2. Reviewers #2

Review #2 Summary: This manuscript presents a theoretical study on the interactions between succinic acid (SUA) and sulfuric acid (SA) – ammonia (AM)/dimethylamine (DMA) clusters in presence of water molecules. The application of the results in atmospheric new particle formation (NPF) is discussed. Overall, this study tackles how a multi-component system, which is more realistic in terms of atmospheric NPF, evolves and provides some of the novel insights into the interaction between organic acids and SA-base clusters. On the other hand, the results and their implication could have been presented in a way that is easier to be followed. The authors are advised to address the following concerns before a recommendation can be made.

Thanks the reviewer for insightful comments.

-Comment #1. The atmospheric concentrations of NPF precursors are especially important when one wants to discuss the implication of a theoretical calculation. In fact, the authors failed to find a reliable source for the key species that appear in this study. The concentration of SUA is referred from Kawamura and Kaplan, 1987, which actually presents concentrations of particulate SUA and should not be used in a clustering system. The concentration of SA is set at 10ˆ5 molecule cmˆ(-3), which is at least one order of magnitude lower than many measurement values.

Thanks the reviewer for pointing out the misuse of the particle-phase concentration for (SUA) for calculations of atmospheric-relavent cluster concentration ratio. However, there is few literatures reporting the gas-phase concentrations for dicarboxylic acids, since these acids are belived semi-volatile and primarily partion into the particle phase. Only one available study was by *Limbeck et al.* [2001], which based on in-situ observations has derived particle/gas partitions for several primary dicarboxylic acid species under the atmospheric condition, including succinic acid we are looking at. Based on their's study, the gas-phase concentration of SUA is about 6.7 ng/m^3, which corresponds to $3x10^7$ molecules/cm^3. Therefore, we assume a value of $1x10^7$ molecules/cm^3 to represent the gas-phase concentration of SUA in calculation in this work. Please refer to Table 3 in the answer to comment #1 of reviewer 1 for the typical values of atmospheric concentrations.

Also, the reported concentrations for sulfuric acid in the atmosphere is typically about 10^5-10^7 molecules cm^{-3} (Weber et al., 1999; Nieminen et al., 2009; Zhang et al.,2012). Therefore, in the revised manuscript, we used the updated concentrations of SUA and SA to re-estimate the SUA/SA ratio range.We have modified the desciription in section 2. "**Computational Methods**", and the related discussions in section 3.4 "**Atmospheric Implication**". Please refer to the answer to comment #3 of reviewer 1 for the modifications of manuscript since the first reviewer have similar concern.

-Comment #2. In many cases, the authors compare delta(G) and then conclude that SUA (and/or other molecules) either promote or hinder the growth of clusters. This is fine when the difference between two delta(G) is large. On the other hand, one probably wants to include the concentrations of gaseous precursors and clusters, do the math, and then obtain something like a branching ratio when the difference is small, instead of simply using "promotion or hindrance". Following this point, I would like to see a clear definition of "promotion or hindrance" in the manuscript. Is it a

comparison between the current step of reaction/clustering or a comparison of the further growth of formed cluster from the current step?

Thank the reviewer for the helpful suggestion. We agree with the reviewer that a branching ratio-like parameter can help us to get a clearer result of "promotion or hindrance" from dynamical view. Hence, future works are needed to get the dynamical data such as rate constants, branching ratio. but in this work, we mainly focused on the thermodynamical study. Considering the reviewer's comment and suggestion, we did additional calculations of bonding ratioes for several primary clustering reactions (Table 6). It also can help us get a clearer result of "promotion or hindrance". Please see the answer to coment #1 of reviewer 1 for more detials about bonding ratios. We have added these discussions to main text (**Lines 369-386**).
The "promotion or hindrance" is a comparison of the further growth of formed cluster from the current steps. When we say "promotion or hindrance", we normally say it from energectic perspetive. For example,
Lines 313-315: "the clusters containing both the base and organic acid (e.g., SA·DMA·SUA) are capable of further binding with acid molecules to promote their subsequent growth."
Here we conclude that the clusters containing both the base and organic acid promote their subsequent growth because the SA addition free energies to SA·DMA·SUA are negative, showing a potential to bind more SA moelcules.

-Comment #3. Given the comprehensive calculation that has been performed, I suppose the authors could suggest a pathway (or multiple possibilities with relative weight for each) on how the complex clusters are formed? e.g., how is (SA)(DMA)(AM)(SUA)(W)6 formed? Will water be added to cluster at the beginning? A summary like this would be welcome, even for a smaller cluster if such a pathway is too complex for a big cluster.

According to the reviewer's helpful suggestion, the summary and the figure about the possible pathways have been added in the revised manuscript (Fig. 9). If we consider the effect of atmospheric concentrations, SA most likely binds to water molecule rather than other precursors (SA, AM, DMA, or SUA), because water vapor is much more abundant than other precursors. For example, the number concentration of water molecules at RH=50% and T=298K is at 10^{17} order of magnitude, with a bonding ratio of 0.1, which is much higher than that for other precursors shown in Table 6. Therefore, the disscussions about clustering pathways in main text are mainly carried on from energy perspective.

Lines 389-392:
"Fig. 9 depicts the relative stability of cluster formation from the interaction among SUA, SA, base, and W molecules, showing that the SA•DMA cluster is most stable for the dimers and the SA•DMA•SUA or $(SA)_2$•DMA is most stable for the trimers."

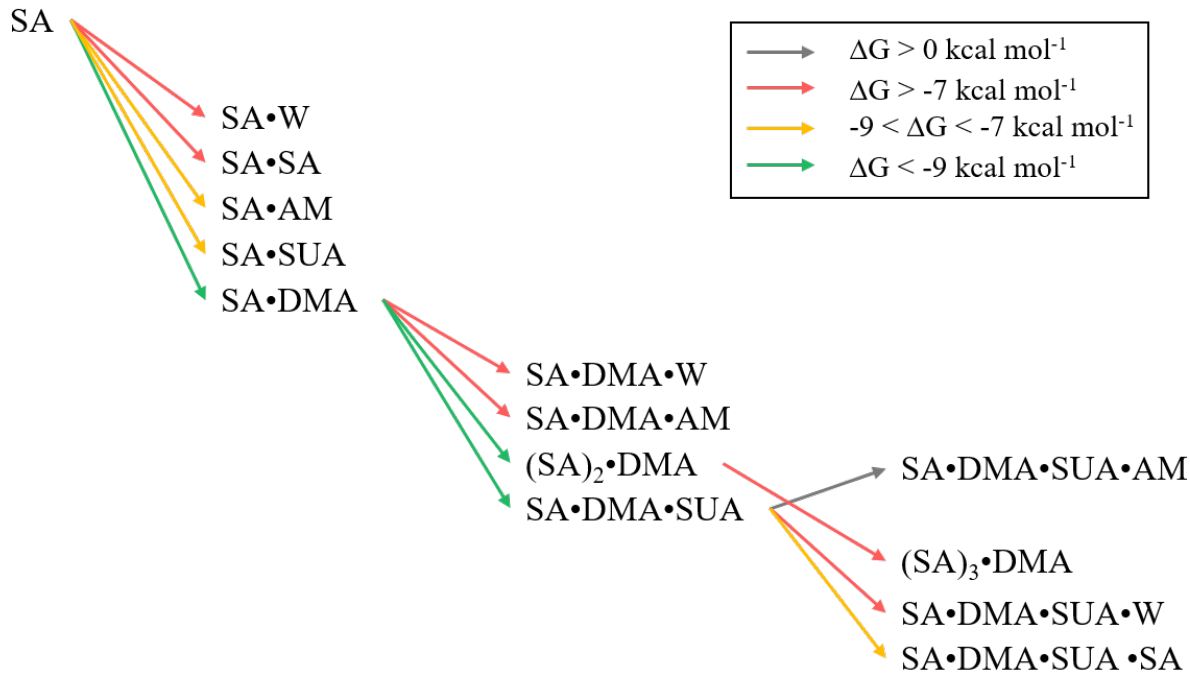

Fig. 9. Possible pathways for formation of the complex clusters.

-Minor comments 4. The reference list should be carefully checked. Some of the references are not in an alphabetical order. Also, I suppose what in Line 75 should be "Xu and Zhang (2012)".

We have revised the reference citing format accordingly.

Reference

Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J. , Chow, J. C., and Watson, J. G.: Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, *J. Geophys. Res.*, *112*, D22S27, https://doi.org/10.1029/2006JD008011, 2007.

Nieminen, T., H. E. Manninen, S. L. Sihto, T. Yli-Juuti, I. R. L. Mauldin, T. Petäjä, I. Riipinen, V. M. Kerminen, and M. Kulmala (2009), Connection of Sulfuric Acid to Atmospheric Nucleation in Boreal Forest, *Environmental Science & Technology*, *43*(13), 4715-4721, doi:10.1021/es803152j.

Weber, R. J., P. H. McMurry, R. L. Mauldin III, D. J. Tanner, F. L. Eisele, A. D. Clarke, and V. N. Kapustin (1999), New Particle Formation in the Remote Troposphere: A Comparison of Observations at Various Sites, *Geophys. Res. Lett.*, *26*(3), 307-310, doi:doi:10.1029/1998GL900308.

Zhang, R., A. Khalizov, L. Wang, M. Hu, and W. Xu (2012), Nucleation and growth of nanoparticles in the atmosphere, *Chem. Rev.*, *112*(3), 1957-2011, doi:10.1021/cr2001756.