



Dear editor and referee 2,

We sincerely thank referee 2 for their valuable feedback and corrections. Their comments helped us to recognize the areas where our manuscript could be improved and have revised the manuscript accordingly. In the following, we provide point-by-point responses to general and specific comments. Referee comments are given in *bold italic*, while responses are given in roman (non-bold, non-italic). Excerpts from the revised manuscript to support our responses are written in yellow highlight. The line and page number to which a response refers to, is indicated by (L### P#).

We hope that the revisions in the manuscript and our accompanying responses prove sufficient, rendering our manuscript suitable 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,

Huan Yang

Referee 2 comments

General comments

This manuscript focuses on extending the “Central field approach” to collision rate calculations to monomer-cluster calculations. It is somewhat dense- it took several readthroughs to fully understand manuscript. However, in the end I found the manuscript well-written, thorough in its presentation (both of prior work and the present model), and I believe it to be a substantial contribution to the literature. I only have a few remarks for the authors to consider in revision:

We thank the referee for their kind words and favorable assessment. It is true that the manuscript is quite dense, dealing with both collision and sticking rate coefficients, as well as computational and analytical models and their applicability. We, however, felt it important to be thorough in our discussion to define precisely what the advantages and limitations of our methods are. We are, therefore, happy to hear that the referee recognizes the merit of the manuscript after multiple readthroughs.

Recent trajectory calculation models (by the authors and others) have shown that the sticking rate is very weakly sensitive to temperature- at higher temperatures the Maxwell Boltzmann distribution is shifted to higher speeds, but the influence of potential interactions is diminished. I suggest also including plots for fixed cluster size as a function of temperature, perhaps over a wider temperature range, to see what temperature dependencies result here.

We thank the referee for the suggestion. We have added two plots to the supplementary materials to illustrate the temperature dependence of collision and sticking rates. The two plots correspond to collisions of $\text{H}_2\text{SO}_4 + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ and $(\text{CH}_3)_2\text{NH} + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ ($n = 1, 2, 4, 8, 16, \text{ and } 32$), respectively. We opted to plot a temperature range of 200 – 400 K, as it covers the relevant range for atmospheric acid-base cluster formation.

Changes made in the supplementary materials:

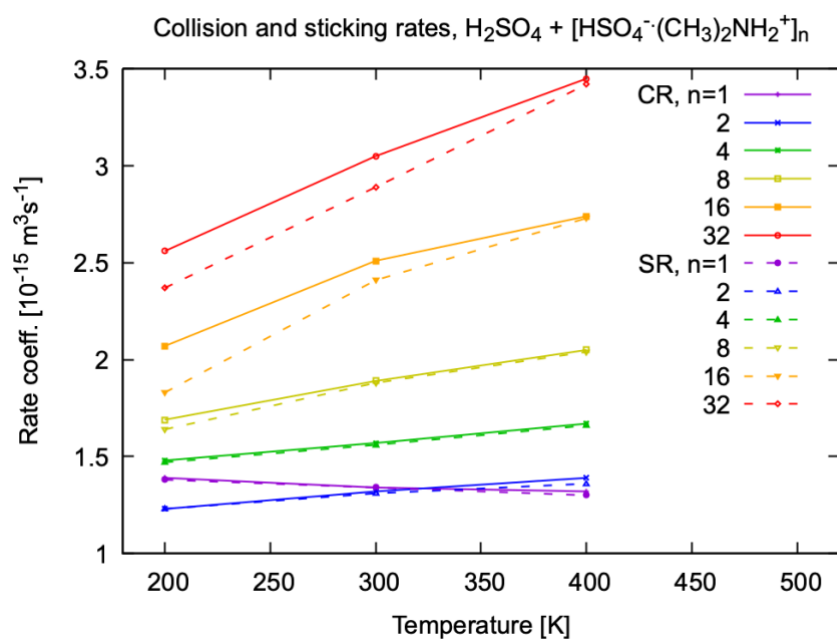


Figure S4. Temperature dependence of collision (CR) and sticking rates (SR) for $\text{H}_2\text{SO}_4 + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions ($n = 1, 2, 4, 8, 16,$ and 32).

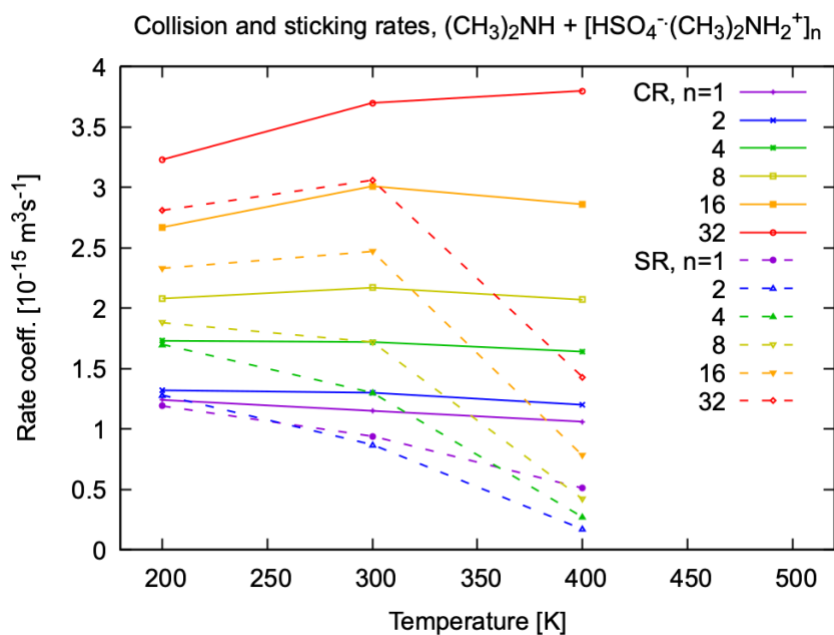


Figure S5. Temperature dependence of collision (CR) and sticking rates (SR) for $(\text{CH}_3)_2\text{NH} + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions ($n = 1, 2, 4, 8, 16,$ and 32).

When the temperature is increased, the Maxwell Boltzmann distribution is shifted to higher speeds, which has two consequences: First, the monomer flux per unit collision cross section is increased due to higher average relative velocities. Second, the area of the collision cross section is decreased due to the diminished influence of the attractive forces at higher relative velocities. The rate of collision and sticking is hence the net effect of

the above two competing factors. The second factor (i.e., decreased collision cross section due to increased temperature) is more significant for small clusters, as the attractive forces play a greater role (leading to higher collision enhancement factors). Therefore, the collision rate decreases with temperature for small clusters, while it increases with temperature for larger clusters.

For $\text{H}_2\text{SO}_4 + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions, the temperature dependence of the collision and sticking rates are similar, as the mass accommodation coefficient is always close to 1 in the studied temperature range. For $(\text{CH}_3)_2\text{NH} + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions, the mass accommodation coefficient decreases sharply with temperature, hence the sticking coefficient also drops sharply with temperature. (Supplementary Materials)

Can the approach be extended to non-pairwise potentials? This was not clear to me in reading the manuscript how to do this.

The approach in its current form is unfortunately not suitable for non-pairwise interactions. One restriction comes from our use of Hamaker's approach to derive the effective monomer-cluster potential based on the monomer-monomer potential. Here, the monomer-monomer potentials must be pairwise so their individual contributions can be summed to obtain the effective monomer-cluster potential. Furthermore, the interaction potential is required to be pairwise when we derive the radius of the collision cross section (the critical impact parameter) from analyzing binary collision trajectories.

The following changes have been made in the manuscript to clarify these points:

In Eq. 13, the effective monomer-cluster potential is essentially a sum over all individual contributions of the monomer-monomer potentials, which has two implications: First, the monomer-monomer potentials must be pairwise in order that their individual contributions are additive. Hence, this approach is not suitable for non-pairwise interactions. Second, the approach can be conveniently extended to multi-component clusters containing several types of monomers. By using Eq. 13 in a similar manner, the corresponding multi-component monomer-cluster potential is $4 \sum_i n_{c,i} \epsilon_i \sigma_i^6 / (r^2 - R_c^2)^3$, where $n_{c,i}$ is the number of monomers of type i in the cluster, and ϵ_i and σ_i are the interaction parameters between a monomer of type i in the cluster and the free monomer colliding with the cluster. (P7 L180)

Specific comments

Figure 3a. While I do not see anything wrong with showing the critical impact parameter for the Coulomb potential, for long range, Coulombically attractive collisions at atmospheric pressure, the free molecular assumption is not valid, and the method the authors are using will not work (this is the problem of ion-ion recombination: doi: 10.5194/acp-22-12443-2022, doi: 10.1063/1.5144772)

We thank the referee for addressing this point. We agree and have clarified in the revised manuscript that the free molecular assumption is not valid for Coulombic attractive collisions at atmospheric pressures, as in such cases the Coulomb force effects the collision dynamics at a distance comparable to the mean free path of the colliding ions.

Changes made in the manuscript:

The Coulomb potential case discussed here is only used to verify Eq. 6 but should not be implemented further in Eqs. 7 and 8 to calculate collision rate coefficients, as the Coulomb potential is non-negligible at distances comparable to the mean free path of the colliding ions at atmospheric pressures, and hence violates the assumption of free molecular regime. (P12 L327)