Rui Wang and co-workers studied the enhancing effect of FSA on SO_3 hydrolysis, both in the gas phase and at the gas-liquid nanodroplet interface, as well as its impact on H_2SO_4-NH_3-driven NPF through quantum chemical calculations, atmospheric clusters dynamics code (ACDC) kinetics combined with Born-Oppenheimer molecular dynamics (BOMD). The present study identified a novel SO_3 hydrolysis pathway involving FSA in the polluted regions and FSA enhanced nucleation mechanism.

The work is quite comprehensive and highly routine in nature which involves substantial workload. However, there are some contradictory points/conclusions that may make the readership confused. Anyway, I hope the authors find the below comments useful.

Line 103: "Initially, the ABCluster program was utilized to randomly produce n $\times$ 1000 initial isomers (where n = 2 to 4)..."
Q1: Why not adopt a unified "n" value for all the clusters ?
Q2: The M06-2X functional with a 6-311++G(2df,2pd) basis set is a reasonable computational level of theory for studying kinetics. However, it would be appreciable if the authors could further motivate their choice. There certainly exist numerous benchmarks of the performance of different DFT functionals for thermochemistry and barrier heights of atmospheric relevant systems.
Q3: CCSD(T)-F12/cc-pVDZ-F12 was used for the single point calculations. Please also specify which basis sets were used for the resolution of identity (RI) and complete auxiliary basis set (CABS) parts?
Q4: To generate more accurate gibbs free energies, the authors calculated the FSA catalytic SO_3 hydrolysis reaction mechanism under the CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311++G(2df,2pd) level of theory. However, the calculations for the nucleation clusters were just under the M06-2X/6-311++G(2df,2pd) level of theory. No further single point calculations were performed, even the CCSD(T)-F12/cc-pVDZ-F12 calculations in ORCA are quite fast. I suggest the authors insist on using CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311++G(2df,2pd) in the whole calculations, including the reactions and the nucleation process, the consistency in the calculation method throughout the study will also make it more scientific and reasonable.

2.2 Rate Coefficient Computations
The studied reactions involves the motion of a hydrogen atom may have a high imaginary frequency. So the tunneling effects could be quite profound. Has the tunneling correction been considered in the rate coefficient computations ? If so, please clarify in section 2.2. If not, I highly recommend taking into account the tunneling correction.

2.3 BOMD Simulations
Q1: Line 126: Please specify the detailed basis set used by the BOMD simulations.
Q2: Line 130 "... to eliminate periodic boundary conditions with step of 0.5 fs..."

Line 135 "...neighbouring water droplets, using a step of 1.0 fs..."
In order to ensure the readability of the manuscript, please briefly explain why two different time steps were used here?

2.4 Molecular Dynamics Simulation of Nucleation
Q1: Line 141 "M06-2X/6-311++G(*2df,2pd*)" → M06-2X/6-311++G(2df,2pd). There's no need for italics here. Please also check the whole manuscript.
Q2: Line 142 "Multiwfn 3.8" Actually, there is no Multiwfn 3.8 version. Please check the Multiwfn website and ensure the exact version which the authors downloaded and used, maybe it is Multiwfn 3.8 (dev).
Q3: Line 151 "Bond lengths were restricted by the LINCS algorithm". Were all the bond lengths in the MD simulations restricted by the LINCS algorithm?

2.5 Atmospheric Cluster Dynamics Code (ACDC) Model
Q1: Lines 160-161 "...while $\beta_{i,j}$ stands for the collision rate between i and j clusters. The term $\gamma_{(i+j)\to i}$ ...". Actually, $\beta_{i,j}$ here is not collision rate but collision coefficient，γ is not evaporation rate but evaporation coefficient. The present misleading expression may confuse readership in their understanding of the birth-death equation. Please revise.
Q2: Line 167 "...were selected as the boundary clusters in the SA-A-FSA system".
Whether a cluster should be selected as a boundary cluster is related to both its evaporation rate and collision rate, as referenced in the article on the ACDC model. Please clarify the selection criteria for boundary clusters in the present study. Furthermore, in lines 313-315, the author pointed out that the evaporation coefficient of $(FSA)_3(A)_3$ $(3.30\times10^{-1}$ $s^{-1})$ was nearly 10^3 times lower than that of $(SA)_3(A)_3$ $(2.25\times10^2$ $s^{-1})$. Then why clusters $(FSA)_4(A)_3$, $(FSA)_4(A)_4$, $(FSA)_3(SA)(A)_3$ were not considered as the boundary clusters ? This is the first contradictory point.

Lines 252-255 "In contrast to the SO_3 hydrolysis with FSA in the gas phase, which does not proceed within 100 ps, the reaction at the gas-liquid nanodroplet interface rapidly proceeds within just a few picoseconds. This indicates that interfacial water molecules at the gas-liquid nanodroplet interface can accelerate the SO3 hydrolysis."
Q1: Since the FSA catalytic SO_3 hydrolysis reaction on the gas-liquid nanodroplet interface is faster, it is more likely to occur on the interface in the case of the low saturated vapor pressure of FSA, making the FSA catalytic reaction in the gas phase relatively less important. And the generated SA molecules at the nanodroplet interface tends to deprotonate rather than evaporate into the gas phase. This is the second contradictory point. Is it possible to calculate the proportion of FSA catalytic reaction occurring in the gas phase versus on the interface? If the proportion of gas phase reaction only accounts for a small fraction, then emphasizing the role of FSA in gas phase reaction and nucleation would appear to have limited significance.
Q2: Since different molecules in the gas phase can catalyze the SO_3 hydrolysis reaction, and water molecules exhibit the fastest catalytic rate due to their higher concentration in the gas phase. So it is necessary to supplement the calculation on the

catalytic effect of water molecules on the interface, where their concentration is even higher. A comparison should hence be made between the catalytic effect of water molecules and FSA molecule on the interface.

Lines 261-264: "As shown, the interactions of FSA$^-$-SA (-21.2 kcal • mol^{-1}) and FSA$^-$-HNO3 (- 12.1 kcal • mol^{-1}) are stronger than that of SA-A (-8.9 kcal • mol^{-1}), illustrating that interfacial FSA$^-$ and H3O$^+$ ions can attract precursor molecules from the gaseous phase to the aqueous nanodroplet surface, and thus facilitating particle growth."

Q: Since the reaction rate for the FSA catalytic SO$_3$ hydrolysis on the aqueous nanodroplet surface is much higher than that in the gas phase. And the generated SA molecules at the nanodroplet interface tends to deprotonate rather than evaporate into the gas phase. Furthermore, interfacial FSA$^-$ ions can also attract precursor molecules from the gas phase to the aqueous nanodroplet surface, and thus facilitate particle growth. Combining with the low saturated vapor pressure of FSA, it seems that FSA is more likely to contribute to the particle growth. In other words, is that possible to calculate the contribution proportion of FSA to the gas phase nucleation and the particle growth ? If the contribution proportion of FSA to the gas phase nucleation only accounts for a small fraction, then the FSA-involved nucleation in Section 3.3 and 3.4 would appear to have limited significance. This is the third contradictory point.

Line 266: SA-A-Y (Y=HOOCCH2COOH, HOCCOOSO3H, CH3OSO3H, HOOCCH2CH(NH2)COOH and HOCH2COOH) clusters.

Q: Such comparison does not seem that fair and reasonable. Y and FSA are all acid molecules which can be deprotonated at the nanodroplet interface. So it is more reasonable to compare the binding free energies of SA-A-FSA$^-$ and SA-A-Y$^-$.

3.3 FSA's Role in Nucleation and Cluster Formation

Q1: Line 283 "In these simulation systems, 5 FSA, 5 SA, 10 A, 20 H2O, 41 O2 and 154 N2 molecules were included."

The ratio of the number of molecules does not seem to be consistent with the real atmospheric concentration condition. Once the number of molecules in the Gromacs MD simulation is large enough, molecular aggregation will take place.

Q2: Fig.4.

The classical MD simulation performed by Gromacs relies on the force field of the molecules, which can only describe physical aggregation. However, during the nucleation process, the proton transfer between acid and base molecules plays an important role in acid-base nucleation which can not be reflected in the classical MD simulation. In this case, the physical aggregation pathways in the MD simulations are not completely consistent with those in ACDC simulations. For example, in the MD simulation shown in Fig. 4, all the clusters containing SA, A and FSA. In the ACDC simulations, there exist pure SA-A paths. The clusters growth pathways are not completely consistent with each other. This is the fourth contradiction in this

manuscript which may make the readership confused.

Line 352: "First, as [A] increases, the interaction between FSA and SA in the ternary cluster may be disrupted, leading to a decrease in the saturation of FSA interaction sites and a reduction in R."

Q: According to the data shown in Fig.5, the ΔG and evaporation coefficient of FSA-based clusters is much lower than that of SA-based clusters. As [A] increases, if the interaction between FSA and SA in the ternary cluster was disrupted, the FSA will interact with the increasing A. The generated FSA-A-based clusters are more thermodynamically stable, and hence the R will increase. This is somewhat inconsistent with the current conclusion.

Line 386: "...with high FSA emissions..."
Q: Is there any emissions sources of FSA?

Line 592: Smith, C. J., Huff, A. K., Ward, R. M., and Leopold, K. R.: Carboxylic sulfuric anhydrides, J. Phys. Chem. A, 124, 601-612, https://doi.org/10.1126/science.1180315, 2020.
Q: The URL (https://doi.org/10.1126/science.1180315) provided does not match this reference, the author wrote a wrong URL. Please revise and also check the whole references section.

Technical corrections:
(1) Line 72: A full stop "." should be added at the end of the paragraph.
(2) Line 102: "The most stable structure of the (FSA)x(SA)y(A)z (z ≤ x + y ≤ 3)...". This is the first time that abbreviation "A" appeared. It will be more clear to clarify that "A" is the abbreviation of NH_3.
(3) Results and discussion: The tense of the sentences throughout the "Results and discussion" should be consistent. If the past tense is used, please use the past tense uniformly. For example, in lines 173 and 176, the authors used "was" and "is", respectively.
(4) Line 376: "low"→"lower". line 386: "high"→ "higher".
(5) Fig.4: "VDW"→"vdW".
(6) Fig.7: "T=278 K"→"T=278.15 K"