**Response to Interactive comment on "Electrical charging changes the composition of sulfuric acid-ammonia/dimethylamine clusters" by A. Nadykto (Referee)**

We want to thank the referee for his useful comments that have helped to improve the quality of our paper. Answers to the comments by the referee (in bold) can be found below.

**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 (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.**

We decided to use the newer parameterization by Su and Chesnavich (1982) instead. We have recalculated all the evaporation rates using this new parameterization and have updated the figures and tables accordingly. However, the uncertainty related to the specific approach used for calculating the ion-neutral collision rates is minor compared to the other uncertainties, and the choice of parameterization does not affect the qualitative conclusions (Kupiainen-Määttä et al., 2013).

**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.**

As we state in the response to referee 1, considering the effect of hydration would be interesting. However, at the moment this is unfortunately not possible due to the lack of large enough datasets of charged hydrated clusters. In this study we focus on understanding the effect of charging on cluster composition in the more simple dry case.

The relative stabilities of neutral clusters with respect to their composition have been discussed by Ortega et al. (2012). The aim of this work is to study the effect of charging on the composition of the most stable neutral clusters by examining the stabilities, *i.e.* the evaporation rates, of the charged counterparts of the stable neutral clusters, and determine the most likely resulting cluster after the charging process and the subsequent loss of molecules with high evaporation rates. The results presented in this work are very

useful in the interpretation of state-of-the art neutral cluster composition measurements conducted with chemical ionization.

**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 semiexperimental 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 referee is correct, in the case of negatively charged pure sulfuric acid clusters, the entropies provided by Froyd and Lovejoy (2003) are calculated by ab initio methods. We have now clarified this in the text.

**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.**

A large number of method comparison papers have been published recently by us, Nadykto et al. and others. The aim of this paper is not to continue the discussion about the superiority of different computational methods,or to compare absolute formation free energies, but instead to explore some general features related to the composition and stability of clusters. Therefore, instead of including a detailed comparison of cluster enthalpies and free energies, we have compared the general trends of evaporation rates versus composition for the two cases where large enough datasets were available. We have removed the computational benchmark section and added the evaporation rates calculated using semi-experimental formation free energies provided by Froyd and Lovejoy (2003 and 2012) and theoretical formation free energies provided by Herb et al. (2011 and 2012) calculated using the PW91PW91 method to the figures and discussion in the results section.

**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.**

**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 ( HSO4-(H2SO4)m(H2O)n, HSO4- (NH3)(H2SO4)m(H2O)n, Entropy, 13, 554-569, 2011 ( DMA-containing H2SO4 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 th 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.**

In general, the magnitude of uncertainties in the thermochemistry obtained with a specific quantum chemical method can be assessed by comparisons with results obtained with a higher level of theory or in the case of charged clusters, also by comparisons with measurement data. However, there is no unambiguous method to determine error limits for quantum chemical data for neutral clusters. We have included in the manuscript extensive discussion about the composition of negatively and positively charged clusters observed in different experiments, and these are in good agreement with our results. General trends in the composition of the most stable neutral clusters predicted with different quantum chemical methods are also in agreement (Herb et al. 2011, Nadykto et al. 2007, Nadykto et al. 2008, Torpo et al. 2007).

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

The parameterization has been changed to that by Su and Chesnavich (1982), so Su and Bowers (1972) reference has been removed from the text.

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