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Reply on RC1

Marcel Zauner-Wieczorek et al.

Author comment on "The ion-ion recombination coefficient α : comparison of temperature- and pressure-dependent parameterisations for the troposphere and stratosphere" by Marcel Zauner-Wieczorek et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-795-AC1>, 2022

***Comments by the referee are in bold print**, answers by the authors are in normal print

This manuscript reviews and then attempts to apply various theories predicting the ion-ion recombination rate in comparison to select experimental data. I think this is certainly a topic worthy of study. However, my recommendation is between major revision and rejection, because I believe this work is misguided in its approach and has more than several inaccurate statements in it. Much of this has to do with the manner in which the authors compare to "Ta20" (which is really a comparison to Fuchs 1963, not Ta20), and I do not believe the "intercomparison" of theories approach with subjective choices in inputs is a reasonable way to go about scientific study. Ultimately, I would like to think the authors can improve upon this work, and endorse major revision.

We would like to thank the referee for their feedback. We believe that thanks to the feedback provided by this referee and the other two referees, severe misconceptions and errors were eliminated, chapters and paragraphs were rearranged to ensure a better comprehensibility, and new ideas were implemented to improve the quality of the manuscript.

Many theories and parameterisations exist to determine the ion-ion recombination coefficient. They yield different results and it is not possible to conclude on one particular theory or parameterisation that covers the whole troposphere and stratosphere, as our study shows. Therefore, we are convinced that it is necessary to discuss and compare those different approaches to better understand their validity/applicability range and to identify further research that is needed.

Comments:

1. As noted in the prior paragraph, I believe the article is quite misguided in its approach. I think this is most apparent in the works presentation and discussion of Tamadate et al (2020). The article devotes quite a bit of time discussing the

work of Tamadate et al (2020), and in fact in looking at Tamadate et al 2020, it looks like a considerable fraction of the review section of this article is based upon the introduction of Tamadate et al. Specifically, a large fraction of the references reviewed in this work are similarly discussed in Tamadate et al, and the symbols and notation in the present manuscript also appear to be taken directly from Tamadate et al in the number of instances (this manuscript even refer readers to Tamadate et al 2020 for Hoppel and Frick's equations, instead of referring readers to Hoppel and Frick!). However, in reading Tamadate et al (2020), I come away thinking the authors completely miss the purpose of that article (or for some reason, do not want others to consider developing and expanding the Tamadate et al 2020 approach). Tamadate et al (2020), and the same researchers subsequent study (doi: 10.1039/D0CP03989F) focus explicitly on leveraging Molecular Dynamics simulations to determine the collision probability needed for implement in Filippov's generalized version of the limiting sphere theory. When the authors attempt to compare their prior measurements to Tamadate et al (2020), they state:

"We calculated Ta_{20} based on the derivations after Fuchs (1963) (Eq. (34) to (36)) and after Filippov (1993) (Eq. (37) to (39)), using Eq. (40) to (42) likewise. However, both derivations yielded the same results within our limits of uncertainty, therefore, for a better overview, for Ta_{20} we only show the results based on Fuchs."

Using the relationship of Fuchs 1963 with the limiting sphere of Wright is nothing more than Fuchs original theory, and not a test of what Tamadate et al did (equations 34-36 are Fuchs's exact theory, Tamadate et al just reiterates them). To be clear, Tamadate et al did not derive new equations, they implement Filippov's equations with Molecular Dynamics simulations, and without using results from MD simulations specific to the ions, gas composition, temperature, and pressure of interest, comparison is not being made appropriate to their work. The simulations in Tamadate et al (2020) agree with Fuchs when they neglect gas molecule-ion interactions (validating their approach), but this is not intended to be an accurate calculation of the recombination rate. Their simulations lead to much higher recombination rates than those of Fuchs and would lead to different values than the predictions here. I suggest correcting this comparison to note it is a comparison to Fuchs's theory, not to Tamadate et al's hybrid continuum-MD simulation approach. Disagreement between measurement and Fuchs's approach when applied to the ion-ion recombination has been known for decades.

In addition to the incorrect comparison, the statements about Tamadate et al are also largely inaccurate:

" Thus, they restricted the MD simulation to the limiting sphere while using the continuum (diffusion) equations outside the limiting sphere...." They actually use a cubic simulation domain of gas molecules that follows both ions. Simulations do not necessarily use Fuchs's definition of the limiting sphere, but they adjust the sphere radius used as the boundary between continuum and MD to ensure that this radius is large enough not to influence results.

"The MD simulations were run for different conditions: with and without the influence of electrostatic forces," Tamadate et al (2020) do not run simulations excluding electrostatic forces (which are extremely important in this problem). They do appear to include and exclude the initial electrostatic velocity for the incoming ions in the limiting sphere theory, but this is very different from including or excluding forces.

“In order to derive the recombination coefficient, they used two different approaches: the theory by Fuchs (1963) and the one by Filippov (1993).” Filippov’s 1993 approach is a more general version of Fuchs 1963 (and earlier) derivation. They are not different approaches. Tamadate et al (2020) very clearly uses Filippov’s equations and states this unambiguously. Tamadate et al do retrace the steps of Fuchs and Filippov, but I believe they appropriately credit where these steps come from.

“In Fig. 5 (e), the limiting sphere theories Na59, HF86, and Ta20 are shown. Whilst Na59 and HF86 agree fairly well with each other, Ta20 yields α values which are one order of magnitude too low ($2.7 \cdot 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at ground level) and is, therefore, not recommended.” To reiterate, the plots displayed are not an accurate test of Ta20, as the probability of Fuchs was used. This statement is hence very inconsistent with the earlier statement in this manuscript, “While the approach of Tamadate et al. (2020) is very promising, they correctly emphasise the need for hybrid continuum-MD simulations with N2 and O2, instead of He, in order to achieve results comparable to atmospheric conditions.” The authors here have not made the appropriate comparison.

We are very thankful to the referee to pointing out these misconceptions of ours. We revised the manuscript thoroughly with regards to the description of the work of Tamadate et al. (2020) and the works by Fuchs (1963) and Filippov (1993), following the referee’s advice and rectifications. For the comparison of theories, we used Fuchs’s (1963) theory and named it accordingly. The description of the work of Tamadate et al. (2020) was completely rewritten and put into a new chapter on numerical model simulations (Section 6). Moreover, we revised the chapter on the theories of Fuchs (1963) and Hoppel and Frick (1986), clearly pointing to the introductory part of Tamadate et al. (2020). We believe it is important to add these theories to the discussion and overview, while also giving proper credit to the work done by Tamadate et al. Where applicable, we used the formulae of the original theories; when the formulae developed by Tamadate et. al appeared to be more convenient to use, we introduced these to the reader, while citing Tamadate et al. Furthermore, we revised the symbols and notations used in the manuscript to ensure consistency.

I also believe the authors are mistaken in the computational power and expertise required to perform such MD calculations. Certainly MD approaches need to be developed further to make use easier. However, it is not unfeasible to use MD calculations to compute and tabulate the ion-ion recombination rate under a variety of conditions. I do not agree with the statement “ Simulation experiments at temperatures and pressures representative of the different layers of the lower atmosphere could provide a better insight into the variation of the ion-ion recombination coefficient α in the atmosphere. Eventually, parameterisations are needed for everyday us because MD simulations require advanced computing power and experience.” The MD simulation approach the authors are discussing is only ~ 1 year old, and notion that this cannot become a common approach to compare to data, or even to predict the recombination rate in the future seems short-sighted and overly dismissive.

We apologise for this misunderstanding. It was never our intention to discredit MD simulations or claim that their area of application cannot be expanded in the future. To avoid any misunderstandings, we did not add further reflections on the complexity of the usage of MD simulations in the newly written chapter about numerical simulations.

2. Second, the comparison to Hoppel & Frick (1986) is odd. Hoppel & Frick specifically developed a theory to describe the ionisation of particles, and use the ion-ion recombination coefficient as an input to bracket results (their concern was ensuring that the rate of small particle-ion recombination agreed with the ion-ion recombination rate and noticed that in Fuchs's theory this would not be the case, so they worked rather hard to develop an approach taking the essence of Fuchs's theory but which would converge to the ion-ion recombination rate). Stated differently, they use the ion-ion recombination rate as an input to their theory, not an output. To quote Hoppel & Frick: "The value of the recombination coefficient for atmospheric ions is here taken to be that given by Nolan (1943) as $1.4 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$. For any value of ionic mass, a corresponding value of the ion-ion trapping distance d can be determined." If the authors choose to compare to Hoppel and Frick, then I believe they should make clear for each comparison what the reference recombination rate being used is and what the temperature and pressure is for it- did they use the same as Hoppel and Frick of $4 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at atmospheric pressure and room temperature?

Indeed, Hoppel and Frick's (1986) theory is concerned with the ionisation of particles. But since it predicts the ion-aerosol attachment so well, it appeared interesting to us to apply this theory to ion-ion recombination, which can be considered as a special case of the ion-aerosol attachment (assuming the "aerosol particle" has the size of an ion and is singly charged).

We re-wrote the description of Hoppel and Frick's (1986) work to accurately account for the purpose of their theory (now in Sect. 5).

We stated the input value of $1.7 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ to retrieve the trapping distance d from Fig. 3 in Hoppel and Frick (1986) in the old manuscript (ll. 484ff.) as well as in the new manuscript (Sect. 7.1, first paragraph). Due to the new arrangement of the chapters, we hope that this information becomes more prominent now. Now, all the input values are listed in one paragraph before discussing the results of the comparisons.

3. Based on comments 1 and 2, I do not agree with the "intercomparison" approach- this treats various theories as fixed and isolated approaches from one another, as opposed to bodies of work building off one another. Rather than perform an intercomparison of different theories where inputs are selected in advance and the theory is determined to be applicable to the data or not, I believe a healthier approach would be to use the data presented to determine the most ambiguous parameters in theories. For example, in the case of limiting sphere theories, the most appropriate thing to do would be to determine $p(\delta)$ in equation (37), the probability needed to find agreement with experimental data. This would be much more useful than an intercomparison, and would enable the authors to discuss how this probability varies. Similarly, the authors can determine the value of " d " needed in equation (26) for agreement with data. I believe Tables of $p(\delta)$ and d for different temperatures, pressures, and relative humidities would be quite useful and referred to extensively by others. I strongly suggest the authors to adjust their approach to provide such tables, as opposed to an intercomparison approach which is skewed by subjective choices in inputs.

We agree that the choice of input values for the different theories does not come without trouble. Indeed, we want to draw attention to this circumstance and argue to take caution when choosing the input values. However, the theories and parameterisations have not been developed without reason. Some of them were explicitly developed to determine the ion-ion recombination coefficient for different altitude or temperature and pressure

regimes. In fact, there is a need to determine concrete values of α for different altitudes; it was our initial motivation to review all the theories on ion-ion recombination because we needed accurate values of α in different altitudes to be able to analyse airborne field data (see Zauner-Wieczorek et al., 2022). To review and compare the available parameterisations and theories to determine these values, thus, appears to be worthwhile and necessary to us.

We stuck to the specifications and input values given in the theories' original works (such as the trapping distance in Hoppel and Frick's article) because we believe that the theories should be evaluated holistically. We, therefore, do not share the referee's view that the input parameters are subjective choices. Of course, suggestions can and should be made how to improve certain parameters. Therefore, and also based on the suggestion to determine values for d and p_δ (now called ε_δ in the manuscript) mentioned above by the referee, we introduced a new chapter (Sect. 8) in which the corresponding values for d and ε_δ were determined for the field data of α reported by Gringel et al. (1978), Rosen and Hofmann (1981), and Morita (1983). The resulting values for d and p_δ are shown in the new Fig. 4 and are listed in Table A1, while we omitted the previous chapter on the sensitivity study of d for Natanson's (1959) and Hoppel and Frick's (1986) theories.

4. I would also encourage the authors to expand the data set they use in comparison. There is no reason to limit to atmospheric air when comparing theories.

We agree that it would be very interesting to compare the different theories with respect to different gases. However, the scope of our work is the applicability to the atmosphere and, thus, we limited ourselves to atmospheric air. Nevertheless, we want to encourage other researchers to expand the comparison to other systems and, thus, added this sentence to the conclusion:

p. 27, l. 273: "Moreover, this work only focussed on the recombination in air; additional gases can be investigated in future studies."

5. The authors do neglect the recent equations of Chahl & Gopalakrishnan (doi: 10.1080/02786826.2019.1614522) who focused on small nanoparticle-ion collisions, but their equations could be extended to ion-ion recombination easily.

The work of Chahl and Gopalakrishnan (2019) is indeed very exciting. In our opinion, its application to ion-ion recombination would justify an article on its own and, thus, we think that it cannot be dealt with appropriately within the limited space in this review article.

Editorial Comments:

1. The line colors in most plots are too similar to one another, and I have a tough time linking the lines in plots to the legend.

We introduced labels next to the lines within the plots and omitted a separate legend to increase the comprehensibility.

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