# Authors’ response to reviewers’ feedback on “Measurement of the rate coefficients between atmospheric ions and multiply charged aerosol particles in the CERN CLOUD chamber”

We thank the two anonymous reviewers for their time and effort engaging with our manuscript and providing us with valuable feedback. We edited our manuscript to address their feedback; below we respond in blue to their reviews in black.

## Reviewer #1

This manuscript investigates the rate coefficients between ions and multiply charged aerosols. Although the particles containing up to 9 elementary charges are not very representative for atmospheric aerosols, the results shown here can still provide further understanding about the theory of collision between ions and charged particles. This study finds that the rate coefficient can be increased by about 15 times when the charge of the particles is increased from 1 to 9 elementary charges. This is very interesting. The multiply charged particles have higher rates to collide with ions and therefore may lead to further changes in particle growth and evolution. However, the discussion about Fig. 3 and Fig. 4 is too general right now. More details need to be provided and the underlying processes need to be explained. The manuscript is well written in most parts, but some parts of the manuscript need to be rewritten. The following issues need to be taken care of:

> We thank the reviewer for the valuable and constructive feedback.

Major issues:

1. There are particles with sizes of 10-40 nm for the steady state as seen in the particle size distribution in Fig. 3a. But this is not seen in multiply charged particles. Please explain why the particles can grow to this size range in the steady state. I suppose the four experiments used the same kind of particles. It is not very straight forward to understand why the multiply charged particles do not have sizes of 10-40 nm while the steady state experiments do.

It is seen in Fig. 3a that the first experiment with multiply charged particles have larger sizes. The modal size is about 7-8 nm. But the other three experiments have modal sizes of 5 nm. I’m not sure if this is just due to experiment uncertainty or there are some other reasons for this.

> All experiments were conducted under the same exact conditions (and using the same exact materials) except for turning on the X-Ray source in the steady-state cases to bring about the charge steady state. The difference between the first experiment (7–8 nm) and the other experiments (5 nm) are likely due to experiment uncertainty as the reviewer points out. We note that the fourth experiment has slightly elevated modal size compared to the third, but less than the first.
>
> The reviewer is correct in pointing out the growth above 10 nm in the steady-state cases. We first note that the particles above 10 nm number significantly less than those under 10

nm (by more than order of magnitude). As we point out in the manuscript, we postulate that these particles are largely a result of instrumental uncertainty in the nSMPS measurements. Additionally, we included all these uncertainties to our error estimation calculation. As discussed and shown in the SI, we allow the nSMPS measurements to vary by 400% to estimate the sensitivity of the calculated coefficients on those uncertainties. We also note that we expect the X-Ray source to be less than 100% efficient at eliminating multiply charged particles (for example, see how the ion ratio panel c is not unity). We thus think the nSMPS conversion algorithm assumes these are singly charged particles and compensate for this erroneous assumption by counting them as bigger particles.

We add the following sentence around after line 365 (in the original manuscript): "The latter assumption is further justified by the presence of the seemingly larger particles in the steady-state cases; the nSMPS inversion algorithm assumes at most singly charged particles after passing the particles through the nSMPS's neutralizer, and compensates for this seemingly erroneous assumption by counting multiply charged particles as larger particles."

2. I think the results would be more complete if the collision rate coefficient between ions and neutral particles can be provided in this study. This means that in Fig. 4, a new data point is added for number of charges = 0. As said in the manuscript, the negatively charged particles are produced through the ion collection of neutral particles, which are approximately 98% in both experiments. Adding this data point may be very relevant to the atmosphere. It is mentioned in the Introduction of this manuscript that previous studies have considered collisions between particles or molecules when only one is charged. This paper focuses on the collision rates between ions and charged particles. Collision rates between ions and neutral particles in this study would make a very nice connection between previous studies and this study. Fig. 4 already shows a nice picture that collision rate increases as number of charge increases. With the new data point, we would see how the collision rate changes when number of charge changes from 0 to 1. Is the rate increased significantly? And how different is the new data point when compared with previous studies?

To obtain the rate coefficient between ions and neutral particles, an equation for the production of negative charged particles due to the collision between ions and neutral particles can be written out similar to Equation (6), but with only one production term. As the concentrations of ions, negatively charged particles and the neutral particles can all be measured, then the collision rate can be estimated. (Number concentration of neutral particles can be obtained using the number concentration of total particles measured with CPC subtracting the number concentration of charged particles.)

We fully agree with the reviewer about this addition leading to a more complete description, but we believe it is outside the scope of this manuscript. Firstly, the collision rates between neutral and charged entities was investigated by He et al. (2021) in the CLOUD chamber. Secondly, our design will likely yield highly uncertain results for any measurements that rely strongly on neutral entities. See our first response about the uncertainty in the nSMPS measurements, which is our main instrument for the neutral particles. Our innovative approach here relies on the NAIS measurements (charged entities) which are more robust to determine the collision rates between charged entities.

He, X.-C., et al.: Determination of the collision rate coefficient between charged iodic acid clusters and iodic acid using the appearance time method, Aerosol Science and Technology, 55, 231–242, https://doi.org/10.1080/02786826.2020.1839013, 2021.

3. It is good that the supplement of this study includes detailed uncertainty estimation of the calculated rate coefficients. However, how would the experimental setup parameters affect the rate coefficients is not discussed. These parameters include temperature, humidity, concentration of gas phase sulfuric acid, and even the flow rates. How sensitive are the collision rates to these parameters? When the humidity or trace gas concentration is changed, would the rate coefficient be changed? I think at least some discussion should be provided in the manuscript. In Line 129, it is only said that the experiments are performed under atmospheric conditions. The exact temperature range, humidity range, and concentration range of trace gases should be summarized in the paper.

We carefully list the experimental conditions in Section 2.1.1 (Lines 140-142).

We further strongly agree with the reviewer's suggestion, and we have plans to conduct these experiments in the near future. Unfortunately, we have not yet conducted any experiments. We do think that these collision coefficients will depend on environmental and experimental conditions and that will offer further insight about their significance to atmospheric conditions.

We added a short outlook to our discussion (line 435 following):

"Furthermore, the comparison with the results by Tamadate et al. (2020b) shows that future studies will need to focus on the dependency of parameters kept constant in this study, for example, relative humidity, chemical composition, and turbulence."

4. The number concentration of positively and negatively charged particles are shown in Fig. 3b and 3c. Is it possible to plot number concentrations of particles with 1, 2, 3, … ,and 9 charges respectively in Fig. 3? Or at least plot the charge status that has the highest number concentration. If more particles have smaller number of charges, then the results in this study may be more relevant to the real atmosphere. But if more particles have larger number of charges, then the result does not have a direct application to the atmosphere but is still useful for understanding the collision theory.

We add the following figure to the SI. We note this includes only the positive particles, measured by NAIS (i.e., the fraction of charges 1–9 of particles in panel d of Figure 3 in the original manuscript). Note how charges are lost as time goes by (from a to b) and how the size grows (as expected). We stress that these figures do not include neutral particles which outnumber the charged ones by far (roughly 98% are neutral overall, but can be as low as 50% at specific sizes (e.g., 8 nm below) at specific times (e.g., 0 seconds below).

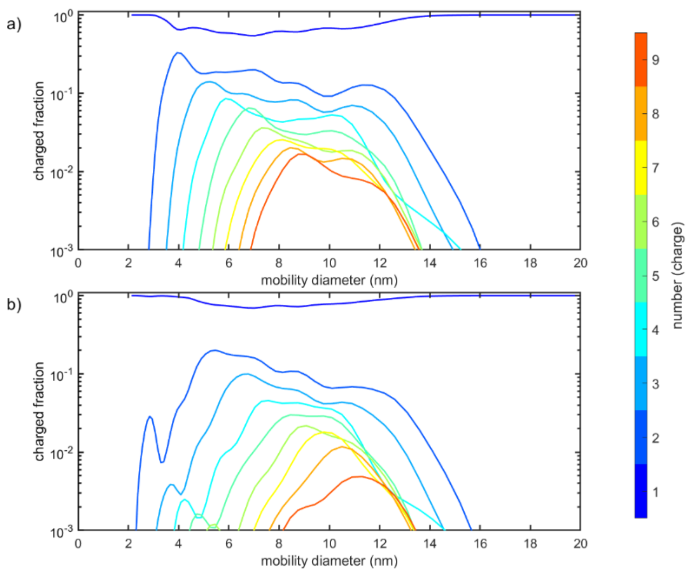



Figure 1: An example of the charge fraction of positive particles (no X-Ray) at a) 0 and b) 500 seconds.

The number concentration of ions should also be given in the paper. In the introduction, it's already said that cosmic rays can lead to an ion pair concentration of 10^3 cm-3. Just from Fig. 5d and 5e, it is not easy for the readers to obtain the ion concentration. So this concentration should be provided in the paper so that we can have an idea if it is representative of the real atmosphere. It's ok if it is not representative. But at least we should know how different the ion concentration in this experiment is from the real atmosphere.

The steady state number concentration of positive ions during all experiments (with and without X-Ray) is comparable and in the range of 1500 $cm^{-3}$ (range: 1166–1684 $cm^{-3}$). The steady state number concentration of negative ions is also reproducible and in the range of 1350 $cm^{-3}$ (range: 1017-1597 $cm^{-3}$). The lower steady state number concentration of negative ions is expected for CLOUD and also discussed in previous publications (see Franchin et al., 2015). Since small negative ions have a higher mobility compared to small positive ions, loss rates (e.g., their wall loss rate) are increased. In steady state, the ratio of positive and negative ions is comparable for both experiments, X-Ray on and X-Ray off.

We add the following two sentences after line 350 in the original manuscript: "We note that the negative and position ion distributions in panel b approach are similar to the canonical value of 1500 cm-3 often reported for ion concentrations in the atmosphere. More precisely, the concentration of positive ions averages around 1500 cm-3 while the negative ions around 1350 cm-3, agreeing with previous studies showing the concentration of negative ions is often lower (Franchin et al. 2015)."

5. The writing of section 2.1 (instrument and experiment) is not organized very well. I strongly suggest to rewrite this part.

I suggest moving all content that is instrument and experiment to section 2.1. In the current version, this content is scattered in various places in section 2.2, and also in section 3. I can understand that the authors put this content in various places in the current manuscript because they want to use this information to explain the data analysis method and results. But it is really difficult for the readers to get a complete picture about the instrument and experiment in the first place. It also does not help understanding the data analysis method and results because the mixing of instrument/experiment with data analysis or results seems to interfere the flow and logics of the paper. Below I list some places that should be revised. But the authors should read through and make sure instrument and experiment are described in 2.1.

First paragraph in 2.2.1 is not data analysis and should belong to section 2.1.

Lines 347-349: should be moved to section 2.

Lines 365-366: Observed distributions in the size distributions …should be moved to section 2.

Line 279: flow rate should be discussed in 2.1.

Line 287: flow rate should be discussed in 2.1.

Lines 132-135 and Lines 168-169: information is kind of repeated.

Section 2.1 presents many instruments. But actually only nSMPS and IAS data are used. It is not clear why other instruments are used. The manuscript also does not explain why one instrument is compared to another instrument and the results of comparison are not discussed at all.

> We apologize for the inconvenience and difficulty in reading our Section 2.1. The feedback is well taken. We have considered this carefully in our revision, and we attempted to rewrite the section as the reviewer suggested. However, we found that we were not able to improve the readability of it and thus reverted to our initial writeup. We have added a brief orienting paragraph atop Sect 2.1 to better orient the reader and emphasize that we are only covering key aspects of the experiment design, and the reader can find more details in a reference with much more details.
>
> While we primarily rely on nSMPS and NAIS data to constrain the evolution of the positively charged particles, we still make use of other data collected to constrain our operating conditions and other confounding factors. For example, we measure sulfuric acid (Figure S1) to ensure that we do not have overly high nucleation and growth and the determining factor in the time evolution of the distribution is due to the collisions between charged aerosols and ions.

Minor issues:

1. The word “collision” should appear in the title. After all, collision rate coefficient is the only rate coefficient between ions and aerosols. Collision rate coefficient is the focus of this study so it is better reflected in the title.

> Done. The title now reads: “Measurement of the collision rate coefficients between atmospheric ions and multiply charged aerosol particles in the CERN CLOUD chamber”

2. Line 38: “may influence cloud dynamics and aerosol processing”, should be changed to “may influence cloud microphysics, dynamics and aerosol processing”.

> Done. The sentence now reads: “… and so may influence cloud microphysics, dynamics, and aerosol processing.”

3. Lines 52-53: “the balance between the loss rates to preexisting particles and growth rates (due to collisions with condensable vapours)” can be changed to “the balance between growth rates due to collisions with condensable vapours and the loss rates to preexisting particles”. What about

Brownian coagulation? The new particles also go through Brownian coagulation for growth but it is not included here.

> Brownian coagulation is indeed the main mechanism for the "loss rates to preexisting particles" (unless charged), but it is often negligible compared to the other growth process (vapor condensation onto particle surface). The sentence now reads: "Consequently, the balance between growth rates due to collisions with condensable vapours and the loss rates to pre-existing particles plays a central role in determining the fraction of new particles that reach CCN sizes and influence climate…"

4. Lines 55-56: "The presence of charges also enhances the growth rate of molecular clusters and newly formed particles." Please use a couple of sentences to explain the mechanism. Presumably this is related to the growth due to condensable vapour as described in Lines 52-53?

> Yes, that is correct. The reader is directed to the references. The mechanism is mostly related to the stabilisation of young clusters mentioned in the previous line.

5. Line 133: "charged small ions": better be changed to "ions".

"in under 1 s", changed to "within 1 s"?

> Done. The sentence now reads: "… which sweeps ions from the chamber in within 1 s."

6. Line 138: "study", should be changed to "obtain", because this instrument is only used for getting particles.

> Correct. Changed to "obtain" instead of "study" in this sentence.

7. GCR in Fig. 1 is better put on the same side as charge electrospray because they both create inputs for the CLOUD chamber. While on the other side, nSMPS and AIS are both measuring the outputs of the CLOUD chamber.

> We agree. We use this updated figure now.

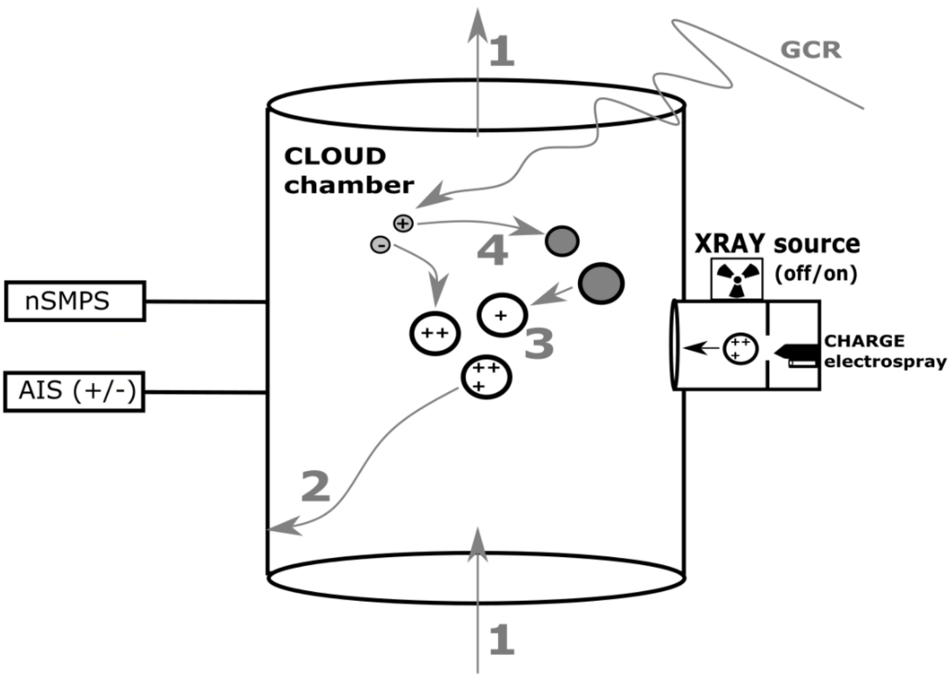


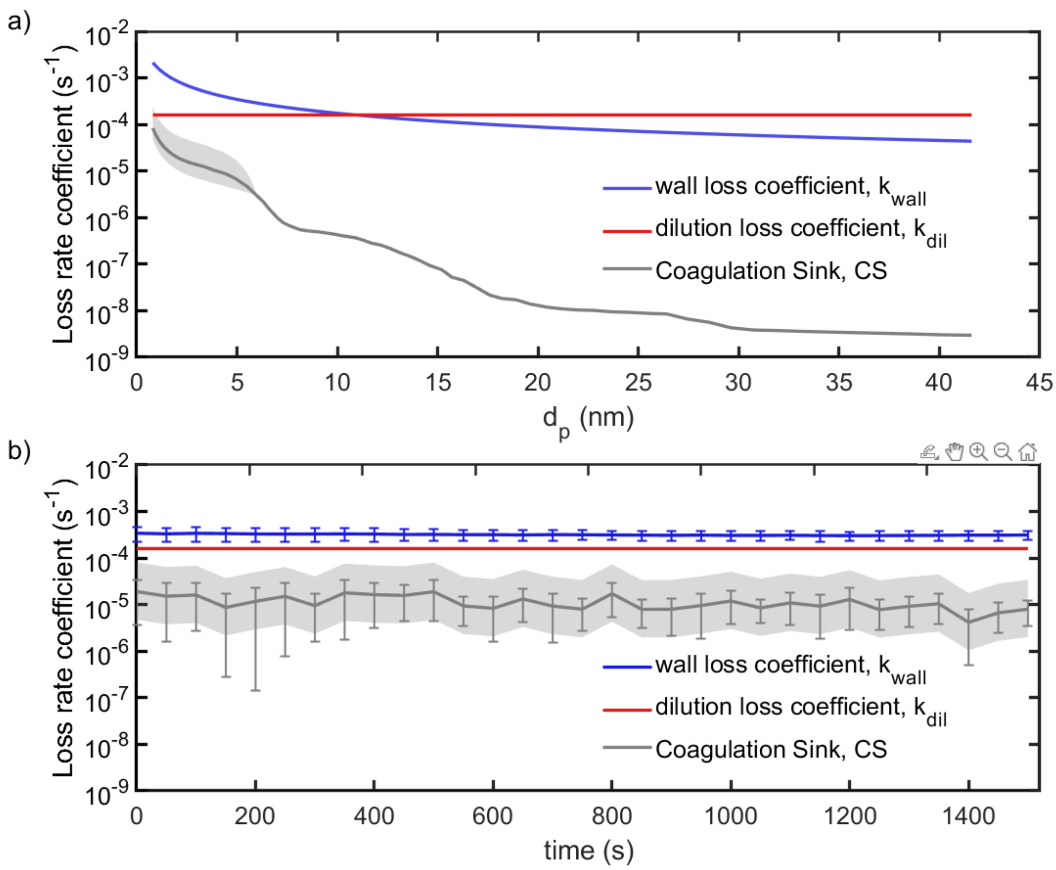
Figure 2. Replacing Figure 1 in the main text.

8. Some place uses "coagulation loss" while Fig. 1 uses "aerosol-aerosol collision loss". Please be consistent when using the terms.

Changed the one in Fig. 1 caption to say "coagulation loss" there.

9. Fig. 2: "condensation sink" should be changed to "coagulation sink".

They are changed interchangeable in the aerosol literature, but we concur with the reviewer and change it.




10. Fig. 3a, 3d, 3e: should use same scale (logarithmic) in the vertical axis. The lower limit of the vertical axis should be shown. It is not easy to compare the data in these figures right now.

Done. We now use the figure below.

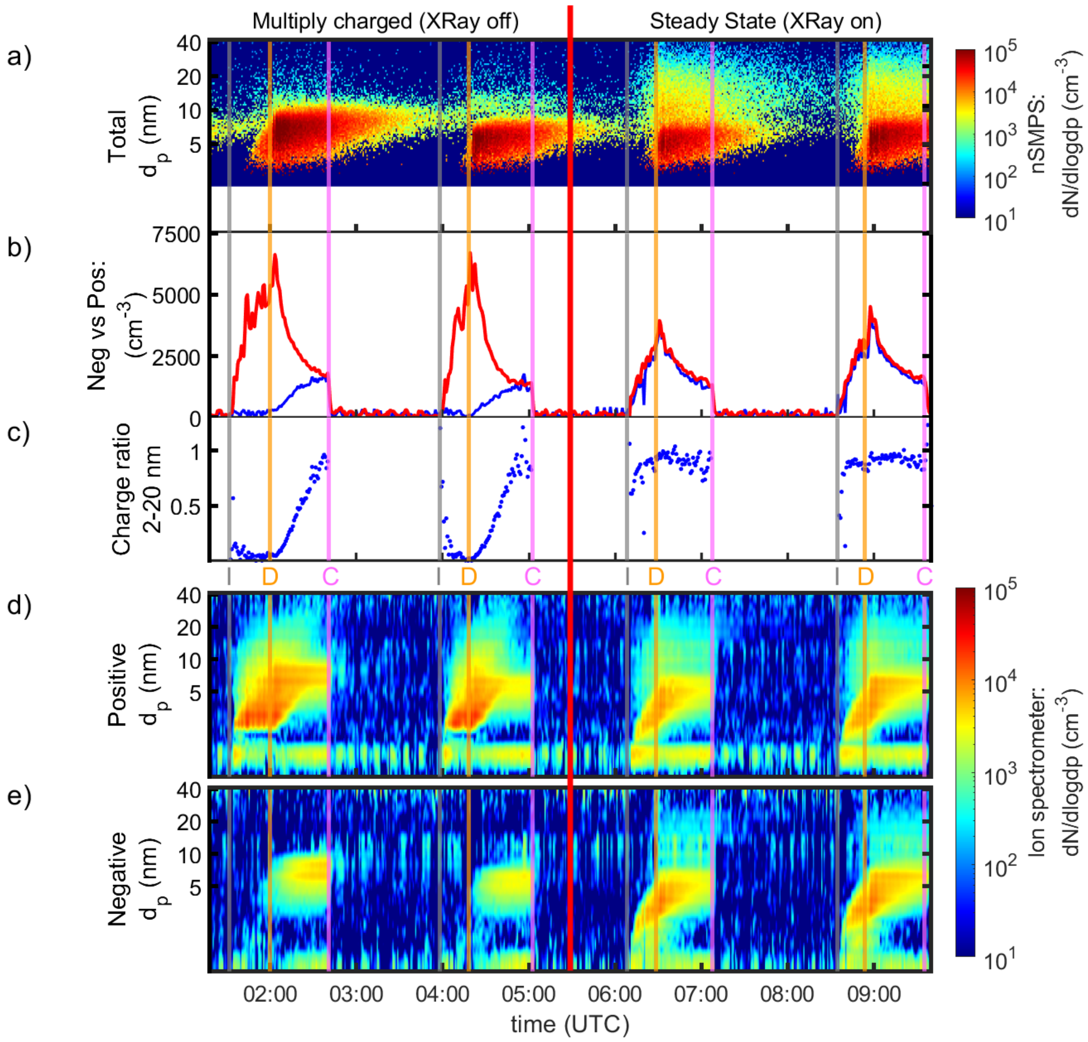



Figure 3. Replacing Figure 3 in the main text.

11. "Ion ratio" in Fig. 3c should be changed to "charge ratio", because "ion ratio" might be mistakenly referred to as gas phase ions.

Done.

12. Should be careful when saying "Total particle concentration".

Line 175: this means the sum of positively and negatively charged particles.

Line 177: this means integration of particles number over size.

Line 185: total distribution, which means the sum of positively and negatively charged particles.

There are many places using "total". Please check and make sure the meaning of it is clear.

We are following the common terminology in aerosol science. We believe our usage is in line with previous studies. When we say "total", we generally mean all polarities. Otherwise, we specify by saying "ion" or "charged" in front of concentration. We have added clarifications in the text to avoid confusion.

13. in Section 2.2.2, why is the charge status from 1 to 11? I guess it should be from 2 to 10? Because there are only 9 charge status.

> This was a typo, thank you for spotting it. We note though that we solve the equations for different charge states in the SI.

14. Line 361: Units should be consistent. Here lpm is used. But other places use L $min^{-1}$.

> Fixed.

15. Lines 407-414 can be reorganized. "we find our results deviate…" is better moved to the place before "moreover…". That is to say, discuss about the consistency between experiment and models first, and then discuss the inconsistency.

> Done. The full paragraph reads as follows: "We compare our results to recent results based on continuum–MD simulations (Tamadate et al., 2020b), which are for multiply charged PEG4600 particles with ions. Our results align well with previous models (López-Yglesias and Flagan, 2013; Gopalakrishnan and Hogan, 2012; Gatti and Kortshagen, 2008; D'yachkov et al., 2007). Additionally, our results align with all models, including the additional one by Tamadate et al. (2020b), for >5 charges where the effect of charge likely outweigh the effects of geometry. Nonetheless, we find our results deviate from those by Tamadate et al. (2020b) especially for a low number of charges (<5). This could be explained by the geometry (and thus size) of the simulated PEG4600 particles. Moreover, the flexible nature of the ions and particles in their study likely plays a central role and cannot be compared directly to our results herein."

## Reviewer #2

The manuscript "Measurement of the rate coefficients between atmospheric ions and multiply charged aerosol particles in the CERN CLOUD chamber" describes a detailed set of experiments aimed at determining the rate coefficients between negatively charged ions and positively charged aerosol particles less than 10 nm in diameter as a function of the number of elementary charges (1-9) on the aerosol particles. In general, the measured rates agree with theory albeit with deviations from some of the theoretical predictions at low aerosol particle charge numbers. Knowing these rate constants is important for understanding the growth of small aerosol particles and ultimately CCN formation. Few measurements of these rate coefficients exist. I find the manuscript to be well-organized and generally easy to follow. I appreciate the careful consideration and explanation of the uncertainty estimation for the rate coefficients. Overall, I think this work is appropriate for ACP and I recommend acceptance following attention to the minor comments below.

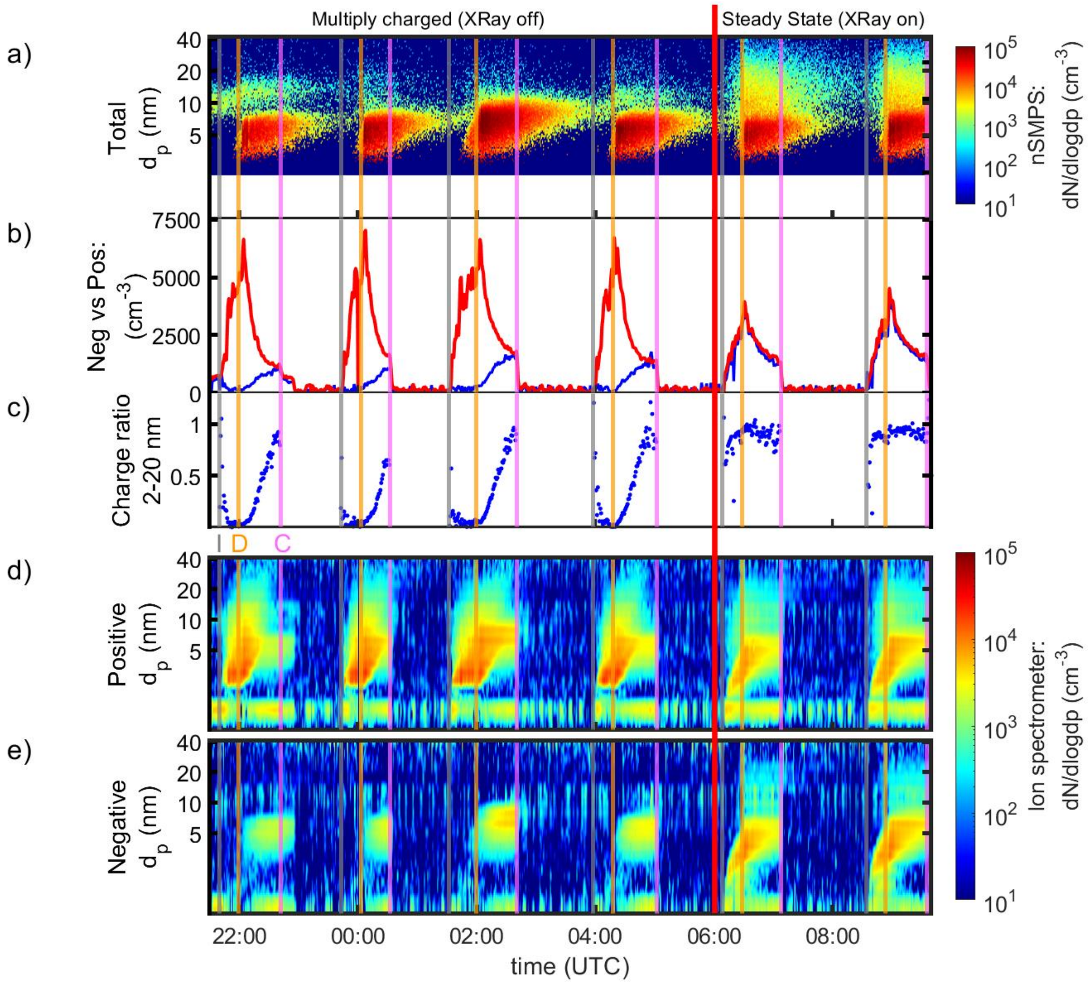
> We thank the reviewer for the valuable and constructive feedback.

## Minor Comments

Figure 3: If only four experiments were performed without X-ray, why not just show the results of all four? Adding the remaining 2 to the SI would be appropriate.

> We have added the remaining 2 to the SI (and can be seen below). Note that we conduct an additional fit to show that the removing one of the experiments (e.g., the second one in the

new figure below where the experiment ends before reaching steady state) has minimal effect on the results.



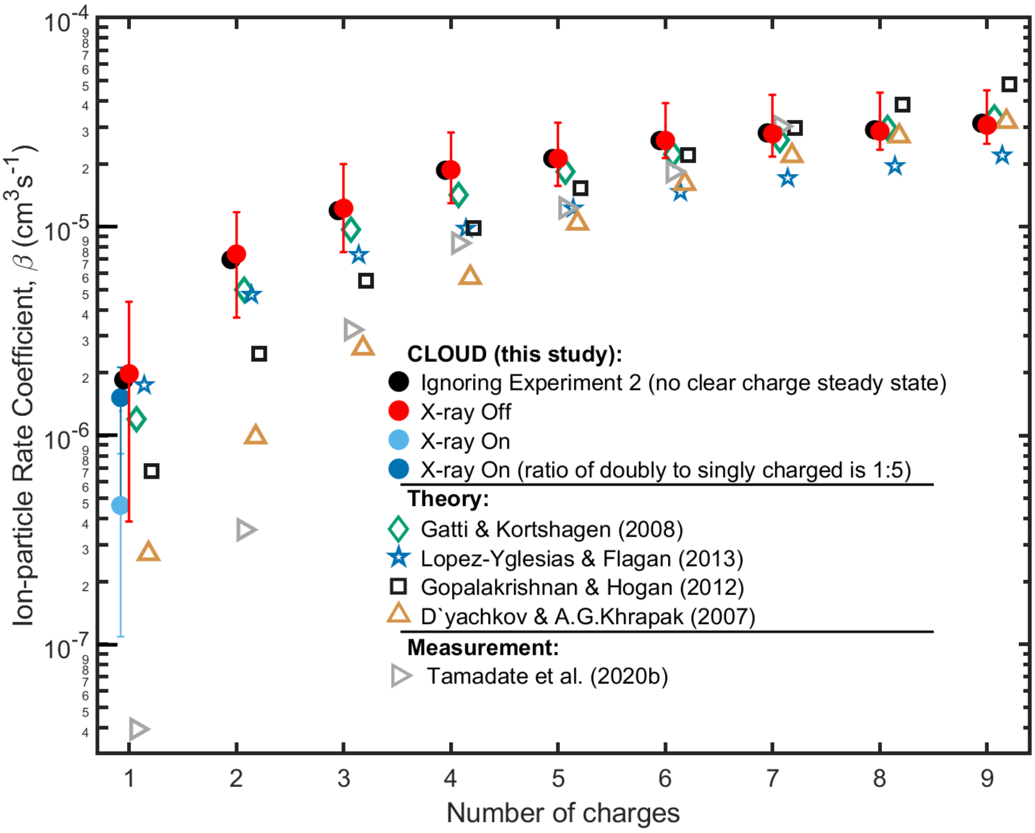



Figure 3: A short explanation of why nSMPS measurements in the X-ray on experiments exhibit a tail towards larger diameters that is absent in the X-ray off experiments is warranted. Does this tail have any impact on deriving the ion-particle rate coefficient for the singly charged aerosols (i.e., blue points in Figure 4).

We have addressed this in our response to the first review and corrected it in the manuscript. We repeat our response here for convenience.

All experiments were conducted under the same exact conditions (and using the same exact materials) except for turning on the X-Ray source in the steady-state cases to bring about the charge steady state. The difference between the first experiment (7–8 nm) and the other experiments (5 nm) are likely due to experiment uncertainty as the reviewer points out. We note that the fourth experiment has slightly elevated modal size compared to the third, but less than the first.

The reviewer is correct in pointing out the growth above 10 nm in the steady-state cases. We first note that the particles above 10 nm number significantly less than those under 10 nm (by more than order of magnitude). As we point out in the manuscript, we postulate that these particles are largely a result of instrumental uncertainty in the nSMPS measurements. Additionally, we included all these uncertainties to our error estimation calculation. As discussed and shown in the SI, we allow the nSMPS measurements to vary by 400% to estimate the sensitivity of the calculated coefficients on those uncertainties. We also note that we expect the X-Ray source to be less than 100% efficient at eliminating multiply charged particles (for example, see how the ion ratio panel c is not unity). We thus think the nSMPS conversion algorithm assumes these are singly charged particles and compensate for this erroneous assumption by counting them as bigger particles.

We add the following sentence around after line 365 (in the original manuscript): “The latter assumption is further justified by the presence of the seemingly larger particles in the steady-state cases; the nSMPS inversion algorithm assumes at most singly charged particles after passing the particles through the nSMPS’s neutralizer, and compensates for this seemingly erroneous assumption by counting multiply charged particles as larger particles.”

Results section: It would be nice to see at least one example of the number distribution of aerosols with differing numbers of elementary charges and how those distributions change over the course of the experiment. Such a figure would be appropriate in the SI and would how some of the various inputs into the equations described in the previous section were changing over the course of an experiment.

We include this in the SI. Please also note our response to the first review which we repeat here for convenience.

We add the following figure to the SI. We note this includes only the positive particles, measured by SI (i.e., the fraction of charges 1–9 of particles in panel d of Figure 3 in the original manuscript). Note the how charges are lost as time goes by (from a to b) and how the size grows (as expected). We stress that these figures do not include neutral particles which outnumber the charged ones by far (roughly 98% are neutral overall, but can be as low as 50% at specific sizes (e.g., 8 nm below) at specific times (e.g., 0 seconds below).

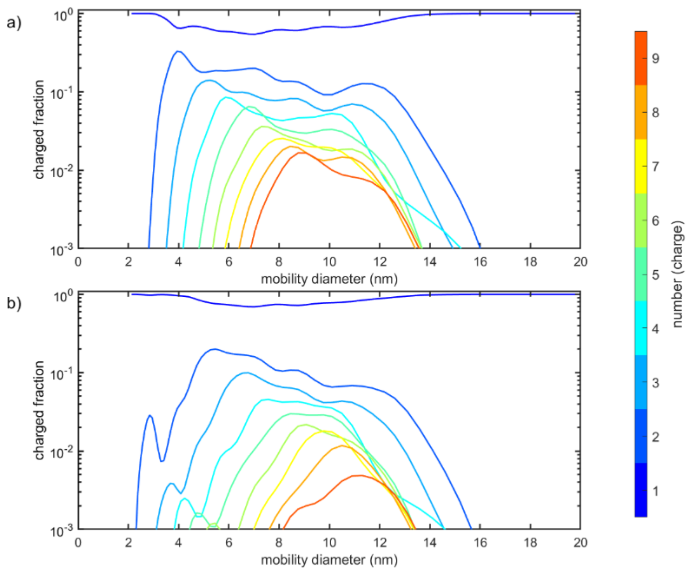



Figure 1: An example of the charge fraction of positive particles (no X-Ray) at a) 0 and b) 500 seconds.

Line 404: Why is it “remarkable” that the results most resemble the analytical model by Gatti and Kortshagen (2008)? Was there something surprising about this agreement or should the work choice “remarkably” just be reconsidered? If the former, then this should be discussed in greater detail.

We have removed the word “remarkable” to avoid confusion.

Technical

Line 173: CI-APi-TOF should be defined.

Added “Chemical Ionization–Atmospheric Pressure interface–Time Of Flight mass spectrometer” to the text.

Figure 2: I believe “Condensation Sink” should be “Coagulation Sink”

Fixed.

Line 274: repeat word “reach reaching”

Removed “reach” from this sentence.

Line 294: Suggest to clarify as ion-charged aerosol rather than just ion-aerosol (may apply elsewhere in the manuscript)

Thank you for spotting this. Corrected.

Lines 425-431: This paragraph reads more like a conclusion to me than a discussion. I suggest merging it into Section 5 (Summary). I also think that some of the implications/impacts of the work are potentially a bit overstated and the wording should perhaps be altered a bit. Since the overall conclusion is that there is general agreement between the measurements and some of the common models, how much of an impact do these results have (beyond potentially reducing uncertainty)? I do not mean to imply that these measurements are unimportant, rather, making such measurements to test theory is extremely important. However, I think as a community we tend to overstate the implications of our results sometimes.

We agree. We are often blinded by out passion for our work. We have decided to remove this entire paragraph because the summary section suffices.

SI line 39: missing a word between “we” and “that”

We add the word “note” here.