison of experimental and theoretical B3RICC2 reaction enthalpies for the formation of negatively charged clusters before or after the Table 1 and discuss the aforementioned issues in some detail.

2. No analysis of uncertainties in the computed values and experimental data was included in the manuscript. The manuscript is too self-referential and does not properly acknowledge the relevant work done by others.

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The paper is based on the data obtained using the B3RICC2 method only. However, many clusters/complexes considered in the manuscript have been studied in the past by other quantum-chemical methods (e.g. J. Phys. Chem., A, 117, 133-152, DOI: 10.1021/jp3088435, 2013 (  $\text{HSO}_4\text{-}(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$  ),  $\text{HSO}_4\text{-}(\text{NH}_3)(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$  , Entropy, 13, 554-569, 2011 ( DMA-containing  $\text{H}_2\text{SO}_4$  clusters), Atmos. Chem. Phys., 9, 4031-4038, 2009, positively charge sulfuric acid-water clusters containing ammonia). The authors should include the data obtained in other studies in comparisons shown in the corresponding Figs. and Tables and a brief discussion on these matters in the revised manuscript.

The absence of any analysis of uncertainties in the computed and experimental data is another serious issue. Uncertainties in both the values produced by the locally developed B3RICC2 method and experimental data should be discussed in the Methods section, while their impacts on theoretical values obtained in the present paper and conclusions made based in the paper should be acknowledged in the Results and Discussion and Conclusion sections.

The large uncertainties in both experimental data and theoretical values related to the thermochemistry of pointed out in J. Phys. Chem., A, 117, 133-152, DOI: 10.1021/jp3088435, 2013. More recently, large uncertainties in the sulfuric acid and amine thermochemistry produced by the B3RICC2 method used in the present study have been pointed out in Chem.Phys.Lett 10.1016/j.cplett.2014.03.036 (2014).

The aforementioned critically important issues should be discussed and addressed in full in the revised manuscript. A thorough analysis of uncertainties and their impacts on the conclusions made in the present paper should also be included in the revised manuscript.

Technical corrections: 1. Page 1321. The cited author's name was misspelled. (Su and Bowers, 1972) should be replaced with ( Su and Bowers, 1972).

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