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## ***Interactive comment on “Observation of neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements” by J. Zhao et al.***

**Anonymous Referee #1**

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Zhao et all have performed an experimental study on clusters containing sulfuric acid and various amines both in the laboratory and in ambient conditions. Such clusters are widely believed to be the major players in atmospheric new-particle formation. The topic of the study is thus interesting, and relevant for a large fraction of the readers of ACP. As far as I can tell (my background is in modeling, not experiments), the study has been diligently carried out using appropriate methods (see below for a few small caveats), and the results have been presented in a clear and concise manner. The manuscript is therefore well worthy of publication in ACP, after some minor revisions.

The experimental methods used seem to have two main weaknesses. Neither of these

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is serious enough to invalidate the authors' analysis and their central conclusions, but they should perhaps be addressed in greater details.

1. First, the sulfuric acid concentrations required for the "SASA" analysis are quite high, in the  $10^8 \text{ cm}^{-3}$  range, which corresponds to rather polluted and sulfur-rich air. How well are the results applicable to cleaner air, with sulfuric acid concentrations in the  $10^6\text{...}10^7 \text{ cm}^{-3}$  range? Might bases such as amines play even greater roles in such conditions, as the barrier for  $\text{H}_2\text{SO}_4$  nucleation is higher due to the lower acid saturation ratios?
2. Second, what is the mass resolution of the mass spectrometer used? Without a time-of-flight (TOF) module, my understanding is that the resolution is only about 1 a.m.u., which does not allow for unambiguous assignment of peaks to elemental compositions. How sure can the authors be that e.g. their "tetramer + amine" peaks really correspond to  $(\text{HSO}_4^-)(\text{H}_2\text{SO}_4)_3^* \text{AMI}$ ?
3. As in many other nucleation studies, the first nucleation theorem is applied a bit too enthusiastically and uncritically. The simplest formulation of the theorem (slope of  $\log J$  versus  $\log [X]$  gives the number of  $X$  in the critical cluster) only applies in an idealized case where the  $N$ -dimensional (where  $N$  is the number of compounds, e.g. 2 or 3 in the case of sulfuric acid nucleating with an amine and possibly water) free energy surface has precisely one saddle point, corresponding to the critical cluster, and no minima, at least not on the nucleation path. For a chemically complicated real system like sulfuric acid - amine - water, it is likely that there exist local minima (and possibly local maxima) smaller than the actual critical cluster - based on computed evaporation rates the cluster with two acids and one or two amines actually seems to be such a local minimum. (Local minima are explicitly known to exist for the case of sulfuric acid hydrates, which can fortunately be fairly simply corrected for in the theory.) In this case, the  $\log J$  versus  $\log [X]$  slopes will not directly correspond to the number of molecules of  $X$  in the critical cluster. One reason for this is that in the presence of local minima, both coagulation (collisions between small clusters) and cluster fission (non-

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monomer evaporation) start to play important roles. The "slope" form of the nucleation theorem has been derived under the assumption that only monomer condensation and evaporation take place. This is not to say that the slope information is useless - it is still definitely valuable information - but a note of caution on the interpretation of the slope data would be warranted.

4. The authors assume that clusters with less than four sulfuric acids, or four acids and more than one amine, always lose amines after charging. This is well supported by both experiments on sulfuric acid - ammonia clusters, and by computed evaporation rates. Thus, the measured amine content of the clusters represents a lower limit for the real amine content of the neutral clusters. This could be explicitly mentioned.

5. The scheme in figure 2 assumes that clusters grow and shrink only by monomer addition or evaporation. How well justified is this given the high stabilities of some of the clusters?

## Minor issues:

-On page 11, lines 24-25, the statement "the high bonding energy of the sulfuric acid dimer exclusively prevents clustering of this ion with other compounds" is a bit ambiguous. Presumably the authors mean that the  $\text{HSO}_4^-$  ion will cluster exclusively with  $\text{H}_2\text{SO}_4$  due to the high bonding energy of the formed cluster? This is a very reasonable assumption, but the sentence ought to be clarified.

-On page 13, line 24, it might be mentioned that the C2 amine could be either dimethylamine or (mono)ethylamine.

-On page 16, line 4, "loose" should be "lose".

-In the caption of figure 2, the authors might explicitly mention that the scan concerns the negative ions. This is of course clear from the text, but should be stated in the caption as well.

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