Concerning the research article:

Methane sulfonic acid enhanced formation of molecular clusters of sulfuric acid and dimethyl amine

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Reply to referee #2:

We thank the referee for the positive review and constructive comments. Here, we present a point-to-point response to all comments (blue colored text).

The authors apply a kinetic model (ACDC) and quantum chemical calculations to study the contribution of gaseous MSA to cluster formation, with and without the presence of dimethyl amine (DMA) and sulfuric acid (H_2SO_4) molecules. Like referee #1 I am not an expert on these methods. However, I find the present paper somewhat incomplete and would like to see appropriate revisions made. My specific comments are as follows:

1. The authors do not consider hydration, i.e. the potential effect of H_2O molecules and associated ligand formation on the overall contribution of MSA to stabilization and growth of clusters. At least one more paragraph and figure should be dedicated to this mechanism to provide a more realistic evaluation (see also their comment on postponing calculations for larger clusters to later work in their Conclusions).

We acknowledge that, under atmospheric conditions, the clusters are likely contain one or more water molecules and we agree that this effect should be discussed. However, obtaining the actual free energies for each hydrated cluster requires vast computational effort, due to increased need of configurational sampling and increased expense of each electronic structure calculation.

However, while water is known to stabilize pure acid clusters strongly, its effect on clusters containing DMA is likely much less significant. As DMA is a much stronger base than water it is unlikely that water will break any of the DMA-MSA bonds, but more likely water will add to the existing cluster by forming new hydrogen bonds. Thus, the main formation pathways and formation rates are likely not significantly affected by hydration. This hypothesis is supported by some recent publications investigating this effect in detail, e.g. Henchel et al (2014).

The following text will be added to a revised manuscript:
"The clusters studied in this work do not contain water molecules due to the considerable additional computational effort required to obtain the necessary thermodynamic data. Hydration can be expected to stabilize weakly bound clusters more than strongly bound cluster and it is therefore conceivable that we will underestimate the contribution from some of the minor growth pathways. However, since DMA is a much stronger base than water, hydration is not likely to have a significant effect on the stability of clusters containing DMA. Therefore, the main growth pathways and growth rates are unlikely to change significantly due to hydration. See e.g. Henschel et al, (J. Phys. Chem. A, 118, 2599−2611, 2014) for further discussion."

2. Again, in the Conclusions the authors state that "The formation mechanism of MSA rich aerosols thus remains unknown". However, they have completely missed previous studies showing that DMS oxidation pathways via DMSO and MSIA produce MSA, in particular at lower temperatures and NOx levels (see, e.g., Davis et al., J. Geophys. Res., 103, 1657,1998; Barnes et al., Chem. Rev., 106, 940, 2006). At least one more paragraph needs to be included to consider these (additional) sources of MSA.

We are completely aware of the extensive literature on the formation mechanisms of MSA from DMS. The sentence: "The formation mechanism of MSA rich aerosols thus remains unknown" only relates to the formation of aerosols from a pre-existing pool of MSA (surely formed from DMS as the referee states). We will rephrase this sentence in the revised manuscript to avoid misunderstandings.

“At present, we are unable to explain MSA/H_2SO_4 ratios up to 30 % observed by Ayers et al. (1991), Huebert et al. (1996) and Kerminen et al. (1997) in small aerosol particles, but we have shown that MSA may enter the aerosol particle at the earliest possible stage and significantly assists in cluster formation”

3. Section 2.2: Only one value (without uncertainty range) has been adopted (from DalMaso et al.) for the condensational loss rate to preexisting particles. In view of the large uncertainties in the evaluation of such loss rates (up to at least a factor of 2, based on CN > 3 nm diameter particle measurement uncertainties alone), a rigorous uncertainty analysis needs to be included and also shown in Figs. 2 and 3. This error source has large implications for all of the following calculations and conclusions.

We acknowledge that the condensational sink is associated with substantial uncertainty. We have conducted the requested uncertainty analysis and have found that the value of the condensational loss rate has a modest, although noticeable effect on the ratio of the particle formation rates. The figure below shows the effect on r_2 and r_3 from varying the condensation sink from 10^{-3} s^{-1} to $5x10^{-3}$ s^{-1}, i.e. about a factor of two around the recommended value of $2.6x10^{-3}$ s^{-1}. These findings will be discussed in the revised manuscript and the figure will be included as supporting information.

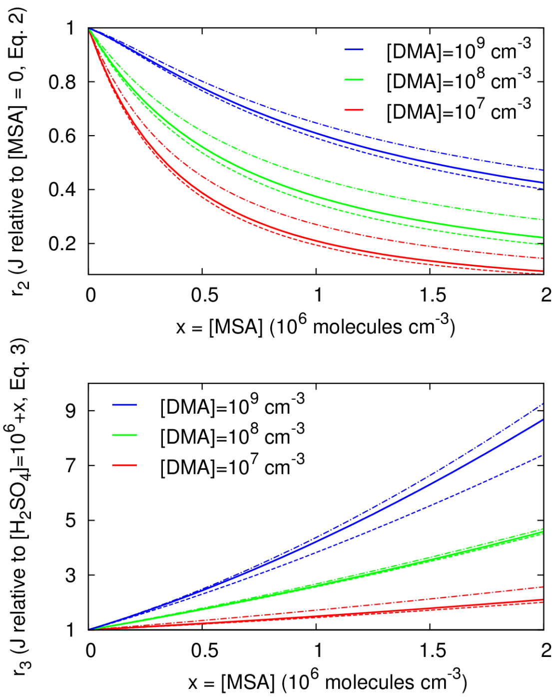

Figure: Plots of r_2 and r_3 ([H_2SO_4]=10^6 cm^{-3} and T=258 K) at varying concentrations of DMA and varying values of of the concensational loss rate of particles due to pre-existing aerosols. The loss rates are 10^{-3} s^{-1} (dotted lines), 2.6x 10^{-3} s^{-1} (solid lines, recommended value) and 5x10^{-3} s^{-1} (dash-dotted lines).

Further comments:

p. 18682, line 16: What are the typical uncertainties / limitations / inaccuracies of these "popular" methods? Discuss this and add at least one reference.

It is very difficult to predict uncertainties for untested systems wherefore a thorough benchmarking is conducted (results presented in Tables 1 and 2). Following, much of Section 2.1 (p. 18683) is dedicated to this question, including also several references. In the revised manuscript, Section 2.1 will be adjusted to clarify this procedure.

line 18: insert: ...is "considered" one of the...

OK

p. 18686, line 19: Explain this "surprise".

It is well known that strong acids and bases tend to form stronger hydrogen bonds and hence form more stable clusters. In terms of pK_a, MSA is a weaker acid than H_2SO_4, wherefore we would expect that the H_2SO_4 dimer was stronger bound than the MSA-H_2SO_4 cluster and that the MSA dimer would be the weakest bound of these three systems. However, the opposite trend is observed which, to us at present, is surprising. This will be clarified in the revised manuscript.

On behalf of all authors,

Nicolai Bork

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