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., H2 O) 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 to 2.0] × 10^{-6} cm^{3} 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 (Tammet 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) considerered 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 the 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 3.2×10^{-4} m^2 V^{-1} 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 3.2×10^{-4} m^2 V^{-1} 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).**

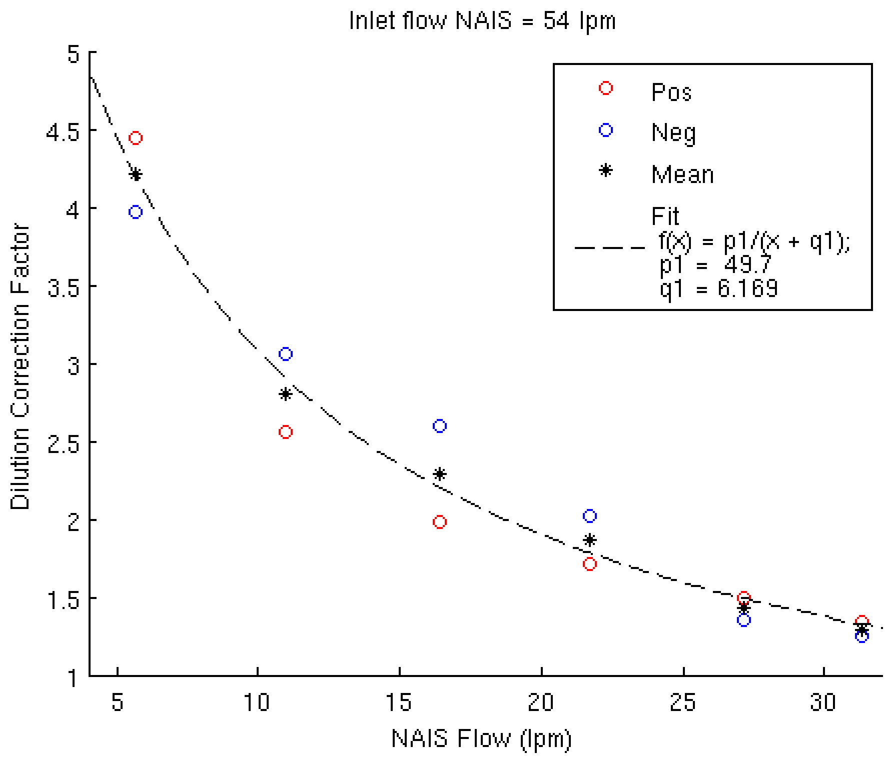

Figure 1. NAIS flow (LPM, flow withdrawn from the chamber) as function of the correction factor for the ion concentration. The correction factor is the valued used for correcting the ion concentration for the dilution of the sample. In the ideal case the correction factor would be equal to NAIS total 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 2.3x10^6 to 9.9x10^6) 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 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 2.0×10^{-4} m^2 V^{-1} 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 $(8.3 \pm 1.6) \times 10^{-3}$ s^{-1} , the value retrieved from the dataset with the best statistics (Fig. 5).

Proposed change:
The linear loss term **β**, equal to $(8.3 \pm 1.6) \times 10^{-3}$ s-^{1}, was calculated based on the dataset with the best statistics (T = 20 ^{o}C, RH = 38 %). **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 that 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.

We thank Referee#2 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**).

Anonymous Referee #2

Received and published: 24 March 2015

The manuscript by Franchin et al. aims investigating ion-ion recombination in laboratory conditions in the Cosmics Leaving Outdoor Droplets (CLOUD) chamber. In their experiments the authors have had excellent facility and suitable instrumentation. The carried experiment and subsequently presented results are well within scope of the journal, and are very interesting for the readership. English of the text was good. Though, I recommend the authors to double check text in the Sections 4 and 5.

I recommend this manuscript to be published in the Atmospheric Chemistry and Physics after the authors have considered, in addition to comments given by referee 1, following minor comments and suggestions to further improve their manuscript.

Minor comments

Abstract

1. Page 3669: Although the abstract nicely reflects made experiments and results of the paper, I would highlight the most important results even more. i) I think that mentioning ion-ion recombination coefficient value that is most commonly used in recent atmospheric applications in literature would put the newly obtained laboratory results into relevant context (lines 12-13). ii) Currently, the reader does not get information how recombination coefficient depends on temperature and RH (lines 15-16, and 18-19).

Answer: We agree with Referee#2 and decided to add the following changes to the text.

Page 3669, lines 12-13.

Current version:

At 20 ^{o}C and 40% RH, the retrieved ion-ion recombination coefficient was (2.3± 0.7) $\times 10^{-6}$ cm^3 s^{-1} .

Proposed changes:

"The best agreement of the retrieved ion-ion recombination coefficient with the commonly used literature value of 1.6×10^{-6} cm^3 s^{-1} was found at a temperature of 5 ^{o}C

and a RH of 40% (1.5 ± 0.6) ×10^{-6} cm^3 s^{-1} . At 20 °C and 40% RH, the retrieved ion-ion recombination coefficient was **instead** (2.3 ± 0.7) ×10^{-6} cm^3 s^{-1}.

Page 3669, lines 15-16.
Current version:
“However, we found a strong dependency of the ion-ion recombination coefficient on temperature.’

Proposed changes:
“However, we **observed a more than fourfold increase** in the ion-ion recombination coefficient **with decreasing** temperature.”

Page 3669, lines 18-19.
Current version:
We observed a strong dependency of the recombination coefficient on relative humidity, which has not been reported previously.

Proposed changes:
“We observed a strong **increase** in the recombination coefficient **for decreasing** relative humidities, which has not been reported previously.”

Introduction

In general, I like style of the introduction and reasonable background information is provided for the readership. However, following improvements could be considered.

1. Page 3669, starting from line 21: I think that the starting paragraph should be revised to make it more interesting, meaningful and to better justify atmospheric relevance of the current study.

Answer: To clarify, we added the following sentence and citation. In addition, some corrections were already made in response for Referee #1 (see comment 1), which also improved the introduction.

Proposed changes:
“Air ions are fundamental to atmospheric electricity and play a central role in the proposed connection between solar activity, Galactic Cosmic Rays (GCRs) and climate (Israël, 1970; Carslaw et al., 2002; Usoskin and Kovaltsov, 2009). Ions are known to enhance nucleation rates in atmospherically relevant vapor mixtures (Kirkby et al., 2011).

In particular, ion-ion recombination has been proposed and studied as a driving force behind atmospheric nucleation (Yu and Turco, 2008; Yu, 2010; Nagato and Nakauchi, 2014).
However, the overall effect of ions on atmospheric new particle formation (NPF), and subsequent production of cloud condensation nuclei,has remained a controversial issue (Gagné ...”

Reference added:

Yu, F., and R. Turco. 2008. “Case Studies of Particle Formation Events Observed in Boreal Forests: Implications for Nucleation Mechanisms.” *Atmospheric Chemistry and Physics* 8 (20): 6085–6102.

Yu, Fangqun. 2010. “Ion-Mediated Nucleation in the Atmosphere: Key Controlling Parameters, Implications, and Look-up Table.” *Journal of Geophysical Research-Atmospheres* 115 (February): D03206. doi:10.1029/2009JD012630.

Nagato, Kenkichi, and Masataka Nakauchi. 2014. “Experimental Study of Particle Formation by Ion–ion Recombination.” *The Journal of Chemical Physics* 141 (16): 164309. doi:10.1063/1.4898376.

Page 3670, lines 15-20: Currently, the text gives very uninformative picture of contributions of various ionization mechanisms and their altitude dependence. Readers of this manuscript would benefit from a schematic figure showing profile(s) of ionization rate(s) through the troposphere (including the lowest part, i.e. the atmospheric boundary layer), and illustrating at least total amount of ionization rate. Such a figure would also put the experiments better into the atmospheric context.
Answer: We added the following text to the manuscript to clarify the contribution of various ionization mechanisms and their altitude dependence. We added Fig. 1, which shows the importance of terrestrial sources and GCR as a function of altitude.

Proposed changes:

“Air ions are continuously produced in the atmosphere from GCRs and terrestrial sources, such as radon decay and gamma radiation from the soil (Laakso et al., 2004). Within the planetary boundary layer, terrestrial sources play an important role in ionization processes, whereas **at altitudes greater than 2 km,** GCRs are the dominant source of ions (Harrison and Carslaw, 2003; Kazil and Lovejoy, 2004; Arnold, 2008; Zhang et al., 2011; Williams et al., 2011).”

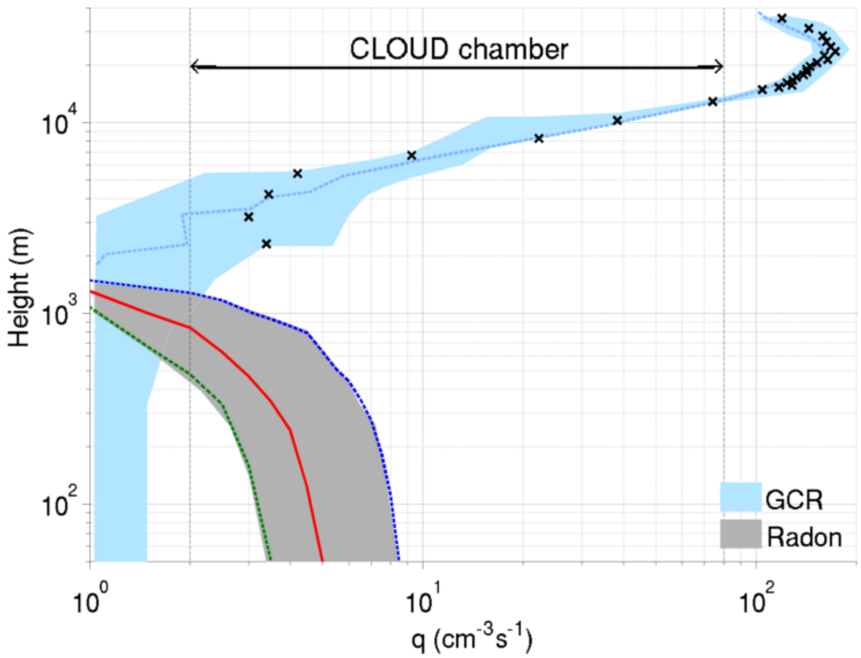

Fig. 1. A vertical profile of the ion production rate *q*, based on literature data. The contribution of radon decay at mid latitudes is shown in gray, accounting for seasonal variation. The minimum is in summer and the maximum is in winter (Zhang et al., 2011). The contribution of galactic cosmic rays at mid latitudes, as presented by Usoskin et al. (2004), is shown in cyan. Black crosses indicate measurements by Harrison et al. (2014). The double arrow at the top shows the range of *q* explored in this study.

Experimental methods

1. Page 3672, line 8: I believe that instead of ’beam settings’ authors mean ’beam intensity’.

Answer: We replaced ’beam settings were’ with ’beam **intensity was**’

2. Page 3675, line 4: I do not think that Kulmala et al. (2007) is right reference for the NAIS. Instead, Manninen et al. (2011), which is already cited in the manuscript elsewhere, Asmi et al. (2009) and Gagné et al. (2011) would be more appropriate references. In order to trace the NAIS to its calibration (e.g. Asmi et al., 2007; Gagné et al., 2011), identification number of the instrument should be mentioned in the text.

Answer: We removed the citation to Kulmala et al. (2007) and added the most appropriate, Gagné et al. (2011). We also added “SER NAIS12” on line 5, page 3675.

Theoretical methods

I think that this section needs substantial revision to better create transparency and facilitate potential repeatability for the applied retrieval.

1. Page 3676, line 22:

Clarify reasons behind number concentration differences between positive and negative ions in Fig. 2 and large variation in time (Page 3698, Figure 3).

Answer: See our answer to comment n.13 by Referee #1.

How was 10 % concentration difference defined? To me variation range seems large, and 25, 50, and 75 percentiles of differences should be shown at least in caption of the Fig. 2.

Answer: 10% is defined as $mean(\frac{|C_{neg}-C_{pos}|}{C_{neg}/2+C_{pos}/2})$, where C_{neg} and C_{pos} are the concentration of negative and positive ions, respectively. 10% corresponds to the 50th percentile. The 25 and 75 percentile values are 5% and 14%, respectively.

A variation of 10% in the concentration is compatible with the ratio of the square root of electrical mobilities sqrt(Zp)/sqrt(Zn) = 0.9, which is proportional to the loss rate of ions to the walls. Moreover, additional variability could be due to variability in the chamber of trace gas concentration, which are difficult to control. Small variations in trace gas concentrations could change the mean mobility of the ions, and therefore their loss rates to the wall of the chamber. We added following sentence for clarification.

Page 3676, line 22.

Suggested changes: ,

"... the **average** difference between the number concentration of positive and negative ions was only about 10 %**. The 25th and 75th percentile are 5 % and 14 %, respectively** (see Fig. 2). **This variation in the concentration of positive and negative polarities is compatible with the ratio of the square root of the mean ion electrical mobilities (Z), which is proportional to the rate at which ions are lost to the walls of the chamber $\frac{\sqrt{Z_{pos}}}{\sqrt{Z_{neg}}}$ = 0.9.**

Are shown ion concentrations of positive or negative ions in Figs. 3-4 and in calculations behind Figs. 3-7?

Answer: The concentrations shown in Figures 3 and 4 are the average between positive and negative ion concentrations. We modified the captions in figure 3,4 to clarify.

Figure 3. Proposed change:

Figure 3. Ion concentration (blue line and circles), the solution to Eq. (1) (red line) and the beam counts (magenta line). **The ion concentration is presented as the average between the concentration of negative and positive ions.** When solving Eq. (1), the recombination coefficient …

Figure 4. Proposed change:

Figure 4. Ion concentration as a function of ion production rate … at a constant temperature of 20 °C. **The ion concentration is presented as the average between the concentration of negative and positive ions.**

2. Page 3677, lines 9-12: This paragraph requires complete revision since it raises so many questions. E.g. what is fraction of analyzed cases when statistics were too poor to determine the linear loss term? Subsequently, what are implications of such poor statics on retrieved ion-ion recombination coefficient?

Answer: We modified the text, as shown below, to clarify the paragraph.

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 ± 1.6) × 10^{-3} s , the value retrieved from the dataset with the best statistics (Fig. 5).

Proposed change:

The linear loss term **β, equal to (8.3 ± 1.6) × 10^{-3} s,** was retrieved from the dataset with the best statistics (T = 20 °C, RH = 38 %). **We assumed β to be the same value for all the other cases. To check our assumption, we performed a sensitivity analysis of the ion-ion recombination coefficient α, shown in Fig. 5. The variation of α for different assumed β is linear and small compared with the observed variation of α due to changing conditions in the chamber.**

3. Page 3677, lines 13-14: Fig. 3 shows that made assumptions work nicely in the particular example case. How representative is this example case? I think Fig. 5 is introduced before Fig. 3.

Answer: In our opinion, the ion decay presented in Figure 3 is representative, as seen in the figure below. The scatter plot below shows all 12 ion decay experiments performed. The measured ion concentrations appear on the x-axis. On the y-axis, the ion concentration is modelled using the analytical solution of the ion balance equation described in the appendix (A5).

76% of the points fall within +/-30% from the 1:1 line, and 92% of the points fall within the +/-50% lines. Therefore, we think that the ion decay presented in Figure 3 is representative.

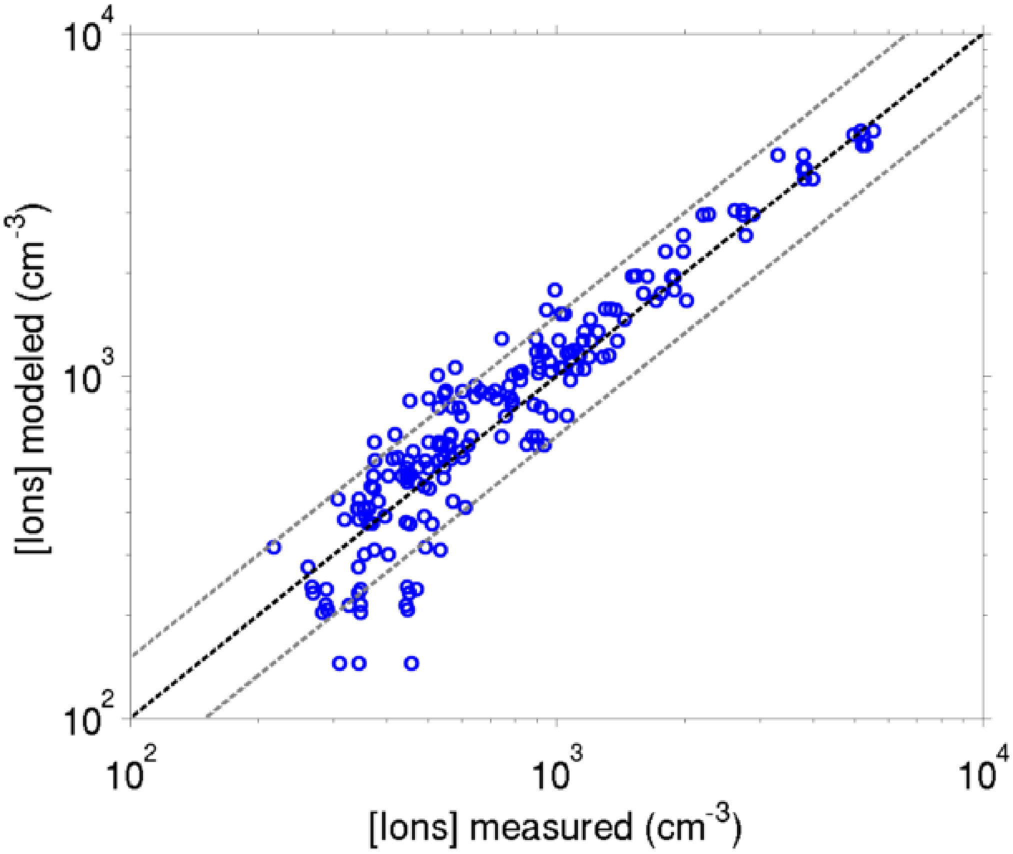

Figure 2. Comparison between the measured and modeled ion concentration during the 12 decay experiments (similar to Fig. 3 in the manuscript). The black line is the 1:1 line, the gray lines are +/-50% from the 1:1 line.

We added following, short clarification to the caption of Fig. 3.

Proposed change:

“Figure 3. **Typical ion decay experiment.** The ion concentration …”

4. Explain uncertainty estimations shown in Figs. 4-5 and Tables 1-2 more in detail.

Answer: We added the following line to the captions of Tables 1 and 2.

The uncertainty is calculated following the error propagation approach, accounting for the uncertainty of the measurements. When the data were averaged, we used the standard deviation.

We added the following line to the caption of Figure 4.

"... at a constant temperature of 20 °C. **The error bar represents the standard deviation over the averaged range.**"

Results

1. Tables 1-2 and Figs. 4, 6-7: The results are very interesting. However, all results for changing RH and temperature are shown only at one temperature and RH, respectively. If the authors cannot create temperature variations of Fig. 4d or RH variations of the Fig. 4c, then more careful and precise discussion of temperature and RH variations in recombination coefficient in Sections 4 and 5 (e.g. on page 3683, lines 17-20) should be provided.

We added the following sentence.

Page 3684, line 2.

Proposed change:

"... supports this explanation, but it fails in reproducing the absolute values. **It is also important to note that our results for the RH dependence of the ion-ion recombination coefficient were studied at only one temperature, 20 °C. The extent of the dependency might be different at different temperatures.**"

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Experimental investigation of ion-ion recombination at atmospheric conditions

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Abstract

We present the results of laboratory measurements of the ion-ion recombination coefficient at different temperatures, relative humidities and concentrations of ozone and sulfur dioxide. The experiments were carried out using the Cosmics Leaving OUtdoor Droplets (CLOUD) chamber at CERN, the walls of which are made of conductive material, making it possible to measure small ions. We produced ions in the chamber using a 3.5 GeV c^{-1} beam of positively-charged pions (π^+) generated by the CERN Proton Synchrotron (PS). When the PS was switched off, galactic cosmic rays were the only ionization source in the chamber. The range of the ion production rate varied from 2 to 100 cm^{-3} s^{-1}, covering the typical range of ionization throughout the troposphere. The temperature ranged from -55 to 20 ^{o}C, the relative humidity from 0 to 70%, the SO_2 concentration from 0 to 40 ppb, and the ozone concentration from 200 to 700 ppb. ~~At 20 ^{o}C and 40% RH, the retrieved ion-ion recombination coefficient was (2.3$\pm$ 0.7) $\times 10^{-6}$ cm^{3}s^{-1}.~~ The best agreement of the retrieved ion-ion recombination coefficient with the commonly used literature value of 1.6$\times 10^{-6}$ cm^{3}s^{-1} was found at a temperature of 5 ^{o}C and a RH of 40 % (1.5 $\pm$ 0.6) $\times 10^{-6}$ cm^{3}s^{-1}. At 20 ^{o}C and 40 % RH, the retrieved ion-ion recombination coefficient was instead (2.3 $\pm$ 0.7) $\times 10^{-6}$ cm^{3}s^{-1}. We observed no dependency of the ion-ion recombination coefficient on ozone concentration and a weak variation with sulfur dioxide concentration. ~~However, we found a strong dependency of the ion-ion recombination coefficient on temperature~~. However, we observed a more than fourfold increase in the ion-ion recombination coefficient with decreasing temperature. We compared our results with three different models and found an overall agreement for temperatures above 0 ^{o}C, but a disagreement at lower temperatures. ~~We observed a strong dependency of the recombination coefficient on relative humidity, which has not been reported previously.~~ We observed a strong increase in the recombination coefficient for decreasing relative humidities, which has not been reported previously.

1 Introduction

~~Air ions are fundamental to atmospheric electricity and play a central role in the proposed connection between solar activity, Galactic Cosmic Rays (GCRs) and climate~~ (Israël, 1970; Carslaw et al., 2002; Usoskin and Kovaltsov, 2008). ~~Ions are known to enhance nucleation rates in atmospherically relevant vapor mixtures~~ (Kirkby et al., 2011) ~~, but the overall effect of ions on atmospheric new particle formation (NPF) and subsequent cloud condensation nuclei production has remained a controversial issue~~

Air ions are fundamental to atmospheric electricity and play a central role in the proposed connection between solar activity, Galactic Cosmic Rays (GCRs) and climate (Israël, 1970; Carslaw et al., 2002; Usoskin and Kovaltsov, 2008). Ions are known to enhance nucleation rates in atmospherically relevant vapor mixtures (Kirkby et al., 2011). In particular, ion-ion recombination has been proposed and studied as the driving force behind atmospheric nucleation (Yu and Turco, 2008; Yu, 2010; Nagato and Nakauchi, 2014). However, the overall effect of ions on atmospheric new particle formation (NPF), and subsequent production of cloud condensation nuclei, has remained a controversial issue (Gagné et al., 2008; Kazil et al., 2010; Manninen et al., 2010; Yu et al., 2010; Hirsikko et al., 2011; Kontkanen et al., 2013; Kulmala et al., 2013). Air ions accumulating near cloud edges may affect cloud microphysics and ultimately climate via several mechanisms that are currently poorly quantified (Tinsley, 2000; Harrison and Amba 2008).

Atmospheric ions are usually classified in three groups depending on their diameter (here, all diameters are reported as Millikan-Fuchs equivalent mobility diameters, Mäkelä et al., 1996): small ions (<1.9 nm), intermediate ions (1.9 - 7.7 nm) and large ions (>7.7 nm). In terms of mobility, they are classified as: small ions (>0.57 cm^2 V^{-1} s^{-1}), intermediate ions (4.3$\times$10^{-2} – 0.57 cm^2 V^{-1} s^{-1}) and large ions (<4.3$\times$10^{-2} cm^2 V^{-1}) (Hõrrak et al., 2000). Small ions have a high mobility, therefore they are the main responsible for the transfer of charge in the atmosphere (Chalmers, 1949; Ogawa, 1985) and play a role in NPF and in aerosol charging processes (Adachi and Kousaka, 1985; Manninen et al., 2011). This work focuses on small ions, from here on simply referred to as “ions” unless specified otherwise.

Air ions are continuously produced in the atmosphere from GCRs and terrestrial sources, such as radon decay and gamma radiation from the soil (Laakso et al., 2004). Within the planetary boundary layer, terrestrial sources play an important role in ionization processes, whereas ~~in the whole troposphere~~ at altitudes greater than 2 km, GCRs are the dominant source of ions (Fig.1 Harrison and Carslaw, 2003; Kazil and Lovejoy, 2004; Usoskin et al., 2004; Arnold, 2008; Zhang et al., 2011; Williams et al., 2011; Harrison et al., 2014).

~~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 electro-negative 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 bonds or other chemical bonds with other molecules and cluster together~~ (Smith and Spanel, 1995). ~~It is only at this point that ions are considered stable and measurable.~~

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 one of 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. Alternatevly, they can establish hydrogen or other chemical bonds with other molecules and cluster (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 be part of 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).

The number concentration of ions depends on the balance between ion sources and sinks. The production rate is proportional to the amount of ionizing radiation present, whereas the loss mechanisms depend on the attachment rate of ions onto aerosol or macroscopic surfaces and on the ion-ion recombination rate (Tammet et al., 2006). The ion-ion recombination rate is the rate at which one ion collides with another ion of opposite charge and get neutralized. It depends on the mobility of ions and possibly on their chemical composition and ambient conditions. ~~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.~~

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 attaching to a neutral aerosol particle ranges from 0.1 to 2.0×10^{-6} cm^3

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.

The aim of this work is to determine the ion-ion recombination coefficient under different conditions. ~~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). ~~In most cases, the ions were studied in noble gases or in pure oxygen. The present work is the first laboratory experiment performed at conditions close to those found in Earth's atmosphere that presents quantitative results about the ion-ion recombination coefficient at varying temperature, relative humidity and trace gas concentrations.~~

In the past, 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 helium and argon at atmospheric densities and found that, in their setup, along with three-body recombination, stabilization by mutual neutralization played 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.

2 Experimental methods

The typical experiment carried out consisted of measuring the ion concentrations at several beam intensities, each time for long enough (about 30 min) to reach steady state conditions while all the other variables were kept constant (Figure 3). 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. The beam intensity was varied from 0 to 1.5×10^5 pions s^{-1}, corresponding to an ion production rate ranging from about 2 to 100 ion pairs $\mathrm{cm}^{-3}\mathrm{s}^{-1}$. The concentration of aerosol particles was constantly monitored with a CPC (TSI 3776) and it remained below 30 cm^{-3} in all experiments. The concentration of ions with $D_\mathrm{p} > 1.9$ nm was negligible as the experiments were carried out in an aerosol-free chamber. Usually, the beam intensity was increased consecutively, generating a series of steps of ion production rate. Each time, at the end of the last step, the beam shutter was closed, and we observed the ion concentration decay (Figure 4). The mobility range of the ions considered in this study was from 3.2 to 0.57 $\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$, that correspons to a size range of $0.8 - 1.9$ nm in mobility equivalent diameter (D_p). In this analysis the signal of the NAIS in ion mode was integrated over all the channels corresponding to $D_\mathrm{p} < 1.9$ nm. The rest of the ion number size distribution was not considered, as it was negligible. From this dataset, we retrieved the ion-ion recombination coefficient under different conditions.

2.1 The CLOUD Chamber

The Cosmics Leaving OUtdoor Droplets (CLOUD) chamber (Kirkby et al., 2011) is a cylindrical vessel with a diameter of 3 m and a volume of 26.1 m^3 made of electro-polished 316L stainless steel (Figure 2.c). Its walls are conductive, which makes it possible to measure small ions that, in a traditional aerosol chamber made of polytetrafluoroethylene (PTFE), would be removed in less than one second by the parasitic electric fields created by the dielectric material (McMurry and Rader, 1985). In the interior of the chamber, all plastic components are avoided using copper o-rings and metallic coating on electrically insulating components. When it is necessary to work in an ion-free environment, two circular grids, one located at the top and one at the bottom of the chamber, are provided with a potential difference of up to 60 kV, generating an axial electric field able to remove the small ions in less than 0.2 s. When the two circular grids are not in use, they are grounded to avoid ground loops or parasitic electric fields.

The total in-flow to the chamber varies between 100 and 150 L min^{-1}. Most of the flow is taken by the instruments connected to the chamber and a portion of it is purged through a valve that controls the pressure inside the chamber. The chamber is kept at 5 mbar above the atmospheric pressure to avoid contamination from the outside. The chamber is equipped with an ultraviolet fiber-optic system that is installed at the top plate of the chamber, allowing OH production (Kupc et al., 2011) without heating up the chamber. The temperature is controlled by air circulating between the chamber and the insulation surrounding it. The temperature ranges from -80 to 100 ^{o}C with a stability inside the chamber of $\pm$ 0.1 ^{o}C for each experiment. The chamber is filled with ultra-pure synthetic air, consisting of N_2 and O_2, obtained from the evaporation of liquid samples. The air is humidified with a Nafion system, using water purified by recirculation through Millipore Super-Q filters and irradiated with UV radiation. Ozone is produced by illuminating a portion of the incoming dry air with UV light. The other trace gases, such as SO_2 and NH_3, are added from gas cylinder reservoirs. These measures aim for the cleanest possible laboratory conditions (Schnitzhofer et al., 2014).

2.2 The particle beam

The particle beam is produced at the CERN Proton Synchrotron. The CLOUD chamber can be exposed to a 3.5 GeV c^{-1} positively-charged pion (π^{+}) beam produced by a secondary target of aluminium or copper (Duplissy et al., 2010). The intensity of the particle beam can be varied to cover the full range of ionization in the troposphere, from an ion production rate of about 2 cm^{-3} s^{-1}, equivalent to boundary layer levels, to 80 cm^{-3} s^{-1}, equivalent to the levels in the free troposphere (Kazil and Lovejoy, 2004; Zhang et al., 2011). The beam consists of pions and muons that have approximately the same energy of about 3.5 GeV and come in spills. Each spill lasts for a few microseconds and delivers 10^8 pions at a time, at intervals of 20 s.

We varied the beam intensity, and thus the ion production rate in the chamber, by varying the aperture of the beam collimator, which consists of two mechanical jaws made of concrete that can slide vertically and horizontally. At full aperture (60 mm × 60 mm) we have the maximum flux of pions through the chamber. When the collimator was partially closed we reduced the flux of pions and we illuminated a smaller part of the chamber. When the collimator was closed, almost no pion could reach the chamber. In this case, only GCRs, which are passing through the chamber vertically, and some residual pions that pass the blocker, hitting the chamber horizontally, were responsible for the ionization. For this reason, the ion production rate in the chamber at GCR conditions was about 30% higher than it would be if the accelerator had been shut down completely.

The pion beam is deliberately defocused to maximize the area where the ionization takes place (Figure 2 .c, shaded area). About 70% of the volume of the chamber is directly ionized and the two mixing fans produce a uniform distribution of ions inside the chamber, the mixing time inside the chamber is estimated to be between 1.7 and 3.6 min (Voigtländer et al., 2012).

2.3 The hodoscope and the B1.2 counter

The hodoscope is an array of scintillation detectors. It measures the pion flux through the chamber and gives accurate positional information on the particle beam. It consists of 9 plastic scintillator slabs adjacent to one another in a vertical orientation and 9 plastic scintillator slabs oriented horizontally (Mizin et al., 2011). The vertical and horizontal slabs form a grid orthogonal to the particle beam, covering an area of about 2 m × 2 m. An ionizing particle, hitting a point on this grid, is located by measuring the coincidence of the signal of two detectors (one vertical and one horizontal). The B1.2 counter consists of two scintillation detectors placed right in front of the beam aperture. It also measures the coincidence of the signal of two detectors in order to count only the pions from the beam. From the number of particles measured per unit time and from the location of the scintillators crossed, we can independently retrieve the beam intensity

(Hz) and its horizontal and vertical profile. This allows us to discriminate between high energy particles coming from the beam, which travel almost horizontally, and the GCRs.

2.4 Neutral cluster and Air Ion Spectrometer (NAIS)

The Neutral cluster and Air Ion Spectrometer (NAIS, Gagné et al., 2011; Mirme and Mirme, 2013, SER NAIS12) is manufactured by Airel Ltd in Estonia and measures atmospheric ions in the range [0.8 - 42] nm and total aerosol particle population in the range [2.5 – 42] nm. It consists of two cylindrical Differential Mobility Analysers (DMAs) working in parallel, classifying negative and positive ions at the same time (Manninen et al., 2009). The ions are simultaneously classified according to their mobility and detected by a stack of 21 electrometer rings for each analyser. The device is equipped with a unipolar charging unit for each analyser that can be switched on and off.

During the CLOUD experiments, the instrument operated in three modes: particle, ion and offset. In particle mode the main charging unit is turned on. In ion mode the main charging unit is turned off. In offset mode the main charger unit stays off and a filter unit is turned on to make a zero measurement. This zero measurement is used to determine the net signal due to ions and particles. To maximize the flow in the tube and reduce the diffusion losses, the NAIS and a mass spectrometer shared part of the 2.54 cm outer diameter sampling line. Outside the chamber, the flow was split (20 L min^{-1} to the NAIS, 10 L min^{-1} to the APi-TOF) using a Y union (Figure 2.b).

The NAIS operates at a 54 L min^{-1} total inlet flow. The high intake of the NAIS is a challenge in aerosol chamber experiments, where it is required to minimize the amount of air withdrawn. For this reason, the NAIS was operated with a recirculation system, which diluted the inlet flow with filtered air coming from the exhaust of the instrument. The filtered air formed an annulus around the sample flow (Figure 2.a). The use of the dilution system allowed us to reduce the withdrawn flow from the chamber from 54 to 20-30 L min^{-1}. In this study, we only present the data recorded in ion mode, in particular the data from of the first 9 electrometers that collect ions with mobility diameter smaller than 1.9 nm (small ions). The detailed setup used for this work is presented in Figure 2.

3 Theoretical methods

3.1 Calculation of the ion-ion recombination rate

Using the balance equation at steady state, the ion-ion recombination rate and a linear loss term were determined using the measured ion concentration and the ion production rate. We can describe the ionization processes inside the chamber using the following balance equation:

$$\frac{dn_\pm}{dt} = q - \alpha n_+ n_- - \beta_\pm n_\pm - k_{\mathrm{CS}}(N, D_{\mathrm{p}}) n_\pm, \tag{1}$$

where $n_\pm$ is the absolute concentration of positive or negative small ions (cm^{-3}), q is the ion production rate (IPR, cm^{-3} s^{-1}), α is the recombination coefficient (cm^3 s^{-1}), β is a first order loss term (s^{-1}) that describes the ion-wall interactions in the aerosol chamber, and other loss mechanisms of the first order, k_{CS} is the coagulation sink, i.e., the rate at which ions are lost by diffusion onto aerosol particles (s^{-1})(Kulmala et al., 2001; Leppä et al., 2011). At a constant q, the steady state that is eventually reached depends on the values of α, β and k_{CS}.

In this study α does not include the effect of initial recombination (Gryzinski et al., 2007). 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 3.2×10^{-4} m^2 V^{-1} s^{-1} (larger than 0.8 nm in mobility equivalent diameter).

We can make some assumptions to simplify Eq.1. By assuming that $n_- \simeq n_+$, and that the ion loss by coagulation is negligible compared with the other sink terms, we get:

$$\frac{dn}{dt} = q - \alpha n^2 - \beta n, \tag{2}$$

These assumptions were well posed in our case, since the average difference between the number concentration of positive and negative ions was 10 %. The 25th and 75th percentile are 5 %

and 14 %, respectively (see Fig. 3) This variation in the concentration of positive and negative polarities is compatible with the ratio of the square root of the mean ion electrical mobilities (Z), which is proportional to the loss rate of ions to the walls of the chamber $\sqrt{\frac{Z_{pos}}{Z_{neg}}}$ = 0.9. During our experiments k_{CS} was constantly below $3\times10^{-7}s^{-1}$, due to negligible aerosol concentration in the chamber. The solution of Eq. 2 can be found analytically (Israël, 1970):

$$n(t)=\frac{n_1(n_0-n_2)-n_2(n_0-n_1)\ \exp(-t\sqrt{\beta^2+4\alpha q})}{(n_0-n_2)-(n_0-n_1)\ \exp(-t\sqrt{\beta^2+4\alpha q})}, \tag{3}$$

where n_0 is the concentration of ions at $t=0$, $n_1=\frac{-\beta+\sqrt{\beta^2+4\alpha Q}}{2\alpha}$ and $n_2=\frac{-\beta-\sqrt{\beta^2+4\alpha Q}}{2\alpha}$.

If we consider steady state conditions, $\frac{dn}{dt}=0$, Eq.2. becomes a second order polynomial. The recombination coefficient α, and the linear loss term β, can be retrieved by fitting a second order polynomial function to the data, treating them as free parameters. The ion concentration was set to zero at q equal to zero. ~~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±1.6)×10^{-3} s^{-1}, the value retrieved from the dataset with the best statistics (Fig. **??**).~~ The linear loss term β, equal to (8.3 ± 1.6) × 10^{-3} s^{-1}, was calculated based on the dataset with the best statistics (T = 20 ^{o}C, RH = 38 %). 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 obseverd variation of α due to changing conditions in the chamber.

Equation 3 was used to check the values of α and β retrieved at steady state by comparing the resulting $n(t)$ to the ion decay data (Figure 4). The ion production rate from the beam (q_b) was calculated using the following equation (Duplissy et al., 2010):

$$q_b=N_bIL/V, \tag{4}$$

where N_b is the number of pions per unit time that hit the chamber. N_b can vary between 0 and 1.5×10^6 s^{-1}. I = 61 i.p. cm^{-1} is the mean ionization per cm for a 3.5 GeV/c π^+ in air at s.t.p. (Smirnov, 2005), L = 284 cm is the path length of a beam particle in the chamber, and V = 26.1×10^6 cm^3 is the chamber volume. The ion production rate was scaled for different air density at different temperatures.

We used a value of 1.84 $\text{cm}^{-3}\text{s}^{-1}$ for the intensity of the GCRs. The total ion production rate q is given by the sum of the GCR contribution q_0 and the beam contribution q_b, $q = q_0 + q_b$. The ion concentration was corrected for sample dilution, due to the dilution system described in section 2.4 and shown in Fig. 2. 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.

3.2 Modelled ion-ion recombination coefficient

The temperature dependency of the calculated ion-ion recombination coefficient was compared to the values computed using three different model approaches. The first model derived by J. J. Thomson (Gardner, 1938; Loeb, 1955; Thomson and Thomson, 2013) considers recombination governed mainly by Brownian motion of ions and molecules and computes the recombination coefficient as:

$$\alpha = \sqrt{2}\pi d^2 C\epsilon. \tag{5}$$

Where $C = \sqrt{3k_bT/m}$ is the root mean square thermal velocity of the ions, $d = e^2/[(3/2)k_BT]$ is the distance where the Coulomb potential energy between the two ions of opposite polarity is equal to their thermal kinetic energy, and ϵ is the probability of the two ions to recombine once they are at distance d. As derived by Thomson, $\epsilon = 2w - w^2$, $w = 1 - 2[1 - \exp(-x)(x+1)]/x^2$, $x = 2d/L$ and L is the mean free path of the ions. The equation for α then becomes:

$$\alpha(cm^3s^{-1}) = 1.90 \times 10^{-5}(273/T)^{\frac{3}{2}}3/2\sqrt{1/M}\epsilon, \tag{6}$$

when T is the temperature in Kelvin and M is the mass of the ion in Da.

The second model taken into consideration and compared with our experimental data is described by López-Yglesias and Flagan (2013). Based on Hoppel and Frick (1986), this model was developed for ion-aerosol attachment, but it can be used to compute the recombination coefficient, if we use an aerosol that is as small as the ion and with opposite charge. The model accounts for Brownian motion, Coulombic interaction, image charging, polarization of the molecules and three-body trapping.

The third model, by Brasseur and Chatel (1983), is a parametrization used for describing the ions in the stratosphere based on earlier work by Bates (1982) and Smith and Adams (1982) that has the expression

$$\alpha(cm^3s^{-1}) = 6\times10^{-8}\sqrt{300/T} + 6\times10^{-26}[M_{air}](300/T)^4, \tag{7}$$

where $[M_{air}]$ is the concentration of air molecules in cm^{-3}.

4 Results and discussion

The ion-ion recombination was measured in the CLOUD chamber at different temperatures, relative humidities and concentrations of ozone and sulfur dioxide. We obtained a value of $2.3 \pm 0.7 \times10^{-6}\mathrm{cm}^3\mathrm{s}^{-1}$, at 298 K and RH = 40%, higher than the constant value of $1.6\times10^{-6}\mathrm{cm}^3\mathrm{s}^{-1}$ usually reported in the literature (Laakso et al., 2004). Interestingly, we found that α depends on both temperature and relative humidity (Table 2 and 1). Figure 5 shows the results of four sets of experiments, where the ion concentration was measured as a function of q. For each set of experiments, we kept all the parameters constant except the one under investigation: the concentration of ozone ($200 - 700$ ppb), sulfur dioxide ($0 - 50$ ppb), temperature (218, 248, 278 and 293 K) and relative humidity (0, 7, 40 and 70%). The measured recombination rate showed a strong dependency (about a factor of 5 change) on temperature and relative humidity and, to some extent (a factor of 2), on the concentration of sulfur dioxide. The variability in the ozone concentration appeared to have little influence, if any, on the measured recombination rate.

The retrieved loss rate for ions ($8.3\times10^{-3}\mathrm{s}^{-1}$, Fig. 6), differs markedly from the linear loss rate retrieved for the sulfuric acid neutral monomer ($1.7\times10^{-3}\mathrm{s}^{-1}$, Almeida et al., 2013). This difference between the loss rates might be partially explained by the image charge effect of the ions with the chamber walls, even though this remains a controversial topic (McMurry and Rader, 1985; Mayya and Sapra, 2002; Vauge, 2002; Chang et al., 2012). Losses might be due to some non-ideal behavior, e.g., retention of surface charge, of some insulator in the clearing field cage region or in proximity to the mixing fans. Yet another possibility is that the mixing in the chamber influences the ion concentrations, creating a higher linear loss rate. Finally, it is possible that sulfuric acid is not lost to the walls with unit efficiency.

4.1 Temperature and relative humidity dependency of the recombination rate

The strongest effect we observed was an increase in the ion-ion recombination coefficient with decreasing temperature (Fig 5). The ion-ion recombination coefficient ~~increased approximately by a factor of 5 (from 11.0×10^{-6} to 2.5×10^{-6} $cm^3\ s^{-1}$)~~ increased by approximately a factor of 4 (from 2.3 to 9.9 $\times10^{-6}$ $cm^3\ s^{-1}$) as temperature decreased from 293 to 218 K. This behavior seems not to be predicted by two of the three models and only partially by the third model, as shown in Figure 7. Interestingly, all the models agree with each other and with the experimental results over a range of temperatures from 273 to 298 K, but there are big discrepancies in the absolute values as well as in the functional form of the temperature dependency at temperatures below 273 K. The model that seems to agree best with our data is the one by Brasseur and Chatel (1983), linked more directly to atmospheric data. The model by López-Yglesias and Flagan (2013) that accounts accurately for all the possible physical processes does not agree with our data. Another option could be related to the evaporation of ions in the line. If the number of ions reaching the instrument was lower because of the losses for evaporation, the resulting recombination would be overestimated. The effect of the mixing fan and the chemical composition of the ions could vary with temperature, which would affect the recombination coefficient.

We observed a strong dependency of the recombination coefficient on relative humidity (RH). The ion-ion recombination coefficient decreases with decreasing RH from 9.4 $\times10^{-6}$ to 2.0 $\times10^{-6}$ $cm^3\ s^{-1}$ as RH drops from 70% to 0%, at a constant temperature of 298 K (Figure 8). The decrease of the ion-ion recombination coefficient at increasing RH values could be related to an increase in size of the small ions: higher values of RH would form larger hydrated ions that would be less mobile, thus decreasing the recombination rate. The change in ion mobility is plausible, as we know that aerosol particles with a diameter larger than 10 nm tend to be hygroscopic, changing their diameter according to the RH (Onasch et al., 1999; Keskinen et al., 2013). We also know, from quantum chemistry calculations, that ions form clusters with water and that the amount of water attached is dependent on RH (Kurtén et al., 2007; Husar et al., 2012; Henschel et al., 2014; Olenius et al., 2014). This explanation matches the observed data qualitatively. In fact, according to quantum calculations shown in Kurtén et al. (2007) for sulfuric acid ions at 20% RH there are mostly 1 or 2 molecules of water in the cluster, whereas at 80% RH there are 3 or 4. We get the equation below if we assume that the ions in the chamber: 1) are mainly sulfuric acid molecules, or behave the same way as sulfuric acid molecules, 2) are perfect spheres, and 3) that their mass is the sum of the masses of the molecules that compose the ions.

$$D_p = \sqrt[3]{\frac{6 \cdot (M_{H_2SO_4} + M_{H_2O} \cdot n_w)}{\pi \rho}} + 0.3nm \tag{8}$$

with

$$\rho = \rho(n_w) = \frac{M_{H_2SO_4} \cdot \rho_{H_2SO_4} + M_{H_2O} \cdot \rho_{H_2O} \cdot n_w}{M_{H_2SO_4} + n_w \cdot M_{H_2SO_4}} \tag{9}$$

Where D_p is the mobility diameter of the ions, $M_{H_2SO_4}$ and M_{H_2O} are the masses in Da of a sulfuric acid molecule and of a water molecule, respectively, n_w is the number of water molecules in a cluster and 0.3 nm is the difference between mobility diameter and mass diameter (Mäkelä et al., 1996; Ku and de la Mora, 2009). This calculation gives a D_p of 0.91 - 0.94 nm at 20% RH and of 0.94 - 1.01 nm at 80% RH. Unfortunately, the effect of RH on the ion diameter could not be observed directly, because this change in diameter is too small to be detected by the NAIS, given its low size resolution (Mirme and Mirme, 2013). However, the RH dependency of the recombination coefficient as a change in ion mobility is unclear, and cannot be predicted satisfactorily by any of the models found in the literature. Only the model described in Gardner (1938) predicts an increase of the recombination coefficient for smaller ions, although it underestimates the absolute values.

4.2 Atmospheric implications

It is important to account for the ion-ion recombination when modelling ion concentrations. As described by equation (1), the term representing the ion-ion recombination is always present and becomes dominant for large ion production rates and when coagulation sinks are small, e.g. in the free troposphere (Volland, 1995).

The possibility of a strong dependency of the ion-ion recombination rate on temperature must be taken into account when interpreting and modelling data of ion concentration or ion production in environments or model domains with a large temperature variability. In fact, a change in temperature from -54 ^{o}C to 20 ^{o}C, a typical temperature change from the free troposphere down to the boundary layer, can cause a change in the recombination rate as high as one order of magnitude.

The RH seems to influence the rate of recombination as well, by decreasing the mobility of ions. In this study, the measurements at different RH were taken at constant temperature and, therefore, changes in RH reflect those in the absolute water vapor concentration. The lower the RH, the faster the ion loss via recombination was. This might be analogous to what happens at high altitudes, where water molecules are scarce.

It should be noted that, in the present study, the pressure was kept constant at +5 mbar above the atmospheric level, during the experiments. In the atmosphere, however, a decrease in temperature with increasing altitude is associated with a decrease in pressure as well. In the CLOUD chamber it is not possible to lower the pressure below typical sea level values, as the chamber is not designed to withstand under-pressure with respect to the outside pressure. So it was not possible to experimentally measure the variation of the ion-ion recombination rate at pressures lower than 900 hPa. It has been shown, however, that the ion-to-particle coefficients are considerably different in ambient conditions at 20 km altitude than at ground level, with the recombination coefficient being an order of magnitude lower at 20 km altitude than at ground level López-Yglesias and Flagan (2013). When moving from ground level to 20 km altitude, the decrease in recombination coefficient due to decrease in pressure is only partly counterbalanced by the increase in recombination coefficient due to decrease in temperature. Consequently, the pressure effect on recombination coefficient needs to be taken into account when interpreting data measured at substantially different pressure than in this work, but investigating the pressure effect is beyond the scope of this study.

5 Conclusions

We carried out an experimental determination of the ion-ion recombination coefficient in the CLOUD chamber at CERN. The retrieved recombination coefficient at 20 ^{o}C and 40% RH agrees with the literature values and with the models. We see no clear dependency of the ion-ion recombination rate coefficient for different ozone concentrations and only a weak variation at varying sulfur dioxide concentrations. Instead, we notice a strong dependency of the ion-ion recombination coefficient on temperature and relative humidity that has not been reported in previous studies. The ion-ion recombination coefficient varied between 9.7×10^{-6} and 2.3×10^{-6} cm^3 s^{-1} over the temperature range 220 to 293 K and between 9.3×10^{-6} and 1.5×10^{-6} cm^3 s^{-1} over the range of relative humidities from 0 % to 70 %. The temperature dependency is not well described by any of the models found in the literature, only the model by Brasseur and Chatel (1983) seems to give results following the temperature dependence of our experimental data within 50% uncertainty. The RH dependency of the ion-ion recombination coefficient is not well understood or described theoretically, but can be interpreted as an effect of ion hydration: ions clustering with water molecules decreases their mobility, and therefore they recombine at a lower rate. Only the model by Gardner (1938) shows a functional dependency that supports this explanation, but it fails in reproducing the absolute values. It is also important to note that our results for the RH dependence of the ion-ion recombination coefficient were studied for only one temperature, 20 ^{o}C, and that the extent of the dependency might be different at different temperatures.

~~This was the first study to investigating experimentally the ion-ion recombination at atmospheric conditions.~~ This was the first study to investigate experimentally the ion-ion recombination in a highly controlled environment at atmospheric relevant temperature, humidity and trace gas concentrations. Our main finding was that the recombination coefficient depends strongly on temperature and relative humidity, quantities that have a large variability in the troposphere. This work can be considered as a starting point for future studies in which pressure, chamber inhomogeneities and ion chemical composition could be taken into account.

Appendix A

Solution of the balance equation

$$\frac{dn}{dt} = Q - \alpha n^2 - \beta n. \tag{1A}$$

The right hand term of Eq.(1A) is a second degree equation, therefore

$$\frac{dn}{dt} = -\alpha(n-n_1)(n-n_2), \tag{2A}$$

where:

$$n_1 = \frac{-\beta + \sqrt{\beta^2 + 4\alpha Q}}{2\alpha}$$

and

$$n_2 = \frac{-\beta - \sqrt{\beta^2 + 4\alpha Q}}{2\alpha}$$

are the solutions. Using the method of separation of variables (2A) becomes:

$$\frac{dn}{(n-n_1)(n-n_2)} = -\alpha dt \tag{3A}$$

Integrating, (3A) can be written as

$$\int_{n_0}^{n}\left(\frac{A}{n-n_1}+\frac{B}{n-n_2}\right)dn=\int_{0}^{t}-\alpha dt \tag{4A}$$

where n_0 is the ion concentration at $t=0$ and $A(n-n_2)+B(n-n_1)=1$. $A(n-n_2)+B(n-n_1)=1$ can be written as $n(A+B)-(An_2+Bn_1)=1$ and its solution is:

$$A=-B=\frac{1}{(n_1-n_2)}=\frac{\alpha}{\sqrt{\beta^2+4\alpha Q}}$$

As

By solving (4A) we obtain:

$$A\ln\left(\frac{|n-n_1|}{|n_0-n_1|}\right)-A\ln\left(\frac{|n-n_2|}{|n_0-n_2|}\right)=-\alpha t$$

We can drop the absolute value because these values are always greater than zero:

$$A\ln\left(\frac{n-n_1}{n_0-n_1}\right)-A\ln\left(\frac{n-n_2}{n_0-n_2}\right)=-\alpha t$$

$$A\ln\left\{\frac{(n-n_1)(n_0-n_2)}{(n-n_2)(n_0-n_1)}\right\}=-\alpha t$$

$$\frac{(n-n_1)}{(n-n_2)}=\frac{(n_0-n_1)}{(n_0-n_2)}\exp\left(-\sqrt{\beta^2+4\alpha Q}t\right)$$

from this we can solve $n(t)$:

$$n(t)=\frac{(n_0-n_2)n_1-n_2(n_0-n_1)\exp(-t\sqrt{\beta^2+4\alpha Q})}{(n_0-n_2)-(n_0-n_1)\exp(-t\sqrt{\beta^2+4\alpha Q})} \tag{5A}$$

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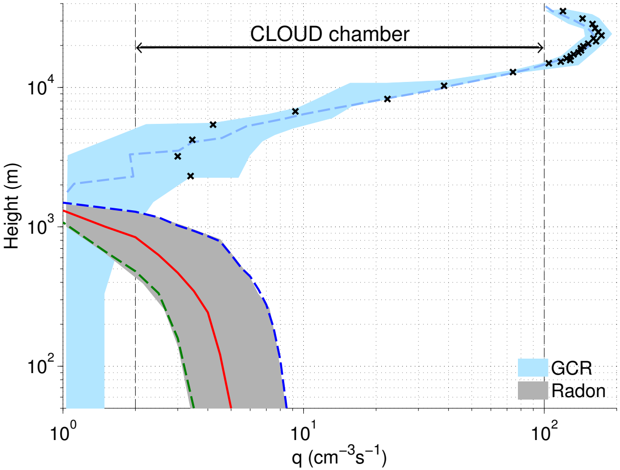

Fig. 1. A vertical profile of the ion production rate q based on literature data. The contribution of radon decay at mid latitudes is shown in gray, accounting for seasonal variation. The minimum is in summer and the maximum is in winter (Zhang et al., 2011). The contribution of galactic cosmic rays at mid latitudes, as presented by Usoskin et al. (2004), is shown in cyan. Black crosses indicate measurements by Harrison et al. (2014). The double arrow at the top shows the range of q explored in this study.

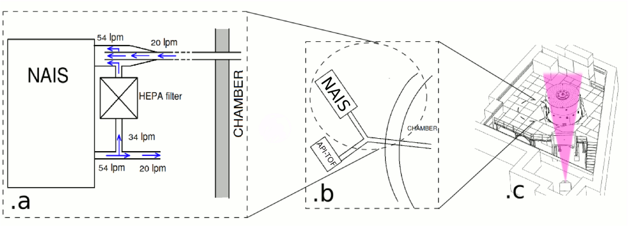

Fig. 2. a) Neutral cluster and Air Ion Spectrometer (NAIS) and its dilution system used during the CLOUD experiments. The sample air flow is withdrawn from the chamber at a flow rate that varies between 20 and 30 L min^{-1} sample air from the chamber is diluted with a portion of the exhaust air of the instrument, which is filtered with a High Efficiency Particulate Air (HEPA) filter and mixed with the sample air. b) Configuration of the NAIS during the CLOUD experiments. c) Sketch of the chamber and the beam. The dashed circle represents the area where the NAIS was located, outside from the beam trajectory. The beam is deliberately defocused to maximize the volume in the chamber where ionization takes place.

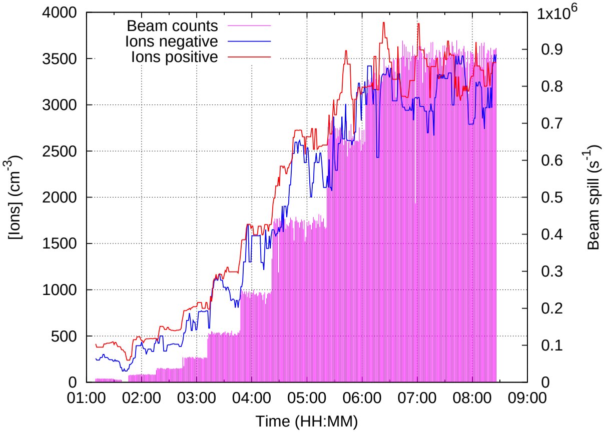

Fig. 3. In a typical experiment, the beam intensity is varied, changing the flux of pions crossing the chamber. The beam intensity is directly proportional to the Ion Production Rate (IPR) and is kept constant for a period of approximately 30 min at each step, to make sure that the ion concentration reaches the steady state. The mean ion concentration is related to the mean IPR at steady state via the balance equation (Eq.1). Blue and red colors correspond to negative and positive ions, respectively. Magenta is the beam intensity.

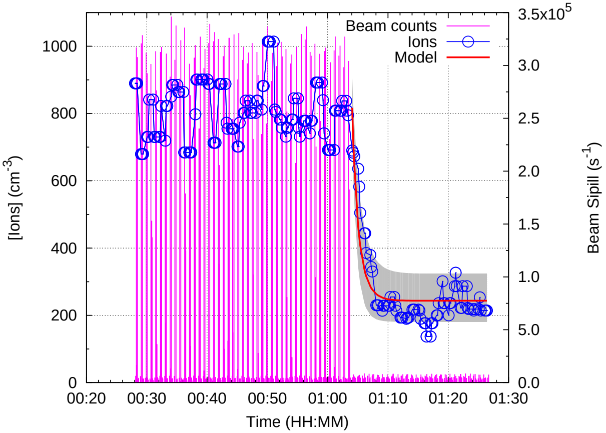

Fig. 4. Typical ion decay experiment. The ion concentration (blue line and circles), the solution to Eq. (1) (red line) and the beam counts (magenta line) The ion concentration is presented as the average between the concentration of negative and positive ions. When solving Eq. (1), the recombination coefficient and linear loss term, retrieved independently by fitting the steady state balance equation at the same conditions (T = 293 K, RH = 0 %), were 9.3×10^{-6} cm^{3}s^{-1} and 8.3e-3 s^{-1}, respectively, and the ion production rate was 8.3 cm^{-3}s^{-1}. The initial concentration of small ions, n_0 (t=01:03), was 810 cm^{-3} (average over time range from 00:24 to 01:03). The grey shaded area is the model uncertainty assuming uncertainty of ± 30 % on n0, α and β.

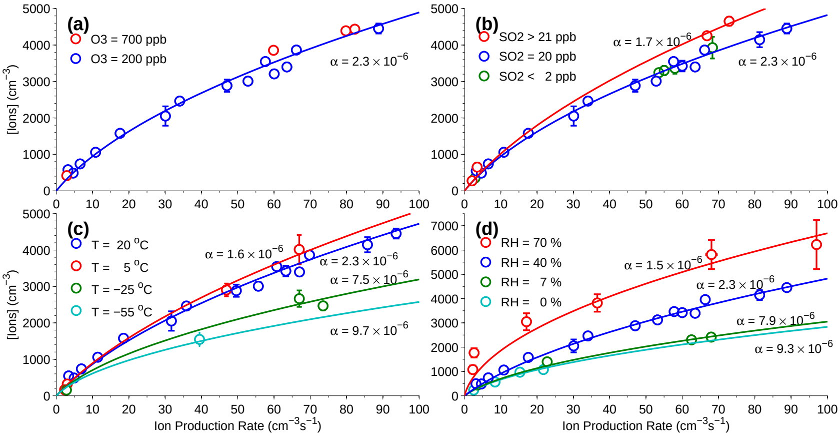

Fig. 5. Ion concentration as a function of ion production rate at (a) two different ozone concentrations (at 200 ppb and at 700 ppb); the other variables were kept constant (T = 20 °C, RH = 40% and [SO_2] = 20 ppb); (b) different SO_2 concentrations between 2 and 30 ppb, temperature, RH and ozone concentration were kept constant (T = 20 °C, RH = 40% and [SO_2] = 20 ppb); (c) different temperatures (20, 5, -25 and -55 °C); and (d) different relative humidities (0, 7, 40 and 70 %) at a constant temperature of 20 °C. The ion concentration is presented as the average between the concentration of negative and positive ions, the uncertainty is calculated as the standard deviation of the mean values at steady state.

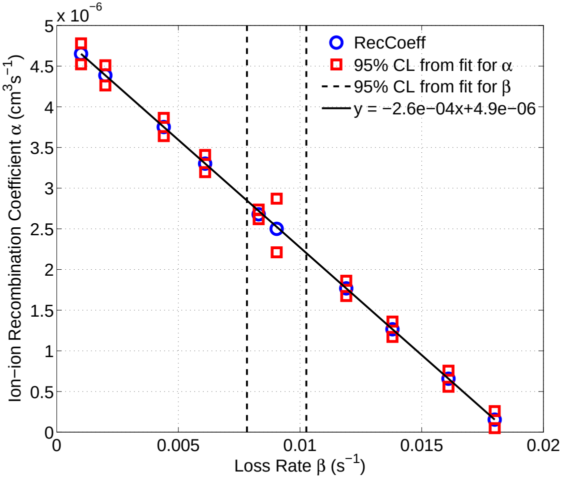

Fig. 6. Variability of the retrieved recombination rate as a function of loss rate. The dataset used here includes experiments performed at T = 20 °C and RH = 40 %. The point at the center presents the larger confidence level interval as the loss term was kept as free parameter. The other points were obtained forcing the loss term β to values varying from 1×10^{-3} to 0.18 s^{-1}.

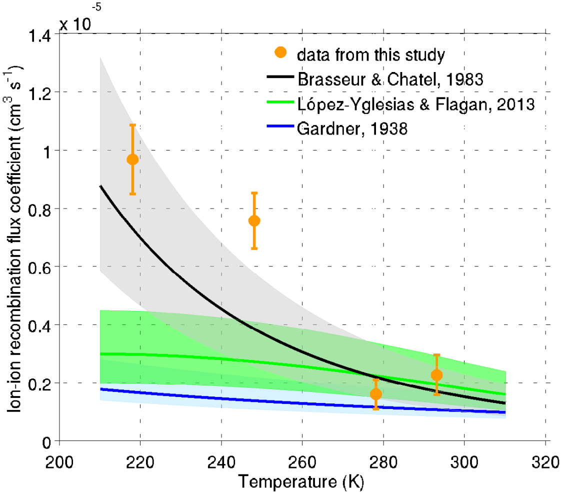

Fig. 7. A comparison between the ion-ion recombination coefficient, measured at different temperatures (points with error bars) and the recombination coefficient modelled using different models. The shaded area represents 50% uncertainty.

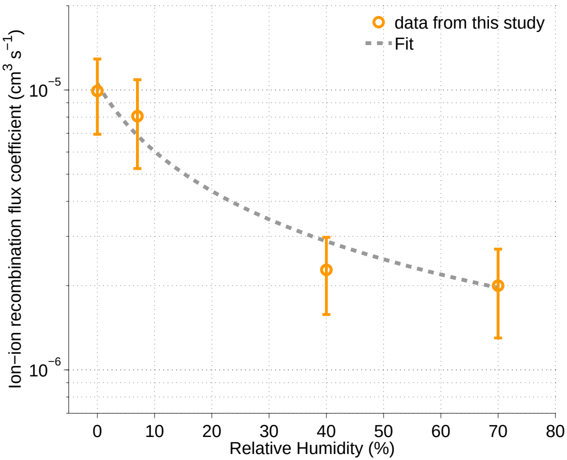

Fig. 8. The ion-ion recombination coefficient measured at different relative humidities, at a constant temperature of 20 °C. The dots are measured points, the dashed line is an exponential fit to guide the eye.

T (°C)	α x10^{-6} (cm^{3}s^{-1})	σ_αx10^{-6} (cm^{3}s^{-1})
20	2.3	0.7
5	1.6	0.6
-25	7.6	1.0
-55	9.7	1.2

Table 1. Values of recombination coefficient and its uncertainty at different temperatures. The uncertainty reported is calculated with error propagation and includes the uncertainty in the fit.

RH (%)	α x10^{-6} (cm^{3}s^{-1})	σ_αx10^{-6} (cm^{3}s^{-1})
70	2.0	0.7
40	2.3	0.7
7	8.1	2.8
0	9.9	3.0

Table 2. Values of recombination coefficient and its uncertainty at different relative humidities. The uncertainty reported is calculated with error propagation and includes the uncertainty in the fit.