# Reply on RC3

Marcel Zauner-Wieczorek et al.

Author comment on "The ion–ion recombination coefficient $a$: 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-AC3, 2022

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

**The manuscript authored by Zauner-Wieczorek et al. presents a good review of the historical theory development on ion-ion recombination under relevant conditions of the troposphere and lower stratosphere. The authors then made a simple sensitivity study on the limiting sphere theories and compared the different parameterisations of the theories to measurement data from a few laboratory and field as well as model results. The content of the work, especially the review part, is valuable. The comparison studies are a bit flimsy, without discussions on why some parametrisations worked poorly and there was no insights given for corrections or improvements. The clarity of the manuscript needs to be improved and the manuscript needs somewhat a major revision.**

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 to improve the readability, the structure, the notations and use of symbols, and the discussion of the inter-comparison.

**Comments:**

**When talk about ion-ion recombination, could you please first of all provide the definition of ion? Do you also consider the recombination of charged aerosol particles as ion-ion recombination?**

We added the definition of ion-ion recombination as opposed to ion-aerosol attachment in the introduction (Sect. 1):

p. 3, l. 42ff.: "While ion-ion recombination concerns the recombination of atomic or molecular ions or small molecular ion clusters, ion-aerosol attachment regards the interaction between an ion and a charged or neutral aerosol particle. Typically, aerosol particles are defined to have a size of 1 nm or bigger. As the ion-aerosol attachment

coefficient depends on the size of the aerosol particle, the ion-ion recombination coefficient can be viewed as a special case of the former if the "aerosol particle" is considered to have ionic size and is singly charged."

**You compared the different parameterisations on ion-ion recombination to a few laboratory, field and model results and demonstrated that some models clearly have poor performance but did not discuss the potential causes. Could you please elaborate on this and provide insights into how they may be corrected or further improved?**

We rewrote the discussion part of the inter-comparison completely (now Sect. 7) and added a discussion of the possible causes for deviations or poor performances.

**Based on the comparisons with laboratory, field and model data, you suggested Brasseur and Chatel 1983 over other parameterisations. Given the fact that it has the semi-empirical nature, it is expected to agree better with measurement data. The measurement data (whether it is Rosen&Hofmann, Gringel et al., Morita or Franchin et al.) are based on probing air ion concentrations. Air conductivity is intrinsically dependent on ion concentration. Then the uncertainty from measurement loss inside the instrumentation or the system cannot be avoided. This was not discussed in the manuscript when making suggestions on the choice of theory.**

We added more information on how the data by Gringel et al. (1978), Rosen and Hofmann (1981), and Morita (1983) were retrieved (see Sect. 4). Furthermore, we pointed out that these data sets can be subject to systematic error in the discussion part of the inter-comparison chapter (Sect. 7.1):

p. 19, l. 541ff.: "In Fig. 2 (a) to (d), the field measurements Gr78, RH81, and Mo83 are shown for a better comparability. Note that the data are inaccurate below 10 km. For RH81, there are two data sets for altitudes above 32 km: one is calculated based on Eq. (2), the other one is based on Eq. (37). One should bear in mind that these data sets, which were determined with similar methods, may also suffer from systematic errors such as losses inside the instrument that were not accounted for, however, these are the most reliable data from field measurements available to this day."

**You did not recommend Tamadate 2020 due to its resulting in large deviation from measurement data. It seems however that the authors did not perform a MD simulation as described in Tamadate et al. 2020, instead the authors used the formula listed in Table 2 and referred that as Tamadate 2020. However, this functional form is merely Filippov's approach, which is similar to Fuchs model, as described in Tamadate 2020.**

We rewrote the former chapter on limiting sphere theories (former Sect. 4), by separating and reorganising it into one chapter on ion-aerosol theories (now Sect. 5) and one on numerical simulations (now Sect. 6). The misconception of the work of Tamadate et al. (2020) was corrected and their work, i.e. a hybrid continuum-MD approach, is now described in Sect. 6. Fuchs's (1963) theory is explained in Sect. 5 and used for the comparison in Sect. 7.1. We renamed and relabelled the main text and the figure (now Fig. 2) accordingly.

**I also find the manuscript was not very carefully prepared. The notations are especially confusing. For example, the mathematical symbol of prime should be used instead of ' (e.g. p6 L137). Also *d* have several definitions through the manuscript, which is confusing. *v*₊ and *v*₋ were not defined where they appear first and definitions of *U*₊ and *U*₋ in eq 8 were missing. It is also unclear what is *x* on p5 L128. A few different notations were used for the same property, e.g. *e* and *e*_T for collision probability, *d* and *d*₃ for three-body trapping distance, etc. It is also sometimes difficult to distinguish between similar symbols like *a* and *a* and *M* for molar mass and [M] for number density of air molecules. Please revise the manuscript carefully and drop off the repeated notions and use symbols that can be better distinguished.**

We are thankful for the suggestions to enhance clarity in notation. We introduced the prime symbol instead of the apostrophe where applicable. We revised all radii and introduced a uniform notation as follows: $d$ is the three-body trapping distance; $\delta$ is the limiting sphere distance; we changed the collision radius from $a$ to $r_{coll}$. Indices further define $d$ and $\delta$ depending on the different theories. We introduced the symbol $\varepsilon$ to all collision probabilities, also using indices to indicate the specific definition of the different theories. For a better distinction, we changed the symbol of the ion mass from M to $m_{ion}$. We introduced $v_+$ and $v_-$ where they first appeared (now Eq. 4) and changed $U_+$ and $U_-$ in former Eq. 8 (now Eq. 9) to $v_+$ and $v_-$, which was a remnant of an older version of the draft. We added an explanatory sentence to define $x$: "In subsequent works, the ratio of the collision sphere radius and the mean free path of the ion, $2d_T \square \lambda_{ion}^{-1}$, is often denoted as $x$." We omitted repeated notions and only introduce the physical quantities in the main text where they first appear. The nomenclature in the end of the manuscript that contains all symbols and their explanations was revised accordingly.

**p7 L160-161. It is confusing that you talk about 'collision probability becomes almost 0' and then 'collision is governed by the collision cross section'. Could you please elaborate what you mean here? How do you distinguish 'collision probability' and 'collision cross section'? To my understanding, the CCS is just a different way to quantify the probability of successful collisions.**

Indeed, the ion-molecule collisions (leading to the dissipation of energy to enable the recombination) and the ion-ion collisions (i.e. the recombination itself) were not clearly distinguished in the former version of the manuscript. We, therefore, adapted the whole paragraph to make this distinction clearer. It now reads as follows:

p. 7, l. 169ff.: "Above atmospheric pressure, Langevin theory is applied. Loeb subclassifies it, firstly, to the range of 20 to 100 atm where there is no diffusional approach of the ions towards each other because they are already within the Coulomb attractive radius $d_T$ and, secondly, to the range of 2 to 20 atm (called Langevin-Harper theory), where the initial distance of the ions $r_0$ is greater than $d_T$ and so they first have to diffuse towards each other. The subsequent collision inside $d_T$ is almost certain because of the high pressure. For the pressure range of 0.01 to 1013 hPa, i.e. for the lower and middle atmosphere, Thomson theory is applicable. Here, the initial distance of the ions is greater than $d_T$ and the mean free path $\lambda_{ion}$, therefore a random diffusive approach is necessary. Within $d_T$, the collision probability $\varepsilon_T$ is less than 1. Below 0.01 hPa, i.e. in the ionosphere, the collision probability becomes almost 0 and, thus, the collision is then governed by the collision cross section. For super-atmospheric pressures (i.e. in the Langevin regime), $a$ is dependent on $p^{-1}$ and proportional to $T$. In the regime where the Thomson theory should be applicable (i.e. from 0.01 to 1013 hPa), $a$ is dependent $T^{-1.5}$, The pressure dependence

of $a$ is different in various Thomsonian theories; while Thomson (1924) stated a proportional dependence (see Eq. (4)), it varies in the parameterisations of Gardner (1938), Israël (1957), and Loeb (1960) (see Eq. (10), (14), (15), respectively, with Eq. (11) to (13)): for approximately 500 to 1000 hPa, $a$ is dependent on $p^{0.5}$ and below 500 hPa, it approaches $p^1$. In the cross section regime (i.e. < 0.01 hPa), $a$ is independent of the pressure and dependent on $T^{-0.5}$."

After Tamadate et al. (2020), the collision probability is the ratio of recombined ions over all ions that entered the limiting sphere; whereas the collision cross section is defined by $\pi\,(r_+ + r_-)^2$ and is, thus, a measure for the probability for binary recombination.

### p7 L177. normal value? what is not normal?

For more clarification, we elaborated more on what the cited authors referred to as "normal" (as compared to "standard") conditions or values in the manuscript. The respective paragraphs now read as followed:

p. 4, l. 82f.: " Lenz (1932) reported $(1.7 \pm 0.1) \cdot 10^{-6}\mathrm{cm}^3\mathrm{s}^{-1}$ for the conditions of 291.15 K and 1013 hPa."

p. 8, l. 192ff.: "In the derivation of the formula he [Israël, 1957] used the value of $1.6 \cdot 10^{-6}\mathrm{cm}^3\mathrm{s}^{-1}$ for $a$ for "normal conditions", however, he neither included a reference for this nor specified the normal conditions. These are probably 273.15 K and 1013.25 hPa."

### P13 L367. what do you mean by 'ion current'?

In Hoppel and Frick's (1986) derivation of their Equation 4, given in our manuscript in former Eq. 32 (now omitted), they state: "Diffusion-mobility theories calculate the current of ions, $I_\mathrm{i}$, to a particle from the steady-state diffusion-mobility equation. […] The inner boundary conditions distinguish the various theories and match the diffusion-mobility flux outside some limiting sphere to the microscopic flux inside. The limiting sphere is concentric with the particle and has a radius $\delta'$ about one mean free path larger than the particle radius. […] Matching the two fluxes at $\delta'$ yields [Equation 4]." In the course of revising the manuscript and the description of Hoppel and Frick's (1986) theory, the manuscript does not mention the ion current anymore.

### p18 L472. what do you mean by 'trapping sphere'? Is it different from limiting sphere?

We added a more detailed explanation of the trapping sphere and the limiting sphere in the introduction of the new Sect. 5 (Application of ion-aerosol theories):

p. 14, l. 380ff.: "While in many ion-ion recombination theories, the concept of the three-body collision radius, or trapping radius, $d$, can be found, many ion-aerosol theories additionally use the concept of the limiting sphere, $\delta$. The limiting sphere and its radius are defined slightly differently depending on the theory. With Fuchs (1963), it is defined as a concentric sphere around the particle with the radius $\delta_\mathrm{F} = r_\mathrm{p} + \lambda\square$, where $r_\mathrm{p}$ is the particle radius and $\lambda\square$ is "the mean distance from the surface of the particle at which the ions collide for the last time with gas molecules before striking this surface" (Fuchs, 1963). Notably, $\lambda\square$ is not equal to the mean free path of one ion, $\lambda_\mathrm{ion}$, or the ion-ion mean free

path, $\lambda$. With Hoppel and Frick (1986), it is defined as the sum of the ion-aerosol three-body trapping sphere and the ion-ion mean free path (see Eq. (44)). Transferred to the ion-ion recombination, the limiting sphere can be defined as the sum of the ion-ion aerosol three-body trapping and one mean free path (see Eq. (45)), as depicted in Fig. 1."


**p24 L587. Ta20 yields $\alpha$ values which are one order of magnitude too low (2.7 · 10−6 cm3 s−1 at ground level). Is it true? 2.7e-6 cm3s-1 does not seem too low.**

We thank the referee for pointing out this typo. It should read $2.7 \cdot 10^{-5}$ $cm^3$ $s^{-1}$, but the main text of the comparison chapter was revised completely for the updated manuscript.


**Fig.1 caption. please consider using open circle instead of white point.**

We appreciate this suggestion, but the white point/circle is not open, but filled white. In the further text, referring to the "open-circle ion" would be more cumbersome than referring to the "white ion", so that we decided to keep the initial wording.


**Fig.3c The color for Tamadate et al. 2020 in legend is different from that in the plot.**

We decided to omit the legends and added labels within the plots to enhance comprehensibility.


**Table 1. please define the symbols in the caption. what is $r_0$?**

We added the definition of symbols in the table caption, including $r_0$, the initial distance of the two ions. We changed $d$ to $d_T$ (Coulombic radius after Thomson) to distinguish it from other radii discussed in the manuscript.


**I also suggest that you consider restructuring some parts of the text. I find organisation of section 2 in the current manuscript does not render a smooth textflow, especially concerning the definition of $d$. Because $d$ appears earlier in the text already but its definition comes quite late. Also in section 4, there is a sudden jump to ion-aerosol attachment without preparing the readers with the purpose.**

We followed the suggestion of the referee and reorganised parts of the manuscript. Now, the three-body trapping distance $d$ is introduced and explained at its first appearance in Sect. 2. We added a chapter (Sect. 8) to determine $d$ numerically by solving Natanson's (1959) equation for $d$, using the field data of $a$ by Gringel et al. (1978), Rosen and Hofmann (1981), and Morita (1983) as input parameters. The short chapter on the sensitivity study of Hoppel and Frick's and Natanson's $d$ (former Sect. 5.1) was replaced by it. Furthermore, we reorganised the chapter on ion-aerosol theories (now Sect. 5), explaining the motivation more clearly why to add this chapter.

References

Fuchs, N. A.: On the stationary charge distribution on aerosol particles in a bipolar ionic atmosphere, Geofisica pura e applicata, 56, 185–193, https://doi.org/10.1007/BF01993343, 1963.

Gardner, M. E.: The Recombination of Ions in Pure Oxygen as a Function of Pressure and Temperature, Physical Review, 53, 75–83, https://doi.org/10.1103/PhysRev.53.75, 1938.

Gringel, W., Käselau, K. H., and Mühleisen, R.: Recombination rates of small ions and their attachment to aerosol particles, Pure and Applied Geophysics, 116, 1101–1113, https://doi.org/10.1007/BF00874674, 1978.

Hoppel, W. A. and Frick, G. M.: Ion—Aerosol Attachment Coefficients and the Steady-State Charge Distribution on Aerosols in a Bipolar Ion Environment, Aerosol Science and Technology, 5, 1–21, https://doi.org/10.1080/02786828608959073, 1986.

Israël, H.: Atmosphärische Elektrizität: Teil 1. Grundlagen, Leitfähigkeit, Ionen, Akademische Verlagsgesellschaft Geest & Portig K.G., Leipzig, 1957.

Lenz, E.: Die Wiedervereinigung von Ionen in Luft bei niederen Drucken, Zeitschrift für Physik (Zschr. f. Physik), 76, 660–678, https://doi.org/10.1007/BF01341939, 1932.

Loeb, L. B.: Basic Processes of Gaseous Electronics, Second edition, revised, University of California Press and Cambridge University Press, Berkeley, Los Angeles and London, 1960.

Morita, Y.: Recent measurements of electrical conductivity and ion pair production rate, and the ion-ion recombination coefficient derived from them in the lower stratosphere, Journal of Geomagnetism and Geoelectricity, 35, 29–38, https://doi.org/10.5636/jgg.35.29, 1983.

Natanson, G. L.: The Theory of Volume Recombination of Ions, Journal of Technical Physics, 4, 1263–1269, 1959.

Rosen, J. M. and Hofmann, D. J.: Balloon-borne measurements of electrical conductivity, mobility, and the recombination coefficient, Journal of Geophysical Research: Oceans, 86, 7406–7410, https://doi.org/10.1029/JC086iC08p07406, 1981.

Tamadate, T., Higashi, H., Seto, T., and Hogan, C. J., J.: Calculation of the ion-ion recombination rate coefficient via a hybrid continuum-molecular dynamics approach, The Journal of Chemical Physics, 152, 94306, https://doi.org/10.1063/1.5144772, 2020.

Thomson, J. J.: XXIX. Recombination of gaseous ions, the chemical combination of gases, and monomolecular reactions, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 47, 337–378, https://doi.org/10.1080/14786442408634372, 1924.