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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Rate enhancement in collisions of sulfuric acid molecules due to long-range intermolecular forces" *by* Roope Halonen et al.

Anonymous Referee #1

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This manuscript discusses calculation of the collision rate between two sulfuric acid molecules in the gas phase using molecular dynamics calculations. The authors find that the binding rate/collision rate is $\sim$ a factor of 2.2 larger than would be expected based on hard sphere calculations. More detailed collision rate calculations are very important for molecules involved in new particle formation, as the resulting collision rate coefficients can be input into models of new particle formation and growth. This improves the accuracy and physical grounding of NPF models.

I think this study is quite promising, very well-written, and the manuscript is easy to follow. However, I do think that calculation of the enhancement factor at a single tem-

perature is of limited use; atmospheric systems are not all at a single temperature, and it is equally important to determine if the collision rate coefficient increases or decreases with temperature (i.e. its derivative). Fortunately, this should be possible to address in revision, and there are similar recent works (in very different systems) the authors could follow to address this issue, as noted below.

1. Section 2.3. and Figure 5. The methods the authors use for binding rate coefficient calculations are nearly identical to those recently used by Yang, Goudeli, and Hogan (2018). Condensation and dissociation rates for gas phase metal clusters from molecular dynamics trajectory calculations. The Journal of Chemical Physics. 164304. It would be good to acknowledge that this approach has been utilized previously. In addition, in presenting results, Yang et al (2018) show collision probability contour plots as a function of (b,v). I find these more intuitive to follow than Figure 5, thus I would recommend the authors look into providing these results as a contour plot.

2. Section 2.5. The collision between two un-ionized molecules in the gas phase at atmospheric pressure conditions is absolutely a free molecular process, and there is really no reason to compare the enhancement factor to the collision rate enhancement factor that applies in the continuum (diffusive or Brownian) limit. I would recommend removing it or altering the discussion to note that this calculation is simply included for reference, as it is not grounded in the correct transport physics for gas phase, molecular scale collisions. How the enhancement factor changes from the free molecular (ballistic) to transition to continuum (diffusive) regimes is discussed in Ouyang, Gopalakrishnan, and Hogan. (2012) Nanoparticle collisions in the gas phase in the presence of singular contact potentials. The Journal of Chemical Physics. 064316.

3. Results and Discussion. I think a key issue to address in the manuscript is that presently the enhancement factor is only calculated at a single temperature. The evolution of it with temperature is of equal interest. Again, following Yang et al (2018) (Figures 5 and 6 of their work, in particular), I think this can be addressed to lead to an improved manuscript. First, using equation (10) of the current manuscript, the authors

can vary the “translational” Temperature by shifting the Maxwell-Boltzmann distribution to see how the enhancement factor changes. Presumably, the enhancement factor decreases with increasing translational temperature, but it is not clear whether the actual collision rate coefficient increases or decreases with increasing temperature (in the hard sphere model it does, but many gas phase reactions have decreasing rates with increasing temperature). Of course, this approach neglects the changes in internal energies of the molecules, and adjusting internal energies the more time consuming effort of rerunning simulations with different initial equilibration temperatures. Still, I would encourage the authors to do these calculations using at least one more temperature, to see how different they are from the results of simply shifting the equation (10) Maxwell-Boltzmann distribution. An enhancement factor calculated at a single temperature is of limited use if the temperature sensitivity is not explored and discussed.

4. Conclusions: After addressing comment 3 it is important to determine if the Langevin model is accurate at all temperatures, or just within 20% of calculations near 300 K. In addition, I think it would be good to discuss the implications of calculations for new particle formation and growth models more explicitly.

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