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Dear Editor and Referee 1,

We sincerely thank Referee 1 for their constructive feedback on our revised manuscript. We greatly appreciate the referee taking the time to include basic Master Equation simulations. It is helpful to demonstrate that the initial dimerization step of neutral cluster formation is not necessarily at the high-pressure limit, and that ideally, a pressure-dependent collision rate coefficient should be used.

Regarding the simulation, we would like to respectfully clarify a nuance regarding the input energies. As far as we are aware, master equation simulations as provided by the referee require the electronic binding energy as input. The well depth of the potential of mean force does not directly correspond to the electronic binding energy (nor the binding free energy). Calculating the electronic binding energy through standard quantum chemistry calculations at the GFN1-xTB for H_2SO_4–H_2SO_4 and H_2SO_4–$(CH_3)_2NH$, we find values of -74.7 and -106.7 kJ mol^{-1}, respectively. We can also find the values at the higher DLPNO level of theory from the Atmospheric Cluster Database (https://github.com/elmjonas/ACDB/tree/master/ACDB_old_v1.0), which gives -94.2 and -101.4 kJ mol^{-1} for the same systems. The electronic binding energies are thus significantly stronger than the potential of mean force well depths presented in our figures, and also stronger than the -66 and -71 kJ mol^{-1} values utilized in the referee's simulation.

Additionally, as the referee correctly anticipates, the subsequent steps in new particle formation, such as the addition of $(CH_3)_2NH$ to $(H_2SO_4)_2$ or H_2SO_4 to $(H_2SO_4)_1((CH_3)_2NH)_1$, exhibit significantly stronger DLPNO electronic binding energies of -145.9 and -138.7 kJ mol^{-1}, respectively. We thus do not expect the later stages of new particle formation to have pressure-dependent collision rate coefficients.

Still, we fully acknowledge the referee's point: the initial dimerization step (especially H_2SO_4 + H_2SO_4) could indeed have a pressure-dependent collision rate coefficient. As stated in our initial response, cluster distribution dynamics modeling based on birth–death equations implicitly assumes that collision and evaporation are separate processes, and thus that thermalization is immediate after collision. While properly investigating this assumption through detailed master equation simulations is outside the scope of the current study, we agree that it should be explicitly noted.

To that end, we have provided revisions to the manuscript text below to clearly acknowledge that the assumption of pressure-independent collision rate coefficients is a potential source of error for the dimerization of small molecules like sulfuric acid.

We hope that these additional incorporated revisions are acceptable, rendering our revised version ready for publication in *Atmospheric Chemistry and Physics*.

We look forward to hearing from you at your earliest convenience and thank you for considering our manuscript for publication.

Best regards,

Ivo Neefjes

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Point-by-point response

However, I'm still concerned about the reaction H_2SO_4 + H_2SO_4 being assumed to be at its high-pressure limit at 1 atmosphere and 300 K.

...

Now for H_2SO_4 system, 66 kJ mol^{-1} binding energy for the dimer is NOT strongly bound; in the atmosphere the equilibrium will favour the monomer over the dimer. For this reason, I have done a basic Master Equation calculation on the system, a vibration only model using frequencies from DFT calculations, and used a high-pressure limit of 7.7e-10, based on your results.

...

XH_2SO_2 is actually H_2SO_4 but is a way to make the system pseudo-first-order, which is required for the calculation. This calculation has an association rate coefficient at 1 atm ca. a factor of three below the capture rate, the high-pressure limit. Only at 100 atm is the system close to its high-pressure limit. I would also expect H_2SO_4 + $(CH_3)_2NH$ to be pressure dependent as its binding energy is similar. The last reaction: H_2SO_4 + HSO_4^- has a binding energy about twice the other 2 reactions, so probably at its high-pressure limit. Therefore, for these first steps of NPT it should be acknowledged that assuming it is purely the capture rate coefficient might not be correct. When you start adding more precursor, H_2SO_4, then it is reasonable to assume only the capture rate coefficient is required. I presume if you considered larger system, e.g. $(H_2SO_4)_2$ + H_2SO_4 this would make it a much more costly calculation?

I note you do state this assumption:

...

I think my above calculation challenges this assumption, but probably only for the first, dimerization step. Perhaps my model to too crude, i.e. vibration only! The authors have done a good job replying to all the other points I made. Overall, if the authors could recognize that the first steps of NPT may not be wholly controlled by the capture rate coefficient then I'm happy to recommend this paper for publication. I know that this assumption is outside the scope of the present study, but it should be acknowledged as a possibility.

We thank the referee for this very detailed response.

Responding to the referee's question about the computational cost of running these simulations for larger systems: Umbrella sampling using machine learning interatomic potentials on larger cluster systems, such as a trimer, is quite straightforward and scales approximately linearly with the number of atoms. In other words, this would be highly feasible. However, it would require training a machine learning model on additional structures of the trimer, which would require some time to create a representative dataset.

Responding to the pressure-dependence of the collision rate coefficients: As stated in the cover

letter, we find a somewhat stronger value for the GFN1-xTB electronic binding energy for the H_2SO_4–H_2SO_4 system than used in the referee's master equation simulations (-75 compared to -66 kJ mol^{-1}), and a significantly stronger value for the H_2SO_4–$(CH_3)_2NH$ system (-107 compared to -71 kJ mol^{-1}).

Still, we expect that, especially for the H_2SO_4–H_2SO_4 system, there will be some pressure-dependence for the collision rate coefficient. In practical applications of cluster distribution dynamic models, such as the atmospheric cluster dynamics code, pressure dependence of the initial dimerization is not accounted for, as the default is to use kinetic gas theory. It would be valuable to interrogate the pressure dependence of the dimerization and how this affects the resulting particle formation rates. However, this would be outside the scope of this manuscript. We propose to make the following revisions to the text to acknowledge the effect of assuming pressure-independence on our results.

We note that while pressure-independent canonical collision rate coefficients, as obtained here, are commonly employed in cluster distribution dynamics models, this relies on the assumption that the system is strongly bound and has enough degrees of freedom to effectively distribute excess collisional energy (Elm et al., 2020). This assumption is likely valid for larger clusters, given that the number of degrees of freedom strictly increases with cluster size, and binding energies generally do as well. However, dimers with fewer degrees of freedom that are less strongly bound, such as the H_2SO_4–H_2SO_4 system, might not effectively thermalize immediately after collision. Consequently, for these collisions, the true collision rate coefficient could be smaller than the coefficient calculated here, due to pressure dependence.

L391 P18

References

Elm, J., Kubečka, J., Besel, V., Jääskeläinen, M. J., Halonen, R., Kurtén, T., and Vehkamäki, H.: Modeling the formation and growth of atmospheric molecular clusters: A review, J. Aerosol Sci., 149, 105 621, https://doi.org/10.1016/j.jaerosci.2020.105621, 2020.