

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

J. Zhao et al.

jzhao@ucar.edu

Received and published: 28 September 2011

The authors would like to thank the reviewer for his/her valuable comments. The reviewer's comments and concerns are addressed point by point below.

1. The purpose of adding high concentrations of sulfuric acid (in the $1\text{e}8\text{ cm}^{-3}$ ranges) in the SASA experiment is to amplify signals corresponding to sulfuric acid-amine clusters so that these clusters can be more easily distinguished from their corresponding backgrounds. In cleaner air, although bases might play even greater roles in helping sulfuric acid clusters to surmount the nucleation barrier, measurements of sulfuric acid-amine clusters are more difficult because these measurements suffer from high

C9446

interferences from other compounds, mainly organics (last paragraph on p19750).

2. The mass resolution of Cluster CIMS is 1 amu. The sulfuric acid-amine clusters were identified according to their nominal masses. However, considering the abundance and high basicity of the amines, they are the best candidates for reactions with sulfuric acid and its neutral clusters compared to other organic compounds with the same nominal masses. To further clarify this, we have added “with a mass resolution of 1 amu” to the last paragraph on p19737.

3. We agree with the reviewer that there might exist local minima smaller than the actual critical cluster for a chemically complicated real system like sulfuric acid - amine - water and that the $\log J$ versus $\log [X]$ slopes might not directly correspond to the number of molecules of X in the critical cluster. We have deleted the sentences and the cited references related to nucleation theorem that are not important for the paper (first paragraph on p19732).

4. We fully agree with the reviewer that the measured content of the sulfuric acid-amine clusters represents the lower limit of the neutral clusters. This has been incorporated on p19744, “Hence, the measured concentrations of the sulfuric acid-amine clusters represent the lower limit values of the corresponding neutral clusters.”

5. The proposed mechanisms in schemes 1 and 2 represent the simplest possible formation pathways for the sulfuric acid-amine clusters by assuming that the clusters grow and evaporate only by monomer addition and evaporation. Direct experimental evidence for the stabilities of most of the neutral clusters is still currently lacking. This has been incorporated into the text on p19748.

-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 HSO_4^- ion will cluster exclusively with H_2SO_4 due to the high bonding energy of the formed cluster? This is a very reasonable assumption, but the sentence ought to be clarified.

C9447

The reviewer is correct. We have reworded the sentence as "For example, the high bonding energy (about 42 kcal mol⁻¹) between HSO₄⁻ and H₂SO₄ in sulfuric acid dimer ion (HSO₄⁻ H₂SO₄) exclusively prevents clustering of this ion (HSO₄⁻) with other compounds (Lovejoy and Curtius, 2001)."

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

We have added "ethylamine" in the text (p19741).

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

It has been corrected.

-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.

The caption has been modified per the reviewer's suggestion.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 19729, 2011.

C9448