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

1 calculation in their Table S6, already this percentage is very small-despite their neglect of many

2 other known candidates for X.)

3 **Response:** Thanks for your valuable comments. According to the reviewer's suggestion, the

4 schematic potential energy surface of the H_2SO_4 formation from the $SO_3 + H_2SO_4$ reaction with

5 H_2O has been added in Fig. 1, while the corresponding effective rate constants have been listed in

6 Table 1. Then, the competition between H_2SO_4 and $H_2S_2O_7$ formations from the $SO_3 + H_2SO_4$

7 reaction with H_2O have been discussed. The corresponding major revision has been made as follows.

8   (a) The $SO_3 + H_2SO_4$ reaction with H_2O can produce two distinct products, labeled (*i*) $H_2S_2O_7$

9 (DSA, Channel DSA_WM) and (*ii*) H_2SO_4 (SA, Channel SA_SA). A single water molecule in (*i*)

10 acts as a catalyst, while it plays as a reactant in (*ii*). So, based on the $H_2S_2O_7$ formation from the

11 $SO_3 + H_2SO_4$ reaction with H_2O, the schematic potential energy surface for the H_2SO_4 formation

12 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

13 revised manuscript, the corresponding discussion has been reorganized as "The $SO_3 + H_2SO_4$

14 reaction with H_2O produced two distinct products, labeled (*i*) $H_2S_2O_7$ (DSA, Channel DSA_WM)

15 and (*ii*) H_2SO_4 (SA, Channel SA_SA). A single water molecule in (*i*) acted as a catalyst, while it

16 played as a reactant in (*ii*). The schematic potential energy surface for the $SO_3 + H_2SO_4$ reaction

17 with H_2O was shown in Fig. 1."

18   (b) Similar with the $H_2S_2O_7$ formation from the $SO_3 + H_2SO_4$ reaction with H_2O (Fig. 1 (b),

19 Channel DSA_WM), the H_2SO_4 formation from the $SO_3 + H_2SO_4$ reaction with H_2O (Fig. 1 (c),

20 Channel SA_SA) can be considered as a sequential bimolecular process. In other words, Channel

21 SA_SA occurs via the collision between SO_3 (or H_2SO_4) and H_2O to form dimer ($SO_3\cdots H_2O$ and

22 $H_2SO_4\cdots H_2O$) first, and then the dimer encounters with the third reactant H_2SO_4 or SO_3. However,

23 the $SO_3\cdots H_2O + H_2SO_4$ reaction in Channel SA_SA can be neglected as its effective rate constant

24 is smaller by 1.02-3.05 times than the corresponding value in the $H_2SO_4\cdots H_2O + SO_3$ reaction.

25 Therefore, we only consider the $H_2SO_4\cdots H_2O + SO_3$ bimolecular reaction in Channel SA_SA. In

26 Lines 21-29 Page 8 to lines 1-17 Page 9 of the revised manuscript, two sequential bimolecular

27 processes, $H_2SO_4\cdots H_2O + SO_3$ and $SO_3\cdots H_2O + H_2SO_4$, have been considered, which has been

28 reorganized as "As the probability of simultaneous collision (Pérez-Ríos et al., 2014; Elm et al.,

29 2013) of three molecules of SO_3, SA and H_2O is quite low under realistic conditions, both Channel

30 DSA_WM and Channel SA_SA can be considered as a sequential bimolecular process. In other

1 words, both Channel DSA_WM and Channel SA_SA occur via the collision between SO_3 (or H_2SO_4)

2 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

3 third reactant H_2SO_4 or SO_3. The computed Gibbs free energies of dimer complexes $SO_3\cdots H_2O$ and

4 $H_2SO_4\cdots H_2O$ were respectively 0.8 $kcal\cdot mol^{-1}$ and -1.9 $kcal\cdot mol^{-1}$, which were respectively

5 consistent with the previous values (the range from -0.2 to 0.62 $kcal\cdot mol^{-1}$ for $SO_3\cdots H_2O$ complex

6 (Bandyopadhyay et al., 2017; Long et al., 2012) and the range from -1.82 to -2.63 $kcal\cdot mol^{-1}$ for

7 $H_2SO_4\cdots H_2O$ complex (Long et al., 2013b; Tan et al., 2018)). The Gibbs free energy of $H_2SO_4\cdots H_2O$

8 was lower by 2.7 $kcal\cdot mol^{-1}$ than that of $SO_3\cdots H_2O$, thus leading to that the equilibrium constant of

9 the former complex is larger by 1-2 orders of magnitude than that of the latter one in Table S2.

10 Additionally, the larger equilibrium constant of $H_2SO_4\cdots H_2O$ complex leads to its higher

11 concentration in the atmosphere. For example, when the concentrations of SO_3 (Yao et al., 2020),

12 H_2SO_4 (Liu et al., 2015) and H_2O (Anglada et al., 2013) were 10^6, 10^8 and 10^{17} molecules$\cdot cm^{-3}$,

13 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

14 5.01×10^5-3.01×10^8 molecules$\cdot cm^{-3}$ within the temperature range of 280-320 K (see Table S3),

15 respectively. So, we predict that Channel DSA_WM and Channel SA_SA mainly take place via the

16 collision of $H_2SO_4\cdots H_2O$ with SO_3. In order to check this prediction, the effective rate constants for

17 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

18 details were shown in *SI Appendix*, Part 3 and Table 1. As seen in Table 1, the $SO_3\cdots H_2O + H_2SO_4$

19 reaction in both Channel DSA_WM and Channel SA_SA can be neglected as their effective rate

20 constants are smaller by 16.7-48.5 and 1.02-3.05 times than the corresponding values in the

21 $H_2SO_4\cdots H_2O + SO_3$ reaction within the temperature range of 280-320 K, respectively. Therefore,

22 we only consider the $H_2SO_4\cdots H_2O + SO_3$ bimolecular reaction in both Channel DSA_WM and

23 Channel SA_SA."

24 (c) As for the H_2SO_4 formation from the $SO_3 + H_2SO_4$ reaction with H_2O, the discussion of

25 the stepwise $H_2SO_4\cdots H_2O + SO_3$ reaction has been added in Lines 8-21 Page 10 of the revised

26 manuscript, which has been reorganized as "Regarding Channel SA_SA, the stepwise reaction

27 occurred firstly via the ring enlargement from six-membered ring complex IM_{SA_SA}' to a cage-like

28 hydrogen bonding network IM_{SA_SA}, and then took place by going through a transition state, TS_{SA_SA},

29 to from the product complex $(H_2SO_4)_2$. TS_{DSA_WM} was in the middle of a double hydrogen transfer,

30 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.

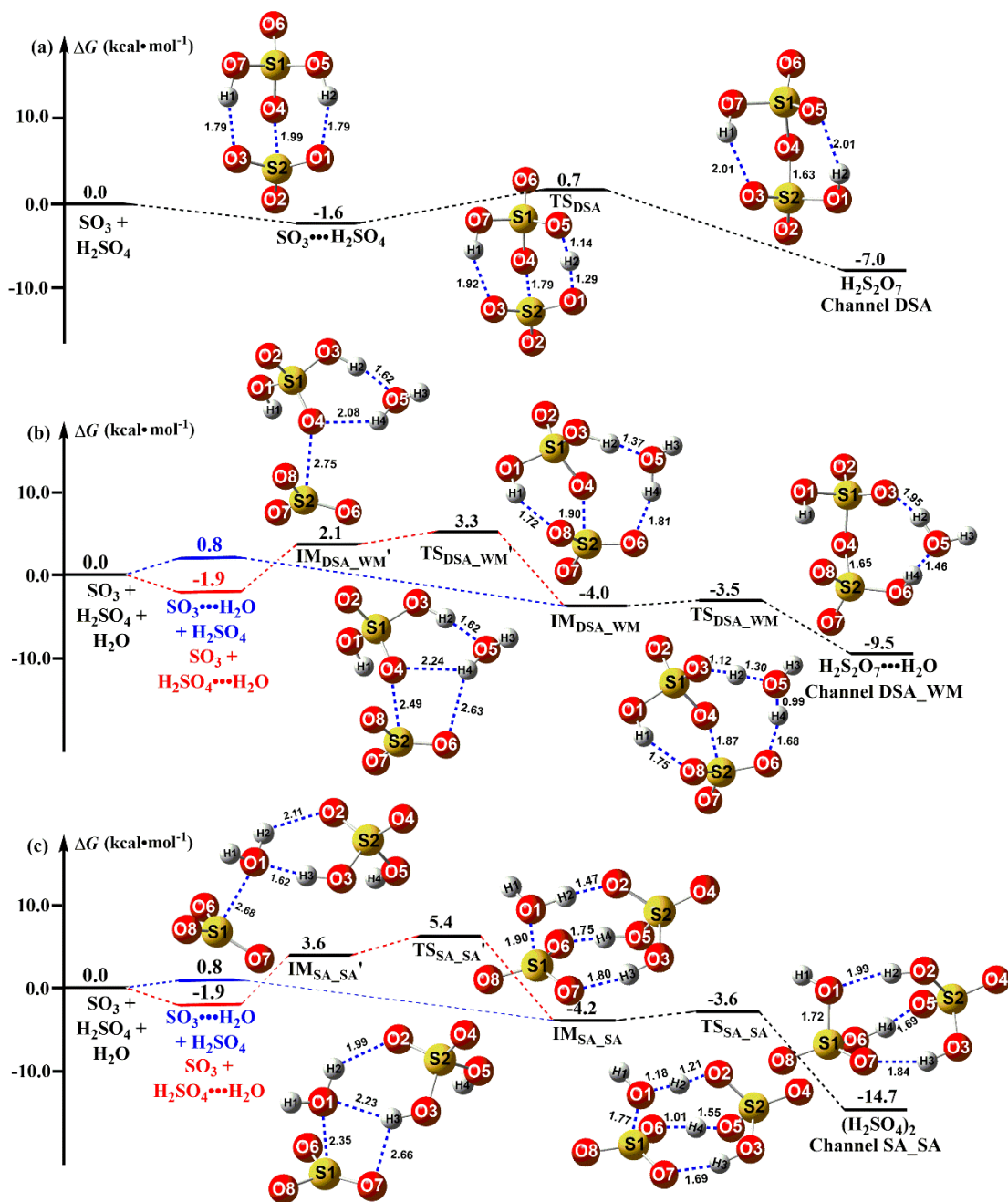



Fig. 1 Schematic potential energy surface of the $SO_3 + H_2SO_4$ reaction without and with H_2O at the CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311+G(2df,2pd) level

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$_2$COOH, HOCCOOSO$_3$H, CH$_3$OSO$_3$H, HOOCCH$_2$CH(NH$_2$)COOH and HOCH$_2$COOH) 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$_2$COOH, HOCCOOSO$_3$H, CH$_3$OSO$_3$H, HOOCCH$_2$CH(NH$_2$)COOH and HOCH$_2$COOH) 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".

1 **Response:** Thanks for your valuable comments. The reason for using a constant SO_3 source is not

2 reasonable has been explained firstly. Meanwhile, the corresponding discussion on "enhancement

3 factors" have been condensed and the analysis of the absolute formation rate with temperature and

4 concentration changes after the addition of $H_2S_2O_7$ has been added. The corresponding major

5 revision has been made as follows.

6 (a) It is not reasonable to use a constant SO_3 source since there are many pathways for the

7 removal of SO_3 removal processes. the hydrolysis of SO_3 to product H_2SO_4 is the most major loss

8 route of SO_3 in the atmosphere. As a complement to the loss of SO_3, ammonolysis reaction of SO_3

9 in polluted areas of NH_3 can form H_2NSO_3H, which can be competitive with the formation of H_2SO_4

10 from the hydrolysis reaction of SO_3. Besides, the reactions of SO_3 with CH_3OH, HNO_3, and organic

11 acids (e.g., formic acid, acetic acid and acrylic acid). These reactions consume some SO_3 in the

12 atmosphere and inhibit the hydrolysis of SO_3 (H_2SO_4 formation) to some extent. Thus, it is not

13 suitable to use a constant source of SO_3.

14 The concentration of $H_2S_2O_7$ has been re-evaluated within the altitude range of 0-30 km. Then,

15 the analysis of the absolute formation rate with temperature and concentration changes after the

16 addition of $H_2S_2O_7$ has been added in Lines 28-30 Page 14 to Lines 1-13 Page 15 of the revised

17 manuscript, which has been organized as "The potential enhancement influence of DSA to the SA-

18 A-based particle formation was shown in Fig. 6. The formation rate (J, $cm^{-3} \cdot s^{-1}$) of SA-A-DSA-

19 based system illustrated in Fig. 6 was negatively dependent on temperature, demonstrating that the

20 low temperature is a key factor to accelerate cluster formation. It is noted that, at low temperatures

21 of 218.15 K (Fig. S12) and 238.15 K (Fig. S13), the actual ΔG of clusters has been calculated to

22 ensure meaningful cluster dynamics of the 3 × 3 systems, where the actual ΔG surface represented

23 that the simulated set of clusters always included the critical cluster. In addition to temperature, the

24 J of SA-A-DSA-based system shown in Fig. 6 rise with the increase of [DSA]. More notably, the

25 participation of DSA can promote J to a higher level, indicating its enhancement on SA-A

26 nucleation. Besides, there was significantly positive dependence of the J of SA-A-DSA-based

27 system on both [SA] and [A] in Fig. 7 (238.15 K) and Fig. S15-Fig. S18 (218.15, 258.15, 278.15

28 and 298.15 K). This was because the higher concentration of nucleation precursors could lead to

29 higher J. Besides, Fig. S19 showed the nucleation rate when the sum ([SA] + [DSA]) was kept

30 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 $H_2S_2O_7 + H_2O => H_2SO_4 + H_2SO_4$ 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.

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

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

1 cluster, will thus collide with DSA molecules about once per 1E9 seconds or so (as the pseudo-

2 unimolecular collision rate is k_coll times the concentration, and the lifetime with respect to

3 collisions is the inverse of this). This is more than 30 YEARS. Even for a DSA concentration of 10

4 per cm^3, the timescale of a given molecule or cluster colliding with a DSA molecule is more than 3

5 YEARS. Or for 100 per cm^3, more than 3 months. It is quite clear from this that the pseudo-steady-

6 state assumed by ACDC simulations will simply never have time to form, when some of the

7 participating molecules have such low concentrations. Or in other words, the basic assumptions

8 required for modelling clustering with ACDC do not apply in these cases (or, to put it yer another

9 way, an ACDC - type code needs to be run in a very different way, explicitly accounting for these

10 timescales).

11 **Response:** Thanks for your valuable comments. We agree with the reviewer that at some of the

12 participating molecules such low concentrations that the pseudo-steady-state assumed by ACDC

13 simulations will simply never have time to form. Based on this, Considering the concentration of

14 sulfuric acid at the end and outside the aircraft engine and flight (up to 600 pptv), the concentration

15 of $H_2S_2O_7$ has been re-evaluated within the altitude range of 0-30 km. Specifically, the steady-state

16 concentration of DSA was calculated using the calculated equilibrium constant listed in Eq. S5.

$$K_{eq3} = \frac{[DSA]}{[SO_3][SA]} \tag{S5}$$

18 where K_{eq3} is the equilibrium constant of DSA with respect to SO_3 and H_2SO_4 within the altitude

19 range of 0-30 km shown in Table S9; [SO_3], [SA] and [DSA] are the concentrations of SO_3, H_2SO_4,

20 and $H_2S_2O_7$, respectively. Although the concentration of sulfur trioxide remains unknown at

21 different altitudes, experimental observations have shown that the concentration of sulfur trioxide

22 can reach 10^6 molecules cm^{-3} in the troposphere. Moreover, water vapor concentrations significantly

23 decrease with increasing of altitude. Consequently, the concentration of sulfur trioxide should be

24 higher in the stratosphere than in the troposphere, and its concentration would increase as a result

25 of geoengineered injection of SO_2 or SO_3. Besides, it is worth noting that H_2SO_4 can form at the

26 end and outside the engine, and flight measurements in the exhaust plume have measured sulfuric

27 acid abundances up to a value of 600 pptv. When an average flight altitude of 10 km is considered,

28 this corresponds to a concentration of 5.1×10^9 molecules·cm^{-3}. Therefore, we have calculated the

29 concentrations of DSA according to concentrations of sulfur trioxide in the range from 10^7 to 10^{14}

1 molecules cm^{-3} and the concentrations of H$_2$SO$_4$ in the range of 10^4-10^9 molecules cm^{-3} as shown

2 in Fig. S9.

3   The maximum concentration of DSA displayed in Fig. S9 can be up to 10^8 molecules·cm^{-3}.

4 However, it should be noted that the concentration of water in the troposphere is abundant, and

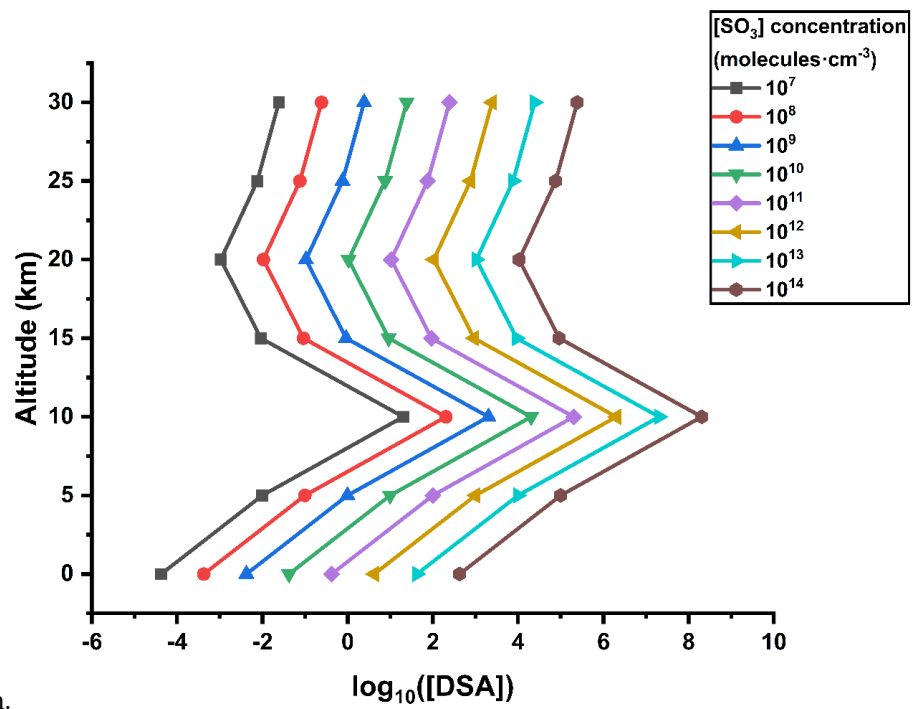
5 DSA is easily hydrolyzed to form H$_2$SO$_4$. Based on this, the concentration of DSA listed in Fig. S9

6 was overestimated. The extent and proportion of DSA hydrolysis remains unclear, and the

7 hydrolysis behavior of DSA needs to be further investigated in subsequent studies. Therefore, the

8 maximum concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of H$_2$S$_2$O$_7$,

9 the product of the reaction between SO$_3$ and H$_2$SO$_4$, on new particle formation (NPF) in various

10 environments by using the Atmospheric Cluster Dynamics Code kinetic model and the QC

11 calculation.

12 **Fig. S9** Concentration (unit: molecules·cm^{-3}) of DSA with respect to different concentrations of SO$_3$

13 as function of altitude. We consider the possible concentrations of SO$_3$ with the injection of SO$_3$.

15   The maximum concentration of DSA displayed in Fig. S9 can be up to 10^8 molecules·cm^{-3}.

16 However, it should be noted that the concentration of water in the troposphere is abundant, and DSA

17 is easily hydrolyzed to form H$_2$SO$_4$. Based on this, the concentration of DSA listed in Fig. S9 was

18 overestimated. The extent and proportion of DSA hydrolysis remains unclear, and the hydrolysis

19 behavior of DSA needs to be further investigated in subsequent studies. Therefore, the maximum

20 concentration of DSA (10^8 molecules·cm^{-3}) was not included in the effect of H$_2$S$_2$O$_7$, 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 → $H_2S_2O_7$ reaction without

and with H_2O illustrated in Fig. 1, the reaction without H_2O has only a barrier height of 2.3 kcal·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·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 introducing 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.