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

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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 $(2.3\pm 0.7)\times 10^{-6}$ $cm^3\ s^{-1}$.

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)."

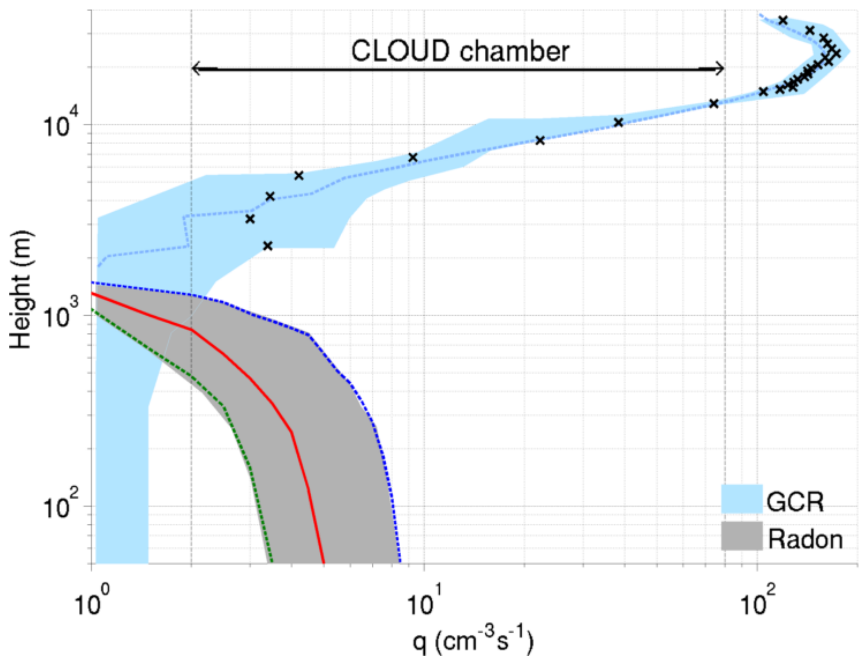

Fig. 1. A vertical profile of the ion production rate *q*, based on literature data. The contribution of radon decay at mid latitudes is shown in gray, accounting for seasonal variation. The minimum is in summer and the maximum is in winter (Zhang et al., 2011). The contribution of galactic cosmic rays 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 $(8.3 \pm 1.6) \times 10^{-3}$ s , the value retrieved from the dataset with the best statistics (Fig. 5).

Proposed change:

The linear loss term **β, equal to $(8.3 \pm 1.6) \times 10^{-3}$ 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.

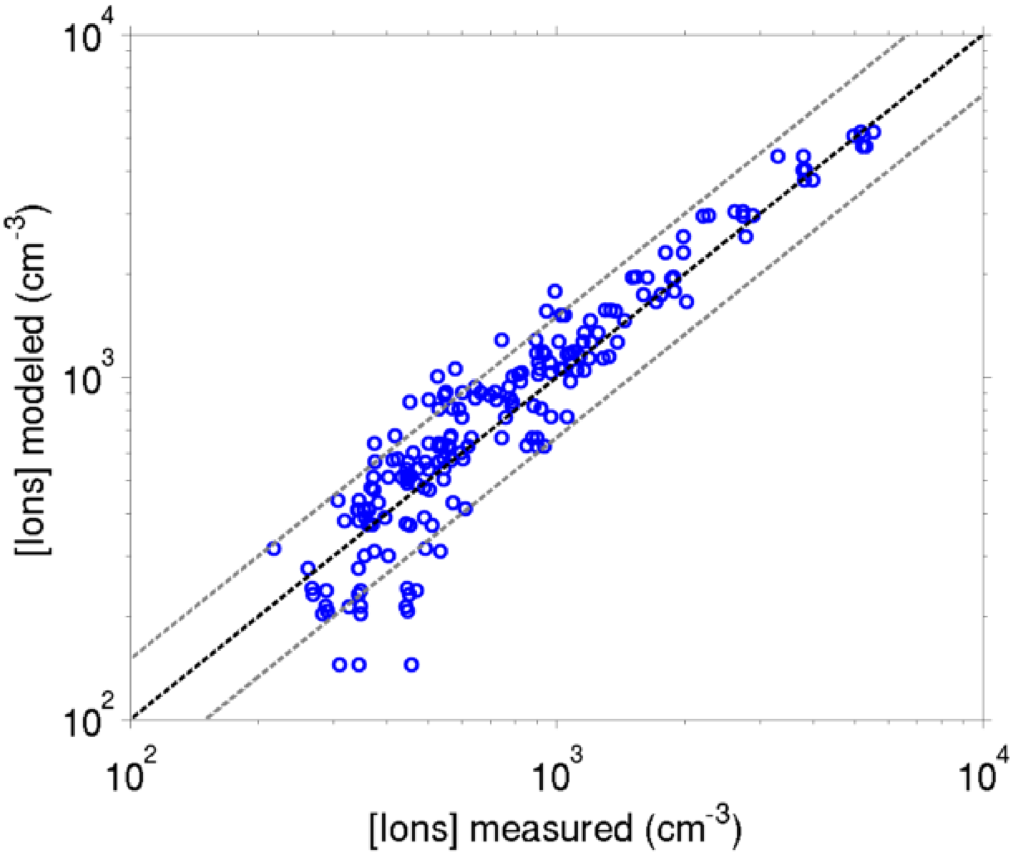

Figure 2. Comparison between the measured and modeled ion concentration during the 12 decay experiments (similar to Fig. 3 in the manuscript). The black line is the 1:1 line, the gray lines are +/-50% from the 1:1 line.

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.**"