

We thank Referee#1 for their comments regarding our manuscript. Below we provide our answers (shown in Blue) to the comments (shown in Black), and where changes were made to the manuscript, the modified text is given (**Blue Bold**).

I think the authors of „Experimental investigation of ion-ion recombination at atmospheric conditions“ have studied a very important topic. Justified and accurate results about the ion-ion recombination characteristics are essential for understanding several atmospheric processes. Nevertheless, the in the current form the manuscript contains several declarations, statements and/or results that should be justified and/or explained and/or discussed better and/or more in detail. I think these shortcomings should be eliminated.

1. Introduction:

The discussion about the formation of small ions in the air is supported only by one (old) reference (Smith and Spanel, 1995). I do not think that this is the only available choice; nether this is not the absolutely best choice. I suggest to put a proper phrase (e.g., "model chemical composition air ions") into Google and to use/discuss other/newer references/studies (as well).

Answer: We agree with the referee and decided to add the following changes to the text and references.

Current version:

When ionizing radiation interacts with the air, a primary positive ion (e.g., N_2^+ , O_2^+) and an electron are generated (Smith and Spanel, 1995). The positive ion has roughly the same diffusion coefficient as the surrounding molecules.

After the interaction with the ionizing radiation, its change in momentum is negligible and we can picture it as in Brownian motion around its initial position. The electron, however, gains a finite momentum in the interaction. It starts to interact with atmospheric molecules, exciting and ionizing them, until its energy decreases and it binds to an electronegative molecule, for example O_2 , creating O_2^- . This process takes place in a few nanoseconds.

Once two molecular ions of opposite polarity are created, they can interact with molecules that have higher electronegativity or proton affinity (e.g., H_2O) and transfer their charge, or they can establish hydrogen or other chemical bonds with other molecules and cluster (Smith and Spanel, 1995). It is only at this point that ions are considered stable and measurable.

Proposed changes:

When ionizing radiation **hits an air molecule, an ion-electron pair is formed. The primary positive ion can be a molecular ion (e.g., N_2^+ , O_2^+), but it can also be N^+ or O^+ , as the ionizing radiation is very energetic** (Smith and Spanel, 1995; Volland, 1995; Leblanc et al., 2008). After the interaction **between an air molecule and ionizing radiation, the newly formed positive ion stays** in Brownian motion around its initial position. **Its diffusion coefficient is similar to the surrounding molecules and its change in momentum is negligible.**

The electron, however, gains a finite momentum in the interaction. **If the energy gained is sufficiently high, the electron** starts to interact with atmospheric molecules, exciting and ionizing them, until its energy decreases **to thermal levels** and it binds to an electronegative molecule (for example an electron and an O_2 molecule, **combining to form O_2^-**). This process takes place in a few nanoseconds.

Once molecular ions of opposite polarity are created, they can interact with molecules that have higher electronegativity or proton affinity (e.g., H_2O) and transfer their charge, or they can establish hydrogen bonds or other chemical bonds with other molecules and cluster together (Smith and Spanel, 1995). **Positive ions are transformed into hydronium-water clusters and ammonium-water clusters, reaching their equilibrium concentrations after about 10 μs (Luts and Salm, 1994; Luts, 1998). After 1 s, less abundant trace gases (such as pyridine and dimethylamine) start to join the clusters.**

Negative primary ions (mainly O_2^-) cluster with water molecules in 0.1 μs and reach their equilibrium around 0.1 s after the interaction between air and ionizing radiation. Once at equilibrium reactions with NO , NO_2 and O_3 start to create nitric acid-water clusters. If present, iodine is known to cluster at longer time scales (several seconds) (Luts and Salm, 1994; Luts et al., 2011).

References added:

- Leblanc, François, Karen Aplin, Yoav Yair, Giles Harrison, Jean Pierre Lebreton, and M. Blanc. 2008. *Planetary Atmospheric Electricity*. Springer Science & Business Media.
- Luts, A., and J. Salm. 1994. "Chemical Composition of Small Atmospheric Ions near the Ground." *Journal of Geophysical Research: Atmospheres* 99 (D5): 10781–85. doi:10.1029/93JD03225.
- Luts, Aare. 1998. "Temperature Variation of the Evolution of Positive Small Air Ions at Constant Relative Humidity." *Journal of Atmospheric and Solar-Terrestrial Physics* 60 (18): 1739–50. doi:10.1016/S1364-6826(98)00151-5.

Luts, Aare, Tiia-Ene Parts, Urmas Horrak, Heikki Junninen, and Markku Kulmala. 2011.

“Composition of Negative Air Ions as a Function of Ion Age and Selected Trace Gases: Mass- and Mobility Distribution.” *Journal of Aerosol Science* 42 (11): 820–38.

doi:10.1016/j.jaerosci.2011.07.007.

Volland, Hans. 1995. *Handbook of Atmospheric Electrodynamics*. CRC Press.

2) The overview of the former studies of the conditions where ion-ion recombination can be dominant sink of small ions is too vague. I suggest to put a proper phrase (e.g. "new aerosol particle formation ion driven processes") into Google and discuss some more results about the conditions where ion-ion recombination can be dominant.

Answer: We added the following changes to the text and references to give better background for when the ion-ion recombination is the dominant sink.

Current version:

Ion-ion recombination becomes dominant in extremely clean environments, where the integral of the aerosol surface distribution is negligible with respect to the ion-ion recombination rate, and the probability for ion-aerosol attachment is low (Volland, 1995).

Recombination is also important at high ionization rates, when the production of ion pairs is so high that the probability of colliding with a neutral aerosol particle is minimal with respect to the probability of colliding with an ion of opposite charge.

Proposed changes:

Ion-ion recombination becomes dominant in extremely clean environments, where the integral of the aerosol surface distribution is negligible with respect to the ion-ion recombination rate, and the probability for ion-aerosol attachment is low (Volland, 1995). **The attachment coefficient for an ion to a neutral aerosol particle ranges from $[0.1 \text{ to } 2.0] \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$, for an ion of 1.1 nm and an aerosol particle ranging from 10 to 100 nm mobility equivalent diameter (Tammet and Kulmala, 2005).**

Recombination is also important at high ionization rates, when the production of ion pairs is so high that the probability of colliding with an aerosol particle is minimal with respect to the probability of colliding with an ion of opposite charge.

Reference added:

Tammet, H., and M. Kulmala. 2005. “Simulation Tool for Atmospheric Aerosol Nucleation Bursts.” *Journal of Aerosol Science* 36 (2): 173–96. doi:10.1016/j.jaerosci.2004.08.004.

3) It is hard to understand, what do the authors mean by "In past studies, the ion-ion recombination rate was calculated for understanding aerosol diffusion charging...". In case

they want to say "... ONLY for understanding aerosol diffusion" then this is not true, e.g., consider (Tamm et al., 2006) (already referred by the authors). In case the authors want to say that the presented references (Natanson, 1960; Bates and Flannery, 1969) are the ONLY STUDIES, where the recombination rate was (remarkably) considered then this is not true, neither. I think the authors should express their meaning more clearly. Also, I wonder why the authors state "...was measured primarily for dosimetry purposes" and provide only one (old) reference (McGowan, 1965). I think the authors should present more extensive discussion about that key topic (about previous studies of ion-ion recombination) and the authors should discuss a larger number of proper references (e.g. Pageoph, 116, 1101-1113; J. Chem. Phys., 90(11), 6328-6334; Adv. At. Mol. Phys., 20, 1-40; Can. J. Chem., 47, 1711-1724; DOI: 10.1039/c2an35849b; ...).

Answer: We agree that the sentence is not clear. We extended the paragraph adding references, as suggested by Referee#1, and explained each cited reference in a more point-by-point way.

Current version:

In past studies, the ion-ion recombination rate was calculated for understanding aerosol diffusion charging (Natanson, 1960; Bates and Flannery, 1969) and it was measured primarily for dosimetry purposes (McGowan, 1965, and references therein) ... concentrations.

Proposed changes:

Bates and Flannery (1969) defined the equations to describe ion-ion recombination as a sink for air ions, continuing the theoretical work initiated by Thomson (1924) and continued by Natanson (1960). Hoppel and Frick (1986) studied the theory of ion-aerosol attachment, and its limiting case, ion-ion recombination, with the aim to enable the use of differential mobility analysis to measure the aerosol population. McGowan (1965) studied ion-ion recombination in laboratory air to improve dosimetry techniques for ion chambers. Gringel et al. (1978) measured vertical profiles of air conductivity and showed good agreement up to 20 km altitude, using a theoretical recombination coefficient of small ions based on a three-body recombination process. Lee and Johnsen (1989) investigated ion-ion recombination in ambient helium and argon at atmospheric densities and found that, in their setup, along with three-body recombination, stabilization by mutual neutralization plays an important role. Heptner et al. (2012) conducted experiments to study relative changes in ion-ion recombination in dry filtered air at atmospheric pressure. In most of these cases, the ions were studied under conditions that were either far from those found in the atmosphere, or allowed little control over trace gas concentrations and ion production rates. In this work, we present the results of laboratory experiments performed at conditions close to those found in the Earth's atmosphere, providing quantitative results about the ion-ion recombination coefficient at varying temperature, relative humidity and trace gas concentrations.

References added:

- Heptner, Andre, Philipp Cochems, Jens Langejuergen, Frank Gunzer, and Stefan Zimmermann. 2012. "Investigation of Ion-Ion-Recombination at Atmospheric Pressure with a Pulsed Electron Gun." *The Analyst* 137 (21): 5105–12. doi:10.1039/c2an35849b.
- Lee, H. S., and R. Johnsen. 1989. "Ion-ion Recombination Studies in Ambient Helium and Argon at Atmospheric Densities." *The Journal of Chemical Physics* 90 (11): 6328–34. doi:10.1063/1.456349.
- Gringel, W., K. H. Käselau, and R. Mühleisen. 1978. "Recombination Rates of Small Ions and Their Attachment to Aerosol Particles." *Pure and Applied Geophysics* 116 (6): 1101–13. doi:10.1007/BF00874674.

4) Section 2.

Pg 3672. The authors state "The concentration of aerosol particles was below 30 per cubic cm...". What is the basis of such a statement? "Aerosol-free" can maybe sound well, but is this phrase the only proof?

Answer: We agree with Referee#1 that this sentence needs to be clarified.

Current version:

The concentration of aerosol particles was below 30 cm⁻³

Proposed change:

The concentration of aerosol particles was **constantly monitored with a CPC (TSI 3776) and it remained below 30 cm⁻³ in all experiments.**

5) Several former studies have distinguished between "initial recombination" and "volume recombination" (e.g, NUKLEONIKA 2007;52(1):7-12). Is this "initial recombination" taken into account?

Answer:

No correction for initial recombination was used in this paper. Initial recombination is important and will be considered in future studies where we aim to investigate inhomogeneities generated by the fan and by convection in the chamber in general. However, because we used a pulsed pion beam, our source had a low linear energy transfer, compared to, for example, an alpha source. Therefore, we posit that the effect of initial recombination is small for cluster ions, and is well within the total uncertainty of our measurements. A confirmation is given by our fits for the decay lifetime (see figure 2 in answers to Referee#2),

which support that our recombination rates are practically independent from initial recombination. Furthermore, initial recombination would mainly affect primary ions, which are not considered in our study that focuses on cluster ion-ion recombination, as the NAIS measures cluster ions with electrical mobility smaller than $3.2 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ (larger than 0.8 nm in mobility equivalent diameter).

We added the following sentence on page 3676, line 17.

Proposed change: “Initial recombination would mainly affect primary ions, which are not considered in our study that focuses on cluster ion-ion recombination, as the NAIS measures cluster ions with electrical mobility smaller than $3.2 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ (0.8 nm in mobility equivalent diameter).”

References added:

Gryzinski, M. A., N. Golnik, and M. Zielczynski. 2007. “Initial Recombination of Ions in Ionization Chambers Filled with Hydrocarbon Gases.” *Nukleonika* 52 (1): 7–12.

6) How the authors estimate the uncertainty of the obtained (raw) results, e.g. uncertainty of NAIS results?

Answer: The uncertainty of the obtained (raw) results is calculated as standard deviation of the mean values at steady state. We added the following line in the caption of Fig. 5.

Proposed change: “ ... the uncertainty is calculated as the standard deviation of the mean values at steady state.”

7) Section 2.4

Pg 3675-3676. Is there any proof that the "dilution system" functioned just the way and only the way it was expected to function? Are the authors convinced that the dilution system did not cause any disturbing turbulence?

Answer: The dilution system was tested in the laboratory and, for the flow range that was used in the experiments (20 - 25 lpm), it agreed within 28% with the ideal system used for our calculations (see plot below).

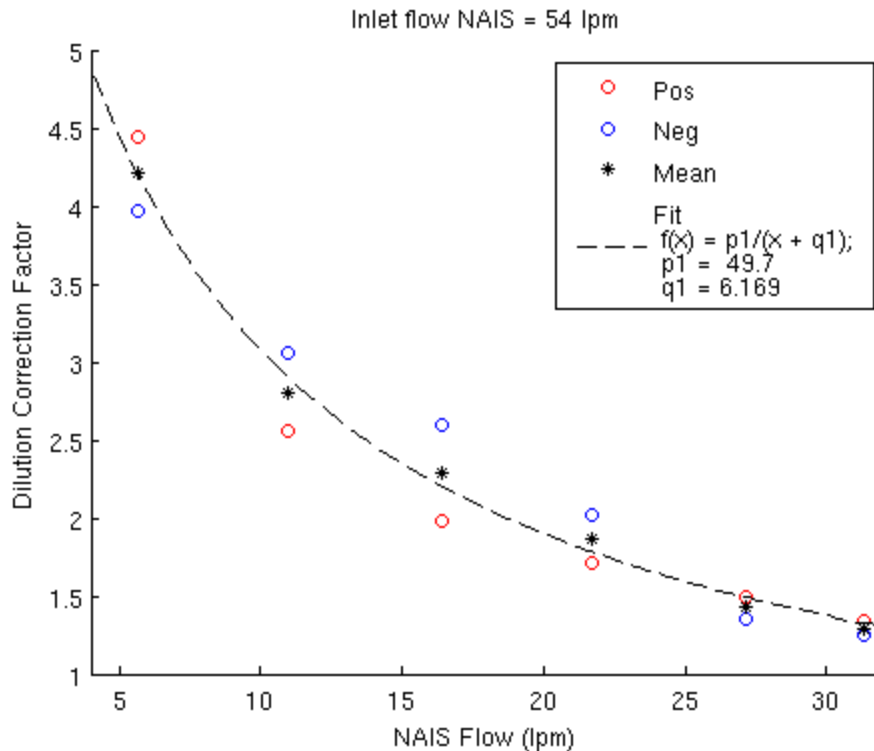


Figure 1. NAIS flow (LPM, flow withdrawn from the chamber) as function of the correction factor for the ion concentration. The correction factor is the valued used for correcting the ion concentration for the dilution of the sample. In the ideal case the correction factor would be equal to NAIS total inlet flow (54 LPM) divided the flow withdrawn from the chamber.

We added one sentence on page 3678, line 2 to clarify the text.

Suggested changes: "... The dilution system was tested in the laboratory and agreed within 28% with the ideal dilution correction factor."

8) Section 3.1.

Pg 3676. Commonly, beta (or beta as a function of diameter) marks the sink, attributed to ambient (aerosol) particles (e.g., Tammet et al., 2006, already referred by the authors). Do the authors have any solid reason to drop the common notations?

Answer: Referee #1 is correct. Usually, beta is used for sinks attributed to aerosol particles. However, the authors decided to use the same notation to refer to all first order losses in the chamber. In this way, there is a logical notation in the balance equation: alpha for the second degree term, and beta for the first degree term.

9) pg 3676-3677. The equation (2) has been already solved by Israël (1970, Atmospheric Electricity, vol 1, p. 167). True, it contains a misprint.

Answer: Due to the misprint, the authors feel motivated to keep the solution of equation (2) in the Appendix. We added the reference to Israël's book on page 3677, line 3.

10) Section 4.1.

pg 3680. "...increased approximately by a factor of 5 (from 11×10^6 to 2.5×10^6)..." How I should understand this?

Answer: Referee#1 is correct, there is a mistake in the sentence. The sentence was corrected. We modified it to: "... **increased** approximately by a factor of **4** (from 2.3×10^6 to 9.9×10^6) as temperature decreased from 293 to 218 K."

11) section 5.

Pg 3684. I do not agree with the statement "... first study to experimentally investigate the ion-ion recombination at atmospheric conditions"; see examples of potential references to former studies above. Also, this investigation is not "...at atmospheric conditions". Yes, the authors have used air-like mixture(s), but this is not exactly "atmospheric conditions". It is still an additional question, how well the experimental conditions correspond to atmospheric conditions.

Answer: We modified the sentence according to the Referee#1's suggestion.

Current version:

"This was the first study to experimentally investigate the ion-ion recombination at atmospheric conditions."

Proposed changes:

"This was the first study to investigate experimentally the ion-ion recombination in a highly controlled environment at atmospherically relevant temperature, humidity and trace gas concentration."

12) Fig.1. (b) The font for NAIS and API-TOF is very small.

Answer: The font was increased.

13) Fig.2. The concentrations of positive ions behave rather differently from the ones of negative ions. For example, shortly after 6:00 the concentration of negative ions has brief but deep depression, accompanied by upward spike in the concentration of positive ions. In general, positive and negative ions should be born in pairs and recombine in pairs, therefore they should be strongly correlated. Also, the ion concentrations at Beam=0.9 are at times even lower than the ones at Beam=0.65. What are the reasons of these odds?

Answer: Referee#1 raises a fair point. We think that the overall concentrations of positive and negative ions are reasonable within the uncertainty of the measurements (around 20% uncertainty of the NAIS electrometers). Because the beam is pulsing, the source of ions is discontinuous and some local, temporary fluctuations can occur. Moreover, the air inside the chamber is stirred by 2 fans, one at the top and one at the bottom. This could also cause fluctuations that are difficult to predict as a consequence of transport inside the chamber. Finally, positive and negative ions have different mean mobility (1.4×10^{-4} and $2.0 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively, in mobility equivalent diameter 1.2 nm and 1 nm). This difference also affects the difference in concentrations for the two different polarities, as the ions will be lost to the walls at different rates.

We added the following sentence to clarify the matter on page 3672, line 4.

Proposed changes: “The ion concentrations were averaged over the last 10-15 minutes, before changing the beam intensity. The averaging time allowed us to compensate for occasional fluctuations in the ion concentrations that were caused by beam pulses, or by convective transport due to the two fans stirring the air inside the chamber.”

15) Fig.5. How can loss rate (constant beta) depend on recombination coefficient alpha ? Is there any unrevealed theoretical link ?

The presented dependence tends to imply that these both quantities are some functions of some other unrevealed quantity (perhaps some functions of some systematic error ?). I think the authors should explain this circumstance more in detail.

Answer: In Fig. 5 we wanted to present a sensitivity study for the fit. Therefore, we repeated the fit using different first order loss rate beta. To clarify, we added a sentence on page 3677, line 9-12 as shown below.

Current version:

The linear loss term was retrieved for each given condition and, when the statistic was too poor to determine the linear loss term, we assumed β to be equal to $(8.3 \pm 1.6) \times 10^{-3} \text{ s}^{-1}$, the value retrieved from the dataset with the best statistics (Fig. 5).

Proposed change:

The linear loss term β , equal to $(8.3 \pm 1.6) \times 10^{-3} \text{ s}^{-1}$, was calculated based on the dataset with the best statistics ($T = 20 \text{ }^\circ\text{C}$, $\text{RH} = 38 \text{ \%}$). **We assumed that the value of β did not change in other cases. To check our assumption, we performed a sensitivity analysis**

of the ion-ion recombination coefficient α , shown in Fig. 5. The variation in α for different assumed values of β is linear and small compared with the observed variation of α due to changing conditions in the chamber.

16) Fig.6. According to the figure, the number results near 280 K are below the ones near 290 K. According to the figure, the recombination coefficient should have a strange temperature dependence: nearly constant below about 250 K, deep depression between 250 K and 280 K and slow uptrend above 280 K. Any explanation?

Answer: We recognize that the measured point at 250 K is higher than one would expect, but we think that the main message of the data is that the ion-ion recombination coefficient decreases at increasing temperatures in the investigated range, quite steeply between 220 and 260 K, more mildly between 250 and 300 K.