

Interactive comment on “The effect of trimethylamine on atmospheric nucleation involving H₂SO₄” by M. E. Erupe et al.

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General comments:

The authors present results of laboratory measurements of the effect of trimethylamine (TMA) on water-sulfuric acid nucleation with atmospherically relevant concentrations of sulfuric acid and TMA. The topic of nucleation participating compounds is a hot topic as quantum chemical calculations has suggested that water-sulfuric acid nucleation can be enhanced by amines or other base molecules. The manuscript is well within the scope of the paper. The results of this kind of experiment can help identifying the compounds involved in the nucleation process. There are some issues that might need considering or revising before publication.

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RE: We thank the reviewer for helpful comments. Below we provide point to point response to each comment.

Specific comments:

1) p. 27678, line 27 is said that this UV-method for productions of sulfuric acid serves as a calibration. What about after adding amine? According to Kurten et al. (2010), CIMS might not be able to measure sulfuric acid if it is bound to base molecule as the charging is not possible. The same should be considered when using other CIMS for measuring the TMA concentration (p. 27680, lines 9-12), because it can be bound to sulfuric acid and though, not be charged in the CIMS.

RE: Keurten et al. (2001) show thermodynamics calculations of sulfuric acid-amine clusters and from these results, they made a conclusion that “CIMS may not be measuring all H₂SO₄”. First, there are a large variety of different types of “CIMS” instruments. Some CIMSs measure only gas phase free-H₂SO₄ molecules (which are not bound to any base molecules and water and therefore, they are not clusters and are in the gas phase); some are designed to measure clusters including those H₂SO₄ containing neutral clusters (naturally existing in the atmosphere or made in the flow reactor via nucleation), sometimes together with gas phase H₂SO₄; some intend to measure H₂SO₄ containing charged ion clusters (as opposed to neutral clusters); then there are also several different types of CIMSs that measure H₂SO₄ containing species from nanometer or micron size aerosol particles (much larger than clusters). Even only for gas phase H₂SO₄-CIMSs alone, there are several different types (e.g., depending on how made in each group; there are about 7-8 groups, to our knowledge), depending on ionization source, ionization cell’s pressure, type of collision dissociation, and focusing lense used. There are also numerous technical details and aspects, which also distinctively differentiate the instrument capabilities (sensitivity for free-H₂SO₄ gas phase, selectivity against other species including clusters, and interferences from artificial OH from water in the ionization cell, etc.). Even for the same CIMS instrument, depending on flow rate, pressure and voltage settings, the performances vary dramatically.

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Secondly, whether H₂SO₄ makes clusters or not is NOT relevant to the measuring of gas phase free-H₂SO₄. What we are trying to do is in our studies, we want to measure only free-H₂SO₄ molecules (present in the gas phase, not at clusters and not in aerosols) with CIMS. We want to compare our nucleation data with classical homogeneous nucleation theory (which has been used in this type of studies for years so far), and based on this theory, we want to know saturation ratio of H₂SO₄. This is the ratio of “free-H₂SO₄ molecule” contents present in the gas phase (which we like to measure) divided by the saturation vapor pressure of H₂SO₄ in a certain temperature. It is not that to measure the cluster concentrations is not important; on the contrary, it is extremely important and necessary when we look at nucleation at the molecular level. But not in the context when we want to measure saturation ratio of H₂SO₄. If H₂SO₄ molecules are bound to ammonia or amines, then we consider that they are already making small clusters, which is in fact a part of nucleation (at the early stage), and we don't consider them to calculate saturation ratio. On the hand, this can be an entirely different case for the CIMS which targets to measure clusters. This becomes serious issues in this case, due to a vast variety of different types of H₂SO₄ clusters (some of them are unidentified this moment) present in the atmosphere, low ionization efficiencies and low concentrations (even lower than free-H₂SO₄ gas phase concentrations) and short lifetimes of these clusters.

Additionally, with regard to if H₂SO₄-amine clusters can affect CIMS calibration or not: this is a valuable point. We know from Kurten et al. that this cluster formation is thermodynamically possible, but we don't know the kinetics information (how fast these reactions actually take place and how much they will produce clusters within short reaction times). But we know, from H₂SO₄ instrumentation development by Eisele-Tanner-Huey and measurements provided by our own group [Young et al., 2008], that cluster formation (e.g., H₂SO₄-H₂O leading to BHN) does not affect calibration within short reaction times (e.g., < 10 s). Considering that ammonia and amines commonly exist in water vapor, we can also assume that these calibrations were conducted under similar conditions where these base molecules likely also existed. But we need more

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systematic studies with accurate information of amine/ammonia concentrations which requires high sensitivity of detection (a new instrument needs to be developed), to determine such effects properly.

2) Here is the main issue of the whole manuscript: TMA is seen to enhance nucleation according to the slopes (fig. 2a and p. 27680, results) but no information of the sizes of the nucleated particles is provided. As Sipilä et al. (2010) suggested, the detection efficiency of the particle detector depends greatly on the size of the particles. Here, TSI model 3776 CPC is used which has a d₅₀ at 3 nm, so if the mean size of the particles before adding TMA is around 2 nm and assuming a log-normal distribution the tail of the distribution is measured by the CPC. When adding the TMA the particles will grow even if the TMA is not participating on the nucleation, but gets bound on the sulfuric acid molecules, which are condensed on the surface of the particle after nucleation. This also explains the different slopes compared to the ones found in Sipilä et al.. This also would explain the fact that higher sulfuric acid concentrations means lower enhancement due to the larger particles caused by condensed sulfuric acid. The dependence of the EF of the RH in figure 3a) can also be explained with this same issue due to the fact that particles are lot smaller at lower RH. Also the condensed sulfuric acid on the surface of the particles are more accessible for the TMA to get bound to when there is less water molecules shielding the sulfuric acid molecules.

RE: These are valuable points. To answer directly some of these questions, we need aerosol size distribution data – unfortunately due to some technical problems, we don't provide size distributions in the present study. We have included this paragraph in Discussion (Lines 250-268): “The TMA EF dependence on [H₂SO₄] and RH is similar to the case of NH₃ [Benson et al., 2009], indicating that these ternary base species are more important at lower RH and lower [H₂SO₄]. However, there may be also additional technical issues related to this trend. Depending on different aerosol sizes, CPC has different counting efficiencies especially for sizes close to 3 nm, which can affect the determination of relative importance of ternary species in nucleation (or EF); for in-

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stance, under different RH. It is also possible that ammonia or amine molecules directly condense or are adsorbed on particles to further interact with H₂SO₄ (via acid-base reactions or heterogeneous reactions), which can likely affect the size (and growth) after nucleation. If this is the case, however, then one would expect that these molecules also can participate in nucleation at the cluster level. Whether low or high RH will promote more such effects is unclear. Base molecules (or any ternary species) can compete with water on sulfuric acid particles, but usually the interactions between acid and base are much stronger than between H₂O and H₂SO₄. There are also always much more H₂O molecules than base molecules present in the atmosphere and in the nucleation reactor. Also, these “hygroscopic” or “water-soluble” base molecules, on the other hand, may prefer higher RH, because in wetter conditions (more “liquid-like”) they can stick more easily and acid-base reactions can be more plausible even for small size particles. Additionally, the dependence of the EF of the RH, can be also in part due to different ammonia impurities at different RH [Benson et al., 2010a; Benson et al., 2010b] [Benson et al., 2010a; Benson et al., 2010b], although this cannot explain the same trend for EF vs. [H₂SO₄].”

3) The concept of using slopes to determine the number of different molecules in the critical cluster (p. 27680-27681) might not be plausible with multicomponent systems due to the possible local minimums and maximums. This does not mean that the numbers presented here wouldn't be right but this approach should not be used so straight forward without any consideration and justification.

RE: We agree. We have replaced the sentence “An examination of the slope, which according to [Kashchiev, 1982; McGraw and Zhang, 2008], can be interpreted as the number of molecules of H₂SO₄ in the critical cluster ($n_{\text{H}_2\text{SO}_4}$) reveals similarities between TMA and NH₃ on H₂SO₄ nucleation.” with “We have used the slope of Log J vs. Log [H₂SO₄] to determine the number of H₂SO₄ molecules ($n_{\text{H}_2\text{SO}_4}$) in the critical cluster based on the classical nucleation theory by assuming that there is only one maximum of Gibbs free energy for nucleation [Kashchiev, 1982; McGraw and Zhang,

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2008]. But recent theoretical study has also suggested that such assumption may not be valid for a multicomponent nucleation system and there may be several local minima and maxima [Vehkamäki, 2010].” (Lines 175-180)

4) Brilliant observation (p. 27681, lines 20-21) that the ammonia will arise always from the water used for BHN and though, these measurements are always, as said here, pseudo-BHN. Another good observation is that comparing slopes taken from field measurements and from laboratory measurements are not necessarily comparable and these field measurements should always be classified and filtered according to temperature and RH.

RE: From these reasons, it is possible that we have underestimated the effects of amines in nucleation. Therefore, it is critical to thoroughly measure aerosol precursors including ammonia and amines and we have to be careful when we try to compare different studies directly.

5)p. 27683, line 24 is said that “it is commonly believed that species other than sulfuric acid and water is needed to explain aerosol nucleation in the atmosphere. . .”. This might be pretty strongly said, as looking for the third compound has lead to very minor advances and it is known (and also mentioned in this manuscript) that sulfuric acid is the key.

RE: We agree. We have reworded this as: “In some atmospheric conditions, species other than H₂SO₄ and H₂O are also needed . . .”.

References:

Kurtén, T., Petäjä, T., Smith, J., Ortega, I. K., Sipilä, M., Junninen, H., Ehn, M., Vehkamäki, H., Mauldin, L., Worsnop, D. R. and Kulmala M.: Chemical ionization mass spectrometry (CIMS) may not measure all gas-phase sulfuric acid if base molecules are present Atmos. Chem. Phys. Discuss., 10, 30539-30568, 2010.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski,

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J., Mauldin III, Roy L., Hyvärinen, A.-P., Lihavainen, H. and Kulmala, M.: The role of sulphuric acid in atmospheric nucleation, *Science*, 327, 5970, 1243-1246.

Additional References:

Benson, D., et al. (2010a), Ternary homogeneous nucleation of H₂SO₄, NH₃, and H₂O under conditions relevant to the lower troposphere, *Atmos. Chem. Phys. Discuss.*, 10(9), 22395-22414.

Benson, D. R., et al. (2009), Laboratory-Measured H₂SO₄-H₂O-NH₃ Ternary Homogeneous Nucleation Rates: Initial Observations, *Geophysical Research Letters*, 36, L15818.

Benson, D. R., et al. (2010b), Atmospheric homogeneous nucleation of H₂SO₄ and H₂O, *Atmos. Chem. Phys. Discuss.*, 10.

Kashchiev, D. (1982), On the relation between nucleation work, nucleus size, and nucleation rate, *J. Phys. Chem.*, 76, 5098-5012.

McGraw, R., and R. Zhang (2008), Multivariate analysis of homogeneous nucleation rate measurements. Nucleation in the p-toluic acid/sulfuric acid/water system, *J. Chem. Phys.*, 128.

Vehkamäki, H. (2010), Molecular Modeling of Atmospheric Clusters, in 2010 International Aerosol Conference, edited, Helsinki, Finland.

Young, L. H., et al. (2008), Laboratory studies of sulfuric acid and water binary homogeneous nucleation: Evaluation of laboratory setup and preliminary results, *Atmos. Chem. Phys.*, 8, 1-20.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 27673, 2010.