Reply to Comment on acp-2021-784
Anonymous Referee #2

We thank the Referee for their constructive comments. Here, we present a point-to-point response to all the comments. For clarity, the Referee's comments are reproduced in blue color text, authors' reply are in black color and modifications to the manuscript are in red color text.

The manuscript titled "Pyruvic acid, an efficient catalyst in SO3 hydrolysis and effective clustering agent in sulfuric acid-based new particle formation" by Tsona et al. discusses the role of pyruvic acid as a catalyst in SO3 hydrolysis. The investigation of whether pyruvic acid can take part in cluster formation brings an interesting addition to the article. The paper is well written and it fits to the scope of the journal.

Specific comments:
1. I would like to see a section in the Methodology on how the cluster conformers were found for the ACDC calculations. Presumably the clusters containing only sulfuric acid and ammonia can be found somewhere in the literature, but how about the clusters containing pyruvic acid? I can see that for the hydrolysis calculations, different conformers of the pyruvic acid were used, but the clusters should have a lot of conformers due to the higher number of molecules as well as the 4 different pyruvic acid conformers, which should be considered in finding the lowest energy cluster.

To select the cluster structures, several initial configurations were generated manually by arranging the participating molecules in different directions and pre-optimizing them. By step-wise addition of monomer to a cluster, larger clusters were built. Depending on the cluster size, 10-30 initial configurations of each cluster were pre-optimized at the M062X/6-31+G(d) level of theory and the best structures with energies within 3 kcal mol^{-1} similar to the lowest energy configuration were re-optimized at the M062X/6-31++G(d,p) level of theory. Although the 6-31++G(d,p) basis set is somewhat smaller than the 6-311++G(3df,3pd) basis set used in the thermodynamics and reaction kinetics part, a benchmark study has shown that the use of the 6-31++G(d,p) basis set instead of 6-311++G(3df,3pd) in modeling sulfuric acid-based clusters only introduces low errors in the Gibbs free energy, yet significantly reducing the computation cost (Elm and Mikkelsen, 2014). Hence, we chose the M062X/6-31++G(d,p) method for optimizing the modeled clusters.
The following was added in the revised manuscript for clarifications:
Line 135:
A number of initial configurations of SA-NH_3 clusters were taken from previously published results (Ortega et al., 2012) and re-optimized with the M06-2X/6-31++G(d,p), while those containing PA were built by stepwise addition of monomers to the relevant cluster. On this basis, several starting configurations were generated manually by arranging the participating molecules/clusters in different directions. Depending on the cluster size, 10-30 initial configurations of each cluster were pre-optimized at the M062X/6-31+G(d) level of theory and all identified structures within 3 kcal mol^{-1} of the lowest energy structure were thereafter re-optimized with the M06-2X/6-31++G(d,p) method and the vibrational frequency analysis were

subsequently performed at the same level of theory. It has been shown that the reduction from 6-311++G(3df,3pd) to 6-31++G(d,p) basis set for sulfuric acid-based cluster formation induces very little errors in the thermal contribution to the Gibbs free energy, with no further substantial effect on the single point energy, yet sufficiently reducing the computation cost (Elm and Mikkelsen, 2014). The electronic energies of M06-2X/6-31++G(d,p) optimized structures were further corrected with the DLPNO-CCSD(T)/aug-cc-pVTZ method.

2. In Fig. 5 (bottom panel), can you discuss why are the enhancement factors of 238 K at 3 and 4*10^9 PA molecules/cm-3 the same, when all other points seem to have the same linear trend with the same slope?

It should be noted that the enhancement factor is calculated as the ratio of the particle formation rate in the SA-PA-NH_3 system to that in the SA-NH_3 system as shown by **Eq. (6)** in the main manuscript. At [SA] = 10^6 cm^{-3} and [NH_3] = 10^{10} cm^{-3}, with [PA] increasing from 10^9 to 10^{10} cm^{-3}, the increase in particle formation rate is very subtle, with slight differences appearing only from the fifth decimal. As a consequence, the change in the enhancement factor as [PA] increases is also very weak. The seemingly similar PA enhancement factor at [PA] = 3×10^9 cm^{-3} and [PA] = 4×10^9 cm^{-3} is due to the way the data were truncated, being at the third decimal. More accurate values of the enhancement factor can be obtained by truncating the values at fourth decimal. The revised plot is shown below and it has been uploaded in the revised manuscript.

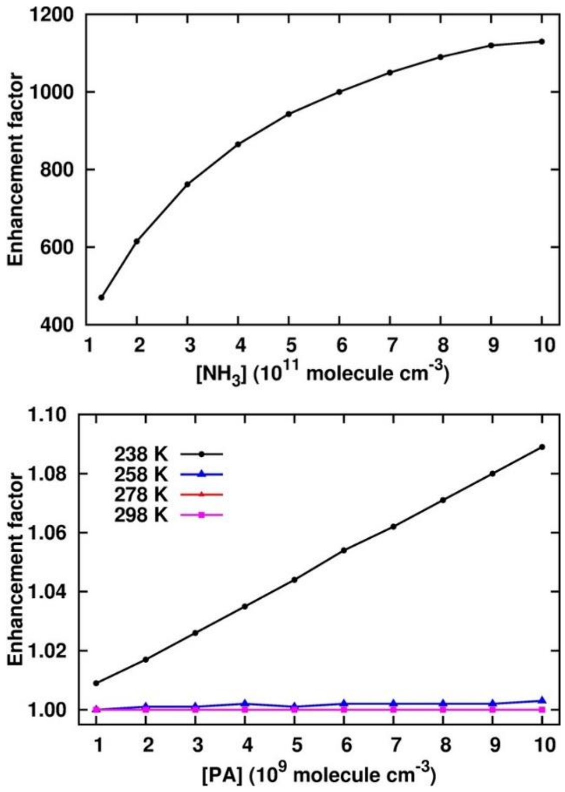

Figure 5: Enhancement of PA in the clusters formation rate in the sulfuric acid-pyruvic acid-ammonia clusters at [SA] = 10^6 cm^{-3}, [NH_3] = 10^{10} cm^{-3}, [PA] = 10^9 -10^{10} cm^{-3} and different temperatures (bottom panel), and T = 238 K, [SA] = 10^6 cm^{-3}, [PA] = 10^{10} cm^{-3}, [NH_3] = 10^{11} -10^{12} cm^{-3} (top panel).

3. Did you run any simulation wher you would have an initial concentration of PASA, formed during the SA formation? Would this have any effect on the cluster formation results or would the PA just evaporate from the cluster, once more SA and NH3 is added through collisions?

We did not simulate the SA•PA concentration from the PA-catalyzed SO_3 hydrolysis, since this would combine not only the kinetics but also dynamics of all involved species, including water for which the concentration is 7 to 10 orders of magnitude higher than the concentrations of other species (SO_3 and PA). Due to this high concentration difference, the kinetic modeling of the studied system would be impossible, as the collision frequency of water with other species would be 7-10 orders of magnitude higher than that of SO_3 of PA, resulting in extremely stiff set of equations that cannot be solved practically (Paasonen et al., 2012).

Instead, the SA•PA concentration was determined in the cluster dynamics simulations by solving the birth-death equations at given monomer concentrations. Fig. 4 indicates that SA•PA concentration would rarely exceed 10^4 cm^{-3} at most relevant monomer concentrations. Our dynamics simulations further indicated that though PA forms clusters with SA in the system, it would rapidly evaporate back unless the cluster has reached a certain size and at low temperatures, exclusively. This was discussed in Section 3.3.2.

Technical corrections:

line 21: "The enhancing effect of PA of examined by evaluating the ratio of the ternary..." There is some typo here.

This has been corrected to “The enhancing effect of PA examined by evaluating the ratio of the ternary…”

line 55, 222, 245: giving -> given

Corrections have been made at the indicated places

line 58: acid in the troposphere -> acids in the troposphere

This has been corrected

line 85: You mention only zero-point energies, though later you use also Gibbs free energies. Did you get them also from this calculation?

Both thermal corrections to the Gibbs free energy and the zero-point energies were calculated in the current study, using the same method. Throughout, we use both zero-point corrected electronic energies and Gibbs free energies to describe the energetics and thermodynamics of the studied systems.

In the revised manuscript, the sentence at Line 85 was modified to highlight the thermal contribution to the Gibbs free energy as follows:

Identified M06-2X/6-31+G(d,p) structures within 3 kcal mol^{-1} of the lowest energy structure were re-optimized, followed by vibrational frequencies analysis at the M06-2X/6-311++G(3df,3pd) level of theory, thereby yielding zero-point energies as well as thermal correction to Gibbs free energies.

line 88: "internal reaction coordinate" should be "intrinsic reaction coordinate" for IRC.
This has been corrected

line 134: Is there a typo in the birth-death equation, the concentration term is missing from end (the cluster evaporation sink term).
The equation has been revised as follows:

$$\frac{dC_{\mathrm{i}}}{dt} = \frac{1}{2}\sum_{\mathrm{j<i}} \beta_{\mathrm{j,(i-j)}} C_{\mathrm{j}} C_{\mathrm{i-j}} + \sum_{\mathrm{j}} \gamma_{\mathrm{(i+j)\rightarrow i,j}} C_{\mathrm{i+j}} - \sum_{\mathrm{j}} \beta_{\mathrm{i,j}} C_{\mathrm{i}} C_{\mathrm{j}} - \frac{1}{2}\sum_{\mathrm{j<i}} \gamma_{\mathrm{i\rightarrow j,(i-j)}} + Q_{\mathrm{i}} - S_{\mathrm{i}} \quad (2)$$

where C_{i} is the concentration of cluster i, $\beta_{\mathrm{i,j}}$ is the collision coefficient of clusters i and j, $\gamma_{k\rightarrow i,j}$ is the rate coefficient of cluster k evaporating into smaller clusters i and j. Q_{i} and S_{i} are possible outside source term and sink term, respectively, for cluster i.

line 156: "second molecule" -> "second H2O molecule"
This has been corrected.

References

Elm, J., and Mikkelsen, K. V.: Computational approaches for efficiently modelling of small atmospheric clusters, Chemical Physics Letters, 615, 26-29, https://doi.org/10.1016/j.cplett.2014.09.060, 2014.
Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225-235, 10.5194/acp-12-225-2012, 2012.
Paasonen, P., Olenius, T., Kupiainen, O., Kurtén, T., Petäjä, T., Birmili, W., Hamed, A., Hu, M., Huey, L. G., Plass-Duelmer, C., Smith, J. N., Wiedensohler, A., Loukonen, V., McGrath, M. J., Ortega, I. K., Laaksonen, A., Vehkamäki, H., Kerminen, V. M., and Kulmala, M.: On the formation of sulphuric acid – amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation, Atmos. Chem. Phys., 12, 9113-9133, 10.5194/acp-12-9113-2012, 2012.