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

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We thank Referee #2 for his/her comments, which helped us improve our manuscript. We respond here point by point to the comments.

1. There are several assumptions used in the kinetic model when calculating the dynamic cluster distribution. The clusters are assumed to be spherical and their radii were calculated from bulk properties. At the microscopic levels, the clusters might not be spherical any more as can be seen from the geometries of the clusters. How good are these assumptions for the bulk-based properties? How these assumptions affect the calculations of the evaporation rates especially for the neutral cluster?

The hard-sphere collision rate used for neutral-neutral collisions is proportional to the

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square of the sum of the radii of the two colliding species. Radii estimated from the coordinates of the clusters are somewhat smaller than those calculated from bulk properties, leading typically to a factor of three difference in collision rates with monomers. On the other hand, dipole-dipole interactions could conceivably increase the collision cross section compared to the simple hard-sphere case. Since the composition of individual neutral clusters cannot be measured, the collision coefficients cannot be determined experimentally, and we have to rely on theoretical approaches. At present, the most accurate way to study collision rates of neutral clusters would be by quantum molecular dynamics, but this is outside the scope of the present study. In any case, the uncertainty in the collision rates is probably within a factor of two or three, and thus smaller than the uncertainty in the evaporation rates due to the uncertainty in the free energies. We will add on page 30858, line 19 a reference to our earlier article (Ortega et al., 2012) where these uncertainties were discussed in more detail.

“The collision rates obtained with this simplified approach are estimated to be accurate to within a factor of 2 or 3 (Ortega et al., 2012).”

2. For the Gibbs free energy calculation, how do the basic set and level of theory affect the accuracy of the geometry and energy calculation? Even for clusters containing a known number of molecules, the potential energy surface is complex and how the authors assure that the pathway found is global? The errors associate with picking a wrong global minimum path may be huge; even several kcal/mol seems to significantly affect the results. Can the authors give an estimation of errors for the calculated free energies and the evaporation rates in Tables 2 and 3?

We have performed a fairly extensive conformational sampling, as described on page 30856, but of course we cannot be perfectly sure that we have found the global minimum energy structure for each cluster. We will move the sentence about the possible error due to limited sampling from page 30862, line 19 closer to the beginning of the Results section (see below). We will also add some more comparison with experiments after the last paragraph on page 30859:

Table 4. 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

“A comparison of computational and experimental free energy changes of ammonia 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^-, $(CH_3)_2NH$ 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}.”

3. The mechanism shown in Figure 1 seems ambiguous: the added or exited molecules are not shown in the scheme. Instead of showing a too-general scheme like Figure 1, the authors should show a potential energy surface to illustrates that the cluster becomes unstable upon addition of an amine to the ammonia cluster and become more stable after the ammonia is kicked out of the cluster;

By “unstable”, we simply mean that a cluster has an evaporation rate that is high compared to the rate at which it would collide with something. In order to clarify this, we have included the relevant collision and evaporation rates in Figure 1.

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Table 5. Experimental and computational (B3LYP/CBSB7//RI-CC2/aug-cc-pV(T+d)Z) proton affinities (kcal/mol)

	experimental	computational	difference
HSO_4^-	309.51[a]	308.63	-0.88
$(CH_3)_2NH$	222.16[b]	220.38	-1.78
NH_3	204.02[b]	202.13	-1.89

(a) Wang et al., 2000

(b) Hunter and Lias, 1998

References

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