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Reply on RC2

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-AC2, 2022

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

The paper by Zauner-Wieczorek, Curtius, and Kueten discusses the history of ion-ion neutralization measurements and theory in the atmosphere. The authors have done a good job of digging up many old references, some of which are new to me and my group although we work in this field. However, I and other members of my group have some serious issues with the paper. I wonder if all this detail on the chemical physics of the process is completely lost on atmospheric chemists.

We would like to thank the referee for their feedback. Based on the feedback provided by this referee and the other two referees, we revised the manuscript, eliminated misconceptions and restructured the manuscript for a better readability.

The manuscript is very hard to read with lots of jargon, many references to various studies that are hard to keep in ones mind.

We have carefully re-organised the paper with the intention to improve the structuring and therefore also the flow and readability of the paper. The revised version was also edited by a native speaker and we have tried to reduce the use of jargon. If the reviewer still has suggestions about the use of jargon or passages that are hard to read then we would be thankful if the specific passages or phrases could be pointed out by the reviewer.

The manuscript is full of confusion between total recombination rate constants without separating what refers to two body and three body contributions are added. I would start with the simpler story of two body recombination and start adding three body processes in the introduction. I realize that some of the early work measures the total rate but going back and forth is difficult so that one compares things that shouldn't be compared.

We followed the referee's suggestion to highlight the differences between binary and ternary recombination more. Thus, we created a separate chapter for the binary theories (Sect. 3). We agree that commencing with the binary process and then introducing the ternary process would be a possible approach. Because the theories build up on each other, however, we found it more comprehensible for the readers if the theories are introduced more or less chronologically, but with a clear separation of the binary theories. We uniformly introduced the index "2" to refer to binary theories (a_2), including Table 2. We kept the index-less *a* for the total recombination coefficient, which most theories and parameterisations in the manuscript describe. Moreover, we expanded the altitude range of the comparison from 0–20 km to 0–50 km; this way, a comparison of the binary theories as well as the total recombination theories in the upper altitude range (where the two-body recombination predominates) is possible. Furthermore, we added some basic information on the binary/ternary processes in the introductory chapter (Sect. 1) to guide the readers from the beginning:

p. 2, l. 38ff.: "There are two important recombination mechanisms: binary recombination, in which two ions of opposite sign recombine upon collision, and ternary recombination, in which one of the ions first has to collide with a neutral gas molecule, i.e. the third body, to dissipate energy in order to recombine successfully with the second ion. The latter process is, therefore, also called three-body trapping. When both the binary and ternary processes are included in a theory or parameterisation, it is called total recombination."

The early history of neutralization is interesting and worth noting, but in my opinion not worth all the detail and equations given in the manuscript. While early researchers like Thomson knew that ion-molecule reactions apparently take place, actual rate constants weren't measured until the 1950s and 1960s, meaning that early researchers couldn't appreciate the complexity of the ion types that were actually involved in the neutralization. It's my opinion that the quantitative similarity of early measurements is mostly a coincidence. Even Loeb in his later books said that it was only after WWII that electronics were advanced sufficiently to make decent measurements. (This from memory; it would take some time to find exactly what Loeb said.)

It is difficult for us to judge if it is a coincidence when the early findings agree with today's findings. Loeb's statement can be found in his textbook that we already cited (Loeb, 1960). We believe it is important to explain the first steps in theory and experiments because the later development is based on those beginnings. However, we added a caveat to our manuscript to highlight this issue so that readers may evaluate the early results cautiously:

p. 4, l. 89ff.: "Moreover, Loeb (1960) pointed out that measurement techniques were not sophisticated enough and gases not pure enough before the 1950s to be able to determine accurately the ion-ion recombination."

p. 9, l. 229ff.: "Furthermore, one has to bear in mind that the capabilities of the instruments and the purity of the gases were less advanced before the 1950s (Loeb, 1960). Therefore, results obtained before that time need to be considered with caution."

The manuscript is mainly concerned with 3-body neutralization, but it seems to me that binary and ternary measurements or theory are not well distinguished, for example, they are mixed in Table 2. An example I know something about: both the Hickman (incorrectly evaluated) and Miller expressions are plotted vs

altitude in Fig. 4(a) even though both are solely for binary neutralization and completely inappropriate for a plot vs altitude.

As mentioned above, we made a clearer distinction between total, ternary, and binary recombination and added the index "2" (α_2) for the purely binary theories. By expanding the altitude plot (former Fig. 4, now Fig. 2) to the altitude range of 0 to 50 km, the discussion of the binary theories becomes relevant for the upper part of the stratosphere. We only show the binary theories above 40 km altitude. Furthermore, we omitted the binary theories from Fig. 3, where only ternary theories apply.

The 3 body work of Smith and Adams has been questioned by Rainer Johnsen.

We added this information and reference where we first present the parameterisation by Smith and Adams (1982):

p. 11, l. 286: "Furthermore, Smith and Adams (1982) presented a parameterisation valid for the altitude range of 10 to 60 km based on laboratory measurements of binary recombination with the flowing afterglow/Langmuir probe (FALP) technique. The resulting parameterisation is simple because it only depends on the altitude and contains two terms that represent the ternary and binary recombination, respectively, as Eq. (30) shows:

[Eq. (30)],

where *h* is the altitude in km. The two terms of Eq. (30) represent the ternary and binary recombination, respectively. Johnsen et al. (1994) later disputed their results because they found that ion-collecting probes, as used by Smith and Adams, are not suitable to obtain data on ion-ion recombination coefficients in flowing-afterglow studies."

Beginning with line 255, the results of Hickman are quoted incorrectly. The formula in Eq. (24) is Hickman's, however, Zauner-Wieczorek et al. says that Hickman's reduced mass is in amu, but that's not right; Hickman used reduced masses in atomic units (the mass of the electron). Use of the formula as stated by Zauner-Wieczorek et al. would lead to rate constants 200 times too large.

Further, some particular data are incorrectly quoted from Hickman's paper. It's important to note that those data were not Hickman's. He was using data from the SRI merged beams experiments. It is now known that the SRI molecular ions were highly vibrationally excited (if not electronically excited), as was later shown by the SRI people themselves with a new collinear ion-laser experiment, which is the reason no further measurements were made with their merged beams apparatus. The important point is that the data quoted are incorrect because Zauner-Wieczorek et al. assumed that the units were E-06 cc/s, but Hickman clearly states that the units are given in Fig. 4, where E-08 cc/s is stated. The same units are specified in Fig. 3 along with the units for m (atomic units).

Beginning with line 260, the results of Miller are quoted incorrectly. The quoted formula is the same as Hickman's except that the reduced mass is given in amu instead of Hickman's atomic units. So the formula should not be attributed to Miller. Miller used flowing afterglow data that existed at that time (1979) to improve on Hickman's parameterization instead of using the faulty SRI merged beams data. The formula developed by Miller is not quoted by Zauner-Wieczorek

et al., namely, a = 3.32E-07 $(T/300)^{-0.5}$ $m^{-0.52}$ $EA^{-0.24}$. The "T<1000K" is a limit imposed because the neutralization cross section is known to depend on 1/E at least for such temperatures.

The results of Hickman and Miller are consequently misstated in Table 2, and even worse in Fig. 3, where Hickman's rate constants lie two orders of magnitude above Miller's. Surely this discrepancy should have tipped off one of the authors to reexamine those two papers. Fig. 4 is likewise misleading.

The 1980 paper of Miller is only of historical interest and shouldn't be considered in this manuscript at all. The type of analysis attempted by Miller in 1980 has been superseded by a more recent paper utilizing far more data: T. M. Miller, N. S. Shuman, and A. A. Viggiano, "Behavior of rate coefficients for ion-ion mutual neutralization, 300-550 K" J. Chem. Phys. 136, 204306 (2012), in which these parameterizations were given (m in amu, EA in eV):

a = (2.8 ± 1.0)E-07 cc/s $(T/300)^{-0.9\pm0.1}$ $m^{-0.5\pm0.1}$ $EA^{-0.13\pm0.04}$ for polyatomic ions

a = (3.2 ± 1.4)E-08 cc/s $(T/300)^{-1.1\pm0.2}$ $m^{-0.01\pm0.09}$ $EA^{-0.04\pm0.23}$ for diatomic ions.

We are thankful to the referee to point out the misunderstanding and misinterpretation in the use of the units of Hickman's (1979) formula and the essential background information regarding Miller's (1980) data. The concept of the Hartree atomic unit (a.u.), i.e. the relative mass based on the mass of the electron, was indeed misinterpreted as atomic mass unit (a.m.u.). We now changed the units of Hickman's formula. We had not made use of the new formula presented in Miller (1980) because it was given for $T \geq 1000$ K. In the article of Miller et al. (2012), we found a footnote that this was a misprint and it should read $T \leq 1000$ K.

We follow the referee's suggestion and do not consider Miller (1980) any more, but include the work by Miller et al. (2012). We changed the text in the main body accordingly.

We also modified Fig. 4 (now Fig. 2), which now spans an altitude range of 0 to 50 km, to account for correct values for Hickman (1979) and to include the more recent parameterisation by Miller et al. (2012) for polyatomic ions above 40 km altitude because in the upper stratosphere, the binary recombination process is predominant and it is, thus, interesting to compare binary theories.

Besides the more recent work of the AFRL group using the VENDAMS technique to derive the above parameterizations, they also miss exciting new work from the Urbain Group and DESIREE group in Stockholm. Also the Prague group has done the most fundamental work on three body increases to the overall rate constants. No mention of product formation is mentioned. Not always is the process a simple electron transfer.

Apart from Miller et al. 2012, we also included references to Shuman et al. (2014a), Shuman et al. (2014b), and Wiens et al. (2015) from the AFRL group who extended the dataset to experiments with several other ions. We believe that the referee means Smith and Španěl when mentioning the Prague group. By citing Smith's earlier works (Smith and Church, 1977; Smith and Adams, 1982), we believe that we ascribe credit to his fundamental contribution to this field of research. We also reviewed the publications by the Urbain group (UC Louvain) and the DESIREE Group in Stockholm. While their work is extremely fascinating, its scope of application – as they state themselves – are astrophysical or stellar systems. The sub-thermal conditions they studied are beyond the scope of this paper that is concerned with the applicability of theories and parameterisation to the Earth's lower atmosphere. To guide the readers to more information on the product formation and the processes other than electron transfer, we added the following sentences to the manuscript:

p. 10, l. 267ff.: "While most research in the field has been carried out on the recombination process itself, some works have also been devoted to study the product formation. For instance, Shuman et al. (2010) investigated the different product channels of the recombination of $SF_{4–6}^-$ with Ar^+. Besides simple electron transfer reactions, the elimination of F atoms was also observed."

The electron affinity of NO3- is 4 eV not 1eV.

We changed the value accordingly to 3.94 eV (Weaver et al., 1991).

Why is H3O+(H2O)3 represented by mass 150? I know the answer is other positive ions exist but that should be clear.

In the revised version of the manuscript, we decided to use the mass of 90 Da for positive and negative ions and the related values according to López-Yglesias and Flagan (2013) to ensure uniformity in the calculations throughout the manuscript.

Given that the work we know well is misrepresented, we, of course, worry that more work has also been misrepresented.

This paper needs at least a major rewrite and I don't believe it belongs in this journal.

Based on the feedback by this referee and the other two referees, we included major changes to our manuscript to remove errors and misinterpretations and to enhance the readability of the manuscript. We are convinced that this review is well placed in ACP. While most of the works we cited were published in other journals, we believe it is important to bring this information to atmospheric chemists and physicists who study ions in the atmosphere and make use of the ion-ion recombination coefficient; especially because, apart from the value of $1.6 \,\square\, 10^{-6}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ at standard conditions, the extensive field of fundamental research on this topic is unknown to many atmospheric scientists. Therefore, we tailored the scope of our review manuscript to compare and evaluate the existing theories and parameterisations for conditions of the troposphere and stratosphere. In fact, it was our initial motivation to review 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)). We would like to make the existing knowledge available to the atmospheric science community.

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