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Review for Chee et al.

Anonymous Referee #2

Referee comment on "A predictive model for salt nanoparticle formation using heterodimer stability calculations" by Sabrina Chee et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-84-RC2, 2021

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.

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.

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.

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.

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.

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.

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?

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.

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

Page 4 line 30: and collected from

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.

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.

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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.

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