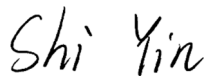


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Dear Prof. Jason Surratt,

Many thanks for your attention to our manuscript. We have revised our manuscript (egosphere-2023-1649) “*Organosulfate Produced from Consumption of SO<sub>3</sub> Speeds up Sulfuric Acid-Dimethylamine Atmospheric Nucleation*”, according to reviewers’ comments. We appreciate the reviewer’s suggestions and comments, and have addressed all their issues and questions. We list below the corresponding changes and explanations we have added to the text, as requested by the reviewers. A marked copy of the manuscript with yellow highlight annotation for our changes were also uploaded for the Editor and Reviewers convenience.

Best regards,



Shi Yin

## Response to referee #1:

### Referee's Comments to Author:

*The manuscript entitled 'Organosulfate produced from consumption of SO<sub>3</sub> speeds up sulfuric acid-dimethylamine atmospheric nucleation' by Zhang et al. presents a detailed theory of the potential role of gas-phase glycolic acid (and its organosulfate derivatives) in new particle formation (NPF). The authors rely on quantum chemical calculations to define the most reasonable pathway and formation product of the reaction between glycolic acid and SO<sub>3</sub>, leading to organosulfates. Also, kinetic modeling is used to understand the most efficient clustering with dimethyl amines. Their findings are backed up with atmospheric observations from Mt. Tai in China where intense NPF events have been observed. The authors also report observations from other locations around the world where the role of glycolic acid in NPF might be important but has been not evaluated earlier. First of all, I would like to acknowledge the authors for a very detailed, easy to follow manuscript. As mentioned by the authors, there are very few studies which tackle the role of organic acids in NPF, mainly due to the scarcity of their measurements. The results presented in this manuscript improve our understanding of the formation pathway of organosulfates from glycolic acid and sulfate and the role of the most stable organosulfate product in clustering with dimethyl amine and its role in NPF. The paper calls for an inclusion of organosulfate chemistry in global models when evaluating NPF and for more studies tackling hydroxyl acids in the gas phase from an observational and measurement point of view. The paper is well written and the findings are sound, I recommend publication after tackling the suggestions listed below.*

### General comments:

1. *Could the authors comment on the role of relative humidity (availability of H<sub>2</sub>O clusters) and how these affect the formation of GAS and GASA. Please see results by Tsona et al. (<https://doi.org/10.1016/j.atmosenv.2019.116921>)*

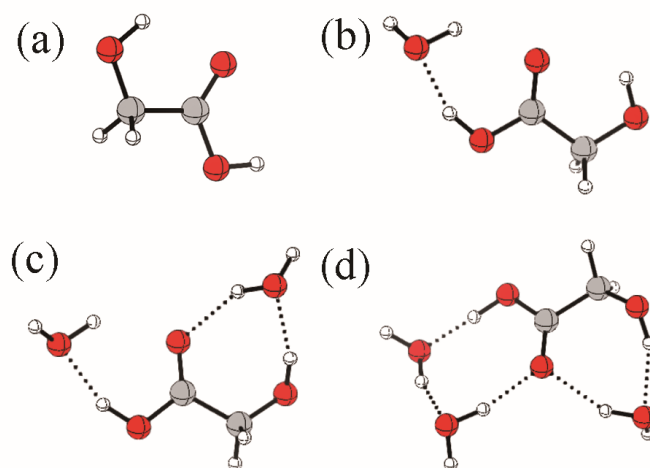
### Author reply:

Thanks for the referee's question and suggestions. In order to comment the role of relative humidity (availability of H<sub>2</sub>O clusters) and how these affect the formation of GAS and GASA, we further explored hydration process of glycolic acid (GA) in the gas phase, according to the method reported by Tsona et al. (Tsona and Du, 2019) at tropospheric temperatures (258 K, 278 K, 298 K) and ambient pressure. The lowest-energy structure of clusters GA-*n*(H<sub>2</sub>O) (*n* = 0 - 3) (Figure S2), equilibrium distribution of GA hydrates (Figure S3), thermodynamic data of the stepwise hydration of GA (Table S2), and relative equilibrium abundance of GA hydrates at different degrees of humidity (Table S3) were obtained and added to the revised supporting information of the manuscript. Following discussions were added to page S7 in our modified supporting information materials.

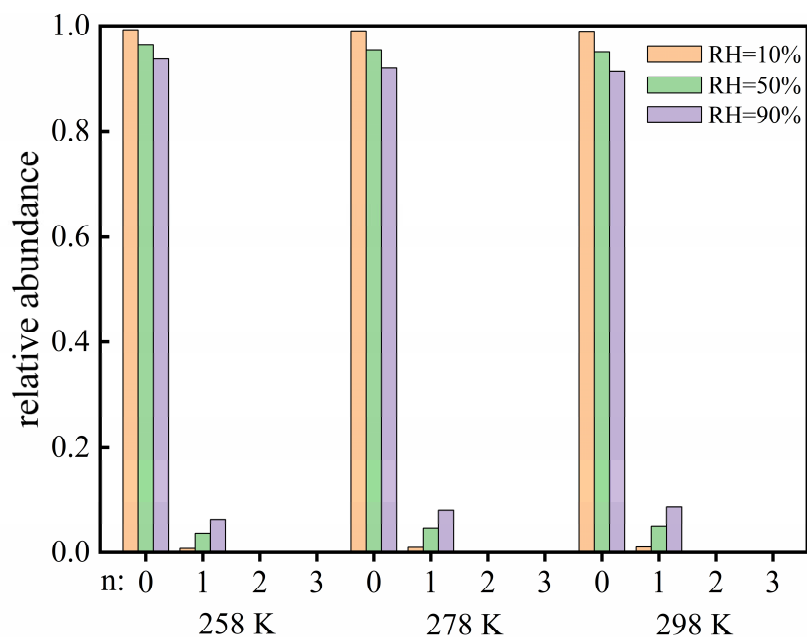
“As shown in Table S2, the first water addition to GA at 298 K, with a Gibbs free energy change of  $-0.71 \text{ kcal mol}^{-1}$ , are more favorable compared to the second and the third water additions, having free energy changes of  $2.98$  and  $0.18 \text{ kcal mol}^{-1}$ , respectively. Additionally, the energies decrease as the temperature decreases, and the energy of first water addition reaches to  $-1.96 \text{ kcal mol}^{-1}$  at 258 K. Although the abundances of hydrated GA clusters, including mono-, di- and tri-hydrates, are slightly increased with increasing RH (relative humidity) (Figure S3 and Table S3), the hydration of GA is still weak at high RH. For example, the relative equilibrium abundance of GA hydrates is less than 7% at  $\text{RH} = 90\%$  and 298 K. Therefore, the relative abundance of unhydrated GA is dominant at varying temperature and RH considered.”

Following sentences were also added to line 175 in page 6 in our modified manuscript.

“These results indicate that both reaction pathways for  $\text{GA} + \text{SO}_3$  are favorable with the catalysis of  $\text{H}_2\text{O}$  to generate GAS and GASA, respectively. Therefore, as the relative humidity (RH) increases, it should be conducive to the formation of GAS and GASA. The abundances of hydrated GA clusters  $\text{GA}-n(\text{H}_2\text{O})$  ( $n = 0 - 3$ ) were also calculated at different RH (Figure S3 and Table S3). The relative equilibrium abundance of GA hydrates is less than 7% at  $\text{RH} = 90\%$  and 298 K. Since the hydration of GA is weak, the effect of the hydrated GA clusters to the formation of GAS and GASA is not further considered.”



**Figure S2** Lowest energy geometries of  $(\text{GA})(\text{H}_2\text{O})_n$ , optimized with the M06-2X/6-311++G(3df,3pd) method. The color coding is red for oxygen, grey for carbon, and white for hydrogen. The number of water molecules increases from (a) where  $n = 0$  to (d) where  $n = 3$ .



**Figure S3** Equilibrium distribution of glycolic acid hydrates at different degrees of humidity (RH = 10%, 50% and 90%) and different temperatures (258 K, 278 K, and 298 K).

**Table S2** Thermodynamic data (in kcal mol<sup>-1</sup>) of the stepwise hydration of glycolic acid (GA) calculated by the M06-2X/6-311++G(3df,3pd) method.

n	$\Delta G$		
	258 K	278 K	298 K
	$(GA)(H_2O)_{n-1} + H_2O \leftrightarrow (GA)(H_2O)_n$		
1	-1.96	-1.33	-0.71
2	1.77	2.38	2.98
3	-1.07	-0.44	0.17

**Table S3** Relative equilibrium abundance of GA hydrates at different degrees of humidity (RH = 10%, 20%, 40%, 50%, 90% and 100%) and different temperatures (258 K, 278 K, and 298 K)

**258 K**

RH	10%	20%	40%	50%	90%	100%
n=0	0.98970000	0.97970000	0.96020000	0.95070000	0.91460000	0.90600000
n=1	0.01026766	0.02032661	0.03984325	0.04931278	0.08539284	0.09398853

n=2	0.00000006	0.00000025	0.00000098	0.00000151	0.00000472	0.00000577
n=3	0.00000002	0.00000018	0.00000139	0.00000268	0.00001504	0.00002044

### 278 K

RH	10%	20%	40%	50%	90%	100%
n=0	0.99050000	0.98120000	0.96310000	0.95430000	0.92070000	0.91260000
n=1	0.00948502	0.01879180	0.03689036	0.04569154	0.07934438	0.08738994
n=2	0.00000001	0.00000004	0.00000015	0.00000023	0.00000073	0.00000089
n=3	0.00000000	0.00000001	0.00000009	0.00000017	0.00000095	0.00000130

### 298 K

RH	10%	20%	40%	50%	90%	100%
n=0	0.99260000	0.98530000	0.97100000	0.96400000	0.93700000	0.93050000
n=1	0.00741927	0.01472926	0.02903091	0.03602716	0.06303219	0.06954867
n=2	0.00000000	0.00000000	0.00000001	0.00000002	0.00000006	0.00000008
n=3	0.00000000	0.00000000	0.00000000	0.00000000	0.00000002	0.00000003

### Reference

Tsona, N. T., and Du, L.: Hydration of glycolic acid sulfate and lactic acid sulfate: Atmospheric implications, *Atmospheric Environment*, 216, 116921, <https://doi.org/10.1016/j.atmosenv.2019.116921>, 2019.

2. *Could the authors comment on the role of coagulation sink? Eg. Line 134, it is a reasonable assumption to use the values from Hyytiälä for Mt. Tai for example?*

Author reply:

Thanks for the referee's question. According to the reviewer's suggestion, the following detail descriptions about coagulation sink were clarified and modified in line 155 page 6 in our revised manuscript. "A constant coagulation sink of  $2.6 \times 10^{-3} \text{ s}^{-1}$  was applied to account for scavenging by larger particles. The simulations were mainly run at 278 K, with additional runs at 258 K and 298 K to investigate the influence of temperature. These conditions correspond to a typical sink value and temperature in the boreal forest environment (Olenius et al., 2013; Maso et al., 2008)." A constant

coagulation sink was applied in the cluster distribution dynamics simulations to account for scavenging by larger particles. The coagulation sink used in this work is the major loss by particles in the assumed atmospheric conditions. Mt. Tai is located in northern China, and its landscape is dominated by forests. Unfortunately, we did not find the measurement coagulation sink report in Mt. Tai. We chose a constant coagulation sink coefficient of  $2.6 \times 10^{-3} \text{ s}^{-1}$ , which is the median condensation sink coefficient of sulfuric acid vapor on pre-existing aerosol particles, based on measurements in the boreal forest environment in Hyytiälä, Finland (Maso et al., 2007). On the other hand, the cluster size dependent coagulation sink coefficient did not have a significant effect on the steady-state cluster concentrations, according to the parametrized formula from Kulmala et al. (Kulmala et al., 2001; Kulmala and Wagner, 2001). Additionally, this coagulation sink value is widely used for a typical sink for molecular sized clusters in continental background areas (Paasonen et al., 2012), and taking into account external losses of organic compound-sulfuric acid-dimethylamine cluster system (Li et al., 2017). Therefore, we think it is a reasonable assumption to use this coagulation sink value in this work.

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- Kulmala, M., Maso, M. D., Mäkelä, J. M., Pirjola, L., Väkevä, M., Aalto, P., Mikkilainen, P., Hämeri, K., and O’Dowd, C. D.: On the formation, growth and composition of nucleation mode particles, *Tellus B*, 53, 479-490, <https://doi.org/10.1034/j.1600-0889.2001.530411.x>, 2001.
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V. M., and Kulmala, M.: On the formation of sulphuric acid - amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation, *Atmos. Chem. Phys.*, 12, 9113-9133, 10.5194/acp-12-9113-2012, 2012.

3. *The products GAS and GASA are better introduced in the main text. Could the authors move page S3 from the supplementary information to the main text in the methods section?*

Author reply:

We appreciated the referee's suggestion. According to the suggestion, we moved the page S3 to the methods section (2.3 The concentration of glycolic acid sulfate (GAS) and glycolic acid sulfuric anhydride (GASA) ) of main text in page 4 in our revised manuscript.

4. *References to studies who tackled the role of organosulfates and other similar organic acids in NPF are missing e.g. Katz et al. (<https://doi.org/10.5194/acp-23-5567-2023>) and Zhang et al. (<https://doi.org/10.5194/acp-22-2639-2022>)*

Author reply:

Thanks for the referee's comments. According to the suggestion, we have read articles, introducing the role of organosulfates and other similar organic acids in NPF by Katz et al. and Zhang et al. The following sentences and references were added to line 37 and line 51 page 2 in the Introduction part of the revised manuscript, respectively.

“Organosulfates have been identified as the most abundant class of organosulfur compounds, accounting for 5-30% of the organic mass fraction in atmospheric particles (Brüggemann et al., 2017; Tolocka and Turpin, 2012; Shakya and Peltier, 2015; Froyd et al., 2010; Mutzel et al., 2015; Glasius et al., 2018). Katz et al. measured the presence of organosulfates and identified its importance to new particle formation (Katz et al., 2023).”

“Organic acids, which are frequently observed in the atmosphere, have been expected to participate in the process of atmospheric nucleation, with a focus on the thermochemical properties of clusters between organic acids and common atmospheric nucleation precursors (Zhang et al., 2022).”

#### Reference

Brüggemann, M., Poulain, L., Held, A., Stelzer, T., Zuth, C., Richters, S., Mutzel, A., van Pinxteren, D., Iinuma, Y., Katkevica, S., Rabe, R., Herrmann, H., and Hoffmann, T.: Real-time detection of highly oxidized organosulfates and BSOA

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Froyd, K. D., Murphy, S. M., Murphy, D. M., de Gouw, J. A., Eddingsaas, N. C., and Wennberg, P. O.: Contribution of isoprene-derived organosulfates to free tropospheric aerosol mass, *Proc. Natl. Acad. Sci. U.S.A.*, 107, 21360, <https://doi.org/10.1073/pnas.1012561107>, 2010.

Mutzel, A., Poulain, L., Berndt, T., Iinuma, Y., Rodigast, M., Böge, O., Richters, S., Spindler, G., Sipilä, M., Jokinen, T., Kulmala, M., and Herrmann, H.: Highly Oxidized Multifunctional Organic Compounds Observed in Tropospheric Particles: A Field and Laboratory Study, *Environ. Sci. Technol.*, 49, 7754-7761, <https://doi.org/10.1021/acs.est.5b00885>, 2015.

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Katz, D. J., Abdelhamid, A., Stark, H., Canagaratna, M. R., Worsnop, D. R., and Browne, E. C.: Chemical identification of new particle formation and growth precursors through positive matrix factorization of ambient ion measurements, *Atmos. Chem. Phys.*, 23, 5567–5585, <https://doi.org/10.5194/acp-23-5567-2023>, 2023.

Zhang, R., Shen, J., Xie, H. B., Chen, J., and Elm, J.: The Role of Organic Acids in New Particle Formation from Methanesulfonic Acid and Methylamine, *Atmos. Chem. Phys. Discuss.*, 2021, 1-18, <https://doi.org/10.5194/acp-2021-831>, 2022.

*Technical comments:*

1. *In figure 3, could the authors write in the figure caption that the GA-SA-DMA lines are the same in a and b, but the y scale is different?*

Author reply:

Thanks for the referee's suggestion. In our modified manuscript, we made a detailed description in the figure caption of Figure 3 that the GA-SA-DMA lines are same in a and b, but the Y-axis scale is



different.

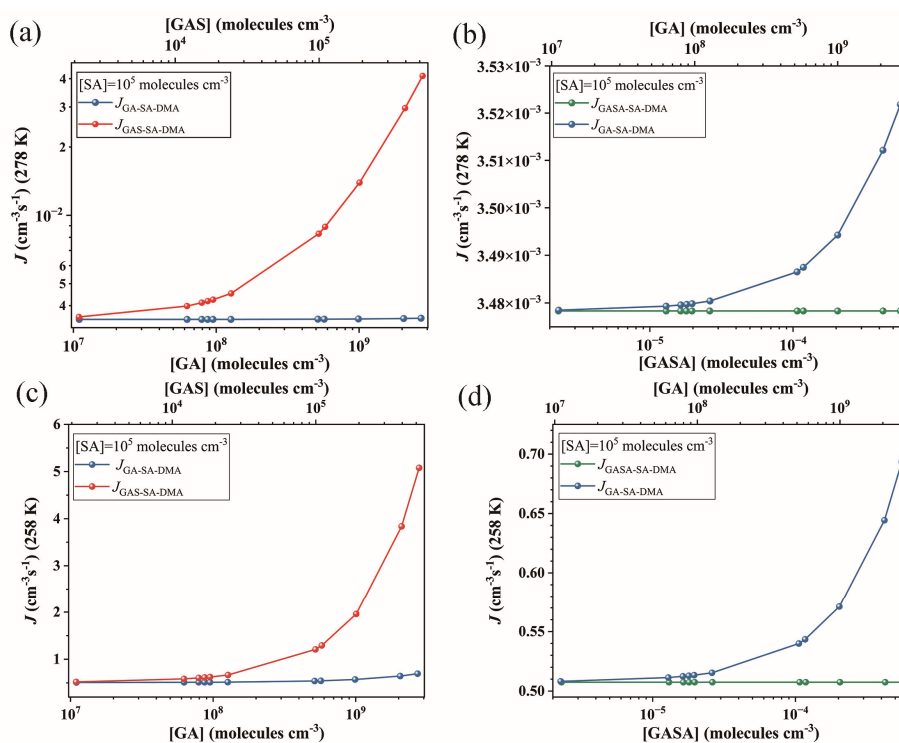


Figure 3. Simulated cluster formation rates  $J$  ( $\text{cm}^3\text{s}^{-1}$ ) as a function of monomer concentrations ( $[GA]$ ,  $[GAS]$ , and  $[GASA]$ , respectively) at (a) (b) 278 K and (c) (d) 258 K under the condition of  $[DMA] = 10^8$  molecules  $\text{cm}^{-3}$  and  $[SA] = 10^5$  molecules  $\text{cm}^{-3}$ . Note that the simulated  $J_{GA-SA-DMA}$  are the same data, but the Y-axis scale are different at (a) (b) and (c) (d), individually.

2. *References format needs to be checked. In some cases, e.g. line 149, 150 the citation is starting the sentence.*

Author reply:

Thanks for the referee's comment. According to the comment, we made an effort to check and correct all reference format in our modified manuscript. The sentence of line 149,150 "With high abundance ( $\sim 10^{17} \text{ cm}^{-3}$ ) being detected in the troposphere,(Huang et al., 2015)  $\text{H}_2\text{O}$  has been reported to effectively act as a catalyst in chemical reactions.(Liu et al., 2019)" was corrected to "With high abundance ( $\sim 10^{17} \text{ cm}^{-3}$ ) being detected in the troposphere (Huang et al., 2015),  $\text{H}_2\text{O}$  has been reported to effectively act as a catalyst in chemical reactions (Liu et al., 2019)." in line 171 page 6 of our revised manuscript.

3. *Line 369, 'sight'. I guess the authors mean 'slight'?*

Author reply:

Thanks for the referee's suggestion. According to the suggestion, we corrected the above spelling error. The sentence of "Given the fact that GA has only a sight influence on the nucleation and growth processes of atmospheric clusters, the reaction between GA and SO<sub>3</sub> may provide a secondary source of the potential precursor since high concentrations of sulfur oxides being detected." in line 398 page 16 was corrected to "Given the fact that GA has only a slight influence on the nucleation and growth processes of atmospheric clusters, the reaction between GA and SO<sub>3</sub> may provide a secondary source of the potential precursor since high concentrations of sulfur oxides being detected." in our revised manuscript.

We appreciate the reviewer's suggestions very much improving our presentation.

## Response to referee #2:

Referee's Comments to Author:

*The paper investigates if organic acids, organic sulfates or organic sulfuric anhydrides could enhance new particle formation driven only by sulfuric acid (SA) and dimethyl amine (DMA). The authors present quantum chemical calculations of the reaction of SO<sub>3</sub> with glycolic acid to glycolic acid sulfate (GAS) and glycolic acid sulfuric anhydride (GASA). They demonstrate that the addition of a catalyst (e.g. water) makes this reaction almost barrierless and thus could be a potential pathway to form GAS and GASA in the gas phase. Furthermore, lowest free energy structures of (GA)<sub>x</sub>-(SA)<sub>y</sub>-(DMA)<sub>z</sub>, (GAS)<sub>x</sub>-(SA)<sub>y</sub>-(DMA)<sub>z</sub>, and (GASA)<sub>x</sub>-(SA)<sub>y</sub>-(DMA)<sub>z</sub> clusters, their formation Gibbs Free Energies and evaporation rates have been calculated. It is shown that (GA)<sub>x</sub>-(SA)<sub>y</sub>-(DMA)<sub>z</sub> clusters are least stable, while mixed clusters with GAS and GASA are similar to or more stable than pure SA-DMA clusters. In a next step the authors calculate mixed cluster formation rates and determine an enhancement effect of GAS on SA-DMA driven new particle formation (NPF). Cluster growth pathways are then shown for different concentrations of SA, GAS and DMA. Finally, the authors compare their theoretical results with ambient observations at Mount Tai in China and conclude, that GAS could explain deviations between pure SA-DMA driven NPF and observations. Furthermore, they propose that the formation of organosulfates by this gas phase reaction may be a source of organosulfates often observed in secondary organic aerosols.*

*The first part of the manuscript including the quantum chemical calculations of the thermodynamic parameters of the organosulfates, as well as the mixed cluster geometries and stabilities is fine. However, the second part has some serious issues. There are no quantitative measurements of GAS and GASA in the atmosphere. Thus, the authors assume for SO<sub>3</sub> a concentration of 10<sup>5</sup> cm<sup>-3</sup> and a range of measured ambient GA concentrations to calculate potential equilibrium concentrations for GAS and GASA. GASA levels would be negligibly small while GAS concentrations could reach 10<sup>3</sup>-10<sup>5</sup> cm<sup>-3</sup>. The authors do not give a reference for their assumed SO<sub>3</sub> concentration of 10<sup>5</sup> cm<sup>-3</sup>.*

Author reply:

Thanks for the referee's question and comments. In order to reconsider the issue of GAS and GASA concentrations in the atmosphere more carefully, we did our best to search for reports on their measurements again. Due to the current lack of observations of organic sulfates in gas phase in the atmosphere, we found only one relevant report. Ehn et al. have made the observation of an organosulfate (glycolic acid sulfate, GAS) in the gas phase, and reported its ion concentration in the gas phase (6.7 molecules cm<sup>-3</sup>) in the boreal forest (Ehn et al., 2010). In the same observation, the gas phase H<sub>2</sub>SO<sub>4</sub> (SA) ion concentration was identified to be 242.7 molecules cm<sup>-3</sup>, which is two orders

of magnitude higher than that of GAS. Unfortunately, we did not find more reports on gas phase concentrations of neutral organosulfates. For the concentration of SA, Kulmala et al., Weber et al. and other researchers have reported that the typical tropospheric concentration of ambient sulfuric acid range from  $10^5$  to  $10^7$  molecules  $\text{cm}^{-3}$  (Kulmala et al., 2000; Weber et al., 1999; Weber et al., 1998; Riipinen et al., 2007). In Ehn et al.'s observation (Ehn et al., 2010), they found the ion concentration of GAS is two orders of magnitude lower than that of SA in the gas phase. If it is assumed that the concentrations of their neutral species have similar proportions, the concentration of gas phase GAS in the atmosphere can be estimated to be  $\sim 10^3$  to  $10^5$  molecules  $\text{cm}^{-3}$ , which agrees well with the GAS calculated concentrations in our work.

For  $\text{SO}_3$  concentrations in the atmosphere, the ambient  $\text{SO}_3$  was detected by Yao et al. from two field measurements in urban Beijing in the atmosphere, and showed that the concentration of  $\text{SO}_3$  varied from  $\sim 4.0 \times 10^4$  to  $1.9 \times 10^6$  molecules  $\text{cm}^{-3}$  during the winter (Yao et al., 2020). Many works, which investigated the reaction mechanisms of organic compounds and  $\text{SO}_3$  at the aerosol surface by Tan et al., Zhong et al. and Liu et al., have theoretically evaluated the concentration of organic sulfate considering  $\text{SO}_3$  concentration at  $10^5$  molecules  $\text{cm}^{-3}$  (Tan et al., 2022; Zhong et al., 2019; Liu et al., 2019). Tsona Tchinda et al. discussed the catalyzed effect of organic acid on the pyruvic acid-catalyzed  $\text{SO}_3$  hydrolysis at the  $\text{SO}_3$  concentration of  $10^5$  molecules  $\text{cm}^{-3}$  (Tsona Tchinda et al., 2022). Li et al. has also investigated the self-catalytic reaction of  $\text{SO}_3$  and  $\text{NH}_3$  in the atmosphere at the  $\text{SO}_3$  concentration of  $10^5$  molecules  $\text{cm}^{-3}$  (Li et al., 2018).

Considering above measurements and theoretical publications about atmospheric  $\text{SO}_3$ , we think  $10^5$  molecules  $\text{cm}^{-3}$  is a reasonable concentration for  $\text{SO}_3$  investigated in our work. According the referee's comments and concerns, the following sentences and references were modified and added in page 5 Line 121 in our revised manuscript.

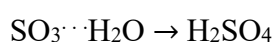
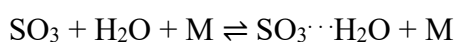
“We use the reactant concentrations of  $[\text{GA}] = 1.11 \times 10^7$ - $2.72 \times 10^9$  molecules  $\text{cm}^{-3}$  according to the values of some field observations (Mochizuki et al., 2019; Miyazaki et al., 2014; Stieger et al., 2021; Mochizuki et al., 2017). Considering field measurements (Yao et al., 2020) and theoretical investigations (Tan et al., 2022; Zhong et al., 2019; Liu et al., 2019; Tsona Tchinda et al., 2022; Li et

al., 2018) of atmospheric SO<sub>3</sub>, its concentration is assumed to be 10<sup>5</sup> molecules cm<sup>-3</sup> here. Based on the above equations, the estimated concentration of the reaction product, GAS, is about 2.14 × 10<sup>3</sup>-5.24 × 10<sup>5</sup> molecules cm<sup>-3</sup>, and GASA is about 2.30 × 10<sup>-6</sup>-5.62 × 10<sup>-4</sup> molecules cm<sup>-3</sup>.”

*In fact, SO<sub>3</sub> is very rapidly converted by water vapor to sulfuric acid, which in turn is condensing on aerosol. Let's assume a condensation sink for SA of 0.01 s<sup>-1</sup>, k(s<sup>-1</sup>) = 3.90 × 10<sup>-41</sup> exp(6830.6/T)[H<sub>2</sub>O]<sup>2</sup> (J.Phys. Chem. A 1997, 101,10000-10011), [H<sub>2</sub>O]= 2·10<sup>17</sup> cm<sup>-3</sup>, an SO<sub>3</sub> level of 10<sup>5</sup> cm<sup>-3</sup> would then yield a steady state concentration of SA = 5.6 ppb. Ambient SA levels are at least a factor 1000 lower. Therefore, possible GAS concentrations would be much lower in the ambient. Furthermore, SO<sub>3</sub> and SA scale with each other. It is very unlikely that [SO<sub>3</sub>]=[SA]=10<sup>5</sup>cm<sup>-3</sup> as assumed in Figure 3. The simulated cluster formation rates in Figures 3 and S6 are only a theoretical exercise but not at all relevant for ambient conditions.*

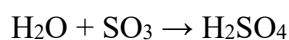
Author reply:

Thanks for the referee's comments. Since the main source of sulfuric acid in the atmosphere is the reaction of SO<sub>3</sub> and H<sub>2</sub>O, considering this reaction to evaluate the concentration of atmospheric SO<sub>3</sub> is a good point. As reported, the reaction of SO<sub>3</sub> with water vapor is believed to be the principal mechanism for gas phase sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) formation in the atmosphere (Stockwell and Calvert, 1983;Castleman Jr et al., 1975;Kolb et al., 1994). The relevant reaction equation between SO<sub>3</sub> and water (H<sub>2</sub>O) can be described by:



According to both of the theoretical calculations and laboratory experiments, the direct reaction between SO<sub>3</sub> and H<sub>2</sub>O is thermodynamically unfavorable owing to the high energy barrier, clearly indicating that a facilitator molecule M, acting as a catalyst, is required in the gas-phase reaction (Kolb et al., 1994;Lovejoy et al., 1996;Morokuma and Muguruma, 1994;Jayne et al., 1997;Torrent-Sucarrat et al., 2012;Hazra and Sinha, 2011;Bandyopadhyay et al., 2017). Theoretical calculations further revealed that this above-mentioned mechanism, involving a four-member ring transition state, has a large activation energy barrier (~28 to 32 kcal mol<sup>-1</sup>) and consequently was not favored as a possible route for atmospheric H<sub>2</sub>SO<sub>4</sub> production (Chen and Plummer, 1985;Hofmann and Schleyer, 1994;Morokuma and Muguruma, 1994;Stuedel, 1995). Hazra et al. have demonstrated the presence of

formic acid could substantially reduce the energy barrier between SO<sub>3</sub> and H<sub>2</sub>O (Hazra and Sinha, 2011). We have carefully read the reference (J. Phys. Chem. A 1997, 101, 10000-10011) the referee mentioned. We are very sorry for not understanding the calculations. For the equation  $k(s^{-1}) = 3.90 \times 10^{-41} \exp(6830.6/T)[H_2O]^2$ , it is an experimentally obtained rate constant equation for the reaction between SO<sub>3</sub> and H<sub>2</sub>O to form H<sub>2</sub>SO<sub>4</sub>. We did not get how to obtain a steady state concentration of SA from H<sub>2</sub>O and SO<sub>3</sub> concentration according to this equation. Hence, we try to estimate the concentration of SA by the following method. Given above previous identified mechanisms, the formation of H<sub>2</sub>SO<sub>4</sub> can be described by following reaction:



The equilibrium constant  $K_{eq}$  for the formation of H<sub>2</sub>SO<sub>4</sub> is

$$K_{eq} = \frac{[H_2SO_4]}{[H_2O][SO_3]} = e^{\frac{-\Delta G}{RT}}$$

And the equilibrium concentration of H<sub>2</sub>SO<sub>4</sub> can be roughly estimated theoretically using the following expression:

$$[H_2SO_4] = K_{eq}[H_2O][SO_3]$$

where  $K_{eq}$  is equal to the equilibrium constant from the formation Gibbs energy of the H<sub>2</sub>SO<sub>4</sub>. According to the results calculated by Liu et al., the Gibbs free energy barrier of reaction between SO<sub>3</sub> and H<sub>2</sub>O is 24.11 kcal mol<sup>-1</sup> at 280 K (Liu et al., 2019). [H<sub>2</sub>O] and [SO<sub>3</sub>] are the concentrations of H<sub>2</sub>O and SO<sub>3</sub> monomer, respectively. According to the reactant concentrations suggested by referee and previous work, the concentration of [H<sub>2</sub>O] is  $2 \times 10^{17}$  molecules cm<sup>-3</sup>, and that of [SO<sub>3</sub>] is  $10^5$  molecules cm<sup>-3</sup> (~0.0037 ppt). Based on the above equations, the estimated concentration of the reaction product, H<sub>2</sub>SO<sub>4</sub>, is about  $7 \times 10^4$  molecules cm<sup>-3</sup>, which is quite close to the reported SA concentration in range from  $10^5$  to  $10^7$  molecules cm<sup>-3</sup> (Kulmala et al., 2000; Weber et al., 1999; Weber et al., 1998; Riipinen et al., 2007). This result also suggests  $10^5$  molecules cm<sup>-3</sup> is reasonable for the SO<sub>3</sub> concentration in the atmosphere.

In Figure 3, it is not mean that  $10^5$  molecules cm<sup>-3</sup> SA is generated from  $10^5$  molecules cm<sup>-3</sup> SO<sub>3</sub>. In the atmosphere, species like SA, GA, SO<sub>3</sub>, and so on all should be in a certain concentration range. Since we are trying to discuss the nucleation of the ternary system, we can only assume that two of the

species are reasonably certain values, and discuss the concentration of the third species within a certain range. Hence, the condition of  $[DMA] = 10^8$  molecules  $\text{cm}^{-3}$  and  $[SA] = 10^5$  molecules  $\text{cm}^{-3}$  were assumed for the discussion. To discuss the concentration of GAS in a range, we use the reactant concentrations of  $[GA] = 1.11 \times 10^7$ - $2.72 \times 10^9$  molecules  $\text{cm}^{-3}$  according to the values of some field observations (Mochizuki et al., 2019; Miyazaki et al., 2014; Stieger et al., 2021; Mochizuki et al., 2017). The concentration of  $\text{SO}_3$  is assumed to be  $10^5$  molecules  $\text{cm}^{-3}$  here. The estimated concentration of the reaction product, GAS, is about  $2.14 \times 10^3$ - $5.24 \times 10^5$  molecules  $\text{cm}^{-3}$  as displayed in Figure 3. The results for different SA concentrations were also given in Figure S8 in our revised manuscript.

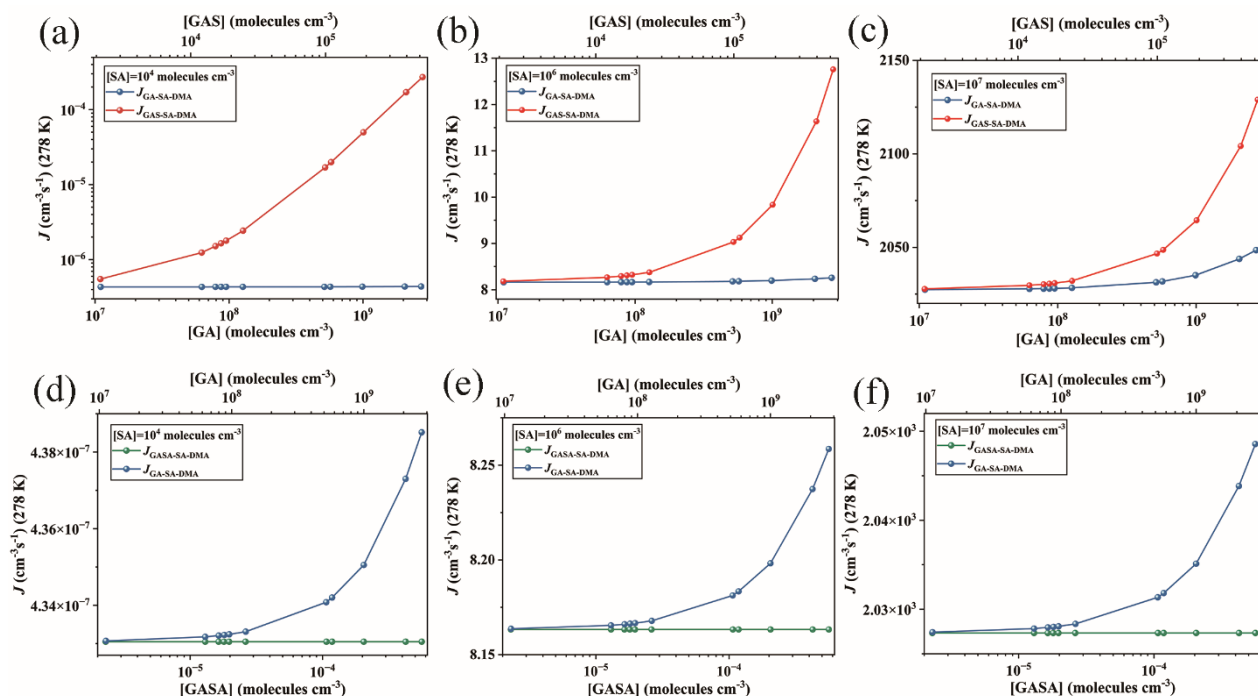
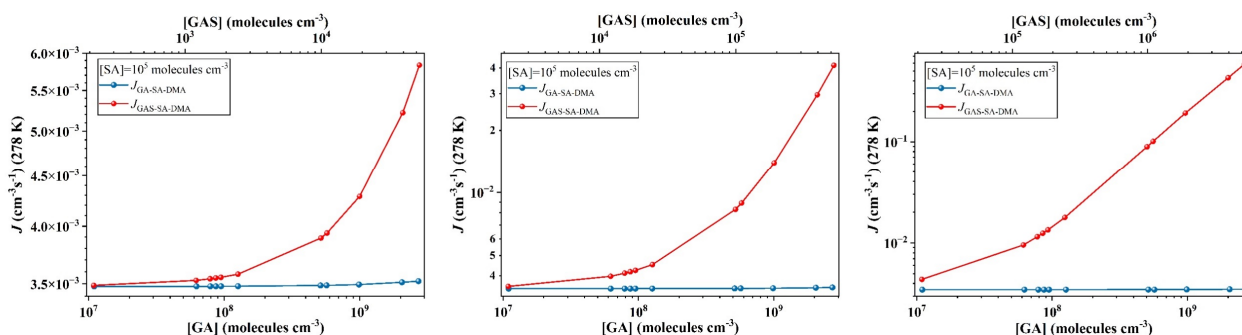


Figure S8. Simulated cluster formation rates  $J$  ( $\text{cm}^{-3}\text{s}^{-1}$ ) as a function of monomer concentrations ( $[GA]$ ,  $[GAS]$ , and  $[GASA]$ , respectively) under different  $[SA]$  (a) (d)  $[SA] = 10^4$ , (b) (e)  $[SA] = 10^6$ , and (c) (f)  $[SA] = 10^7$  molecules  $\text{cm}^{-3}$  at 278 K,  $[DMA] = 10^8$  molecules  $\text{cm}^{-3}$ .

In order to further consider the effect of different concentrations of  $\text{SO}_3$  according to the referee's comments, we investigated the formation rates ( $J_{GAS-SA-DMA}$  and  $J_{GA-SA-DMA}$ ) at the conditions of varying level  $[\text{SO}_3]$  ( $[\text{SO}_3] = 10^4$  molecules  $\text{cm}^{-3}$ ,  $[\text{SO}_3] = 10^5$  molecules  $\text{cm}^{-3}$ , and  $[\text{SO}_3] = 10^6$  molecules  $\text{cm}^{-3}$ ). The following results and descriptions were added in page S14 in the revised SI of

our manuscript. “As the results displayed in Figure S9, we found that the cluster formation rate of GAS-SA-DMA system markedly increases with the increasing concentration of [GAS] compared to that of GA-SA-DMA system, especially in the case of  $[\text{SO}_3] = 10^6 \text{ molecules cm}^{-3}$ , which  $J_{\text{GAS-SA-DMA}}$  could be up to 2 orders of magnitude higher than  $J_{\text{GA-SA-DMA}}$ .”



**Figure S9.** Simulated cluster formation rates  $J \text{ (cm}^{-3}\text{s}^{-1}\text{)}$  as a function of monomer concentrations ( $[\text{GA}]$  and  $[\text{GAS}]$ ) at 278 K and  $[\text{SO}_3] = 10^4 \text{ molecules cm}^{-3}$  (left panel)  $[\text{SO}_3] = 10^5 \text{ molecules cm}^{-3}$  (center panel)  $[\text{SO}_3] = 10^6 \text{ molecules cm}^{-3}$  (right panel) under the condition of  $[\text{DMA}] = 10^8 \text{ molecules cm}^{-3}$  and  $[\text{SA}] = 10^5 \text{ molecules cm}^{-3}$ .

*The authors also argue that measured new particle formation rates at Mt. Tai could not be explained by pure SA-DMA nucleation. For the comparison the authors use theoretical NPF-rates from ACDC calculations at a cluster size of only about 1.2-1.4 nm, while the measurements were made at 3 nm. The authors apparently assume that the nucleation rate at the two different cluster sizes should be the same. That is not at all the case.  $J(3\text{nm})$  is probably more than a factor of 10 slower than  $J(1.3\text{nm})$  (see e.g. Xiao et al., ACP 21, 14275–14291, 2021). Thus, this comparison does not provide evidence that GAS could explain the fast NPF rate.*

Author reply:

Thanks for the referee’s comments on the consideration of the different nucleation rate for different cluster size. Due to the lack of accurate observational data, the relationship between the formation rates of particles of different sizes under different environmental conditions is difficult to accurately quantify. In Xiao et al.’s work (ACP 21, 14275–14291, 2021), they calculated the ratio between the formation rates at 2.5 and 1.7 nm as the survival probability in CLOUD chamber experiments. In their experiments, it is obvious that the survival probability is closely related to various experimental conditions such as nucleation precursor species and concentrations, temperature, condensation sink and so on. Unfortunately they did not give a quantitative relationship between the formation rates of clusters of different sizes, so we cannot use it to correct our calculated results. In order to consider this



issue more rigorously, we searched the relevant literatures. According to the revised Kerminen–Kulmala equation (Anttila et al., 2010;Lehtinen et al., 2007;Kulmala et al., 2012), cluster formation rates for 3.0 nm clusters ( $J_{3.0}$ ) relate to those for 1.2-1.4 nm clusters ( $J_{1.2}$ ) by

$$J_{1.2} = J_{3.0} \exp\left[\gamma \left(\frac{1}{1.2} - \frac{1}{3.0}\right) \frac{CS}{GR}\right]$$

where GR is the initial cluster growth rate from 1.0 to 3.0 nm, CS represents condensation sink of clusters by preexisting particles and  $\gamma$  is a coefficient with a value of approximately  $0.23 \text{ m}^2 \text{ nm}^2 \text{ h}^{-1}$  (Riipinen et al., 2007;Xia et al., 2020). GR was measured to be  $1.5\text{--}3.1 \text{ nm}\cdot\text{h}^{-1}$  in the 1.0–3.0 nm size range during the observed events (Riipinen et al., 2007). CS was between  $0.01$  and  $0.04 \text{ s}^{-1}$  (Xia et al., 2020).  $J_{1.2}$  was then calculated to be 1.0003–1.0031 times of  $J_{3.0}$ . This result suggests that the  $J_{1.2}$  and  $J_{3.0}$  are close at above conditions, which are similar with that considered in our work. However, because always  $J_{1.2} > J_{3.0}$ , using the  $J_{3.0}$  value instead of  $J_{1.2}$  should lead to slight underestimation of  $J_{1.2}$ . As precursor concentrations ( $[\text{H}_2\text{SO}_4]$ ,  $[\text{DMA}]$ , and  $[\text{GAS}]$ ) positively correlate with  $J_{\text{GAS-SA-DMA}}$ ,  $J_{\text{GA-SA-DMA}}$  and/or  $J_{\text{GA-SA-DMA}}$ , the required precursor concentrations calculated by ACDC simulations for the observed 3.0 nm clusters may be slightly underestimated. The following sentences were added in our revised manuscript and SI respectively.

“Noted that the calculated cluster formation rates via ACDC in this work are at a cluster size about 1.2-1.4 nm. The observed cluster formation rates ( $J_{\text{obs}}$ ) at Mt. Tai were measured at 3 nm. According to the revised Kerminen–Kulmala equation (Anttila et al., 2010;Lehtinen et al., 2007;Kulmala et al., 2012), the cluster formation rate for 1.2 nm cluster ( $J_{1.2}$ ) is slightly larger than that for 3.0 nm clusters ( $J_{3.0}$ ) ( $J_{1.2}$  is calculated to be 1.0003–1.0031 times of  $J_{3.0}$ ). The above required precursor concentrations calculated by ACDC simulations for the observed 3.0 nm clusters may be slightly underestimated (see details in the SI).” were added in page 18 line 436 in our modified manuscript.

“According to the revised Kerminen–Kulmala equation (Anttila et al., 2010;Lehtinen et al., 2007;Kulmala et al., 2012), cluster formation rates for 3.0 nm clusters ( $J_{3.0}$ ) relate to those for 1.2-1.4 nm clusters ( $J_{1.2}$ ) by

$$J_{1.2} = J_{3.0} \exp\left[\gamma \left(\frac{1}{1.2} - \frac{1}{3.0}\right) \frac{CS}{GR}\right]$$

where GR is the initial cluster growth rate from 1.0 to 3.0 nm, CS represents condensation sink of clusters by preexisting particles and  $\gamma$  is a coefficient with a value of approximately  $0.23 \text{ m}^2 \text{ nm}^2 \text{ h}^{-1}$  (Riipinen et al., 2007; Xia et al., 2020). GR was measured to be  $1.5\text{--}3.1 \text{ nm}\cdot\text{h}^{-1}$  in the 1.0–3.0 nm size range during the observed events (Riipinen et al., 2007). CS was between  $0.01$  and  $0.04 \text{ s}^{-1}$  (Xia et al., 2020).  $J_{1.2}$  was then calculated to be 1.0003–1.0031 times of  $J_{3.0}$ . This result suggests that the  $J_{1.2}$  and  $J_{3.0}$  are close at above conditions, which are similar with that considered in our work. However, because always  $J_{1.2} > J_{3.0}$ , using the  $J_{3.0}$  value instead of  $J_{1.2}$  should lead to slight underestimation of  $J_{1.2}$ . As precursor concentrations ( $[\text{H}_2\text{SO}_4]$ ,  $[\text{DMA}]$ , and  $[\text{GAS}]$ ) positively correlate with  $J_{\text{GAS-SA-DMA}}$ ,  $J_{\text{GA-SA-DMA}}$  and/or  $J_{\text{GA-SA-DMA}}$ , the required precursor concentrations calculated by ACDC simulations for the observed 3.0 nm clusters may be slightly underestimated.” were added in page S4 line 61 in our modified SI.

*Overall, I think the second part of the paper about the potential role and importance of GAS for ambient NPF is untenable. I do not see how this hypothesis could be substantiated. Since the first part is only QC calculations, I think the first part alone is not suited for ACP.*

*Minor comments*

*Line 57: it is not proven so far that  $\text{SO}_3$  is a major oxidant in the atmosphere. It is also not emitted but formed as an intermediate species through oxidation of  $\text{SO}_2$ .*

Author reply:

Thanks for the referee’s comments. For  $\text{SO}_3$  concentration in the atmosphere, the ambient  $\text{SO}_3$  was detected by Yao et al. from two field measurements in urban Beijing in the atmosphere, and showed that the concentration of  $\text{SO}_3$  varied from  $\sim 4.0 \times 10^4$  to  $1.9 \times 10^6 \text{ molecules cm}^{-3}$  during the winter (Yao et al., 2020). It has been reported that sulfur trioxide ( $\text{SO}_3$ ) is a major air pollutant and is mainly produced by the gas-phase oxidation of  $\text{SO}_2$  (Stockwell and Calvert, 1983; Mauldin Iii et al., 2012; Zhong et al., 2017; Li et al., 2018). Furthermore,  $\text{SO}_3$  is a highly reactive gas and one of the most common acid oxides (Fleig et al., 2012), which can lead to both acid rain and atmospheric aerosol (Sipila et al., 2010; England et al., 2000).

*Figure 3: For J rates you should say at what cluster size they have been calculated*

Author reply:

Thanks for the referee's suggestions. In order to clarify this issue, following sentences were added in page 18 line 436 in our modified manuscript. "Noted that the calculated cluster formation rates via ACDC in this work are at a cluster size about 1.2-1.4 nm."

*Line 311: high mountain sites and polar regions are usually not places with high amine concentrations, do you have references?*

Author reply:

We appreciated the referee's comments and questions. Liu et al. observed high amines concentrations in gas phase which could be up to  $307 \pm 196.7 \text{ ng m}^{-3}$  at Nanling Mountains, southern China in summer (298 K) (Liu et al., 2018). Specifically, the measured dimethylamine concentration is up to  $300 \text{ ng m}^{-3}$  ( $\sim 4 \times 10^9 \text{ molecules cm}^{-3}$ ). And a forested site on the northern foot of Mt. Fuji, Japan has measured the dimethylamine with the concentration of  $226.5 \text{ pmol m}^{-3}$  (Matsumoto et al., 2023). Baumgardner et al. have reported high atmospheric amine concentrations and amines were quantified with concentrations of  $0.36\text{-}1.42 \text{ }\mu\text{g m}^{-3}$  from the mountain site, and other research groups have also measured high amine concentration in the atmosphere and/or particulate matter (Ge et al., 2011; Kürten et al., 2014; Drewnick et al., 2007; Baumgardner et al., 2009; Roth et al., 2016; Liu et al., 2023). Of particular note, alkylamines in the surface ocean and atmosphere of the Antarctic sympagic environment have been detected from  $0.01 \text{ ng m}^{-3}$  to  $7.1 \text{ ng m}^{-3}$  (Dall'Osto et al., 2019). Baumgardner et al. have reported high atmospheric amine concentrations and amines were quantified with concentrations of  $0.36\text{-}1.42 \text{ }\mu\text{g m}^{-3}$  from the mountain site (Ge et al., 2011; Kürten et al., 2014; Drewnick et al., 2007; Baumgardner et al., 2009). Following sentences and citations were modified and added in page 10 line 264 in our modified manuscript. "The concentration of DMA is selected to be  $10^8 \text{ molecules cm}^{-3}$ , according to the typical concentrations observed in the gas phase at high mountains (Liu et al., 2018b, Matsumoto et al., 2023)."

*Figure S1: there is no red line. The blue line should read green. "the pathway to form H<sub>2</sub>SO<sub>4</sub> with as a catalyst" should read "the pathway to form H<sub>2</sub>SO<sub>4</sub> with H<sub>2</sub>O as a catalyst"*

Author reply:

Thanks for the referee's suggestion. According to the suggestion, we corrected the above spelling error. The caption of Figure S1 "The red line represents the pathway through SO<sub>3</sub> attacking the -OH group of GA with H<sub>2</sub>O as a catalyst;" was corrected to "The green line represents the pathway through SO<sub>3</sub> attacking the -OH group of GA with H<sub>2</sub>O as a catalyst;" in our revised supporting information for the manuscript.

*Table S1: how do you get the  $\Delta G$  values from Figure 1?*

Author reply:

Thanks for the referee's question. To clarify the data of our calculation results, the  $\Delta G$  values under different temperatures (278 K, Table S4 and 298 K, Table S5) were added in page S20 and S21 in our revised SI of manuscript as below.

**Table S4.** Calculated Gibbs free energy changes ( $\Delta G$ ) of the formation of heterotrimers consisting of H<sub>2</sub>SO<sub>4</sub>, base (ammonia/DMA), and GA/GAS/GASA at the temperature of 278 K and pressure of 101.3 KPa.

clusters	$\Delta G$ (kcal mol <sup>-1</sup> ) GA-SA-ammonia <sup>a</sup>	$\Delta G$ (kcal mol <sup>-1</sup> ) GA-SA-DMA	$\Delta G$ (kcal mol <sup>-1</sup> ) GAS-SA-DMA	$\Delta G$ (kcal mol <sup>-1</sup> ) GASA-SA-DMA
Org-base	-2.74	-4.23	-7.83	-3.06
Org-SA	-7.55	-7.97	-2.58	-5.27
Org-SA-base	-14.90	-23.12	-29.90	-34.54
Org-SA-2base	-16.68	-32.66	-50.48	-52.57
Org-2SA	-14.55	-11.70	-13.58	-15.75
Org-2SA-base	-28.21	-37.71	-41.62	-40.26
Org-2SA-2base	-36.81	-55.95	-65.39	-71.31
Org-2SA-3base	-41.21	-67.68	-82.56	-90.30
2Org	-5.37	-5.17	-6.68	-0.77
2Org-base	-4.33	-10.05	-18.20	-27.65
2Org-2base	-2.35	-11.59	-50.36	-64.19

2Org-SA	-14.87	-15.04	-16.86	-14.54
2Org-SA-base	-19.96	-26.48	-38.94	-44.23
2Org-SA-2base	-20.99	-39.72	-62.20	-68.50
2Org-SA-3base	-23.42	-44.48	-76.48	-90.80
3Org	-5.24	-1.81	-7.71	-11.82
3Org-base	-6.87	-13.61	-29.49	-40.64
3Org-2base	-6.98	-20.11	-54.73	-69.36
3Org-3base	-3.20	-27.43	-78.18	-98.00

**Table S5.** Calculated Gibbs free energy changes ( $\Delta G$ ) of the formation of heterotrimers consisting of  $\text{H}_2\text{SO}_4$ , base (ammonia/DMA), and GA/GAS/GASA at the temperature of 298 K and pressure of 101.3 KPa.

clusters	$\Delta G$ (kcal mol <sup>-1</sup> )	$\Delta G$ (kcal mol <sup>-1</sup> )	$\Delta G$ (kcal mol <sup>-1</sup> )	$\Delta G$ (kcal mol <sup>-1</sup> )
	SA-GA-ammonia <sup>a</sup>	SA-GA-DMA	SA-GAS-DMA	SA-GASA-DMA
Org-base	-2.11	-3.50	-7.10	-2.37
Org-SA	-6.83	-7.28	-1.78	-4.51
Org-SA-base	-13.51	-21.76	-28.35	-32.90
Org-SA-2base	-14.55	-30.36	-48.13	-50.06
Org-2SA	-12.94	-10.10	-11.86	-14.04
Org-2SA-base	-25.95	-35.22	-39.15	-37.64
Org-2SA-2base	-33.76	-52.74	-62.14	-67.93
Org-2SA-3base	-37.48	-63.71	-78.55	-86.19
2Org	-4.62	-4.40	-5.76	0.13
2Org-base	-2.97	-8.64	-16.54	-25.84
2Org-2base	-0.32	-9.03	-47.82	-61.62
2Org-SA	-13.39	-13.60	-15.13	-12.75
2Org-SA-base	-17.74	-24.08	-36.49	-41.54
2Org-SA-2base	-17.78	-36.51	-58.92	-65.15
2Org-SA-3base	-19.65	-40.59	-72.36	-86.50
3Org	-3.76	-0.12	-5.99	-10.01

3Org-base	-4.67	-11.16	-26.82	-37.95
3Org-2base	-3.94	-16.80	-51.34	-65.78
3Org-3base	-17.78	-23.60	-74.01	-93.69

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We appreciate the referee's comments and suggestions for clarifying and improving our presentation.

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