



EGUsphere, referee comment RC1
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Comment on egusphere-2022-93

Kai Leonhard (Referee)

Referee comment on "Modeling approaches for atmospheric ion–dipole collisions: all-atom trajectory simulations and central field methods" by Ivo Neefjes et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-93-RC1>, 2022

General comments:

The present work describes molecular Dynamics (MD) simulations of collisions of molecules / clusters and ions and the determination of collision rate constants from these simulations as well as from theory, using analytical equations with different approximations. The study increases our understanding of the validity range and limitations of these approximations.

Specific comments:

Eq 11: to my understanding, β_L is the rate constant for the collision of an ion with a polarizable molecule and β_{SC} that for an ion with a polarizable dipolar molecule. Hence, I would expect that K should approach one for μ_d (and hence x) approaching 0, but it seems to be 0.025. Please comment on this behaviour.

I find the description of the equilibration process difficult to follow (lines 222-233). There is a statement "The collision partners were first separately equilibrated for 50 ps using a Langevin thermostat with a damping factor of 0.1 ps. During the equilibration, both the center-of-mass motion of each collision partner and the angular momentum of the total system were removed ... Both collision partners were then given a velocity along the x-direction" If they are equilibrated separately (i.e. in separate simulations), both fragments should not have any rotational angular momentum. I have the impression rather "together, but separated with a large distance" is meant. If the latter is the case, have you checked the correct distribution of rotational angular momenta? Only a check of the energy distribution is mentioned. This this is a scalar and the angular momentum is a vector, therefore this may not be sufficient.

Line 261: "The center-of-mass distance criterion for a successful collision was determined for each system by taking the distance at which the value of the PMF was $5k_B T$ (≈ 0.13 eV at 300 K) higher than its minimum," There are two such distances, right and left from the minimum. Which one have you chosen?

Line 270, Discarding and adding new trajectories in case of dissociation: Is that the correct procedure? To me, it would seem most appropriate to define 3 outcomes of the encounters: no collision, association, and dissociation of an existing dimer. Then one would use the total number of trajectories in the denominator for each of the rate calculations. This would seem in line with what is done in Master Equation calculations for barrierless reactions. Please comment on the justification for your approach.

Line 279: What do you mean by "small oscillations in the interaction energy"?

Can you specify statistical uncertainties, for the MD results, e.g. in table 2?

Technical comment:

Figs 4 and 5: The Circles do not show up on my Adobe Acrobat on android, but they do on windows.