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Comment on acp-2021-795

Anonymous Referee #2

Referee 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-RC2>, 2021

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.

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

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.)

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.

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

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):

$$a = (2.8 \pm 1.0)E-07 \text{ cc/s } (T/300)^{-0.9 \pm 0.1} m^{-0.5 \pm 0.1} EA^{-0.13 \pm 0.04} \text{ for polyatomic ions}$$

$$a = (3.2 \pm 1.4)E-08 \text{ cc/s } (T/300)^{-1.1 \pm 0.2} m^{-0.01 \pm 0.09} EA^{-0.04 \pm 0.23} \text{ for diatomic ions.}$$

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.

The electron affinity of NO₃⁻ is 4 eV not 1eV. Why is H₃O⁺(H₂O)₃ represented by mass 150? I know the answer is other positive ions exist but that should be clear.

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.