Department of Chemistry

1102 Natural Sciences 2
University of California, Irvine
Irvine, CA 92697-2025

June 29, 2021

Dear Editor:

We highly appreciate the constructive comments from the reviewers, and we have addressed the comments in the revised paper. We hope that the following responses are satisfactory and that the paper can be accepted for publication in Atmospheric Chemistry and Physics without further delay. The reviewers' comments have been reproduced in blue text below, followed by our point-by-point replies.

Reviewer comments:

Reviewer: 2

Chee et al. present a detailed review on how various atmospheric bases react with sulfuric acid/methane sulfonic acid/nitric acid to nucleate particles. They use the previous published computational chemistry data on cluster formation energies for these acid-base systems to draw several conclusions on what type of molecule is needed to nucleate with atmospheric acids. They found gas-phase acidity to be the best indicator of how stable the heterodimer was and thus nucleation rates. It is quite satisfying to read a paper that shows that vapor pressure is not a good predictor of (acid-base) nucleation. This paper fits ACP well and is a great article on how to think about acid-base nucleation in the atmosphere. There a few points the authors should address before this manuscript should be accepted for publication.

Author reply:

We are grateful of these relevant comments and suggestions.

Specific comments:

Why did the authors decide on J1.5 nm? This size makes it difficult to compare with published observations of J1.7 nm or J1.0 nm. Along this same line, the authors compare their calculated J1.5 nm to CLOUD's J1.7 nm. The authors should comment on how the smaller diameter size will impact that comparison.

Author reply:

The value J1.5nm corresponds a formation rate of clusters larger than 4 acid and 4 base molecules, for which the diameter is around 1.5 nm. In ACDC simulations we define a simulation box size (4 acid and 4 base) and the growing out criteria (stable clusters larger than 4 acid 4 base clusters, specific criteria for each system is given in SI). Thus, in contrast to measurements, simulations do not have an exact diameter which are detected, but a combination of molecules in cluster, and we approximated the size of clusters larger than 4 acid and 4 base molecules to be 1.5 nm, which might be underestimated for large bases such as putrescine and overestimated for small bases such as ammonia. We have changed J1.5 to J4x4 to reduce overanalysis of the data.

The CLOUD data does not span enough orders of magnitude to merit the statement that their model for J1.5 nm to be accurate to measurements within 2 orders of magnitude. It would be helpful if the authors could either compare to more observations or re-evaluated their conclusion from comparing to CLOUD data. The authors mention that they can only compare to data where acid concentrations are approximately equal to base concentrations. Dr. Hanson at Augsburg College has published results where acid and base concentrations are approximately equal and has explored numerous bases.

Author reply:

We agree that more comparison with measurements would be useful. In future, we aim to further develop our model and include effect of ions and hydration which allows wider comparison with experimental results.

This may be outside the scope of the study but several papers have been published recently examining organic acid+base nucleation: Chen et al., 2017; Kumar et al., 2019 and other papers from Hansen and Francisco. If possible, it would be helpful to put their energy calculations into context with the results shown here.

Author reply:

We agree that organic acid+base nucleation is worth of studying in the future.

The authors present their J1.5 model as a function of [heterodimer] as simple and relatively accurate. 10 orders of magnitude is quite large. Though Pierce and Adams (2009) show 6 orders of magnitude may not be a big deal in predicting particle concentrations, what about 10 orders of magnitude? Also the presented model is based on their calculated J1.5 from their computational chemistry results. The comparison with CLOUD data does not provide a good indication how accurate their J1.5nm is to observed J1.5 (which would include water). It would be helpful if the authors could provide a short discussion on uncertainties in their J1.5 calculation so the reader knows how well equation 4 does in predicting observed J1.5.

Author reply:

We agree that 10 orders of magnitude is quite large and have removed the recommendation for the equation to be used in global models. We added a brief discussion on the effect of water: "It is important to keep in mind that this model was calculated in the absence of relative humidity, which may enhance \ce{J_{4x4}} rates for those acid--base pairs with many free HBD~\citep{directlink}."

From the abstract, I was expecting the normalized heterodimer concentration to estimate nucleation rates. However, it seems this is not true as it really only works for ammonia and methylamine. Basically all the other bases presented here fall off the linear curve presented in figure 12 and 13. In addition, the authors provide quite a few caveats to using this parameter to estimate J, like acid and base concentrations need to be approximately equal. In the atmosphere, ammonia is almost always higher in concentration than sulfuric acid. (The other bases are so poorly measured around the world that it is hard to say how their concentration varies.) In which case, I am not quite sure the purpose of this normalized concentration parameter? If the authors are very committed to keeping this parameter, it would be helpful then to define what a weak salt is in the abstract. Also it would be very helpful to include an equation showing how to calculate J from Φ.

Author reply:

We agree that the applicability of the parameter is limited with its current caveats as mentioned. We believe this to be a good starting point for future studies that can explore more atmospherically relevant conditions to provide better estimations of J from heterodimer stability (or some permutation thereof). A weak salt has been defined in the abstract as a salt with a $\Delta GA > 95$ kcal/mol, which encapsulates both ammonium sulfate (109 kcal/mol) and methylaminium sulfate (97 kcal/mol).

From the SI, the CLOUD that is being used also includes ion nucleation experiments. How are ion nucleation reactions taken into account with the heterodimer energies used in this study? Wouldn't ion cluster formation energies be drastically different than their electrically neutral counterpart?

Author reply:

That is a good point. We purposely did not take into account ion nucleation reactions in order to see if the nucleation experiment was still able to be described by the model we have proposed, and only one experiment has a large ionization rate. We aim to explore ion cluster formation energies compared to neutral clusters, as well as their effect on J rates in the future.

Technical Comments:

Page 2 line 20: Heterodimer stability reminds me of papers from (Kürten et al., 2014; Jen et al., 2014). Worth referencing them as they measured sulfuric acid heterodimer concentrations for the abundant atmospheric bases and concluded that how the dimer forms (and if they evaporate) is an important controlling factor for nucleation.'

Author reply:

Thanks for the added citations.

Page 4 line 10: how do the authors know 4 acids and 4 bases is 1.5 nm? Is this geometric diameter?

Author reply:

We have approximated the stable clusters larger than 4 acid and 4 base molecules to be 1.5 nm. The geometric diameters of 4 acid 4 base clusters are given in SI.

Page 4 line 30: and collected from

Author reply:

Thanks for spotting this.

Page 17 line 20: The normalized heterodimer concentration has units of cm^-1.5. Is this correct? I thought it would have units of cm^0.5.

Author reply:

The normalized heterodimer concentration is calculated from

$[heterodimer]/([acid][base]/Cref)^{1/2}$,

or,

$cm^{-3} / (cm^{-3} * cm^{-3} / cm^{-3})^{1/2}$,

which can be simplified to:

$cm^{-3} / cm^{-1.5} = cm^{-1.5}$

Figure 12: what are the dashed lines? Concentrations of what? Also it's really difficult to tell the difference between the different shades of gray.

Author reply:

The dashed lines are the monomer concentration of the acid and base in molec cm^{-3}. The lines have been changed to different dashed line types to help differentiate them.

References used in this review:

Chen, J., Jiang, S., Liu, Y.-R., Huang, T., Wang, C.-Y., Miao, S.-K., Wang, Z.-Q., Zhang, Y., and Huang, W.: Interaction of oxalic acid with dimethylamine and its atmospheric implications, RSC Adv., 7, 6374–6388, https://doi.org/10.1039/C6RA27945G, 2017.

Jen, C. N., McMurry, P. H., and Hanson, D. R.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, J. Geophys. Res. Atmospheres, 119, 2014JD021592, https://doi.org/10.1002/2014JD021592, 2014.

Kumar, M., Burrell, E., Hansen, J. C., and Francisco, J. S.: Molecular insights into organic particulate formation, Commun. Chem., 2, 1–10, https://doi.org/10.1038/s42004-019-0183-7, 2019.

Kürten, A., Jokinen, T., Simon, M., Sipilä, M., Sarnela, N., Junninen, H., Adamov, A., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., Heinritzi, M., Hutterli, M., Kangasluoma, J., Kirkby, J., Laaksonen, A., Lehtipalo, K., Leiminger, M., Makhmutov, V., Mathot, S., Onnela, A., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L., Schobesberger, S., Seinfeld, J. H., Steiner, G., Tomé, A., Tröstl, J., Winkler, P. M., Williamson, C., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K. S., Kulmala, M., Worsnop, D. R., and Curtius, J.: Neutral molecular cluster formation of sulfuric acid–dimethylamine observed in real time under atmospheric conditions, Proc. Natl. Acad. Sci., https://doi.org/10.1073/pnas.1404853111, 2014.