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Comment on acp-2022-805

Anonymous Referee #1

Referee comment on "Measurement of the collision rate coefficients between atmospheric ions and multiply charged aerosol particles in the CERN CLOUD chamber" by Joschka Pfeifer et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-805-RC1, 2023

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:

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.

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.)

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.

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.

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.

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.

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.

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

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?

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

“in under 1 s”, changed to “within 1 s”?

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

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.

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

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

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.

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

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.

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.

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

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.