**Atmospheric
Chemistry
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Discussions**

Interactive comment on "Amine substitution into sulfuric acid – ammonia clusters" *by* O. Kupiainen et al.

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We thank Dr. Nadykto for his thorough referee comments, which helped us improve our manuscript. We respond here point by point to the comments.

1. Experimental value of the dipole moment of the sulfuric acid (Table 1, Kuczkowski et al. (1981)) is outdated and should be replaced with the one from more accurate recent measurements of Leopold et al. 2008 [1]. References: 1. Sedo, G.; Schultz, J; Leopold, K.R. (2008) J. Mol. Spectrosc., 251, 4-8.

We thank Dr. Nadykto for pointing out the more resent value for the sulfuric acid dipole moment, and we have recalculated the collision and evaporation rates using it. This increases the sulfuric acid evaporation rates by 3%, but does not change our results

qualitatively.

2. Amines are not the only organic species that may enhance nucleation rates in the Earth's atmosphere. A brief review of the frontier research on organics-enhanced nucleation should be included in the Introduction to the revised manuscript. The literature review should be written in a balanced way and should cover not only work done by the Helsinki group but also research published by others.

We will add the following paragraph about other nucleation mechanisms into the revised manuscript before the paragraph starting on page 30855, line 10.

"Once the initial sulfuric-acid-containing clusters have been formed, their growth is manly due to various organic vapors (O'Dowd et al., 2002a; Shantz et al., 2003; Maria et al., 2004). Organic compounds can also take part in the initial steps of sulfuric acid cluster formation (Zhang et al. 2004; Metzger et al., 2010; Nadykto et al., 2007; Xu et al., 2010). In coastal areas nucleation can also be driven by iodine compounds (O'Dowd et al., 2002b)."

3. The main problem of the paper is that the application of "a multi-step quantum chemistry method" (Ortega et al. 2012)[2]. The authors use non-standard composite B3LYP /CBSB7 /RI-CC2/augcc- pV(T+d)Z method , citing their previous work [2] as the only study supporting the validity of their newly invented multi-step method. This sort of the justification is at best questionable. Composite methods, such as G2, G3, G4 and their modifications are widely used in the computational quantum chemistry. However, they have been tested on a hundreds of species and validated against experimental data, while Ortega et al. (2012) [2] used theoretical calculations of only 4 reaction free energies and no experimental data to evaluate the predictivity of their new method. References: 2. Ortega, I. et al. (2012) Atmos. Chem. Phys., 12, 225–235

Dr Nadykto is correct that the validation of calculated complexation free energies, especially for neutral clusters/complexes, is quite difficult. There are very few direct experimental values available for neutral cluster reactions – that is indeed the main reason

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why so many calculations are being performed by different groups. Furthermore, the few experimental data that do exist are not completely reliable either, due to multiple issues – such as the van't Hoff linearization issue mentioned by Dr Nadykto, or the assumption that only certain clustering reactions take place. (For example, the diffusion-based measurement of the free energy for sulfuric acid – water complexation, often used as a validation benchmark, ignores the clustering of sulfuric acid with any other trace gases than water, which may be a quite significant error.) Thus, comparison to higher-level computational data is one of the few ways by which at least electronic energies (though not necessarily free energies) can be validated. However, also this has its problems, as discussed at length in previous studies by both Dr Nadykto's group and ours. Ultimately, the best test of any computational approach is whether or not it works, i.e. whether or not it matches the experimental observations of the overall phenomenon being modeled. For this work, the experiments directly corresponding to the simulations are the measurements of Bzdek et al on amine/ammonia exchange in sulfuric acid clusters. As shown in the article, agreement between experimental and computational results is extremely good.

In addition to the four clusters mentioned above, we compared the formation free energies of eight other clusters computed with our method and the widely used and well tested CBS-QB3 method (Montgomery et al., 1999) in the supplementary material of Ortega et al. (2012). The results were in good agreement, while our method was substantially faster. In addition, we have added comparison to more experimental data, see below for details.

For some reason, their new composite method include B3LYP density functional , which is incapable, according to their recent study (Kurten et al. 2006) [3], to describe the hydrogen bonding in large weakly-bonded complexes such as e.g. neutral anime-sulfuric clusters studied in their work. The B3LYP density functional was used in the pioneering studies of Bandy and Ianni (1999-2001) and was shown to fail in predicting the hydration free energies of small and simple atmospheric sulfuric acid hydrates [3]. Ref-

erences: 3. Kurten, T. et al. (2006) J Phys Chem A. 110(22):7178- 88.

According to Kurtén et al. (2006), the main error source in the formation free energy of the $H_2SO_4 \cdot H_2O$ cluster was the inaccuracy of the B3LYP electronic energy. They concluded that the best approach was to use a high-level correction to the electronic energy. They also concluded that the PW91 functional (used for instance by Herb et al., 2011 and Nadykto et al., 2011) does not describe cluster formation adequately, either. In our study, we use the B3LYP functional for geometry optimizations and frequency calculations, but, as opposed to Herb et al., (2011) and Nadykto et al., (2011), we use a higher level single-point energy calculation to correct the free energy.

A comparison of methods used in some recent studies for small sulfuric acid – ammonia and sulfuric acid – DMA clusters (Table 1) reveals that sulfuric acid addition energies computed with our composite method B3RICC2 are relatively close to those obtained with other methods using a high level of theory for the electronic energy, while pure density functional theory calculations result in significantly lower binding energies with no systematic difference between the B3LYP and PW91 functionals. This suggests that the differences between our results and results by Herb et al., (2011) and Nadykto et al., (2011) are not explained by the different choice of density functional in the geometry optimizations, but rather by the choice whether to use a high-level correction to the electronic energy.

Moreover, the comparison of their B3LYP /CBSB7 /RI-CC2/aug-cc-pV(T+d)Z method [2] with other composite methods generally makes little to no sense (Herb et al. 2011) [6]. The main problem is that while both high level ab initio methods with large basis sets and composite methods such as e.g. G3, G2 reproduce enthalpy changes within chemical accuracy, their predictions of stepwise changes in the Gibbs free energies have never been studied systematically and validated against large sets of experimental data. On the other hand, the agreement of enthalpies predicted by ab -initio and composite methods with experimental values may not necessarily be a sign of perfection. Although reaction enthalpies reported in the literature are denoted as 'experimen-

Table 1. Gibbs free energies (at 298 K and 1 atm reference pressure) for the addition of sulfuric acid to form ammonia and dimethylamine containing clusters. All values in kcal/mol.

	B3RICC2[a]	RI-CC2[b]	CBS-QB3[c]	B3LYP[d]	PW91[e]
$H_2SO_4 + H_2SO_4 \rightarrow (H_2SO_4)_2$	-7.89	-6.93	-8.66	-5.86	-5.59
$NH_3 + H_2SO_4 \rightarrow H_2SO_4 \cdot NH_3$	-6.41	-6.64	-7.19	-2.42	-3.32
$(CH_3)_2NH + H_2SO_4 \rightarrow H_2SO_4 \cdot (CH_3)_2NH$	-15.4	-13.66	-14.37	-11.07	-11.38
$H_2SO_4 \cdot NH_3 + H_2SO_4 \rightarrow (H_2SO_4)_2 \cdot NH_3$	-16.21	-14.43	-17.13	-10.96	-11.66
$H_2SO_4 \cdot (CH_3)_2NH + H_2SO_4$ $\rightarrow (H_2SO_4)_2 \cdot (CH_3)_2NH$	-19.48	-19.29	-20.71	-15.78	-14.3

(a) B3LYP/CBSB7//RI-CC2/aug-cc-pV(T+d)Z (Ortega et al., 2012)

(b) RI-MP2/aug-cc-pV(D+d)Z//RI-CC2/aug-cc-pV(T+d)Z (Kurtén et al., 2008)

(c) (Ortega et al., 2012)

(d) B3LYP/CBSB7

(e) PW91/6-311++G(3df,3pd) (Herb et al., 2011 and Nadykto et al., 2011)

tal thermochemical values', they are usually obtained indirectly, from the experimental reaction rates using the linearized form of the van't Hoff equation. The van't Hoff plot typically appears quite linear, with a correlation coefficient close enough to unity to be taken as indicating linearity within experimental uncertainty. However, if one subjects the same data to a non-linear least-squares analysis, employing the more general form of the van't Hoff equation the curvature of the van't Hoff plot may become evident. The difference between reaction enthalpies obtained from the same experimental data set using the oversimplified linear and 1more accurate non-linear form of the van't Hoff equation can be very large (>5 kcal/mol) [6]. The uncertainties in the van't Hoff analysis and discrepancies between direct calorimetric and indirect van't Hoff estimates of enthalpies are well-known; however, as for now, these issues remain unresolved. The authors should perform simple calculations of free energies small neutral clusters containing water and sulfuric 'acid for which experimental data are available, for example sulfuric acid monohydrates and di-hydrates. It would also be useful to include data for water dimer and a few complexes of H3O+ with (H2SO4) and (H2O), for which experimental data of Froyd and Lovejoy (2003) [7] are available, in the comparison. The deviation of B3LYP /CBSB7 /RI-CC2/aug-cc-pV(T+d)Z [2] from the experimental data should be estimated. References: 2. Ortega, I. et al. (2012) Atmos. Chem. Phys., 12, 225–235 6. Herb., J., A. Nadykto, and F. Yu (2011) Chem. Phys. Lett., 518, 7-14, 10.1016/j.cplett.2011.10.035 7. Froyd, KD, and Lovejoy, ER (2003) J. Phys. Chem. A 107, 9812–9824.

We agree with Dr. Nadykto that the ultimate way to evaluate the performance of a quantum-chemistry method is by comparison to experiments. However, in the case of the clusters we have studied, there have been very few experimental thermochemical data to compare to. After the submission of our manuscript, Froyd and Lovejoy (2012) published reaction free energies of ammonia addition to positively charged sulfuric acid – ammonia clusters. We have compared these with our computational results, and found good agreement (Table 2). We will include this comparison in the revised manuscript.

Table 2. (Table 4 in revised manuscript.) Experimental (Froyd and Lovejoy, 2012) and computational (B3LYP/CBSB7//RI-CC2/aug-cc-pV(T+d)Z) ΔG values (kcal/mol) for ammonia addition.

	exp. ΔG	comp. ΔG	difference
$NH_4^+ + NH_3 \rightarrow NH_4^+ \cdot NH_3$	-9.92	-8.79	1.13
$NH_4^+ \cdot H_2SO_4 + NH_3 \rightarrow NH_4^+ \cdot NH_3 \cdot H_2SO_4$	-9.95	-10.53	-0.58
$NH_4^+ \cdot NH_3 \cdot (H_2SO_4)_2 + NH_3 \rightarrow NH_4^+ \cdot (NH_3)_2 \cdot (H_2SO_4)_2$	-8.17	-8.83	-0.66

We have also performed some test calculations on negatively charged sulfuric acid – water clusters up to $HSO_4^- \cdot (H_2O)_4$ and $HSO_4^- \cdot H_2SO_4 \cdot (H_2O)_2$, and obtained water addition ΔG values mostly within 1 kcal/mol of experimental values by Froyd and Lovejoy (2003). We do not, however, wish to publish these results, because they are not related to the present study, and they are part of another manuscript under preparation. Furthermore, water addition energies to these clusters are much lower than addition energies of clustering reactions relevant for the present study. Thermochemical properties of water-containing clusters may be strongly related to large-amplitude motions of floppy water ligands (Partanen et al, 2012). Good agreement between measurements on water clusters and rigid-rotor-harmonic-oscillator (RRHO) based quantum-chemical calculations does not, therefore, necessarily imply that the quantum-chemistry method performs well (in the sense of accurately predicting e.g. electronic energies), but may simply be due to coincidental error cancellation. On the other hand, acid-base clusters are more strongly bound, and use of the RRHO approximation is, therefore, better justified even though it is certainly not perfectly valid even in this case.

As another justification for our multi-step method, we have compared our proton affinities with measured values (Table 3). Both our multi-step method and the PW91PW91/6-311++G(3df,3pd) method used by Herb et al. (2011) give values within 2 kcal/mol of the experimental results. The B3LYP/CBSB7 values without the higher

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Table 3. (First three columns as table 5 in revised manuscript.) Proton affinities (kcal/mol)

	experimental	B3LYP/CBSB7// RI-CC2/aug-cc-pV(T+d)Z	PW91PW91/ 6-311++G(3df,3pd)	B3LYP/CBSB7
HSO_4^-	309.51[a]	308.63	311.1	316.86
$(CH_3)_2NH$	222.16[b]	220.38	220.08	223.97
NH_3	204.02[b]	202.13	202.74	207.86

(a) Wang et al. (2000)

(b) Hunter and Lias (1998)

level single-point energy correction are somewhat further away. This shows that while B3LYP energies are, as pointed out by Dr. Nadykto, not accurate enough for hydrogen-bonded clusters, B3LYP geometries combined with higher-level energies still give quite good results. Since the bonding between acid and base molecules is closely connected to the relative proton affinities, these results also suggest that our multi-step method can adequately describe the proton-transfer reactions relevant to the clusters considered in this study. We will add these data to the revised manuscript.

Finally, we would like to emphasize that a major aim of this study was to compare our results with available experimental data. The experiments by Bzdek et al. (2010a,b) provided the clearest existing dataset concerning the competition between ammonia and DMA bound to sulfuric acid clusters. Our results on positively charged clusters are in excellent agreement with the experimental data.

4. The impact of the propagation of the uncertainties in the computed Gibbs free energies should be investigated thoroughly and conclusions about the role of amines made in the paper should be modifief with accounting for the aforementioned uncertancies.

We will add the following paragraph and tables after the last paragraph on page 30859:

"A comparison of computational and experimental free energy changes of ammonia

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addition to form small positively charged ammonia-containing clusters is presented in Table 4. The differences between the computational and experimental values are around 1 kcal mol^{-1} or less, but for larger clusters the error in the computational free energies may be larger. Computational proton affinities of HSO$_4^-$, (CH$_3$)$_2$NH and NH$_3$ are all within 2 kcal mol^{-1} of the experimental values (Table 5). Based on these comparisons and the benchmark calculations by Ortega et al. 2012, we estimate that the errors in free energy changes for adding a molecule to a cluster are below 2 kcal mol^{-1}. This corresponds to an error below two orders of magnitude in the evaporation rates. Finally, there remains the possibility that we have not found the global minimum energy structure for some cluster, which can lead to an error of even several kcal mol^{-1}."

and change the sentence on page 30862, line 21:

"We have roughly estimated the effect of such errors on the modeled concentrations by lowering the Gibbs free energy of one species at a time by 1 kcal mol^{-1} and rerunning the simulation."

into

"We have roughly estimated the effect of such errors on the modeled concentrations by lowering the Gibbs free energy of one species at a time by 1 kcal mol^{-1} (corresponding to a factor of 5.4 in evaporation rates) and rerunning the simulation."

and the paragraph on page 30863, line 5:

"In general, if a cluster is extremely stable or if it is extremely unstable with respect to one evaporation pathway, small errors in its evaporation rates are unlikely to affect the overall process. However, if a cluster can participate in different collision and evaporation processes with similar rates, the accuracy of the rate coefficients can be crucial."

into

"In general, if a cluster is extremely stable or if it is extremely unstable with respect to one evaporation pathway, even an error of one or two orders of magnitude in its

evaporation rates, due to an error of two or three kcal mol^{-1} in the corresponding free energy differences, is unlikely to affect the overall process. However, if a cluster can participate in different collision and evaporation processes with similar rates, the accuracy of the free energies can be crucial."

5. A brief discussion on the recently discovered controversy (Nadykto et al. 2011 [4]; Kurten, 2011 [5]) over the role of amines in the atmospheric nucleation should be included in the revised manuscript. References: 4. Nadykto, A.B. et al. (2011) Entropy, 13(2):554-569 5. Kurten, T. (2011) Entropy, 13, 915-923

We will change the sentence about amines in the introduction (page 30855, line 5)

"Recent results from the CLOUD experiment in CERN suggest that ammonia does not enhance the growth of sulfuric acid clusters enough to account for the nucleation rates observed in the boundary layer (Kirkby et al., 2011), but it has been seen in earlier modeling studies that amines stabilize sulfuric acid clusters significantly more than ammonia (Kurtén et al., 2008; Loukonen et al., 2010)."

to include a comment about the controversy

"Recent results from the CLOUD experiment in CERN suggest that ammonia does not enhance the growth of sulfuric acid clusters enough to account for the nucleation rates observed in the boundary layer (Kirkby et al., 2011). However, it has been seen in earlier modeling studies that amines stabilize sulfuric acid clusters significantly more than ammonia (Kurtén et al., 2008; Loukonen et al., 2010), although different quantum-chemistry methods give somewhat different results concerning the magnitude of the stability difference (Nadykto et al., 2011; Kurtén et al., 2011)."

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