

Responses to Referee #1's comments

We are grateful to the reviewers for their valuable and helpful comments on our manuscript "Enhancing SO₃ Hydrolysis and Nucleation: The Role of Formic Sulfuric Anhydride" (MS No.: **egusphere-2024-3275**). We have revised the manuscript carefully according to reviewers' comments. The point-to-point responses to the Referee #1's comments are summarized below:

General comments:

This manuscript reports that the formic sulphuric anhydride molecule (FSA) is able to catalyze the hydration of SO₃ to form sulphuric acid in the atmosphere. This should not be a surprise to anyone in this field, since it seems that any molecule which is able to form a complex with SO₃ and H₂O and help the double proton transfer happen will catalyze this process. It was still worth doing this work to get some quantitative data for this new system, though, and it should be published with some minor revisions.

Specific Comments:

Comment 1.

I have some concerns about the simulations done to demonstrate the propensity of the pre-reactive cluster to sit on the interface (results shown in Fig S6). I was glad to see this done, since it is often omitted from similar work, but it is very important to do; who cares if the reaction is faster at the interface, if the pre-reactive complex never resides there?

However, I could not find any discussion of the simulation methods used. I assume that these were not ab initio simulations, since they were quite long (150ns). But the only force-field based simulations described in the manuscript were the clustering simulations described in section 2.4. Simulating the interfacial preference of different species is known to be difficult, it is sensitive to, for example, whether polarizability is included in the force field, as well as the analysis methods used to define the interface (see eg. <https://doi.org/10.1080/08927022.2021.1980215> for a recent review) so it is crucial that these details be included.

Response: Thanks for your valuable comments. As stated by the reviewer, the surface preference of the SO₃-FSA complex was studied using classical molecular dynamics (MD) simulations rather than ab initio simulations. The corresponding revision has been respectively made as follows.

(a) The MD simulations were performed using GROMACS 2024.3 software package with the general AMBER force field (GAFF). GAFF is a complete force field; it covers almost all the organic chemical space that is made up of C, N, O, S, P, H, F, Cl, Br and I. The GAFF force field has been widely used in studies involving the air-water interface, demonstrating its suitability for predicting the properties of species at air-water interface. So, in Lines 144-155 on Page 5-6 of the revised manuscript, the sentence of “MD simulations were conducted using the GROMACS 2024.3 software package (Abraham et al., 2024) with the general AMBER force field (GAFF). GAFF is a comprehensive force field that encompasses nearly all of organic chemical space, including elements such as C, N, O, S, P, H, F, Cl, Br, and I. This force field has been widely utilized in studies of the air-water interface, with the results confirming its suitability for predicting the properties of species at this interface (Li et al., 2024b; Cheng et al., 2025; Zhao et al., 2019). To get the force field parameters, geometry optimization at the M06-2X/6-311++G(2df,2pd) level were performed, following Electrostatic potential (ESP) calculations at the same level. Geometry optimization and electrostatic potential (ESP) calculations were carried out with the Gaussian 09 software. The restrained electrostatic potential (RESP) charges were calculated using Multiwfn 3.8 (dev) (Lu and Chen, 2012). Subsequently, the AMBER parameter and coordinate files were generated using Packmol (Martínez et al., 2009) and Sobotop (Lu, 2023), respectively.” has been reorganized.

(b) A cubic box of 4 nm side length with 2165 water molecules was firstly built. The water box was extended to 9 nm along the z axis direction, we put the water slab in the middle of the box with the COM coordinate of (2.0 nm, 2.0 nm, 4.5 nm) and a SO₃-FSA complex at (2.0 nm, 2.0 nm, 7.5 nm) (Fig. S6(c)). A 150 ns NVT simulation was performed. So, in the section of “2.4.1 Surface preference of SO₃, FSA and SO₃-FSA” of the revised manuscript, in Lines 157-161 on Page 6, the sentence of “A cubic box with a side length of 4 nm, containing 2165 water molecules, was initially constructed. The box was then extended along the z-axis to a length of 9 nm. The water slab was positioned at the center of the box with the COM coordinates of (2.0 nm, 2.0 nm, 4.5 nm), while the SO₃, FSA and SO₃-FSA complexes were placed at (2.0 nm, 2.0 nm, 7.5 nm) (Fig. S6(c)). Subsequently, a 150 ns NVT simulation was conducted.” has been added.