Responses to Referee #1's comments

We are grateful to the reviewers for their valuable and helpful comments on our manuscript "Reaction of SO_3 with H_2SO_4 and Its Implication for Aerosol Particle Formation in the Gas Phase and at the Air-Water Interface" (MS No.: **egusphere-2023-2009**). We have revised the manuscript carefully according to reviewers' comments. The point-to-point responses to the Referee #1's comments are summarized below:

Referee Comments:

Rui Wang and co-authors have used computational methods to study the formation and clustering of $H_2S_2O_7$-known (depending on the source) as either disulfuric acid, pyrosulfuric acid, or oleum. The technical methods used in the study are broadly appropriate, and the context (atmospheric new-particle formation involving different sulfur compounds) is certainly relevant and broadly interesting. The study is thus without doubt publishable. However, I have some critical notes about the interpretation of the results, and their atmospheric implications (which I believe to the overstated, at least in the context of Earth's lower atmosphere).

Response: We would like to thank the reviewer for the positive and valuable comments, and we have revised our manuscript accordingly.

Major issues

Comment 1.

As shown by Torrent-Sucarrat (JACS 2012; cited in the present study), the SO_3 + H_2SO_4 reaction in the presence of water can also lead directly to H_2SO_4 + H_2SO_4 (instead of $H_2S_2O_7$). Given that H_2SO_4 is pretty much always hydrated, water is - as the authors themselves argue here - essentially always present in the reaction system, at least in the lower troposphere. Thus, an explicit consideration of the competition between the two channels would be warranted - however this seems to be missing in the study. The authors should try to estimate what percentage of SO_3 + H_2SO_4 collisions, in different hydration environments, we can expect to yield (at least transiently, see below) $H_2S_2O_7$, as compared to H_2SO_4 + H_2SO_4? (Note that this question should be asked on top of the question that they DO address, i.e. "what fraction of SO_3 will collide with H_2SO_4 as opposed to H_2O, or H_2O*X, where X is any other catalyst for the SO_3 hydration reaction. As per the authors own

calculation in their Table S6, already this percentage is very small-despite their neglect of many other known candidates for X.)

Response: Thanks for your valuable comments. According to the reviewer's suggestion, the schematic potential energy surface of the H_2SO_4 formation from the SO_3 + H_2SO_4 reaction with H_2O has been added in Fig. 1, while the corresponding effective rate constants have been listed in Table 1. Then, the competition between H_2SO_4 and $H_2S_2O_7$ formations from the SO_3 + H_2SO_4 reaction with H_2O have been discussed. The corresponding major revision has been made as follows.

(a) The SO_3 + H_2SO_4 reaction with H_2O can produce two distinct products, labeled (*i*) $H_2S_2O_7$ (DSA, Channel DSA_WM) and (*ii*) H_2SO_4 (SA, Channel SA_SA). A single water molecule in (*i*) acts as a catalyst, while it plays as a reactant in (*ii*). So, based on the $H_2S_2O_7$ formation from the SO_3 + H_2SO_4 reaction with H_2O, the schematic potential energy surface for the H_2SO_4 formation from the SO_3 + H_2SO_4 reaction with H_2O is also involved in Fig. 1. In Lines 18-21 Page 8 of the revised manuscript, the corresponding discussion has been reorganized as "The SO_3 + H_2SO_4 reaction with H_2O produced two distinct products, labeled (*i*) $H_2S_2O_7$ (DSA, Channel DSA_WM) and (*ii*) H_2SO_4 (SA, Channel SA_SA). A single water molecule in (*i*) acted as a catalyst, while it played as a reactant in (*ii*). The schematic potential energy surface for the SO_3 + H_2SO_4 reaction with H_2O was shown in Fig. 1."

(b) Similar with the $H_2S_2O_7$ formation from the SO_3 + H_2SO_4 reaction with H_2O (Fig. 1 (b), Channel DSA_WM), the H_2SO_4 formation from the SO_3 + H_2SO_4 reaction with H_2O (Fig. 1 (c), Channel SA_SA) can be considered as a sequential bimolecular process. In other words, Channel SA_SA occurs via the collision between SO_3 (or H_2SO_4) and H_2O to form dimer (SO_3···H_2O and H_2SO_4···H_2O) first, and then the dimer encounters with the third reactant H_2SO_4 or SO_3. However, the SO_3···H_2O + H_2SO_4 reaction in Channel SA_SA can be neglected as its effective rate constant is smaller by 1.02-3.05 times than the corresponding value in the H_2SO_4···H_2O + SO_3 reaction. Therefore, we only consider the H_2SO_4···H_2O + SO_3 bimolecular reaction in Channel SA_SA. In Lines 21-29 Page 8 to lines 1-17 Page 9 of the revised manuscript, two sequential bimolecular processes, H_2SO_4···H_2O + SO_3 and SO_3···H_2O + H_2SO_4, have been considered, which has been reorganized as "As the probability of simultaneous collision (Pérez-Ríos et al., 2014; Elm et al., 2013) of three molecules of SO_3, SA and H_2O is quite low under realistic conditions, both Channel DSA_WM and Channel SA_SA can be considered as a sequential bimolecular process. In other

words, both Channel DSA_WM and Channel SA_SA occur via the collision between SO_3 (or H_2SO_4) and H_2O to form dimer ($SO_3\cdots H_2O$ and $H_2SO_4\cdots H_2O$) first, and then the dimer encounters with the third reactant H_2SO_4 or SO_3. The computed Gibbs free energies of dimer complexes $SO_3\cdots H_2O$ and $H_2SO_4\cdots H_2O$ were respectively 0.8 kcal·mol^{-1} and -1.9 kcal·mol^{-1}, which were respectively consistent with the previous values (the range from -0.2 to 0.62 kcal·mol^{-1} for $SO_3\cdots H_2O$ complex (Bandyopadhyay et al., 2017; Long et al., 2012) and the range from -1.82 to -2.63 kcal·mol^{-1} for $H_2SO_4\cdots H_2O$ complex (Long et al., 2013b; Tan et al., 2018)). The Gibbs free energy of $H_2SO_4\cdots H_2O$ was lower by 2.7 kcal·mol^{-1} than that of $SO_3\cdots H_2O$, thus leading to that the equilibrium constant of the former complex is larger by 1-2 orders of magnitude than that of the latter one in Table S2. Additionally, the larger equilibrium constant of $H_2SO_4\cdots H_2O$ complex leads to its higher concentration in the atmosphere. For example, when the concentrations of SO_3 (Yao et al., 2020), H_2SO_4 (Liu et al., 2015) and H_2O (Anglada et al., 2013) were 10^6, 10^8 and 10^{17} molecules·cm^{-3}, respectively, the concentrations of $SO_3\cdots H_2O$ and $H_2SO_4\cdots H_2O$ were 2.41×10^3-2.01×10^4 and 5.01×10^5-3.01×10^8 molecules·cm^{-3} within the temperature range of 280-320 K (see Table S3), respectively. So, we predict that Channel DSA_WM and Channel SA_SA mainly take place via the collision of $H_2SO_4\cdots H_2O$ with SO_3. In order to check this prediction, the effective rate constants for two bimolecular reactions of $H_2SO_4\cdots H_2O + SO_3$ and $SO_3\cdots H_2O + H_2SO_4$ were calculated, and the details were shown in *SI Appendix*, Part 3 and Table 1. As seen in Table 1, the $SO_3\cdots H_2O + H_2SO_4$ reaction in both Channel DSA_WM and Channel SA_SA can be neglected as their effective rate constants are smaller by 16.7-48.5 and 1.02-3.05 times than the corresponding values in the $H_2SO_4\cdots H_2O + SO_3$ reaction within the temperature range of 280-320 K, respectively. Therefore, we only consider the $H_2SO_4\cdots H_2O + SO_3$ bimolecular reaction in both Channel DSA_WM and Channel SA_SA."

(c) As for the H_2SO_4 formation from the $SO_3 + H_2SO_4$ reaction with H_2O, the discussion of the stepwise $H_2SO_4\cdots H_2O + SO_3$ reaction has been added in Lines 8-21 Page 10 of the revised manuscript, which has been reorganized as "Regarding Channel SA_SA, the stepwise reaction occurred firstly via the ring enlargement from six-membered ring complex IM_{SA_SA}' to a cage-like hydrogen bonding network IM_{SA_SA}, and then took place by going through a transition state, TS_{SA_SA}, to from the product complex $(H_2SO_4)_2$. TS_{DSA_WM} was in the middle of a double hydrogen transfer, where H_2SO_4 acted as a bridge of hydrogen atom from the H_2O to SO_3 along with O1 atom of H_2O

addition to the S atom of SO_3. It is worth noting that the energy barriers of two elementary reactions involved in the stepwise route of Channel SA_SA were only 1.8 and 0.6 kcal·mol^{-1}, respectively, showing that the stepwise route of Channel SA_SA is feasible to take place from energetic point of view.

(d) The discussion of the competition between the $SO_3 + H_2SO_4$ reaction with H_2O and the hydrolysis of SO_3 with H_2SO_4 have been discussed in Lines 8-14 Page 9 of the revised manuscript, which has been reorganized as "To check whether Channel DSA_WM is more favorable than Channel SA_SA or not, their rate ratio listed in Eq. 4 has been calculated in Table 1. The calculated rate ratio $v_{DSA\_WM\_s}/v_{SA\_SA\_s}$ shows that Channel DSA_WM is more important than Channel SA_SA because the rate ratio $v_{DSA\_WM\_s}/v_{SA\_SA\_s}$ is 1.53-3.04 within the temperature range of 280-320 K. So, we predicted that the $SO_3 + H_2SO_4$ reaction with H_2O producing $H_2S_2O_7$ is more favorable than that forming H_2SO_4.

$$\frac{v_{DSA\_WM}}{v_{SA\_SA}} = \frac{v_{DSA\_WM\_s} + v_{DSA\_WM\_o}}{v_{SA\_SA\_s} + v_{SA\_SA\_o}} = \frac{k_{DSA\_WM\_s} \times K_{eq(H_2SO_4 \cdots H_2O)} + k_{DSA\_WM\_o} \times K_{eq(SO_3 \cdots H_2O)}}{k_{SA\_SA\_s} \times K_{eq(H_2SO_4 \cdots H_2O)} + k_{SA\_SA\_o} \times K_{eq(SO_3 \cdots H_2O)}} \quad (4)"$$

Overall, in the $SO_3 + H_2SO_4$ reaction with H_2O, a single water molecule both acting as a catalyst and a reactant has been investigated. Meanwhile, these two kinds of reactions mainly take place via the collision of $H_2SO_4 \cdots H_2O$ with SO_3. Moreover, the $SO_3 + H_2SO_4$ reaction with H_2O producing $H_2S_2O_7$ is more favorable than that forming H_2SO_4 as the rate ratio v_{DSA_WM}/v_{SA_SA} is 1.53-3.04 within the temperature range of 280-320 K.

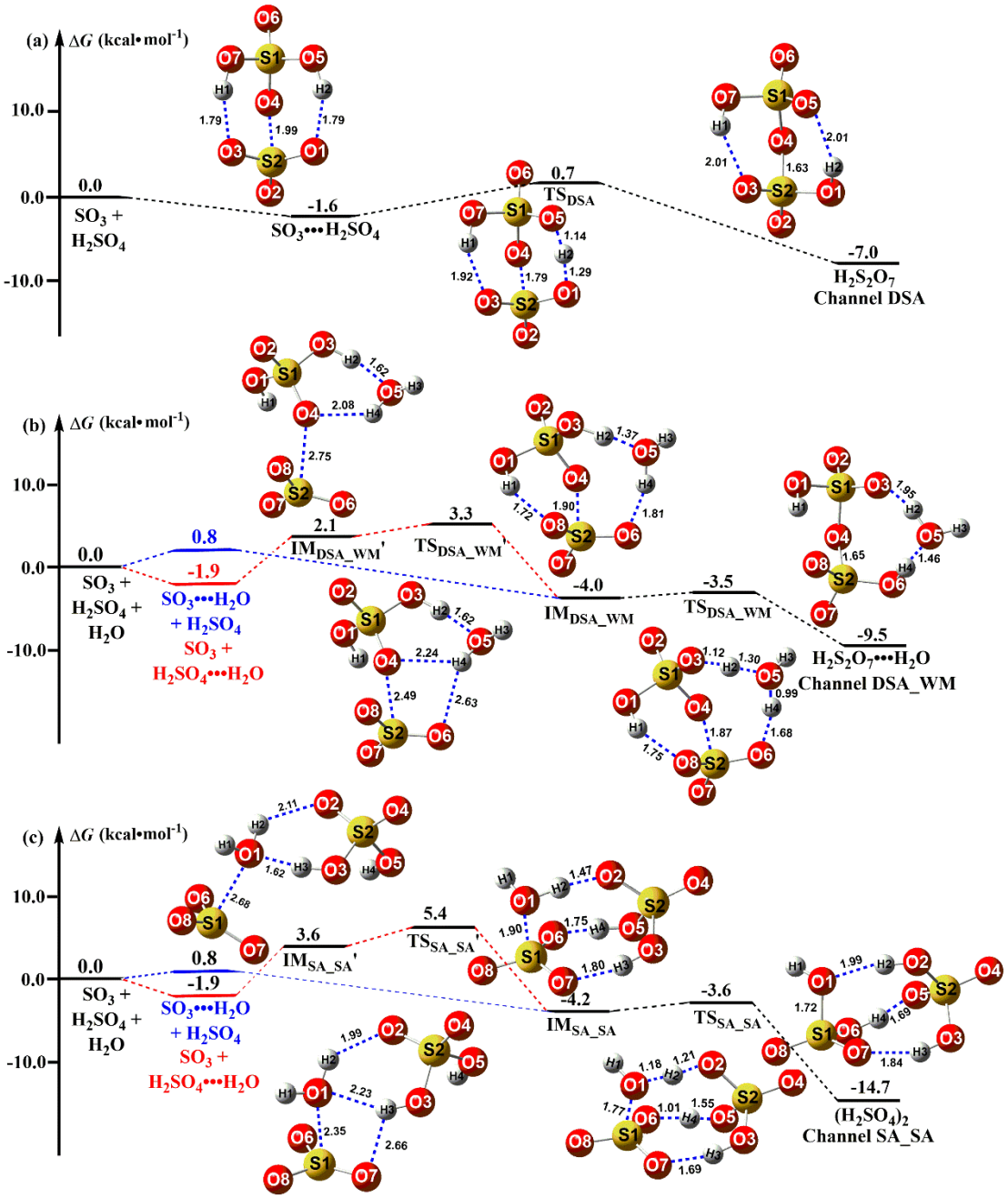


Fig. 1 Schematic potential energy surface of the SO_3 + H_2SO_4 reaction without and with H_2O at the CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311+G(2*df*,2*pd*) level

Table 1 The rate constant ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for the SO_3 + H_2SO_4 reaction along with the effective rate constant ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for the SO_3 + H_2SO_4 reaction with H_2O (100%RH) within the temperature range of 280-320 K

T/(K)	280 K	290 K	298 K	300 K	310 K	320 K
k_{DSA}	5.52×10^{-12}	4.60×10^{-12}	3.95×10^{-12}	3.80×10^{-12}	3.13×10^{-12}	2.57×10^{-12}
$k'_{DSA\_WM\_o}$	2.12×10^{-13}	2.68×10^{-13}	2.88×10^{-13}	2.89×10^{-13}	2.89×10^{-13}	2.75×10^{-13}
$k'_{DSA\_WM\_s}$	1.03×10^{-11}	8.55×10^{-12}	7.42×10^{-12}	7.11×10^{-12}	5.79×10^{-12}	4.60×10^{-12}
$k'_{SA\_SA\_o}$	1.29×10^{-21}	8.69×10^{-22}	6.00×10^{-22}	5.37×10^{-22}	3.47×10^{-22}	2.28×10^{-22}

$k'_{SA\_SA\_s}$	3.93×10^{-21}	1.82×10^{-21}	1.01×10^{-21}	8.62×10^{-12}	4.42×10^{-12}	2.34×10^{-12}
v_{DSA_WM}/v_{SA_SA}	3.04	2.61	2.30	2.22	1.85	1.53

k_{DSA} is the rate constant for the $SO_3 + H_2SO_4$ reaction; $k'_{DSA\_WM\_o}$ and $k'_{DSA\_WM\_s}$ are respectively the effective rate constants for H_2O-assisted $SO_3 + H_2SO_4$ reaction occurring through one-step and stepwise routes. $k'_{SA\_SA\_o}$ and $k'_{SA\_SA\_s}$ are respectively the effective rate constants for the hydrolysis reaction of SO_3 with H_2SO_4 occurring through one-step and stepwise routes. v_{DSA_WM}/v_{SA_SA} is the rate ratio between Channel DSA_WM and Channel SA_SA.

Comment 2.

While interesting, I'm not sure the BOMD simulations are saying much about the relevance of $H_2S_2O_7$ for actual new-particle formation: $H_2S_2O_7$ formed in water droplets will presumably stay there, and never evaporate to participate in NPF. (Overall, "air-water interfaces" have little to do with actual NPF, as the interfaces are by definition found in particles that *have already formed*: many of the claims of "NPF-relevance" made in the study are thus by definition incorrect). While there may be some relevance of the studied process to particle growth, even H_2SO_4 has an essentially zero evaporation rate from any particles larger than a few nanometers - so it may make little difference to the growth of larger aerosol whether the sulfur is taken up as H_2SO_4 or $H_2S_2O_7$ (also see issue 4 for a further caveat).

Response: Thanks for your valuable comments. We agree with the suggestion of the reviewer that the reaction of $H_2S_2O_7$ or H_2SO_4 formations at air-water interface is not directly related to new particle formation. However, the reaction of $H_2S_2O_7$ or H_2SO_4 formations at air-water interface is necessary to investigate by using BOMD simulations. This is because that

(a) Many investigations (***J. Am. Chem. Soc.***, 2016, 138, 1816-1819; ***Proc. Natl. Acad. Sci. U.S.A***, 2017, 114, 12401-12406.; ***J. Am. Chem. Soc.***, 2018, 140, 6456-6466.; ***J. Am. Chem. Soc.***, 2018, 140, 14, 4913-4921.; ***Chem. Sci.***, 2019, 10, 743-751.; ***Chem. Sci.***, 2017,8, 5385-5391.) suggest that interfacial environment not only triggers the arrangement and aggregation of hydrophilic groups, but also provides a good medium for many atmospheric reactions. Notably, due to the induction of proton transfer pathways by interfacial water molecules, many atmospheric reactions that occur on the surface of aerosols and droplets are faster, and sometimes are different from the corresponding processes in the gas phase. Based on this, the differences in the reactivity of SO_3 with H_2SO_4 in the gas phase and at the air-water interface were evaluated by using BOMD simulations.

(b) The BOMD simulation results at the air-water interface suggest that three different types of interfacial reaction mechanisms (*i*) H_2O-induced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair; (*ii*) HSO_4^- mediated the formation of $HSO_4^-\cdots H_3O^+$ ion pair and (*iii*) the deprotonation of $H_2S_2O_7$ were observed. These interfacial reactions occurred through stepwise mechanism to form the ion pair of $S_2O_7^{2-}\cdots H_3O^+$ and $HSO_4^-\cdots H_3O^+$, and proceed on the picosecond time scale. These interfacial mechanisms are in contrast to the gas phase reaction mechanisms in which loop-structure mechanism were involved in $SO_3 + H_2SO_4$ reaction without and with H_2O. Thus, the $SO_3 + H_2SO_4$ reaction behavior at the air-water interface is different from that of the gas phase, and some new and different mechanisms have been found.

(c) Although the formation routes of the $S_2O_7^{2-}\cdots H_3O^+$ and $HSO_4^-\cdots H_3O^+$ ion pair at air-water interface is not directly related to new particle formation, the $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation potential as the following reasons. One reason is that the interactions of $S_2O_7^{2-}\cdots H_2SO_4$, $S_2O_7^{2-}\cdots HNO_3$, $S_2O_7^{2-}\cdots (COOH)_2$, $H_3O^+\cdots NH_3$, $H_3O^+\cdots H_2SO_4$, $SA^-\cdots H_2SO_4$, $SA^-\cdots (COOH)_2$, and $SA^-\cdots HNO_3$ listed in Table 2 are stronger than those of $H_2SO_4\cdots NH_3$ (major precursor of atmospheric aerosols). These results reveal that interfacial $S_2O_7^{2-}$, SA^- and H_3O^+ can attract candidate species from the gas phase to the water surface. The other reason is that as compared with $(SA)_1(A)_1(X)_1$ (X = $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$) clusters (Zhong et al., 2019; Zhang et al., 2018; Rong et al., 2020; Gao et al., 2023; Liu et al., 2021a; Zhang et al., 2017), the number of hydrogen bonds in $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster presented in Fig. S8 increased and the ring of the complex was enlarged. Meanwhile, comparing to $(SA)_1(A)_1(X)_1$ (X = $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$) clusters (Table 2), the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster is lower, showing $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation ability than X in the gas phase. Based on this, the sentence of "and thus in turn accelerates the growth of particle." has been deleted in Line 14 Page 14 of the revised manuscript. Similarly, the sentence of "enhancing potential of $S_2O_7^{2-}$ on SA-A cluster" has been changed as "the nucleation potential of $S_2O_7^{2-}$ on SA-A cluster" in Line 15 Page 16 of the revised manuscript. Moreover, the sentence of "the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster is lower. Therefore, we predict that $S_2O_7^{2-}$ at the air-water interface has important implication to the aerosol NPF in highly industrial polluted regions with high concentrations of SO_3." has been

changed as "the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster is lower, showing $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation ability than *X* in the gas phase. Therefore, we predict that $S_2O_7^{2-}$ at the air-water interface has stronger nucleation potential." in Lines 23-26 Page 16 of the revised manuscript.

Overall, the BOMD simulations of three different types of interfacial reaction mechanisms (*i*) H_2O-induced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair; (*ii*) HSO_4^- mediated the formation of $HSO_4^-\cdots H_3O^+$ ion pair and (*iii*) the deprotonation of $H_2S_2O_7$ were studied. These interfacial reactions occurred through stepwise mechanism and were in contrast to the gas phase reaction mechanisms in which loop-structure mechanism were involved in $SO_3 + H_2SO_4$ reaction without and with H_2O. Then, the nucleation potential of $S_2O_7^{2-}$ at the air-water interface has been investigated by considering the adsorption capacity of the $S_2O_7^{2-}$, H_3O^+ and SA^- to gasous precursors in the atmosphere as well as the geometrical structure and the formation free energies of the $(SA)_1(A)_1(S_2O_7^{2-})_1$ clusters.

Comment 3.

The authors spend much time discussing the results they obtain for the "enhancement factor" R (equation 5). As cautioned in Elm et al. (https://www.sciencedirect.com/science/article/abs/pii/S0021850220301099), the excessive use of such abstract "enhancement factors" is questionable and risky. In this particular case, I don't believe the results are actually technically badly wrong - for example including the effect of H_2SO_4 depletion (caused by a fraction of the SO_3 forming DSA rather than H_2SO_4) would probably not change the qualitative results, as the clustering ability of DSA is much greater than that of H_2SO_4. (For completeness sake, I would nevertheless recommend this is done). However, many of the presented "results" are in reality rather trivial consequence of how the simulation is set up, and the parameters defined. For example, the R values are quite obviously "greater than or equal to 1", as the J values with added DSA cannot (in the way the authors run ACDC) be lower than the J values without the added DSA. Similarly, the various correlations between R and different parameters are not particularly informative or novel. I recommend the authors first of all account for all relevant effects (including sulfur depletion - ie run the code with a constant SO_3 source rather than constant $[H_2SO_4]$), and also condense the discussion on "enhancement factors".

Response: Thanks for your valuable comments. The reason for using a constant SO_3 source is not reasonable has been explained firstly. Meanwhile, the corresponding discussion on "enhancement factors" have been condensed and the analysis of the absolute formation rate with temperature and concentration changes after the addition of $H_2S_2O_7$ has been added. The corresponding major revision has been made as follows.

(a) It is not reasonable to use a constant SO_3 source since there are many pathways for the removal of SO_3 removal processes. the hydrolysis of SO_3 to product H_2SO_4 is the most major loss route of SO_3 in the atmosphere. As a complement to the loss of SO_3, ammonolysis reaction of SO_3 in polluted areas of NH_3 can form H_2NSO_3H, which can be competitive with the formation of H_2SO_4 from the hydrolysis reaction of SO_3. Besides, the reactions of SO_3 with CH_3OH, HNO_3, and organic acids (e.g., formic acid, acetic acid and acrylic acid). These reactions consume some SO_3 in the atmosphere and inhibit the hydrolysis of SO_3 (H_2SO_4 formation) to some extent. Thus, it is not suitable to use a constant source of SO_3.

The concentration of $H_2S_2O_7$ has been re-evaluated within the altitude range of 0-30 km. Then, the analysis of the absolute formation rate with temperature and concentration changes after the addition of $H_2S_2O_7$ has been added in Lines 28-30 Page 14 to Lines 1-13 Page 15 of the revised manuscript, which has been organized as "The potential enhancement influence of DSA to the SA-A-based particle formation was shown in Fig. 6. The formation rate (J, $cm^{-3}\cdot s^{-1}$) of SA-A-DSA-based system illustrated in Fig. 6 was negatively dependent on temperature, demonstrating that the low temperature is a key factor to accelerate cluster formation. It is noted that, at low temperatures of 218.15 K (Fig. S12) and 238.15 K (Fig. S13), the actual ΔG of clusters has been calculated to ensure meaningful cluster dynamics of the 3 × 3 systems, where the actual ΔG surface represented that the simulated set of clusters always included the critical cluster. In addition to temperature, the J of SA-A-DSA-based system shown in Fig. 6 rise with the increase of [DSA]. More notably, the participation of DSA can promote J to a higher level, indicating its enhancement on SA-A nucleation. Besides, there was significantly positive dependence of the J of SA-A-DSA-based system on both [SA] and [A] in Fig. 7 (238.15 K) and Fig. S15-Fig. S18 (218.15, 258.15, 278.15 and 298.15 K). This was because the higher concentration of nucleation precursors could lead to higher J. Besides, Fig. S19 showed the nucleation rate when the sum ([SA] + [DSA]) was kept constant. $J_{DSA/SA}$ at substituted condition was higher than that at unsubstituted condition. These

results indicated that DSA may can greatly enhance the SA-A particle nucleation in heavy sulfur oxide polluted atmospheric boundary layer, especially at an average flight altitude of 10 km with high [DSA]."

Comment 4

The most problematic part of the overall claim for atmospheric relevance is the neglect of $H_2S_2O_7$ decomposition by hydration (i.e. the $H_2S_2O_7 + H_2O \Rightarrow H_2SO_4 + H_2SO_4$ reaction), which is very well known (e.g. from industrial sulfur chemistry) to be rapid and spontaneous. (Indeed, $H_2S_2O_7$ is one of the strongest dehydrating agents in the known universe - its hydration reaction is so strong and favourable that it can even extract water molecules from sugar.) The BOMD simulations indicate that $H_2S_2O_7$ is stable for 10 picoseconds - but this is nowhere near enough time for a $H_2S_2O_7$ to, for example, collide with a H_2SO_4 (timescale: seconds) in the gas phase (and thus participate in NPF). Recently, another group showed that preliminary results on the role of sulfamic acid in new-particle formation are invalidated by rapid hydrolysis (https://pubs.acs.org/doi/full/10.1021/acs.jpca.3c04982) - I anticipate something very similar may end up being the case for di/pyrosulfuric acid in the Earth's lower atmosphere. Having said that, the presented results may very well have relevance for stratospheric chemistry, as well as for cloud chemistry on Venus (where there is much less water, and much more H_2SO_4). I recommend the atmospheric implications and relevance discussion be reformulated to target the appropriate atmospheres /or regions of them. Or at the very least, the possible (even likely) rapid hydrolysis of $H_2S_2O_7$ should be mentioned as a major caveat of the results (and as a strongly recommended subject for follow-up studies!)

Response: Thanks for your valuable comments. According to the reviewer's suggestion, the importance of the $SO_3 + H_2SO_4$ reaction has been investigated in the atmospheres of Earth and Venus. Meanwhile, the concentration of $H_2S_2O_7$ has been re-evaluated where the end and outside the aircraft engine and flight was considered. The corresponding revision has been made as follows.

(a) To understand the competition between the $SO_3 + H_2SO_4$ reaction and H_2O-assisted hydrolysis of SO_3 in the Earth's atmosphere, the rate ratio (v_{DSA}/v_{SA}) between the $SO_3 + H_2SO_4$ reaction and H_2O-assisted hydrolysis of SO_3 has been calculated and was expressed in Eq. (5).

$$\frac{v_{DSA}}{v_{SA}} = \frac{k_{DSA} \times [SO_3] \times [H_2SO_4] + k_{DSA\_WM\_s} \times K_{eq1} \times [SO_3] \times [H_2SO_4] \times [H_2O]}{k_{SA\_WM} \times K_{eq2} \times [SO_3] \times [H_2O] \times [H_2O]} \quad (5)$$

In Eq. (5), K_{eq1} and K_{eq2} were the equilibrium constant for the formation of $H_2SO_4\cdots H_2O$ and $SO_3\cdots H_2O$ complexes shown in Table S2, respectively; k_{DSA}, $k_{DSA\_WM\_s}$ and k_{SA_WM} were respectively denoted the bimolecular rate coefficient for the $H_2SO_4 + SO_3$, $H_2SO_4\cdots H_2O + SO_3$ and $SO_3\cdots H_2O + H_2O$ reactions; $[H_2O]$ and $[H_2SO_4]$ were respectively represented the concentration of H_2O and H_2SO_4 taken from references (***J. Phys. Chem. A***, 2013, 117, 10381-10396.; ***Environ. Sci. Technol.***, 2015, 49, 13112-13120.). The corresponding rate ratio have been listed in Table S7 (0 km altitude) and S8 (5-30 km altitude). As seen in Table S7, at 0 km altitude, the hydrolysis reaction of SO_3 with $(H_2O)_2$ is more favorable than the $SO_3 + H_2SO_4$ reaction as the $[H_2O]$ (10^{16}-10^{18} molecules·cm^3) is much larger than that of $[H_2SO_4]$ (10^4-10^8 molecules·cm^3). Although the concentration of water molecules decreases with the increase of altitude in Table S8, the concentration of $[H_2O]$ is still much greater than that of $[H_2SO_4]$, resulting in the $SO_3 + H_2SO_4$ reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 5-30 km. Moreover, the $SO_3 + H_2SO_4$ reaction is not also the major sink route of SO_3, even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight. Based on this, the sentence of "The value of v_{DSA}/v_{SA} was listed in Table S7 (0 km altitude) and S8 (5-30 km altitude). As seen in Table S7, at 0 km altitude, the hydrolysis reaction of SO_3 with $(H_2O)_2$ is more favorable than the $SO_3 + H_2SO_4$ reaction as the $[H_2O]$ (10^{16}-10^{18} molecules·cm^3) is much larger than that of $[H_2SO_4]$ (10^4-10^8 molecules·cm^3). Although the concentration of water molecules decreases with the increase of altitude in Table S8, the concentration of $[H_2O]$ is still much greater than that of $[H_2SO_4]$, resulting in the $SO_3 + H_2SO_4$ reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 5-30 km. Even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight at 10 km, the $SO_3 + H_2SO_4$ reaction is not also the major sink route of SO_3." has been added in Lines 24-29 Page 13 to Lines 1-4 Page 14 of the revised manuscript.

(b) It has been proposed that the concentration of sulfuric acid is even greater than that of water vapor in the atmosphere of Venus (***Science***, 1990, 249, 1273.; ***Planet. Space Sci.***, 2006, 54, 1352.; ***Icarus***, 1994, 109, 58.; ***Nat. Geosci.***, 2010, 3, 834.), which may lead to that the $SO_3 + H_2SO_4$ reaction is probably favorable than the H_2O-assisted hydrolysis of SO_3 in the Venus' atmosphere. To check whether the $SO_3 + H_2SO_4$ reaction is more favorable than H_2O-assisted hydrolysis of SO_3 or not in the Venus' atmosphere, the rate ratio of v_{DSA}/v_{SA} listed in Eq. 4 has been calculated in Table 2. It

can be seen from Table 2 that the rate ratio of v_{DSA}/v_{SA} is 3.24×10^8-5.23×10^{10} in the 40-70 km altitude range of Venus, which indicates that the $SO_3 + H_2SO_4$ reaction is significantly more favorable than the hydrolysis reaction of $SO_3 + (H_2O)_2$ within the altitudes range of 40-70 km in the Venus' atmosphere. Based on this, the sentence of "Notably, as the concentration of sulfuric acid is even greater than that of water vapor in the atmosphere of Venus, the SO_3 + SA reaction is probably favorable than the H_2O-assisted hydrolysis of SO_3 in the Venus' atmosphere. To check whether the $SO_3 + H_2SO_4$ reaction is more favorable than H_2O-assisted hydrolysis of SO_3 or not in the Venus' atmosphere, the rate ratio of v_{DSA}/v_{SA} listed in Eq. 4 has been calculated in Table 2. It can be seen from Table 2 that the rate ratio of v_{DSA}/v_{SA} is 3.24×10^8-5.23×10^{10} in the 40-70 km altitude range of Venus, which indicates that the $SO_3 + H_2SO_4$ reaction is significantly more favorable than the hydrolysis reaction of $SO_3 + (H_2O)_2$ within the altitudes range of 40-70 km in the Venus' atmosphere." has been added in Lines 4-11 Page 14 of the revised manuscript.

(c) Considering the concentration of sulfuric acid at the end and outside the aircraft engine and flight (up to 600 pptv), the concentration of $H_2S_2O_7$ has been re-evaluated within the altitude range of 0-30 km. Specifically, the steady-state concentration of DSA was calculated using the calculated equilibrium constant listed in Eq. S5.

$$K_{eq3} = \frac{[DSA]}{[SO_3][SA]} \quad (S5)$$

where K_{eq3} is the equilibrium constant of DSA with respect to SO_3 and H_2SO_4 within the altitude range of 0-30 km shown in Table S9; $[SO_3]$, [SA] and [DSA] are the concentrations of SO_3, H_2SO_4, and $H_2S_2O_7$, respectively. Although the concentration of sulfur trioxide remains unknown at different altitudes, experimental observations have shown that the concentration of sulfur trioxide can reach 10^6 molecules cm^{-3} in the troposphere. Moreover, water vapor concentrations significantly decrease with increasing of altitude. Consequently, the concentration of sulfur trioxide should be higher in the stratosphere than in the troposphere, and its concentration would increase as a result of geoengineered injection of SO_2 or SO_3. Besides, it is worth noting that H_2SO_4 can form at the end and outside the engine, and flight measurements in the exhaust plume have measured sulfuric acid abundances up to a value of 600 pptv. When an average flight altitude of 10 km is considered, this corresponds to a concentration of 5.1×10^9 molecules·cm^{-3}. Therefore, we have calculated the concentrations of DSA according to concentrations of sulfur trioxide in the range from 10^7 to 10^{14}

molecules cm^{-3} and the concentrations of H_2SO_4 in the range of 10^4-10^9 molecules cm^{-3} as shown in Fig. S9.

The maximum concentration of DSA displayed in Fig. S9 can be up to 10^8 molecules·cm^{-3}. However, it should be noted that the concentration of water in the troposphere is abundant, and DSA is easily hydrolyzed to form H_2SO_4. Based on this, the concentration of DSA listed in Fig. S9 was overestimated. However, the extent and proportion of DSA hydrolysis remains unclear, and the hydrolysis behavior of DSA needs to be further investigated in subsequent studies. Therefore, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$, the product of the reaction between SO_3 and H_2SO_4, on new particle formation (NPF) in various environments by using the Atmospheric Cluster Dynamics Code kinetic model and the QC calculation. In Lines 27-29 Page 7 to Lines 1-2 Page 8 of the revised manuscript, the discussion of the DSA concentration has been added as "As the prediction in Table S7, the concentration of DSA is set to 10^4-10^8 molecules·cm^{-3}. However, DSA is easily hydrolyzed with abundant water in the troposphere to form H_2SO_4, the concentration of DSA listed in Fig. S9 was overestimated. So, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$ on new particle formation (NPF) in various environments."

Overall, the SO_3 + SA reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 0-30 km in the Earth's atmosphere, even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight. However, the SO_3 + SA reaction is significantly more favorable than the hydrolysis reaction of SO_3 + $(H_2O)_2$ within the altitude range of 40-70 km in Venus' atmosphere. Moreover, as the extent and proportion of DSA hydrolysis is unclear, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$ on new particle formation (NPF) in various environments by using the Atmospheric Cluster Dynamics Code kinetic model and the QC calculation.

Comment 5.

Another issue to consider is the timescale associated with participation in NPF of compounds with mixing ratios well below a part per quadrillion. The gas-kinetic bimolecular collision rate for small molecules and their clusters is around 1E-10…1E-9 cm^3 per molecule and second. If the DSA concentration is 1 molecule per cm^3, then on average a H_2SO_4 molecule, or a H_2SO_4-containing

cluster, will thus collide with DSA molecules about once per 1E9 seconds or so (as the pseudo-unimolecular collision rate is k_coll times the concentration, and the lifetime with respect to collisions is the inverse of this). This is more than 30 YEARS. Even for a DSA concentration of 10 per cm^3, the timescale of a given molecule or cluster colliding with a DSA molecule is more than 3 YEARS. Or for 100 per cm^3, more than 3 months. It is quite clear from this that the pseudo-steady-state assumed by ACDC simulations will simply never have time to form, when some of the participating molecules have such low concentrations. Or in other words, the basic assumptions required for modelling clustering with ACDC do not apply in these cases (or, to put it yer another way, an ACDC - type code needs to be run in a very different way, explicitly accounting for these timescales).

Response: Thanks for your valuable comments. We agree with the reviewer that at some of the participating molecules such low concentrations that the pseudo-steady-state assumed by ACDC simulations will simply never have time to form. Based on this, Considering the concentration of sulfuric acid at the end and outside the aircraft engine and flight (up to 600 pptv), the concentration of $H_2S_2O_7$ has been re-evaluated within the altitude range of 0-30 km. Specifically, the steady-state concentration of DSA was calculated using the calculated equilibrium constant listed in Eq. S5.

$$K_{eq3} = \frac{[DSA]}{[SO_3][SA]} \quad (S5)$$

where K_{eq3} is the equilibrium constant of DSA with respect to SO_3 and H_2SO_4 within the altitude range of 0-30 km shown in Table S9; [SO_3], [SA] and [DSA] are the concentrations of SO_3, H_2SO_4, and $H_2S_2O_7$, respectively. Although the concentration of sulfur trioxide remains unknown at different altitudes, experimental observations have shown that the concentration of sulfur trioxide can reach 10^6 molecules cm^{-3} in the troposphere. Moreover, water vapor concentrations significantly decrease with increasing of altitude. Consequently, the concentration of sulfur trioxide should be higher in the stratosphere than in the troposphere, and its concentration would increase as a result of geoengineered injection of SO_2 or SO_3. Besides, it is worth noting that H_2SO_4 can form at the end and outside the engine, and flight measurements in the exhaust plume have measured sulfuric acid abundances up to a value of 600 pptv. When an average flight altitude of 10 km is considered, this corresponds to a concentration of 5.1×10^9 molecules·cm^{-3}. Therefore, we have calculated the concentrations of DSA according to concentrations of sulfur trioxide in the range from 10^7 to 10^{14}

molecules cm^{-3} and the concentrations of H_2SO_4 in the range of 10^4-10^9 molecules cm^{-3} as shown in Fig. S9.

The maximum concentration of DSA displayed in Fig. S9 can be up to 10^8 molecules·cm^{-3}. However, it should be noted that the concentration of water in the troposphere is abundant, and DSA is easily hydrolyzed to form H_2SO_4. Based on this, the concentration of DSA listed in Fig. S9 was overestimated. The extent and proportion of DSA hydrolysis remains unclear, and the hydrolysis behavior of DSA needs to be further investigated in subsequent studies. Therefore, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$, the product of the reaction between SO_3 and H_2SO_4, on new particle formation (NPF) in various environments by using the Atmospheric Cluster Dynamics Code kinetic model and the QC calculation.

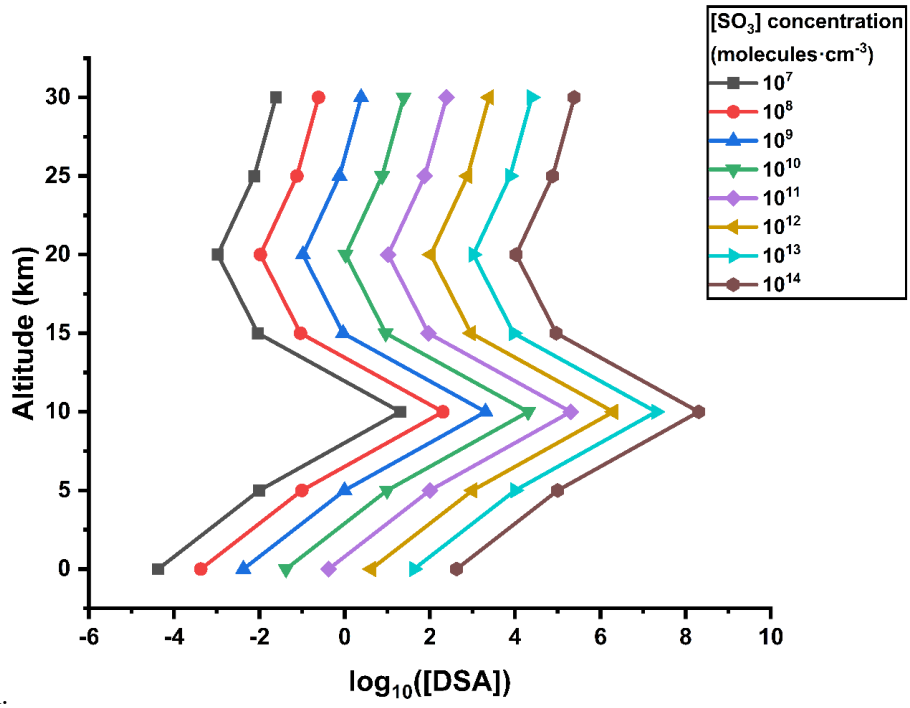


Fig. S9 Concentration (unit: molecules·cm^{-3}) of DSA with respect to different concentrations of SO_3 as function of altitude. We consider the possible concentrations of SO_3 with the injection of SO_3.

The maximum concentration of DSA displayed in Fig. S9 can be up to 10^8 molecules·cm^{-3}. However, it should be noted that the concentration of water in the troposphere is abundant, and DSA is easily hydrolyzed to form H_2SO_4. Based on this, the concentration of DSA listed in Fig. S9 was overestimated. The extent and proportion of DSA hydrolysis remains unclear, and the hydrolysis behavior of DSA needs to be further investigated in subsequent studies. Therefore, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$, the product of

the reaction between SO_3 and H_2SO_4, on new particle formation (NPF) in various environments by using the Atmospheric Cluster Dynamics Code kinetic model and the QC calculation.

Technical issues

Comment 6.

The kinetic approach used here seems quite elaborate, given that the authors are not actually treating (or at least not discussing) any sort of pressure dependence, non-thermalisation, etc. How different are the rates compared to what one would obtain using a simple transition state theory framework (plus assuming kinetic gas theory forward rates for the initial complex formation)? I'm not criticising the use of elaborate methods as such, I'm just trying to assess how much difference they make, compared to a much simpler approach.

Response: Thanks for your valuable comments. The Rice-Ramsperger-Kassel-Marcus based Master Equation (ME/RRKM) model is well suited to calculate the kinetics of the $SO_3 + H_2SO_4$ reaction without and with H_2O. Specifically, as for the $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ reaction without and with H_2O illustrated in Fig. 1, the reaction without H_2O has only a barrier height of 2.3 $kcal \cdot mol^{-1}$ to produce the formation of $H_2S_2O_7$, while the reaction with H_2O only has a lower barrier height of 0.5 $kcal \cdot mol^{-1}$. It is reported that the ME/RRKM model has been used widely to calculate the rate constants of many gas phase reactions (***J. Am. Chem. Soc.***, 2022, 144, 19910-19920.; ***J. Am. Chem. Soc.,*** 2022, 144, 20, 9172-9177.; ***Phys. Chem. Chem. Phys.***, 2022, 24, 18205-18216.; ***Phys. Chem. Chem. Phys.***, 2022, 24, 4966-4977.; ***J. Phys. Chem. A***, 2019, 123, 3131-3141.; ***Chem. Phys. Lett.***, 2020, 742, 137157.) where the rate constants for barrierless or near barrierless bimolecular reactions were evaluated reliably. In this case, the pre-equilibrium approximation used in our calculation is truly obsolete and may not be appropriate.

Meanwhile, to check the reliability of Master Equation (ME/RRKM) model, the rate constants for the $SO_3 + H_2SO_4$ reaction without and with H_2O were also calculated by using transition state theory (TST) coupled with the pre-equilibrium approximation. As seen in Table S6, the rate constants for the $SO_3 + H_2SO_4$ reaction without and with H_2O by using transition state theory is significantly higher than the gas kinetic limit. In addition, as for the rate constants calculated by transition state theory (TST) coupled with the pre-equilibrium approximation, the rate constants for the $SO_3 + H_2SO_4$ reaction without and with H_2O showed appreciably high negative temperature

dependence making the rate constants even larger at lower temperatures. This reveals that the TST coupled with pre-equilibrium approximation used in our calculation is truly obsolete and may not be appropriate. Thus, Using the Master Equation/Rice-Ramsperger-Kassel-Marcus (ME/RRKM) models, the kinetic calculations for the $SO_3 + H_2SO_4$ reaction without and with H_2O were performed by Bartis-Widom method in the MESMER program package (Master Equation Solver for Multi-Energy Well Reactions).

Table S6 The rate constant ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for the $SO_3 + H_2SO_4$ reaction for the $SO_3 + H_2SO_4$ reaction without and with H_2O within the temperature range of 280-320 K by using transition state theory

T/(K)	280 K	290 K	298 K	300 K	310 K	320 K
k_{DSA}	8.98×10^{-9}	4.38×10^{-9}	2.56×10^{-9}	2.25×10^{-9}	1.20×10^{-9}	6.72×10^{-10}
$k'_{DSA\_WM\_o}$	5.77×10^{-8}	2.59×10^{-8}	1.42×10^{-8}	1.23×10^{-8}	6.12×10^{-9}	3.18×10^{-9}
$k'_{DSA\_WM\_s}$	5.20×10^{-5}	2.44×10^{-5}	1.39×10^{-5}	1.21×10^{-5}	6.29×10^{-6}	3.42×10^{-6}

k_{DSA} is the rate constant for the $SO_3 + H_2SO_4$ reaction; $k_{DSA\_WM\_o}$ and $k_{DSA\_WM\_s}$ are respectively the rate constants for H_2O-assisted $SO_3 + H_2SO_4$ reaction occurring through one-step and stepwise routes.

Comment 7

The method references for M06-2X, CCSD(T)-F12, and the ORCA program are not correct - the first is completely wrong, while the latter refer to studies which have also used these approaches. Please refer to the actual publications introducting the methods/codes instead.

Response: Thanks for your valuable comments. We are very sorry for using wrong references for M06-2X, CCSD(T)-F12, and the ORCA program. The references regarding for the M06-2X, CCSD(T)-F12 and the ORCA program has been respectively made as follows.

(a) As for M06-2X method, the correct references have been recited which has been organized as references (Zhao and Truhlar, 2008; Elm et al., 2012).

[1] Zhao, Y., and Truhlar, D. G.: The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor. Chem. Acc., 120, 215-241, 2008.;

[2] Elm, J., Bilde, M., and Mikkelsen, K. V.: Assessment of density functional theory in predicting structures and free energies of reaction of atmospheric prenucleation clusters, J. Chem. Theory Comput., 8, 2071-2077, 2012.

(b) Regarding for CCSD(T)-F12 method, the relevant references have been changed which has been organized as references (Adler et al., 2007; Knizia et al., 2009).

[1] Adler, T. B., Knizia, G., and Werner, H. J.: A simple and efficient CCSD(T)-F12 approximation, J. Chem. Phys., 127, 221106, 10.1063/1.2817618, 2007.

[2] Knizia, G., Adler, T. B., and Werner, H.-J.: Simplified CCSD(T)-F12 methods: Theory and benchmarks, J. Chem. Phys., 130, 054104, 10.1063/1.3054300, 2009.

(c) As for ORCA program, the corresponding reference have been recited which has been organized as references (Neese, 2012).

[1] Neese, F.: The ORCA program system, WIREs Comput. Mol. Sci., 2, 73-78, https://doi.org/10.1002/wcms.81, 2012.

Responses to Referee #2's comments

We are grateful to the reviewers for their valuable and helpful comments on our manuscript "Reaction of SO_3 with H_2SO_4 and Its Implication for Aerosol Particle Formation in the Gas Phase and at the Air-Water Interface" (MS No.: **egusphere-2023-2009**). We have revised the manuscript carefully according to reviewers' comments. The point-to-point responses to the Referee #2's comments are summarized below:

Referee Comments

Using computational methods Wang and co-workers study the reaction between H_2SO_4 and SO_3 leading to the formation of $H_2S_2O_7$. The gas-phase formation mechanism is studied using well-established methodologies, both with and without a water molecule present. The reaction is also studied at the air-water interface using Born-Oppenheimer molecular dynamics simulations. Finally, the authors study the potential of the formed $H_2S_2O_7$ product in "enhancing" new particle formation involving sulfuric acid and ammonia.

Overall, the applied quantum chemical methods are up to the current standard and the study is broadly atmospherically interesting, but I believe many of the conclusions are erroneously drawn and not supported by the data. Remember negative results are equally as important as positive results. So try to frame the results in a more transparent fashion. In addition, there is heavy referencing to the SI, which makes the paper difficult to follow in some places and the reader is left wondering if the claims are actually correct. I believe the paper might be worth publishing, but some critical changes must made.

Response: We would like to thank the reviewer for the positive and valuable comments, and we have revised our manuscript accordingly.

Specific Comments:

Comment 1.

Overall: When referring to the SI, please add the numbers to the text as well and elaborate on what the reader is supposed to look at in the SI. In several places it is very difficult to comprehend how the authors draw the conclusions.

Response: Thanks for your valuable comments. According to the reviewer's suggestion, the numbers have been added to the manuscript in reference to the SI and detailing what the reader should look for in the SI. The corresponding revision has been respectively made as follows.

(a) In Lines 18-19 Page 5 of the revised manuscript, the optimized structures and the formation Gibbs free energy of the stable clusters in the supporting information has been mentioned and organized as "The optimized structures and the formation Gibbs free energy of the stable clusters were summarized in Fig. S9 and Table S8 of the *SI Appendix*, respectively."

(b) In Lines 18-19 Page 5 of the revised manuscript, the details of the equilibrium process for the droplet system with 191 water molecules in the supporting information has been mentioned and organized as "The details of the equilibrium process for the droplet system with 191 water molecules are shown in the *SI Appendix* Part 4."

(c) In Lines 10-12 Page 9 of the revised manuscript, the details for calculations of effective rate constants in the supporting information has been mentioned and organized as "the effective rate constants for two bimolecular reactions of $H_2SO_4\cdots H_2O + SO_3$ and $SO_3\cdots H_2O + H_2SO_4$ were calculated, and the details were shown in *SI Appendix*, Part 3 and Table 1."

Comment 2.

Line 48: *"As a typical inorganic acid, SA can act as an important role in the new particle formation …"*

What is meant by "typical here? Please rephrase this sentence.

Response: Thanks for your valuable comments. It has been reported that H_2SO_4 is a major inorganic acidic air pollutant (***Atmos. Chem. Phys.***, 2011, 11, 10803-10822.; ***Atmos. Chem. Phys.***, 2021, 21, 13483-13536.). So, according to the reviewer's suggestion, "As a typical inorganic acid, SA can act as an important role in the new particle formation…" has been changed as "As a major inorganic acidic air pollutant (Tilgner et al., 2021), SA can act as an important role in the new particle formation…".

Comment 3.

Line 82: *"It has been shown that the products of SO_3 with some important atmospheric species have been identified in promoting NPF process."*

Such reaction would lead to the consumption of an SO_3 molecule potentially at the expense of forming less sulfuric acid. This competition should be further discussed in the manuscript.

Response: Thanks for your valuable comments. According to the reviewer's suggestion, the sentence of "It has been shown that the reaction between SO_3 and some important atmospheric species (Li et al., 2018a; Yang et al., 2021; Liu et al., 2019; Rong et al., 2020) not only can cause appreciable consumption of SO_3 and thus reduce the abundance of SA from the hydrolysis of SO_3 in the atmosphere, but also can promote NPF process by their products." has been added in Lines 1-4 Page 4 of the revised manuscript. Moreover, to study the atmospheric importance of the $SO_3 + H_2SO_4$ reaction without and with H_2O, the rate ratio (v_{DSA}/v_{SA}) between the $SO_3 + H_2SO_4$ reaction and H_2O-assisted hydrolysis of SO_3 was compared which has been organized in Lines 13-29 Page 13 to Lines 1-11 Page 14.

Comment 4.

Line 104: I am missing some justification to why the M06-2X functional has been used and why the 6-311++G(2df,2pd) basis set was chosen. In addition, the M06-2X reference is incorrect.

Response: Thanks for your valuable comments. According to the reviewer's suggestion, the reason that M06-2X method with 6-311++G(2*df*,2*pd*) basis set has been added as follows.

(a) It has been proved that M06-2X functional is one of the best functionals to describe the noncovalent interactions and estimate the thermochemistry and equilibrium structures for atmospheric reactions. In Lines 22-24 Page 4 of the revised manuscript, the sentence of "The M06-2X functional has been proved to be one of the best functionals to describe the noncovalent interactions and estimate the thermochemistry and equilibrium structures for atmospheric reactions." has been added.

(b) The geometric parameters of the SO_3 and H_2SO_4 reactants calculated at the M06-2X/6-311++G(3*df*,2*pd*) level have been shown in Fig. S1. As seen in Fig. S1, the mean absolute deviation of calculated bond distances and bond angles between the M06-2X/6-311++G(3*df*,2*pd*) level and the experimental reports were 0.005 Å and 0.45°, respectively. This reveals that the calculated bond distances and bond angles at the M06-2X/6-311++G(3*df*,2*pd*) level agree well with the available experimental values. So, the method of M06-2X/6-311++G(3*df*,2*pd*) was reliable to optimize the geometries of all the stationary points in the $SO_3 + H_2SO_4$ reaction without

and with H_2O. The corresponding details revision have been shown in Fig. S1. Thus, in Lines 1-2 Page 4 of the revised manuscript, the sentence of "It is noted that the calculated bond distances and bond angles at the M06-2X/6-311++G(3*df*,2*pd*) level (Fig. S1) agree well with the available experimental values." has been added.

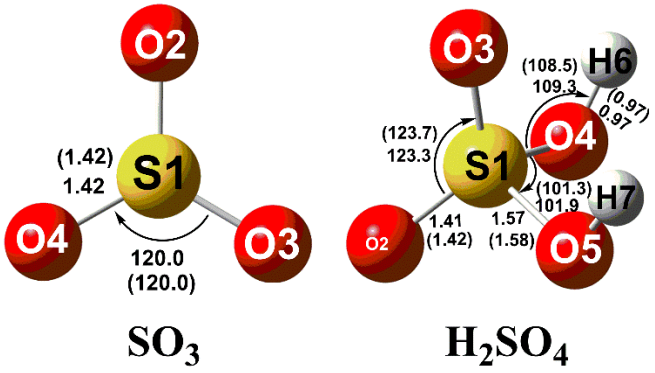


Fig. R1 The optimized geometrical structures for the species of the SO_3 and HCl at M06-2X/6-311++G(3*df*,2*pd*) level of theory. The values in parentheses are the experimental values. Bond length is in angstrom and angle is in degree.

(c) As for M06-2X method, the correct references have been recited which has been organized as references (Zhao and Truhlar, 2008; Elm et al., 2012).

[1] Zhao, Y., and Truhlar, D. G.: The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor. Chem. Acc., 120, 215-241, 2008.;

[2] Elm, J., Bilde, M., and Mikkelsen, K. V.: Assessment of density functional theory in predicting structures and free energies of reaction of atmospheric prenucleation clusters, J. Chem. Theory Comput., 8, 2071-2077, 2012.

Comment 5.

Line 108: The ORCA reference is incorrect.

Response: Thanks for your valuable comments. We are very sorry for using wrong references for the ORCA program. As for ORCA program, the corresponding reference have been recited and organized as references (Neese, 2012).

[1] Neese, F.: The ORCA program system, WIREs Comput. Mol. Sci., 2, 73-78, https://doi.org/10.1002/wcms.81, 2012.

Comment 6.

Line 110-116: I am in doubt whether the applied configurational sampling of the clusters is sufficient to identify the lowest free energy cluster structures. Only calculating 1000 local minima from the ABCluster search sounds a bit low on the low side. How certain are the authors that they have located the global minimum? As the CHARMM forcefield cannot handle bond breaking a more diverse pool of clusters is needed. This is usually done by performing ABCluster runs with ionic monomers as well (see Kubečka et al., https://doi.org/10.1021/acs.jpca.9b03853). Only selecting the lowest 100 cluster configurations based on PM6 could lead to the global minimum cluster being missed (see Kurfman et al., https://doi.org/10.1021/acs.jpca.1c00872).

Response: Thanks for your valuable comments. We are very sorry for missing a '*n*' for the configurational sampling method. Indeed, a multi-path searching approach is adopted in this work, which expands the search range. As for every global minimum cluster, *n* kinds of searching pathways have been considered, and 1000 autogenerated structures in every searching pathway were first carried out using ABCluster software, and were optimized at the semi-empirical PM6 methods using MOPAC 2016. Then, up to *n**100 structures with relatively lowest energy among the *n**1000 ($1 < n < 5$) structures were selected and reoptimized at the M06-2X/6-31+G(*d*,*p*) level. Finally, *n**10 lowest-lying structures were optimized by the M06-2X/6-311++G(2*df*,2*pd*) level to determine the global minimum. So, the method for configurational sampling of the clusters has been corrected as "Specifically, a multistep global minimum sampling technique was used to search for the global minima of the $(SA)_x(A)_y(DSA)_z$ ($0< y \leq x + z \leq 3$) clusters. Specifically, the initial *n**1000 ($1 < n < 5$) configurations for each cluster were systematically generated by the ABCluster program (Zhang and Dolg, 2015), and were optimized at the semi-empirical PM6 (Stewart, 2013) methods using MOPAC 2016 (Stewart, 2013; Stewart, 2007). Then, up to *n**100 structures with relatively lowest energy among the *n**1000 ($1 < n < 5$) structures were selected and reoptimized at the M06-2X/6-31+G(*d*,*p*) level. Finally, *n**10 lowest-lying structures were optimized by the M06-2X/6-311++G(2*df*,2*pd*) level to determine the global minimum. The optimized structures and the formation Gibbs free energy of the stable clusters were summarized in Fig. S9 and Table S8 of the SI Appendix, respectively." in Line 8-19 Page 5 of the revised manuscript.

Comment 7.

Line 116: Here it is stated that the free energies are calculated at the M06-2X/6-311++G(2df,2pd) level of theory. However, Table S8 indicates that DLPNO-CCSD(T) single point energy calculations were carried out on top of the clusters.

Response: Thanks for your valuable comments. We apologize for the reviewer's misunderstanding of the calculation methodology. Indeed, the M06-2X/6-311++G(2*df*,2*pd*) method has been used to optimize the geometries of $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters, while the single-point energy calculations were refined at the DLPNO-CCSD(T)/aug-cc-pVTZ level based on the optimized geometries at the M06-2X/6-311++G(2*df*,2*pd*) level. In order to express the calculated method clearly, in Lines 16-18 Page 5 of the revised manuscript, the sentence of "To obtain the reliable energies, single-point energy calculations were refined at the DLPNO-CCSD(T)/aug-cc-pVTZ level based on the optimized geometries at the M06-2X/6-311++G(2*df*,2*pd*) level" has been added.

Comment 8.

Line 147: How was the 191 water cluster obtained? Has this cluster been equilibrated before the SO_3 and H_2SO_4 was added? Or after? Some more details about how the system was setup is needed. Is a 1 fs timestep adequate to capture the desired dynamics? I.e. can it actually capture the hydrogen bond stretching vibration?

Response: Thanks for your valuable comments. According to the reviewer's suggestion, the reason for selecting the droplet system with 191 water molecules has been explained firstly. Meanwhile, it is pointed out that the droplet system with 191 water molecules has been equilibrated before SO_3 and H_2SO_4 was added at the water surface. Finally, the reason for setting a 1 fs timestep in the dynamic simulations has been explained. The corresponding revision has been respectively made as follows.

(a) The size effect on interfacial mechanism has been reported by Zhong et al. (*J. Am. Chem. Soc.*, 2017, 139, 47, 17168-17174), where the behavior of SO_2 adsorption on droplet with 24, 48, 96 and 191 water molecules has been studied. The work reported by Zhong et al. (*J. Am. Chem. Soc.*, 2017, 139, 47, 17168-17174) shows that the smaller droplet is subjected to large deformation

during the system evolution, and the droplet system with 191 water molecules are sufficient to describe the interfacial mechanism. So, we only consider the droplet system with 191 water molecules in the BOMD simulation. The radius of the water droplet in our system was approximately 10.7 Å and a cubic simulation box of side 35 Å was used. The similar set of simulation box have been found widely in previous works. (*J. Am. Chem. Soc.*, 2016, 138, 1816-1819; *Proc. Natl. Acad. Sci. U.S.A*, 2017, 114, 12401-12406.; *J. Am. Chem. Soc.*, 2018, 140, 6456-6466.; *J. Am. Chem. Soc.*, 2018, 140, 14, 4913-4921.; *Chem. Sci.*, 2019, 10, 743-751.; *Chem. Sci.*, 2017,8, 5385-5391.). So, in Lines 20-22 Page 6 of the revised manuscript, the droplet system with 191 water molecules has been reorganized as "As the droplet system with 191 water molecules are sufficient to describe the interfacial mechanism, the air-water interfacial system here included 191 water molecules, SO_3 and SA in the BOMD simulation.".

(b) The droplet system with 191 water molecules has been equilibrated before SO_3 and H_2SO_4 was added at the water surface. Specifically, a nearly spherical droplet with 191 water molecules was firstly constructed by using the Packmol program (*J. Comput. Chem.*, 2009, 30, 2157-2164.) with a tolerance of 2.0 Å, namely, all atoms from different molecules will be at least 2.0 Å apart. Then, based on the resulting initial structure, the GROMACS software (*J. Comput. Chem.*, 2005, 26, 1701-1718.) with the general AMBER force field (GAFF) (*J. Comput. Chem.* 2004, 25, 1157-1174.) was used to simulate the droplet equilibrium process with two steps. In the first step, a water slab of 35 × 35 × 35 $Å^3$ containing 191 water molecules was built using periodic boundary conditions to avoid the effect of neighboring replicas. In the second step, the water slab was fully equilibrated for 1 ns under NVT ensemble (N, V and T represent the number of atoms, volume and temperature, respectively) to reach equilibrium state. The water molecules were described by the TIP3P model. The isothermal-isochoric (NVT) simulation was executed at 298 K for simulation system. The temperature was kept constant by the V-rescale thermostat coupling algorithm. The coupling time constant is 0.1 ps. Bond lengths were constrained by the LINCS algorithm. The cut-off distance of 1.2 nm was set for van der Waals (vdW) interactions. The Particle Mesh Ewald (PME) summation method was used to calculate the electrostatic interactions. During the whole simulation process, a time step of 2 fs was set and three-dimensional periodic boundary conditions were adopted. Next, to ensure the stability of the system, the droplets were pre-optimized using BOMD at 300 K for 10 ps prior to the simulation of the air-water interfacial

reaction. Using the density functional theory (DFT) method, the electronic exchange-correlation term was described by the Becke-Lee-Yang-Parr (BLYP) functional. The Grimme's dispersion correction (D3) was applied to account for the weak dispersion interaction. The double-ζ Gaussian (DZVP-MOLOPT) basis set and the Goedecker-Teter-Hutter (GTH) norm-conserving pseudopotentials were adopted to treat the valence and the core electrons, respectively. The planewave cutoff energy is set to 280 Ry, and that for the Gaussian basis set is 40 Ry. And the SCF convergence criterion is 1.0E-5 Hartree. All simulations were performed in NVT ensemble with Nose-Hoover thermostat controlling the temperature. Finally, the SO_3 and H_2SO_4 molecule was added at the water surface after the droplet system with 191 water molecules was fully equilibrated. The details of the equilibrium process for the droplet system with 191 water molecules are shown in the *SI Appendix* Part 4. Meanwhile, the sentence of "It is pointed out that the droplet system with 191 water molecules has been equilibrated before SO_3 and H_2SO_4 was added at the water surface. The details of the equilibrium process for the droplet system with 191 water molecules are shown in the *SI Appendix* Part 4." has been added in Lines 22-25 Page 6 of the revised manuscript.

(c) In the interfacial BOMD simulations, the timestep was set to be 1.0 fs, as it has been proved to achieve sufficient energy conservation for the water system (*J. Chem. Theory Comput.*, 2011, 7, 2937-2946.; *J. Am. Chem. Soc.* 2015, 137, 12070.; *J. Am. Chem. Soc.* 2016, 138, 1816.; *J. Am. Chem. Soc.* 2016, 138, 11164.; *Chem. Sci.* 2017, 8, 5385.). So, the sentence of "Notably, the timestep of 1.0 fs has been proved to achieve sufficient energy conservation for the water system." has been added in Lines 27-28 Page 6 of revised manuscript.

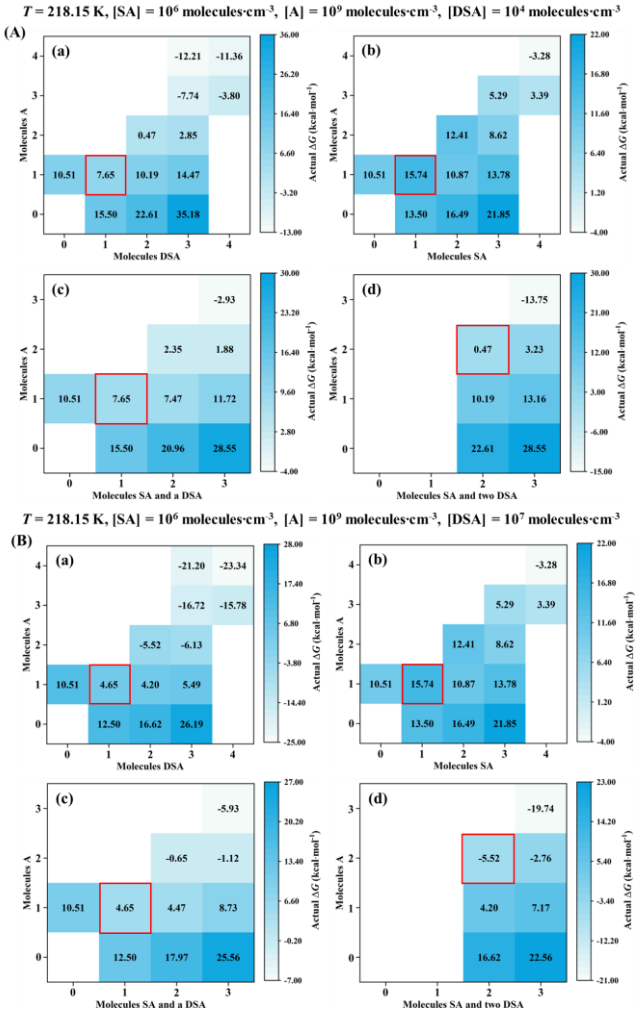
Comment 9.

Line 156: I am not entirely convinced that the 3 × 3 system "box" size is large enough to ensure meaningful cluster dynamics of the systems. For instance, the work by Besel et al. (https://doi.org/10.1021/acs.jpca.0c03984) showed how the sulfuric acid-ammonia system is impacted by the studied box size. Please elaborate on this aspect.

Also is the sulfur concentration constrained in the simulations? A single DSA molecule would consume 2 sulfuric acids. 1 SA and 1 SO_3 that could form SA. Hence, the simulations might actually "push" additional sulfur into the system.

Response: Thanks for your valuable comments. For reviewers' comments, the corresponding revision has been respectively made as follows.

(a) As the work reported by Besel et al. (***J. Phys. Chem. A***, **2020**, 124(28), 5931-5943), the explicitly simulated set of clusters should always include the "critical cluster". Also, the highest barrier on the lowest-energy path connecting the monomers to the outgrowing clusters (a saddle point on the actual ΔG surface) represents the "critical cluster". So, at 218.15 K (Fig. S12) and 238.15 K (Fig. S13), the actual ΔG of $(A)_y(DSA)_z$ ($0 \le y \le z \le 4$), $(SA)_x(A)_y$ ($0 \le y \le x \le 4$), $(SA)_x(A)_y(DSA)_1$ ($0 \le y \le 3$, $0 \le x \le 2$), and $(SA)_x(A)_y(DSA)_2$ ($0 \le y \le 3$, $0 \le x \le 1$) clusters has been calculated to ensure meaningful cluster dynamics of the 3 × 3 systems. As seen in Fig. S12 and S13, the actual ΔG surface represented that the simulated set of clusters always included the critical cluster. So, we conclude that, in atmospherically relevant conditions, a 3 × 3 cluster set is adequate for predicting the particle formation in the SA-A system.



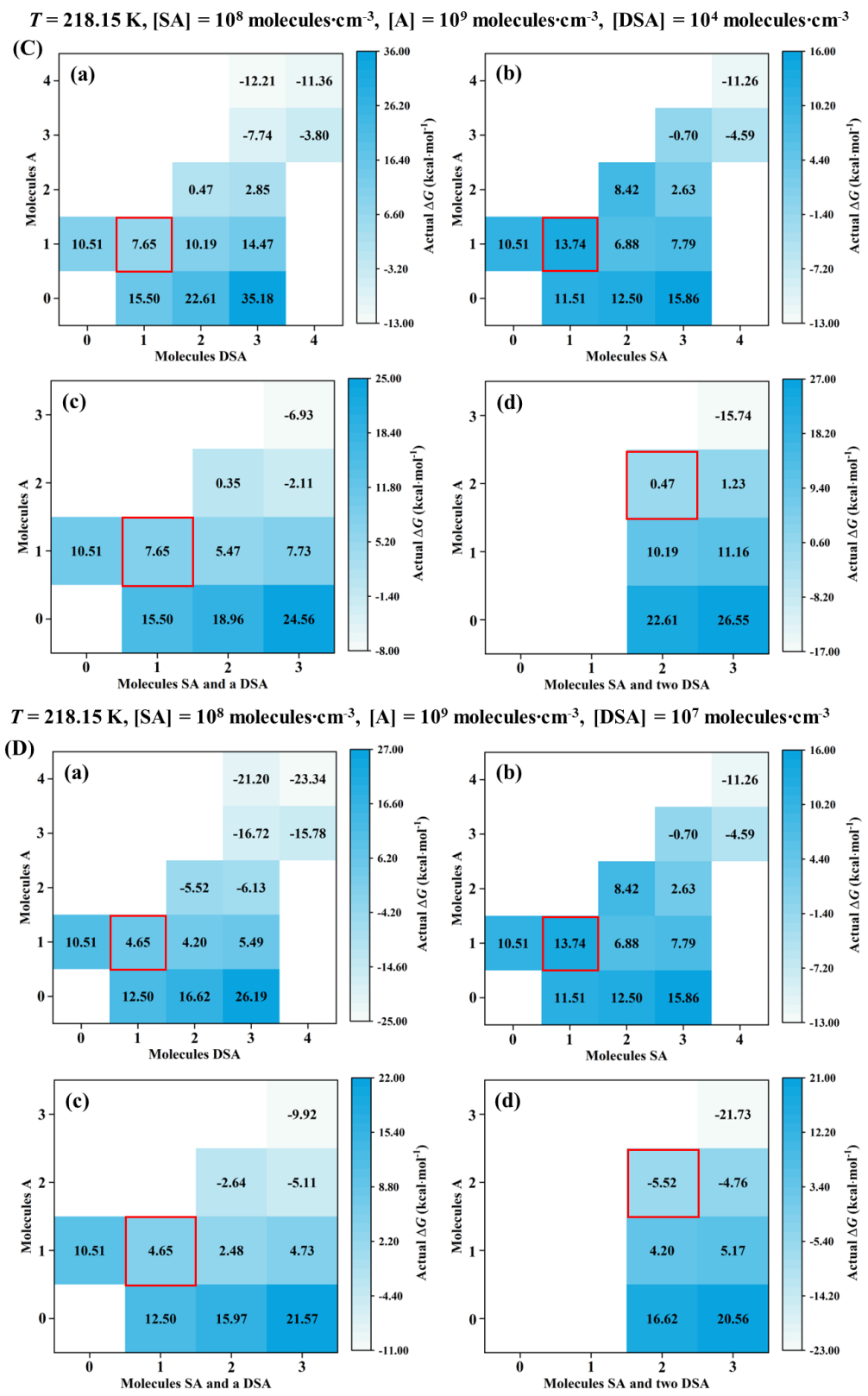
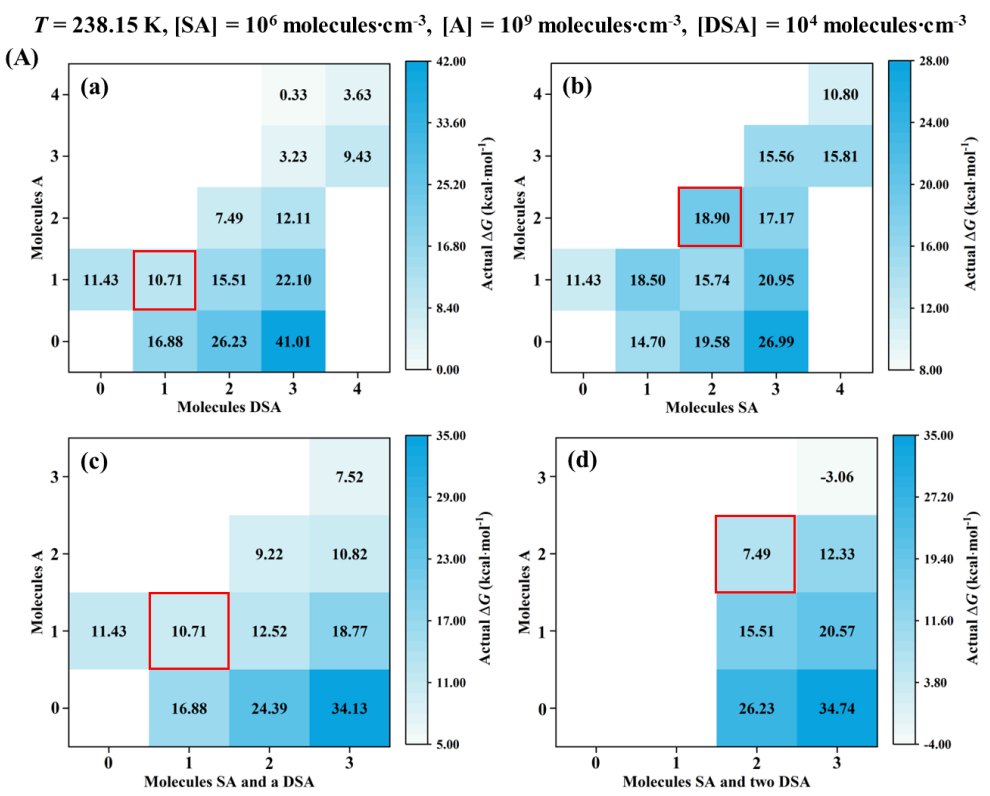


Fig. S12 A typical actual Δ*G* surface at 218.15 K. [SA] is the concentration of sulfuric acid monomers, [A] the concentration of ammonia monomers and [DSA] is disulfuric acid


T = 238.15 K, [SA] = 10^6 molecules·cm^-3, [A] = 10^9 molecules·cm^-3, [DSA] = 10^4 molecules·cm^-3
(A)
(a)
0.33 3.63
3.23 9.43
7.49 12.11
11.43 10.71 15.51 22.10
16.88 26.23 41.01
Molecules A
Molecules DSA
Actual ΔG (kcal·mol^-1)
42.00 33.60 25.20 16.80 8.40 0.00
(b)
10.80
15.56 15.81
18.90 17.17
11.43 18.50 15.74 20.95
14.70 19.58 26.99
Molecules SA
28.00 24.00 20.00 16.00 12.00 8.00
(c)
7.52
9.22 10.82
11.43 10.71 12.52 18.77
16.88 24.39 34.13
Molecules SA and a DSA
35.00 29.00 23.00 17.00 11.00 5.00
(d)
-3.06
7.49 12.33
15.51 20.57
26.23 34.74
Molecules SA and two DSA
35.00 27.20 19.40 11.60 3.80 -4.00
T = 238.15 K, [SA] = 10^6 molecules·cm^-3, [A] = 10^9 molecules·cm^-3, [DSA] = 10^7 molecules·cm^-3
(B)
(a)
-9.47 -9.44
-6.57 -3.64
0.95 2.31
11.43 7.44 8.97 12.30
13.61 19.69 31.21
Molecules DSA
35.00 26.00 17.00 8.00 -1.00 -10.00
(b)
10.80
15.56 15.81
18.90 17.17
11.43 18.50 15.74 20.95
14.70 19.58 26.99
Molecules SA
28.00 24.40 20.80 17.20 13.60 10.00
(c)
4.26
5.95 7.55
11.43 7.44 9.25 15.50
13.61 21.12 30.86
Molecules SA and a DSA
32.00 26.20 20.40 14.60 8.80 3.00
(d)
-9.59
0.95 5.80
8.97 14.04
19.69 28.20
Molecules SA and two DSA
30.00 22.00 14.00 6.00 -2.00 -10.00

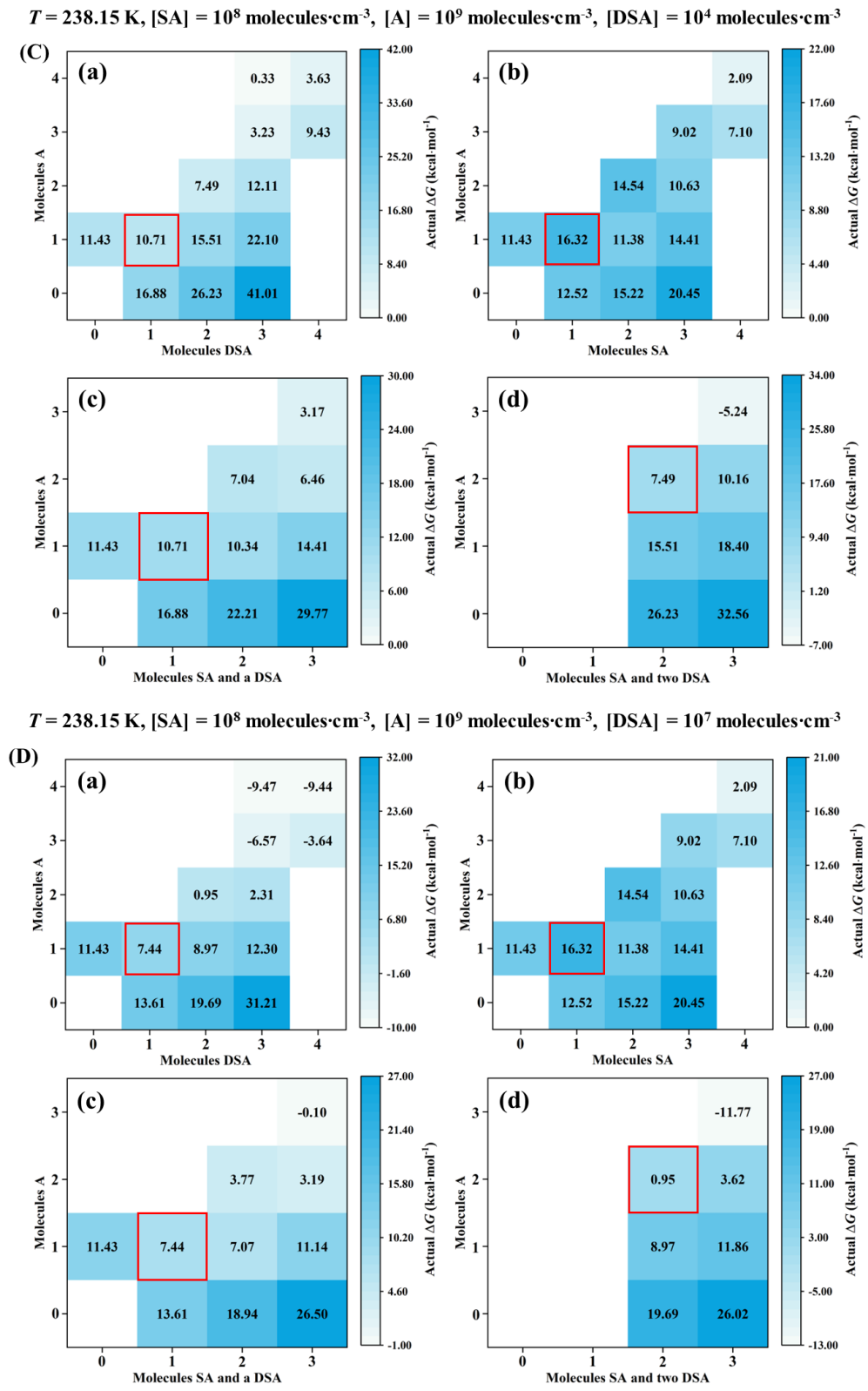


Fig. S13 A typical actual ΔG surface at 238.15 K. [SA] is the concentration of sulfuric acid monomers, [A] the concentration of ammonia monomers and [DSA] is disulfuric acid

(b) As mentioned by the reviewer, each DSA molecule generated consumes one SA molecule, resulting the simulations might "push" additional sulfur into the system. So, when the sum ([SA] +

[DSA]) is kept constant (10^4 - 10^8 molecules·cm^{-3}), Fig. S19 shows particle formation rates (J, cm^{-3}·s^{-1}) with varying ratios of [DSA]:[SA] at 238.15 K under different A concentrations ((a)10^7 molecules·cm^{-3}, (b)10^9 molecules·cm^{-3}, (c)10^{11} molecules·cm^{-3}).

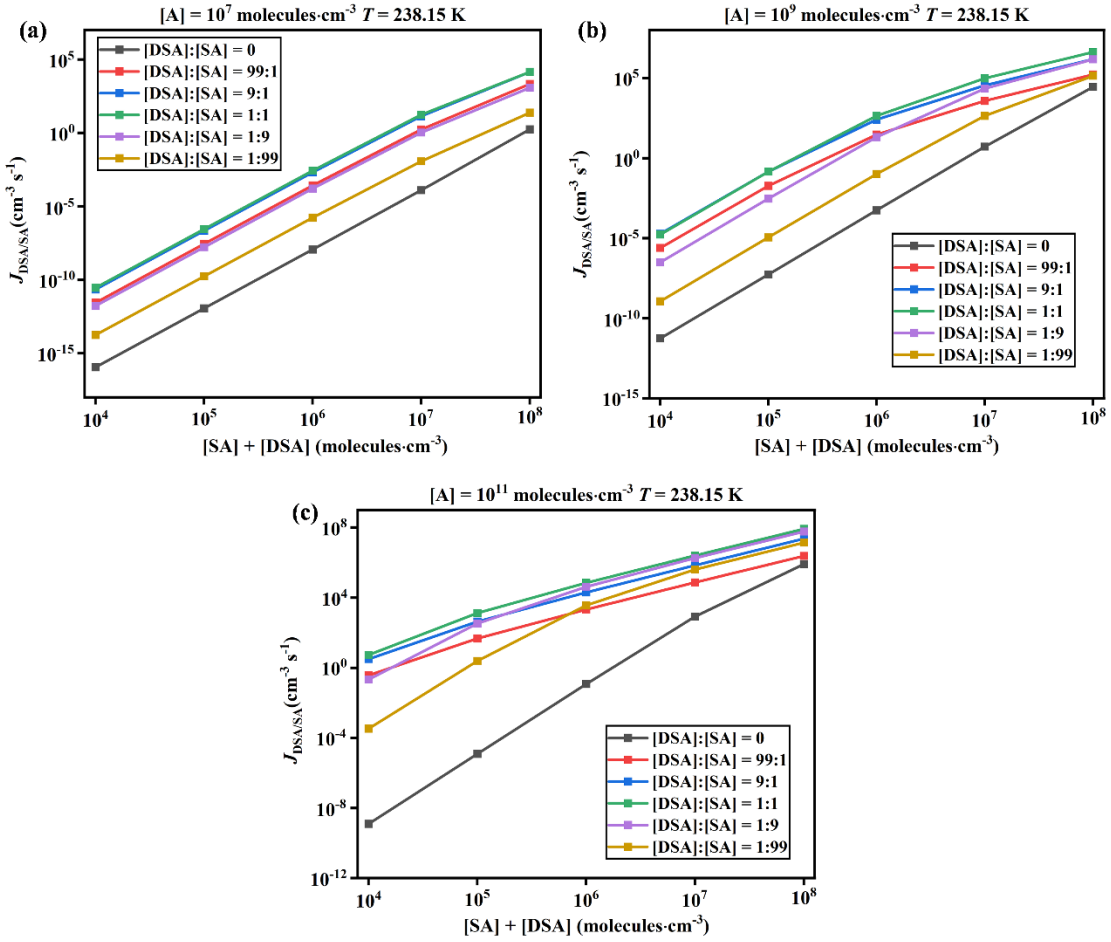


Fig. S19 Particle formation rates (J, cm^{-3}·s^{-1}) with varying ratios of [DSA]:[SA] at 238.15 K under different A concentrations ((a)10^7 molecules·cm^{-3}, (b)10^9 molecules·cm^{-3}, (c)10^{11} molecules·cm^{-3}). [DSA] + [SA] = 10^4-10^8 molecules·cm^{-3}

As shown in Fig. S19(a), at lower atmospheric concentration of A (10^7 molecules·cm^{-3}), the formation rate $J_{DSA/SA}$ at 1% substitution ([DSA]:[SA] = 1:99) was higher than that at unsubstituted condition ([DSA]:[SA] = 0:100). Similarly, $J_{DSA/SA}$ at 10% substitution ([DSA]:[SA] = 1:9) was higher than that at 1% substitution. Moreover, $J_{DSA/SA}$ at 50% substitution ([DSA]:[SA] = 1:1) reach a maximum value (1.41×10^4 cm^{-3}·s^{-1}), which is larger by 4-5 orders of magnitude than the value at unsubstituted condition. These results at lower atmospheric concentration of A show that the enhancement strength of DSA on the particle formation rate of SA-A-based clusters increases with the increasing of the percentage of substitution.

At medium (10^9 molecules·cm^{-3}) and higher (10^{11} molecules·cm^{-3}) atmospheric concentration

of A, $J_{DSA/SA}$ at 50% substitution ([DSA]:[SA] = 1:1) reaches a maximum value. As compared with $J_{DSA/SA}$ at unsubstituted condition, the value of $J_{DSA/SA}$ at 50% substitution ([DSA]:[SA] = 1:1) enhanced by 10 and 11 orders of magnitude, respectively. However, as the percentage of substitution (> 50%) increases, the value of $J_{DSA/SA}$ at medium and higher [A] decreases. This may be due to the fact that in the pure A-DSA nucleation system, large stable clusters $(A)_3 \cdot (DSA)_3$ can only be formed by mutual collisions of A·DSA clusters. So, DSA has the same "acid" molecular properties as SA in the SA-A-DSA ternary nucleation system. We predicted that DSA is a relatively stronger nucleation precursor than SA.

Besides, it should be noted that the concentration of water in the troposphere is abundant, and DSA is easily hydrolyzed to form 2 H_2SO_4 molecules. Based on this, the concentration of DSA listed in Fig. S9 was overestimated. However, the extent and proportion of DSA hydrolysis remains unclear, and the hydrolysis behavior of DSA needs to be further investigated in subsequent studies. Therefore, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$, the product of the reaction between SO_3 and H_2SO_4, on new particle formation (NPF) in various environments by using the Atmospheric Cluster Dynamics Code kinetic model and the QC calculation. In Lines 27-29 Page 7 to Lines 1-2 Page 7 of the revised manuscript, the discussion of the DSA concentration has been added as "As the prediction in Table S7, the concentration of DSA is set to 10^4-10^8 molecules·cm^{-3}. However, DSA is easily hydrolyzed with abundant water in the troposphere to form H_2SO_4, the concentration of DSA listed in Fig. S9 was overestimated. So, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$ on new particle formation (NPF) in various environments."

Comment 10.

Line 162: I do not believe the factors of 1/2 should be in this equation.

Response: Thanks for your valuable comments. The equation has been checked carefully and the equation is correct. This is consistent with the previous literature (***Chemosphere***, **2020**, 245, 125554.; **2018**, 203, 26-33.; ***Phys. Chem. Chem. Phys.***, **2018**, 20, 17406-17414.; **2023**, 25, 16745.; ***Atmos. Chem. Phys.***, **2012**, 12, 2345-2355.; **2022**, 22, 2639-2650.; **2021**, 21, 6221-6230.; **2022**, 22, 1951-1963.; ***J. Chem. Phys.***, **2017**, 146, 184308.)

Comment 11.

Line 168-169: Please explicitly mention the boundary conditions and concentration ranges in the text here instead of referring to the SI.

Response: Thank you for your valuable comments. According to your suggestion, boundary conditions and concentration ranges have been added in Lines 20-29 Page 7 to Lines 1-4 Page 8 of the revised manuscript, which has been organized as "The boundary conditions in the ACDC require that the smallest clusters outside of the simulated system should be very stable so that not to evaporate back immediately (McGrath et al., 2012). Based on cluster volatilization rate (shown in Table S10) and the formation Gibbs free energy of the clusters (shown in Table S8), the cluster boundary conditions simulated in this study were set as $(SA)_4 \cdot (A)_3$, $(SA)_4 \cdot (A)_4$, $SA \cdot (A)_3 \cdot (DSA)_3$, $(SA)_3 \cdot (A)_4 \cdot (DSA)_1$ and $(SA)_2 \cdot (A)_3 \cdot (DSA)_2$. According to field observations, the concentration of SA and A was respectively set in a range of 10^6-10^8 molecules·cm^{-3} and 10^7-10^{11} molecules·cm^{-3} (Almeida et al., 2013; Kuang et al., 2008; Bouo et al., 2011; Zhang et al., 2018). As the prediction in Table S7, the concentration of DSA is set to 10^4-10^8 molecules·cm^{-3}. However, DSA is easily hydrolyzed with abundant water in the troposphere to form H_2SO_4, the concentration of DSA listed in Fig. S9 was overestimated. So, the maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of $H_2S_2O_7$ on new particle formation (NPF) in various environments. Besides, the temperature was set to be 218.15-298.15 K, which span most regions of the troposphere and the polluted atmospheric boundary layer."

Comment 12.

Section 3.1: I am missing some comments on why the titled reaction is of interest and how much the competitive pathway of $SO_3 + H_2O$ matters. Would SO_3 not react with water instead of H_2SO_4? What are the branching ratios between these reaction pathways?

Response: Thanks for your valuable comments. The reason for our interest in $SO_3 + H_2SO_4$ reaction and the importance of the competition between the $SO_3 + H_2SO_4$ reaction and H_2O-assisted hydrolysis of SO_3 have been discussed. The corresponding major revision has been made as follows.

(a) Sulfur trioxide (SO_3) is a major air pollutant and can be considered as the most important oxidation product of SO_2. As an active atmospheric species, SO_3 can lead to the

formations of acid rain and atmospheric aerosol and thus plays a well-documented role in regional climate and human health. In the atmosphere, the hydrolysis of SO_3 to product H_2SO_4 is the most major loss route of SO_3. Meanwhile, SO_3 can also react with NH_3, CH_3OH, HNO_3, HCl, organic acids (such as HCOOH), et al. the products of SO_3 with some important atmospheric species have been identified in promoting NPF process. However, H_2SO_4 plays a significant role as a major inorganic acidic air pollutant in the new particle formation and acid rain. The reaction of SO_3 with H_2SO_4 has not been investigated as far as we know. Thus, it is important to study the mechanism between SO_3 and H_2SO_4.

(b) To understand the competition between the SO_3 + H_2SO_4 reaction and H_2O-assisted hydrolysis of SO_3 in the Earth's atmosphere, the rate ratio (v_{DSA}/v_{SA}) between the SO_3 + H_2SO_4 reaction and H_2O-assisted hydrolysis of SO_3 has been calculated and was expressed in Eq. (4).

$$\frac{v_{DSA}}{v_{SA}} = \frac{k_{DSA} \times [SO_3] \times [H_2SO_4] + k_{DSA\_WM\_s} \times K_{eq1} \times [SO_3] \times [H_2SO_4] \times [H_2O]}{k_{SA\_WM} \times K_{eq2} \times [SO_3] \times [H_2O] \times [H_2O]} \quad (4)$$

In Eq. (4), K_{eq1} and K_{eq2} were the equilibrium constant for the formation of $H_2SO_4\cdots H_2O$ and $SO_3\cdots H_2O$ complexes shown in Table S2, respectively; k_{DSA}, $k_{DSA\_WM\_s}$ and k_{SA_WM} were respectively denoted the bimolecular rate coefficient for the H_2SO_4 + SO_3, $H_2SO_4\cdots H_2O$ + SO_3 and $SO_3\cdots H_2O$ + H_2O reactions; [H_2O] and [H_2SO_4] were respectively represented the concentration of H_2O and H_2SO_4 taken from references (***J. Phys. Chem. A***, 2013, 117, 10381-10396.; ***Environ. Sci. Technol.***, 2015, 49, 13112-13120.). The corresponding rate ratio have been listed in Table S7 (0 km altitude) and S8 (5-30 km altitude). As seen in Table S7, at 0 km altitude, the hydrolysis reaction of SO_3 with $(H_2O)_2$ is more favorable than the SO_3 + H_2SO_4 reaction as the [H_2O] (10^{16}-10^{18} molecules·cm^3) is much larger than that of [H_2SO_4] (10^4-10^8 molecules·cm^3). Although the concentration of water molecules decreases with the increase of altitude in Table S8, the concentration of [H_2O] is still much greater than that of [H_2SO_4], resulting in the SO_3 + H_2SO_4 reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 5-30 km. Moreover, the SO_3 + H_2SO_4 reaction is not also the major sink route of SO_3, even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight. Based on this, the sentence of "The value of v_{DSA}/v_{SA} was listed in Table S7 (0 km altitude) and S8 (5-30 km altitude). As seen in Table S7, at 0 km altitude, the hydrolysis reaction of SO_3 with $(H_2O)_2$ is more favorable than the SO_3 + H_2SO_4 reaction as the [H_2O] (10^{16}-10^{18} molecules·cm^{-3}) is much larger

than that of [H_2SO_4] (10^4-10^8 molecules·cm^{-3}). Although the concentration of water molecules decreases with the increase of altitude in Table S8, the concentration of [H_2O] is still much greater than that of [H_2SO_4], resulting in the SO_3 + H_2SO_4 reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 5-30 km. Even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight at 10 km (Curtius et al., 2002), the SO_3 + H_2SO_4 reaction is not also the major sink route of SO_3." has been added in Lines 24-29 Page 13 to Lines 1-4 Page 14 of the revised manuscript.

(c) It has been proposed that the concentration of sulfuric acid is even greater than that of water vapor in the atmosphere of Venus (***Science***, 1990, 249, 1273.; ***Planet. Space Sci.***, 2006, 54, 1352.; ***Icarus***, 1994, 109, 58.; ***Nat. Geosci.***, 2010, 3, 834.), which may lead to that the SO_3 + H_2SO_4 reaction is probably favorable than the H_2O-assisted hydrolysis of SO_3 in the Venus' atmosphere. To check whether the SO_3 + H_2SO_4 reaction is more favorable than H_2O-assisted hydrolysis of SO_3 or not in the Venus' atmosphere, the rate ratio of v_{DSA}/v_{SA} listed in Eq. 4 has been calculated in Table 2. It can be seen from Table 2 that the rate ratio of v_{DSA}/v_{SA} is 3.24×10^8-5.23×10^{10} within the altitude range of 40-70 km in the Venus' atmosphere, which indicates that the SO_3 + H_2SO_4 reaction is significantly more favorable than the hydrolysis reaction of SO_3 + $(H_2O)_2$ within the altitudes range of 40-70 km in the Venus' atmosphere. Based on this, the sentence of "Notably, as the concentration of sulfuric acid was even greater than that of water vapor in the atmosphere of Venus, the SO_3 + SA reaction was probably favorable than the H_2O-assisted hydrolysis of SO_3 in the Venus' atmosphere. To check whether the SO_3 + H_2SO_4 reaction was more favorable than H_2O-assisted hydrolysis of SO_3 or not in the Venus' atmosphere, the rate ratio of v_{DSA}/v_{SA} listed in Eq. 4 has been calculated in Table 2. It can be seen from Table 2 that the rate ratio of v_{DSA}/v_{SA} was 3.24×10^8-5.23×10^{10} within the altitude range of 40-70 km in the Venus' atmosphere, which indicates that the SO_3 + H_2SO_4 reaction is significantly more favorable than the hydrolysis reaction of SO_3 + $(H_2O)_2$ within the altitudes range of 40-70 km in the Venus' atmosphere." has been added in Lines 4-11 Page 14 of the revised manuscript.

Overall, it is important to study the mechanism between SO_3 and H_2SO_4 and the competition between the SO_3 + H_2SO_4 reaction and H_2O-assisted hydrolysis. The SO_3 + SA reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 0-30 km in the Earth's atmosphere, even considering of high H_2SO_4 concentration at the end and outside the aircraft

engine and flight. However, the SO_3 + SA reaction is significantly more favorable than the hydrolysis reaction of SO_3 + $(H_2O)_2$ within the altitude range of 40-70 km in the Venus' atmosphere.

Comment 13.

Line 181: *"Therefore, it can be said that the direct reaction between SO_3 and SA is more favorable over H_2O-catalyzed hydrolysis of SO_3 energetically and kinetically."*

I believe this conclusion should be based on the "reaction rates" and not the "reaction rate constants".

Response: Thank you for your valuable comments. We agree with the suggestion of the reviewer that the conclusion should be based on the "reaction rates" and not the "reaction rate constants". So, in Lines 16-17 Page 8 of the revised manuscript, the sentence of "Therefore, it can be said that the direct reaction between SO_3 and SA is more favorable over H_2O-catalyzed hydrolysis of SO_3 energetically and kinetically." has been changed as "Therefore, it can be said that the direct reaction between SO_3 and SA occurs easily under atmospheric conditions.".

Comment 14.1.

Section 3.2: The first two sentences are contradicting each other. Is the mechanism lacking or does it have high reactivity? I am also missing some information about how the system was setup.

Response: Thanks for your valuable comments. According to suggestion of reviewers, the first two sentences in the section of "**3.2 Reactions at the Air-water interface**" has been re-organized. The mechanism for the SO_3 + SA reaction at the air-water interface was lacking and thus BOMD simulations were used to evaluate the reaction mechanism of SO_3 with SA at the aqueous interfaces. This reaction on water surface may occur in three ways: (*i*) SO_3 colliding with adsorbed H_2SO_4 at the air-water interface; (*ii*) SO_3 colliding with adsorbed SO_3 at the aqueous interface; or (*iii*) the SO_3-H_2SO_4complex reacting at the aqueous interface. However, due to the high reactivity both of SO_3 and H_2SO_4 with interfacial water, the lifetimes of SO_3 and H_2SO_4 on the water droplet are extremely short (on the order of a few picoseconds). Thus, two possible models were mainly considered for the SO_3 + H_2SO_4 reaction on the water surface: (*i*) gaseous SO_3 colliding with HSO_4^- at the air-water interface and (*ii*) the DSA (the gas-phase product of SO_3 and H_2SO_4) dissociating on water droplet. Based on this, the sentence of "Similar with the interfacial reaction

of SO_3 with organic and inorganic acids (Cheng et al., 2023; Zhong et al., 2016), the reaction between SO_3 and SA at the aqueous interface may occur in three ways: (*i*) SO_3 colliding with adsorbed SA at the air-water interface; (*ii*) SO_3 colliding with adsorbed SO_3 at the aqueous interface; or (*iii*) the SO_3-SA complex reacting at the aqueous interface. However, due to the high reactivity both of SO_3 and SA at the air-water interface, the lifetimes of SO_3 (Zhong et al., 2019) and SA (Fig. S2) (on the order of a few picoseconds) on the water droplet were extremely short and can be formed SA^- ion quickly. Besides, as the calculated result above, $SO_3\cdots H_2SO_4$ complex can be generate DSA easily before it approaches the air-water interface." has been deleted in Lines 17-25 Page 10 of the revised manuscript.

Comment 14.2.

Would the studied compounds (SO_3, H_2SO_4 and $H_2S_2O_7$) actually be at the interface or would they be solvated in the water cluster?

Response: Thanks for your valuable comments. According to suggestion of reviewers, the time evolution of the position (z coordinate) of SO_3, SA and DSA molecules is monitored so as to observe whether these molecules stay at the air-water interface or in the water phase. The pie chart with the occurrence percentages of SO_3, SA and DSA at the air-water interface and in water phase has been displayed in Fig. S2. As seen in Fig. S2, the SO_3, SA and DSA molecules can stay at the interface for 35.8%, 30.1% and 39.2% of the time in the 150 ns simulation (Fig. S2), respectively, revealing that the existence of SO_3, SA and DSA at the air-water interface cannot be negligible.

Comment 14.3.

Is the reaction an artefact of not equilibrating the system before setting up the reaction?

Response: Thanks for your valuable comments. The droplet system with 191 water molecules has been equilibrated before SO_3 and H_2SO_4 was added at the water surface. Specifically, a nearly spherical droplet with 191 water molecules was firstly constructed by using the Packmol program (*J. Comput. Chem.*, 2009, 30, 2157-2164.) with a tolerance of 2.0 Å, namely, all atoms from different molecules will be at least 2.0 Å apart. Then, based on the resulting initial structure, the GROMACS software (*J. Comput. Chem.*, 2005, 26, 1701-1718.) with the general AMBER force field (GAFF) (*J. Comput. Chem.* 2004, 25, 1157-1174.) was used to simulate the droplet

equilibrium process with two steps. In the first step, a water slab of 35 × 35 × 35 $Å^3$ containing 191 water molecules was built using periodic boundary conditions to avoid the effect of neighboring replicas. In the second step, the water slab was fully equilibrated for 1 ns under NVT ensemble (N, V and T represent the number of atoms, volume and temperature, respectively) to reach equilibrium state. The water molecules were described by the TIP3P model. The isothermal-isochoric (NVT) simulation was executed at 298 K for simulation system. The temperature was kept constant by the V-rescale thermostat coupling algorithm. The coupling time constant is 0.1 ps. Bond lengths were constrained by the LINCS algorithm. The cut-off distance of 1.2 nm was set for van der Waals (vdW) interactions. The Particle Mesh Ewald (PME) summation method was used to calculate the electrostatic interactions. During the whole simulation process, a time step of 2 fs was set and three-dimensional periodic boundary conditions were adopted. Next, to ensure the stability of the system, the droplets were pre-optimized using BOMD at 300 K for 10 ps prior to the simulation of the air-water interfacial reaction. Using the density functional theory (DFT) method, the electronic exchange-correlation term was described by the Becke-Lee-Yang-Parr (BLYP) functional. The Grimme's dispersion correction (D3) was applied to account for the weak dispersion interaction. The double-ζ Gaussian (DZVP-MOLOPT) basis set and the Goedecker-Teter-Hutter (GTH) norm-conserving pseudopotentials were adopted to treat the valence and the core electrons, respectively. The planewave cutoff energy is set to 280 Ry, and that for the Gaussian basis set is 40 Ry. And the SCF convergence criterion is 1.0E-5 Hartree. All simulations were performed in NVT ensemble with Nose-Hoover thermostat controlling the temperature. Finally, the SO_3 and H_2SO_4 molecule was added at the water surface after the droplet system with 191 water molecules was fully equilibrated. The details of the equilibrium process for the droplet system with 191 water molecules are shown in the *SI Appendix* Part 4. Meanwhile, the sentence of "It is pointed out that the droplet system with 191 water molecules has been equilibrated before SO_3 and H_2SO_4 was added at the water surface. The details of the equilibrium process for the droplet system with 191 water molecules are shown in the *SI Appendix* Part 4." has been added in Lines 22-25 Page 6 of revised manuscript.

Comment 14.4.

How many trajectories were carried out? Are adequate statistics ensured or can this be considered a "rare event".

Response: Thanks for your valuable comments. In the interfacial reactions of (*i*) gaseous SO_3 colliding with SA^- at the air-water interface and (*ii*) the DSA (the gas-phase product of SO_3 and SA) dissociating on water droplet, sufficient statistical data are available in each reaction mechanism. It is noted that 40 BOMD simulations were carried out in the air-water interface reactions to eliminate the influence of the initial configuration on the simulation results of interfacial reaction. So, the additional BOMD trajectories and snapshots for H_2O-induced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair, HSO_4^- mediated the formation of $HSO_4^-\cdots H_3O^+$ ion pair and the deprotonation of $H_2S_2O_7$ has been added in Fig. S4, Figs. S5-S6 and Fig. S7, respectively. Due to the similarity of the same type of interfacial reaction mechanism, we do not list all the BOMD trajectories and snapshots for H_2O-induced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair, HSO_4^- mediated the formation of $HSO_4^-\cdots H_3O^+$ ion pair and the deprotonation of $H_2S_2O_7$. However, in Fig. S4-Fig. S7, at least 4 BOMD trajectories and snapshots were included in each Figure. Besides, the sentence of "To eliminate the influence of the initial configuration on the simulation results of interfacial reaction, 40 BOMD simulations for the air-water interface reactions were carried out." has been added in Lines 3-5 Page 7 of revised manuscript.

Comment 14.5.

What was the starting geometries? At the transition state?

Response: Thanks for your valuable comments. It is noted that the interfacial starting geometries are not the transition state in the reaction of SO_3 with SA at the air-water interface. Specially, (*a*) in H_2O-induced the formation of $S_2O_7^{2-}\cdots H_3O^+$ ion pair from the reaction of SO_3 with HSO_4^- at the air-water interface illustrated in Fig. 2 and Fig. S4, the starting geometries is the gaseous SO_3 collision with the adsorbed SA^-, where the bond length between S1 atom of SO_3 and O1 atom of HSO_4^- is set within the range of 3.0-4.0 Å; (*b*) In the hydration reaction mechanism of SO_3 mediated by HSO_4^- at the air water interface illustrated in Fig. 3, Fig. S5 and Fig. S6, the starting geometries is the gaseous SO_3 collision with the adsorbed SA^-, where the bond length between O4 atom of SO_3 and H3 atom of HSO_4^- is set within the range of 2.5-3.5 Å; (*c*) In the deprotonation of $H_2S_2O_7$ at the air water interface illustrated in Fig. 4 and Fig. S7, the starting geometries is the

adsorbed DSA, where the distance between DSA and interfacial water molecule is set within the range of 3.0-4.0 Å.

Comment 14.6.

Was the SO_3+H_2O reaction observed in any of the trajectories? The reaction without SA should also be tested.

Response: Thanks for your valuable comments. The interfacial hydration mechanism of SO_3 without H_2SO_4 has been reported previously by Lv et al. (***Atmos. Environ.***, 2020, 230, 117514.) where the SO_3 can react rapidly with water molecules to form the ion pair of HSO_4^- and H_3O^+ or H_2SO_4 within a few picoseconds. Three different reaction pathways, namely no loop-structure formation, loop-structure formation with proton transfer in the loop and loop-structure formation with proton transfer outside the loop, can be found from the results of BOMD simulations reported by Lv et al. (***Atmos. Environ.***, 2020, 230, 117514.). So, the interfacial hydration mechanism of SO_3 without H_2SO_4 has not been restudied here. However, the hydration reaction mechanism of SO_3 at the air-water interface reported by Lv et al. (***Atmos. Environ.***, 2020, 230, 117514.) has been compared with the interfacial hydration mechanism of SO_3 mediated by HSO_4^- reported in the present work.

The interfacial hydration mechanism of SO_3 mediated by HSO_4^- were observed in the BOMD simulations illustrated in Fig. 3, Fig. S5 and Fig. S6. Specifically, both direct (loop-structure formation with proton transfer outside the loop, Fig. 3(a), Fig. S5 and Movie S2) and indirect (no loop-structure formation, Fig. 3(b), Fig. S6 and Movie S3) forming mechanisms were observed in HSO_4^--mediated formation of $HSO_4^-\cdots H_3O^+$ ion pair. The loop-structure formation with proton transfer in the loop was not observed in the BOMD simulations. The direct HSO_4^--mediated formation of $HSO_4^-\cdots H_3O^+$ ion pair was a loop structure mechanism, which was consistent with gas phase hydrolysis of SO_3 assisted by acidic catalysts of HCOOH, HNO_3, $H_2C_2O_4$ and H_2SO_4 in the previous works (Long et al., 2012; Long et al., 2013a; Torrent-Sucarrat et al., 2012; Lv et al., 2019) and the hydration reaction mechanism of SO_3 at the air water interface (***Atmos. Environ.***, 2020, 230, 117514.). During the direct formation route of $HSO_4^-\cdots H_3O^+$ ion pair, HSO_4^- played as a spectator, while interfacial water molecules acted as both a reactant and a proton acceptor. The indirect forming process of $HSO_4^-\cdots H_3O^+$ ion pair contained two steps: (*i*) SO_3 hydration along

with H_2SO_4 formation and (*ii*) H_2SO_4 deprotonation. During the whole indirect forming process of $HSO_4^-\cdots H_3O^+$ ion pair, HSO_4^- played as protons donor and acceptor, and water molecules acted as hydration reactants and proton acceptors. The direct HSO_4^--mediated formation of $HSO_4^-\cdots H_3O^+$ ion pair needs less time than the indirect forming process of $HSO_4^-\cdots H_3O^+$ ion pair. This is consistent with the interfacial reactions of $CH_2OO + HNO_3$ (***J. Am. Chem. Soc.***, 2018, 140, 14, 4913-4921.) and the hydration of SO_3 (***Atmos. Environ.***, 2020, 230, 117514.) where the direct forming mechanism needs less time than indirect forming mechanism.

Based on the discussion above, the sentence of "As compared with the hydration reaction mechanism of SO_3 at the air-water interface reported by Lv et al. (Lv and Sun, 2020), the loop-structure formation with proton transfer in the loop was not observed in the direct mechanism of SA^--mediated formation of $SA^-\cdots H_3O^+$ ion pair. This is probably because SA^- ion is more difficult to give the proton." has been added in Lines 25-28 Page 12 of the revised manuscript. Meanwhile, the sentence of "Compared with the direct mechanism of SA^--mediated formation of $SA^-\cdots H_3O^+$ ion pair, the indirect forming process of $HSO_4^-\cdots H_3O^+$ ion pair required more time. This was consistent with the interfacial reactions of $CH_2OO + HNO_3$ (Kumar et al., 2018) and the hydration of SO_3 (Lv and Sun, 2020) where the direct forming mechanism needed less time than indirect forming mechanism." has been added in Lines 15-19 Page 12 of the revised manuscript.

Comment 15.

Section 3.3: There is heavy referencing to the SI. Please also add the relevant data to the text. For instance, at line 303, how can the $H_2S_2O_7$ formation reaction matter if $SO_3 + (H_2O)_2$ is the major sink?

Response: Thank you for your valuable comments. According to your suggestion, the importance of the $SO_3 + H_2SO_4$ reaction has been discussed and the competition between the $SO_3 + H_2SO_4$ reaction and H_2O-assisted hydrolysis of SO_3 in the atmospheres of Earth and Venus have been discussed. Moreover, the relevant data listed in supporting information has been added to the manuscript. The corresponding revision has been respectively made as follows.

(a) Sulfur trioxide (SO_3) is a major air pollutant and can be considered as the most important oxidation product of SO_2. As an active atmospheric species, SO_3 can lead to the formations of acid rain and atmospheric aerosol and thus plays a well-documented role in regional

climate and human health. In the atmosphere, the hydrolysis of SO_3 to product H_2SO_4 (SA) is the most major loss route of SO_3. As a complement to the loss of SO_3, ammonolysis reaction of SO_3 in polluted areas of NH_3 can form H_2NSO_3H, which not only can be competitive with the formation of SA from the hydrolysis reaction of SO_3, but also can enhance the formation rates of sulfuric acid (SA)-dimethylamine ($NH(CH_3)_2$, DMA) clusters by about 2 times. Similarity, SO_3 can also react with NH_3, CH_3OH, HNO_3, HCl, organic acids (such as HCOOH), and both processes can provide a mechanism for incorporating organic matter into aerosol particles. These reactions between SO_3 and trace atmosphere species above provide some complementary routes to the loss of SO_3 in locally polluted areas. However, the reaction mechanism between SO_3 and H_2SO_4 has yet to be fully understood. Previous studies have shown that the concentration of water vapor decreases significantly with increasing altitude (*J. Phys. Chem. A*, 2013, 117, 10381-10396.; *J. Am. Chem. Soc.*, 2021, 143, 8402-8413.), leading to longer atmospheric lifetimes of SO_3. The gas phase reaction of SO_3 with H_2SO_4 may contribute significantly to the loss of SO_3 in dry areas where [H_2SO_4] is relatively high (especially at lower temperatures) and at higher altitude. So, the reaction mechanism between SO_3 and H_2SO_4 has been studied here, and the competition between the SO_3 + H_2SO_4 reaction and H_2O-assisted hydrolysis of SO_3 have been discussed. Based on this, the sentence of "Previous studies have shown that the concentration of water vapor decreases significantly with increasing altitude, leading to longer atmospheric lifetimes of SO_3. The gas phase reaction of SO_3 with H_2SO_4 may contribute significantly to the loss of SO_3 in dry areas where [H_2SO_4] is relatively high (especially at lower temperatures) and at higher altitude. So, it is important to study the reaction mechanism of SO_3 with H_2SO_4 and its competition with H_2O-assisted hydrolysis of SO_3." has been added in Lines 7-12 Page 3 of the revised manuscript.

(b) In the gas-phase, the main sink route of SO_3 is H_2O-assisted hydrolysis of SO_3. To understand the competition between the SO_3 + H_2SO_4 reaction and H_2O-assisted hydrolysis of SO_3 in the Earth's atmosphere, the rate ratio (v_{DSA}/v_{SA}) between the SO_3 + H_2SO_4 reaction and H_2O-assisted hydrolysis of SO_3 has been calculated and was expressed in Eq. (4).

$$\frac{v_{DSA}}{v_{SA}} = \frac{k_{DSA} \times [SO_3] \times [H_2SO_4] + k_{DSA\_WM\_s} \times K_{eq1} \times [SO_3] \times [H_2SO_4] \times [H_2O]}{k_{SA\_WM} \times K_{eq2} \times [SO_3] \times [H_2O] \times [H_2O]} \quad (4)$$

In Eq. (4), K_{eq1} and K_{eq2} were the equilibrium constant for the formation of $H_2SO_4\cdots H_2O$ and $SO_3\cdots H_2O$ complexes shown in Table S2, respectively; k_{DSA}, $k_{DSA\_WM\_s}$ and k_{SA_WM} were

respectively denoted the bimolecular rate coefficient for the H_2SO_4 + SO_3, H_2SO_4···H_2O + SO_3 and SO_3···H_2O + H_2O reactions; [H_2O] and [H_2SO_4] were respectively represented the concentration of H_2O and H_2SO_4 taken from references (***J. Phys. Chem. A***, 2013, 117, 10381-10396.; ***Environ. Sci. Technol.***, 2015, 49, 13112-13120.). The corresponding rate ratio have been listed in Table S7 (0 km altitude) and S8 (5-30 km altitude). As seen in Table S7, at 0 km altitude, the hydrolysis reaction of SO_3 with $(H_2O)_2$ is more favorable than the SO_3 + H_2SO_4 reaction as the [H_2O] (10^{16}-10^{18} molecules·cm^3) is much larger than that of [H_2SO_4] (10^4-10^8 molecules·cm^3). Although the concentration of water molecules decreases with the increase of altitude in Table S8, the concentration of [H_2O] is still much greater than that of [H_2SO_4], resulting in the SO_3 + H_2SO_4 reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 5-30 km. Moreover, the SO_3 + H_2SO_4 reaction is not also the major sink route of SO_3, even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight. Based on this, the sentence of "The value of v_{DSA}/v_{SA} was listed in Table S7 (0 km altitude) and Table S8 (5-30 km altitude). As seen in Table S7, the hydrolysis reaction of SO_3 with $(H_2O)_2$ is more favorable than the SO_3 + H_2SO_4 reaction at 0 km altitude as the [H_2O] (10^{16}-10^{18} molecules·cm^3) is much larger than that of [H_2SO_4] (10^4-10^8 molecules·cm^3). Although the concentration of water molecules decreases with the increase of altitude in Table S8, the concentration of [H_2O] is still much greater than that of [H_2SO_4], resulting in the SO_3 + H_2SO_4 reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 5-30 km. Even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight at 10 km (Curtius et al., 2002), the SO_3 + H_2SO_4 reaction is not also the major sink route of SO_3." has been added in Lines 24-29 Page 13 to Lines 1-4 Page 14 of the revised manuscript.

(c) It has been proposed that the concentration of sulfuric acid is even greater than that of water vapor in the atmosphere of Venus (***Science***, 1990, 249, 1273.; ***Planet. Space Sci.***, 2006, 54, 1352.; ***Icarus***, 1994, 109, 58.; ***Nat. Geosci.***, 2010, 3, 834.), which may lead to that the SO_3 + H_2SO_4 reaction is probably favorable than the H_2O-assisted hydrolysis of SO_3 in the Venus' atmosphere. To check whether the SO_3 + H_2SO_4 reaction is more favorable than H_2O-assisted hydrolysis of SO_3 or not in the Venus' atmosphere, the rate ratio of v_{DSA}/v_{SA} listed in Eq. 4 has been calculated in Table 2. It can be seen from Table 2 that the rate ratio of v_{DSA}/v_{SA} is 3.24×10^8-5.23×10^{10} in the 40-70 km altitude range of Venus, which indicates that the SO_3 + H_2SO_4 reaction

is significantly more favorable than the hydrolysis reaction of SO_3 + $(H_2O)_2$ within the altitudes range of 40-70 km in the Venus' atmosphere. Based on this, the sentence of "Notably, as the concentration of sulfuric acid was even greater than that of water vapor in the atmosphere of Venus, the SO_3 + SA reaction was probably favorable than the H_2O-assisted hydrolysis of SO_3 in the Venus' atmosphere. To check whether the SO_3 + H_2SO_4 reaction was more favorable than H_2O-assisted hydrolysis of SO_3 or not in the Venus' atmosphere, the rate ratio of v_{DSA}/v_{SA} listed in Eq. 4 has been calculated in Table 2. It can be seen from Table 2 that the rate ratio of v_{DSA}/v_{SA} was 3.24×10^{8}-5.23×10^{10} within the altitude range of 40-70 km in the Venus' atmosphere, which indicates that the SO_3 + H_2SO_4 reaction is significantly more favorable than the hydrolysis reaction of SO_3 + $(H_2O)_2$ within the altitudes range of 40-70 km in the Venus' atmosphere." has been added in Lines 4-11 Page 14 of the revised manuscript.

Overall, it is important to study the reaction mechanism of SO_3 with H_2SO_4 and its competition with H_2O-assisted hydrolysis of SO_3. The SO_3 + SA reaction cannot compete with H_2O-assisted hydrolysis of SO_3 within the altitude range of 0-30 km in the Earth's atmosphere, even considering of high H_2SO_4 concentration at the end and outside the aircraft engine and flight. However, the SO_3 + SA reaction is significantly more favorable than the hydrolysis reaction of SO_3 + $(H_2O)_2$ within the altitude range of 40-70 km in Venus' atmosphere.

Comment 16.

Line 307-308: The "stability analysis" should be added to the manuscript.

Response: Thank you for your valuable comments. According to your suggestion, the Gibbs free energy (kcal·mol^{-1}) diagram of $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) clusters at 278.15K and 1 atm has been added in Fig. 5. Meanwhile, evaporation rate coefficient (γ, s^{-1}) for $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters were calculated in Table S11-12. Based on this, the stability analysis for $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters has been added in Lines 12-27 Page 14 of the revised manuscript, which has been organized as "From the multistep global minimum sampling technique, for $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters, 27 most stable structures in the present system have been found (Fig. S11). To evaluate the thermodynamic stability of these clusters, Gibbs formation free energies (ΔG) at 278.15 K and evaporation rate coefficient (γ, s^{-1}) for $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters were calculated in Fig.

5 and Table S11-12, respectively. As for dimers formed by SA, A and DSA, the ΔG of $(A)_1 \cdot (DSA)_1$ was -16.1 kcal·mol^{-1}, which was lowest in all dimers followed by $(SA)_2$ (-8.5 kcal·mol^{-1}) and then $(SA)_1 \cdot (A)_1$ (-6.3 kcal·mol^{-1}), meanwhile, the γ of $(A)_1 \cdot (DSA)_1$ (1.17×10^{-3} s^{-1}) was lower than those of $(SA)_2$ (3.81×10^{2} s^{-1}) and $(SA)_1 \cdot (A)_1$ (4.19×10^{4} s^{-1}). Regarding for the SA-A-DSA-based clusters, the values of ΔG and γ of SA-A-DSA-based clusters containing more DSA molecules were relatively lower than the corresponding values of other SA-A-DSA-based clusters with the same number of acid and base molecules. In the free-energy diagram for cluster formation steps of the SA-A-DSA system (Fig. 5), thermodynamic barriers were weakened mainly by the subsequential addition of A or DSA monomer. Also, the SA-A-DSA-based growth pathway was thermodynamically favorable with decreasing ΔG. These results indicate that DSA not only can promote the stability of SA-A-DSA-based clusters but also may synergistically participate in the nucleation process."

Comment 17.

Line 312: The application of the enhancement factor yields an incorrect picture of the importance of $H_2S_2O_7$ for cluster formation. Sulfuric acid and ammonia form very weakly bound electrically neutral clusters. Usually, ions are required to facilitate the process. Hence, large enhancement factors (R) are an artefact of dividing with a very small number. Please mention the absolute formation rates to ensure that the cluster formation rate is not zero.

Response: Thank you for your valuable comments. According to your suggestion, the formation rate of SA-A-DSA-based system has been mainly discussed rather than the enhancement factor. So, the influence of temperature and the precursor concentration on the formation rate (J, cm^{-3}·s^{-1}) has been discussed and reorganized in the revised manuscript. The corresponding revision has been mainly made as follows.

(a) In Lines 28-30 Page 14 of the revised manuscript, the analysis of the influence of temperature on formation rate has been discussed and organized as "The potential enhancement influence of DSA to the SA-A-based particle formation was shown in Fig. 6. The formation rate (J, cm^{-3}·s^{-1}) of SA-A-DSA-based system illustrated in Fig. 6 is negatively dependent on temperature, demonstrating that the low temperature is a key factor to accelerate cluster formation.".

(b) In Lines 4-6 Page 15 of the revised manuscript, the analysis of the influence of [DSA] has been discussed and organized as "In addition to temperature, the *J* of SA-A-DSA-based system shown in Fig. 6 rise with the increase of [DSA]. More notably, the participation of DSA can promote *J* to a higher level, indicating its enhancement on SA-A nucleation."

(c) In Lines 6-13 Page 15 of the revised manuscript, the analysis of the influence of on both [SA] and [A] has been discussed and organized as "Besides, there was significantly positive dependence of the *J* of SA-A-DSA-based system on both [SA] and [A] in Fig. 7 (238.15 K) and Fig. S15-Fig. S18 (218.15, 258.15, 278.15 and 298.15 K). This was because the higher concentration of nucleation precursors could lead to higher *J*. Besides, Fig. S19 showed the nucleation rate when the sum ([SA] + [DSA]) was kept constant. $J_{DSA/SA}$ at substituted condition was higher than that at unsubstituted condition. These results indicated that DSA may can greatly enhance the SA-A particle nucleation in heavy sulfur oxide polluted atmospheric boundary layer, especially at an average flight altitude of 10 km with high [DSA]."

Comment 18.

Line 316: An R value of 1.0 will mean that there is no enhancement. Hence, I do not believe that this can be stated. In addition, please add the numbers and explain how this conclusion of DSA being a "better enhancer" is drawn.

Response: Thank you for your valuable comments. We agree with the suggestion of the reviewer that it is incredible to use "enhancement factors" to explain the enhancing effect of the DSA. According to your suggestion, the formation rate of SA-A-DSA-based system has been mainly discussed rather than the enhancement factor. Meanwhile, the absolute formation rate has been used to explain why DSA promotes the nucleation of SA-A particles. The corresponding revision has been mainly made as follows.

(a) To evaluate the thermodynamic stability of these clusters, Gibbs formation free energies (ΔG) at 278.15 K and evaporation rate coefficient (γ, s^{-1}) for $(DSA)_x(SA)_y(A)_z$ ($z \leq x + y \leq 3$) molecular clusters were calculated in Fig. 5 and Table S11-12, respectively. As for dimers formed by SA, A and DSA, the ΔG of $(A)_1 \cdot (DSA)_1$ is -16.1 kcal·mol^{-1}, which is lowest in all dimers followed by $(SA)_2$ (-8.5 kcal·mol^{-1}) and then $(SA)_1 \cdot (A)_1$ (-6.3 kcal·mol^{-1}), meanwhile, the γ of $(A)_1 \cdot (DSA)_1$ (1.17×10^{-3} s^{-1}) is lower than those of $(SA)_2$ (3.81×10^{2} s^{-1}) and $(SA)_1 \cdot (A)_1$ (4.19 ×

10^4 s^{-1}). Regarding for the SA-A-DSA-based clusters, the values of ΔG and γ of SA-A-DSA-based clusters containing more DSA molecules are relatively lower than the corresponding values of other SA-A-DSA-based clusters with the same number of acid and base molecules. In the free-energy diagram for cluster formation steps of the SA-A-DSA system (Fig. 5), thermodynamic barriers are weakened mainly by the subsequential addition of A or DSA monomer. Moreover, the *J* of SA-A-DSA-based system shown in Fig. 6 rise with the increase of [DSA]. More notably, the participation of DSA can promote *J* to a higher level, indicating its enhancement on SA-A nucleation.

(b) The influence of temperature and the precursor concentration on the formation rate (*J*, $cm^{-3}\cdot s^{-1}$) has been discussed in Lines 1-8 Page 15 of the revised manuscript. The detail information is also provided in **Comment 17**.

(c) The contribution of the DSA participation pathway has been increased with increasing temperature. Also, the contribution of the pathway with participation of DSA increases with increasing [DSA], while the number of DSA molecules contained in clusters [$(SA)_2\cdot(A)_3\cdot$DSA, SA$\cdot(A)_2\cdot$DSA, SA$\cdot(A)_3\cdot(DSA)_2$, and $(A)_3\cdot(DSA)_3$] that can contribute to cluster growth has a positive correlation with [DSA]. The corresponding revision has been made in Lines 20-24 Page 15 of the revised manuscript.

Comment 19.

Line 325: Please mention the absolute rates here to let the reader know if this enhancement of many orders of magnitude is actually meaningful.

Response: Thank you for your valuable comments. According to your suggestion, the effects of precursor concentration and temperature are mainly described by the formation rate, meanwhile, the description of "enhancement factors" has been declined in the revised manuscript. The detail information is also provided in **Comment 17**.

Comment 20.

Line 336-339: *"Hence, it can be forecasted that the participation of DSA in SA-A-based NPF can likely enhance the number concentration of atmospheric particulates significantly in the polluted atmospheric boundary layer (278.15 K) areas with relatively high [DSA] and [A]."*

I do not believe this claim is adequately supported by the data. Please report the absolute values to support the conclusion.

Response: Thank you for your valuable comments. According to your suggestion, Meanwhile, the contribution of the DSA participation pathway has been increased with increasing temperature. Also, the contribution of the pathway with participation of DSA increases with increasing [DSA], while the number of DSA molecules contained in clusters [$(SA)_2 \cdot (A)_3 \cdot DSA$, $SA \cdot (A)_2 \cdot DSA$, $SA \cdot (A)_3 \cdot (DSA)_2$, and $(A)_3 \cdot (DSA)_3$] that can contribute to cluster growth has a positive correlation with [DSA]. Based on this, the sentence of "Hence, it can be forecasted that the participation of DSA in SA-A-based NPF can likely enhance the number concentration of atmospheric particulates significantly in the polluted atmospheric boundary layer (278.15 K) areas with relatively high [DSA] and [A]." has been changed as "These results suggested that DSA has the ability to act as a potential contributor to SA-A-based NPF in the atmosphere at low *T*, low [SA], high [A] and high [DSA], and the DSA participation pathway can be dominant in heavy sulfur oxide polluted atmospheric boundary layer and in season of late autumn and early winter.".

Comment 21.

Line 367-368: *"Furthermore, the adsorption capacity of the $S_2O_7^{2-}$, H_3O^+ and SA^- to gasous precursors in the atmosphere was further investigated."*

How was this evaluated? From Table 2 it looks like only the binding free energies were calculated. I guess the addition free energy of a given species should represent adsorption?

Response: Thanks for your valuable comments. Previous studies (***Angew. Chem. Int. Ed.***, 2019, 131, 8439-8443.) have used the interaction free energies to assess the adsorption capacity of interfacial ions. So, we believe that it is reasonable to use the binding free energy to evaluate the adsorption capacity of the $S_2O_7^{2-}$, H_3O^+ and SA^- to gasous precursors in the atmosphere. Our calculated the Gibbs free energies in Table 2 show that the interactions of $S_2O_7^{2-}\cdots H_2SO_4$, $S_2O_7^{2-}\cdots HNO_3$, $S_2O_7^{2-}\cdots (COOH)_2$, $H_3O^+\cdots NH_3$, $H_3O^+\cdots H_2SO_4$, $SA^-\cdots H_2SO_4$, $SA^-\cdots (COOH)_2$, and $SA^-\cdots HNO_3$ are stronger than those of $H_2SO_4\cdots NH_3$ (major precursor of atmospheric aerosols) with their binding free energies enhanced by 18.6-42.8 kcal·mol^{-1}. These results reveal that interfacial $S_2O_7^{2-}$, SA^- and H_3O^+ can attract candidate species from the gas phase to the water surface.

Comment 22.

Line 373-374: I do not believe you can use a charged 2-3 molecular cluster in the gas-phase to draw conclusions about the "acceleration of particle growth"

Response: Thanks for your valuable comments. We agree with the suggestion of the reviewer that it is incorrect to use a charged 2-3 molecular cluster in the gas-phase to draw conclusions about the "acceleration of particle growth". In Line 15 Page 16, of the revised manuscript "and thus in turn accelerates the growth of particle." has been deleted; "enhancing potential of $S_2O_7^{2-}$ on SA-A cluster" has been changed as "the nucleation potential of $S_2O_7^{2-}$ on SA-A cluster" and In Lines 23-26 Page 16 of the revised manuscript "the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster is lower. Therefore, we predict that $S_2O_7^{2-}$ at the air-water interface has important implication to the aerosol NPF in highly industrial polluted regions with high concentrations of SO_3." has been changed as "the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster is lower, showing $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation ability than *X* in the gas phase. Therefore, we predict that $S_2O_7^{2-}$ at the air-water interface has stronger nucleation potential.". The $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation potential as the following reasons. One reason is that the interactions of $S_2O_7^{2-}\cdots H_2SO_4$, $S_2O_7^{2-}\cdots HNO_3$, $S_2O_7^{2-}\cdots(COOH)_2$, $H_3O^+\cdots NH_3$, $H_3O^+\cdots H_2SO_4$, $SA^-\cdots H_2SO_4$, $SA^-\cdots(COOH)_2$, and $SA^-\cdots HNO_3$ listed in Table 2 are stronger than those of $H_2SO_4\cdots NH_3$ (major precursor of atmospheric aerosols). These results reveal that interfacial $S_2O_7^{2-}$, SA^- and H_3O^+ can attract candidate species from the gas phase to the water surface. The other reason is that as compared with $(SA)_1(A)_1(X)_1$ (*X* = $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$) clusters (Zhong et al., 2019; Zhang et al., 2018; Rong et al., 2020; Gao et al., 2023; Liu et al., 2021a; Zhang et al., 2017), the number of hydrogen bonds in $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster presented in Fig. S8 increased and the ring of the complex was enlarged. Meanwhile, comparing to $(SA)_1(A)_1(X)_1$ (*X* = $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$) clusters (Table 2), the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster is lower, showing $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation ability than *X* in the gas phase.

Comment 23.

Line 380-382: *"It was demonstrated that $S_2O_7^{2-}$ has the highest potential to stabilize SA-A clusters and promote SA-A nucleation in these clusters due to its acidity and structural factors such as more intermolecular hydrogen bond binding sites"*

I do not understand how this conclusion is drawn. What is the acidity of each of the compounds?

Response: Thanks for your valuable comments. The $S_2O_7^{2-}$ ion is formed by two deprotonations of $H_2S_2O_7$, where the pK_a1 and pK_a2 of $H_2S_2O_7$ are -16.05 and -4.81 (***Dalton Trans.***, 2013, 42, 5566), respectively. This indicates that $S_2O_7^{2-}$ is a strong acid anion. Moreover, $S_2O_7^{2-}$ ion has many exposed O atoms, which suggests that $S_2O_7^{2-}$ ion has more intermolecular hydrogen bond binding sites. Besides, the pK_a for *X* (*X* = $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$) has been listed in the Table S8.

Table S8 The pK_a for $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$

Compound	pK_a1	pK_a2
$HOOCCH_2COOH$ [a]	2.85	5.89
$HOCCOOSO_3H$ [b]	4.73	-
CH_3OSO_3H [c]	10.2	-
$HOOCCH_2CH(NH_2)COOH$ [d]	1.99	3.90
$HOCH_2COOH$ [e]	3.83	-

[a] The value was taken from reference (*J. Am. Chem. Soc.*, 1994, 116, 10298-10299.)

[b and c] The values were calculated at the M06-2X/6-311++G(3*df*,2*pd*) level.

[d] The value was taken from reference (Data for Biochemical Research, second ed., Oxford University Press, Oxford, 1969)

[e] The value was taken from reference (*Tissue Eng.*, 2007, 13, 2515-2523.)

Comment 24.

Line 384: An ion at a particle interface does not influence NPF.

Response: Thanks for your valuable comments. We agree with the suggestion of the reviewer that an ion at air-water interface is not directly related to new particle formation. Although the reaction of $H_2S_2O_7$ or H_2SO_4 formations at air-water interface is not directly related to new particle formation. In Line 15 Page 14, of the revised manuscript "and thus in turn accelerates the growth of particle." has been deleted; "enhancing potential of $S_2O_7^{2-}$ on SA-A cluster" has been changed as "the nucleation potential of $S_2O_7^{2-}$ on SA-A cluster" and In Lines 23-26 Page 16 of the revised manuscript "the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster is lower. Therefore,

we predict that $S_2O_7^{2-}$ at the air-water interface has important implication to the aerosol NPF in highly industrial polluted regions with high concentrations of SO_3." has been changed as "the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster was lower, showing $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation ability than *X* in the gas phase. Therefore, we predict that $S_2O_7^{2-}$ at the air-water interface has stronger nucleation potential.". The $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation potential as the following reasons. One reason is that the interactions of $S_2O_7^{2-}\cdots H_2SO_4$, $S_2O_7^{2-}\cdots HNO_3$, $S_2O_7^{2-}\cdots(COOH)_2$, $H_3O^+\cdots NH_3$, $H_3O^+\cdots H_2SO_4$, $SA^-\cdots H_2SO_4$, $SA^-\cdots(COOH)_2$, and $SA^-\cdots HNO_3$ listed in Table 2 are stronger than those of $H_2SO_4\cdots NH_3$ (major precursor of atmospheric aerosols). These results reveal that interfacial $S_2O_7^{2-}$, SA^- and H_3O^+ can attract candidate species from the gas phase to the water surface. The other reason is that as compared with $(SA)_1(A)_1(X)_1$ (*X* = $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$) clusters (Zhong et al., 2019; Zhang et al., 2018; Rong et al., 2020; Gao et al., 2023; Liu et al., 2021a; Zhang et al., 2017), the number of hydrogen bonds in $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster presented in Fig. S8 increased and the ring of the complex was enlarged. Meanwhile, comparing to $(SA)_1(A)_1(X)_1$ (*X* = $HOOCCH_2COOH$, $HOCCOOSO_3H$, CH_3OSO_3H, $HOOCCH_2CH(NH_2)COOH$ and $HOCH_2COOH$) clusters (Table 2), the Gibbs formation free energy ΔG of $(SA)_1(A)_1(S_2O_7^{2-})_1$ cluster is lower, showing $S_2O_7^{2-}$ ion at the air-water interface has stronger nucleation ability than *X* in the gas phase.