

We would like to thank reviewer 1, Dr. Luis Ladino, for the helpful comments and suggestions. In line with the comments and suggestions, we revised the manuscript. Below are the comments (in bold) followed by the replies. The parts that are in italic are corrections that are included in the revised version of the paper:

**Major comments:**

**1. I am wondering if the authors accounted for particle losses. What was the transmission efficiency of the particles? Is it possible that the low collection efficiencies observed for particles smaller than 0.2  $\mu\text{m}$  could be due to particle losses in the glass walls, the dryers at the end of the chamber, or in the transition from the chamber to the PALMS? In the absence of droplets is the aerosol particle concentration at the entrance of the chamber and before the PALMS comparable?**

Information on particle losses was added to the paper under the experimental setup section: *Particle losses were calculated by measuring the particle concentration at the entrance and at the bottom of the chamber (i.e., before PALMS). Particle losses were  $14\pm 10\%$ .*

**2. It is mentioned in the text that the flow within the chamber is laminar. Did the authors conduct computational fluid dynamic simulations to support this? If I interpret Figure 2 correctly, the neutralizer was placed inside the chamber. Does it have any effect on the laminar flow?**

Information about the neutralizer was added to the paper under the experimental section: *A neutralizer, containing two Polonium-210 strips (0.64 cm thickness and 15 cm long), is placed in the lower part of the DGN.*

Information on laminar flow was also added to the paper under the result and discussion section: *Calculations of Reynolds number were performed using the experimental conditions and chamber geometry. Reynolds numbers from 0.12 to 0.16 were calculated and, based on this, we assume the aerosol particles and droplets interact in flow condition close to laminar throughout the chamber.*

**3. The authors indicate that the droplet size was 20  $\mu\text{m}$  and that it was measured prior to the experiments. Did you measure the droplet size inside the chamber? Did you monitor the droplet size while running the experiments? What was the droplet size used for the collection efficiency calculations? Given that the RH inside the chamber is below water saturation, droplet evaporation occurred along the chamber. Was this accounted for in the CE calculations? What was the droplet size at the bottom of the chamber?**

**4. What is the residence time of the droplets within the chamber? The authors said: “Average droplet evaporation time was calculated based on the average droplet size and the RH condition: 2.1 and 14.7 s for the Low and High RH cases, respectively”. This means that the residence time of the particles was below 2.1s? I am wondering if the 20  $\mu\text{m}$  droplets did completely evaporate during the low RH experiments (i.e. 15%).**

Information on the droplet size was added to the paper under the experimental setup section: *Due to the position of the camera, droplet size could not be monitored during an experiment or within the chamber. Droplet size was, however, measured before and after the experiment, and the size was constant within the quoted uncertainty. Droplets size during experiments was also verified by the residual size after the droplets evaporated.*

The droplets completely evaporated in both RH conditions; the evaporation was verified by measuring the AS residual sizes with the OPS and by using an evaporation model calculation. Information on droplets residence time was added to the paper under the result and discussion section: *Total droplet evaporation time (i.e., residence in the generator section and experimental chamber) was calculated based on the average droplet size and the RH condition: 2.1 and 16.6 seconds for the Low and High RH cases, respectively. The droplets residence time in the chamber was 0.7 and 6.1 seconds, for the Low and High RH cases, respectively.*

Explanation on the calculation of CE was added to the paper under the result and discussion section: *CE value was calculated for each experiment, based on the average droplet size measured from each experiment and when similar RH, aerosol size and concentration conditions were used.*

Since all three reviewers asked about the droplet sizes due to evaporation and the effect it has on the CE, we decided to change our CE calculation in order to include the fact that droplets evaporate in the chamber. In addition, we include a new paragraph on the subject in the result and discussion section. The droplet size at the time that collection occurred is not measured in our system; therefore, we used different droplets sizes that corresponded to the range of evaporation times in the system in order to calculate theoretical CE values. The following was added to the paper in the result and discussion: *As noted earlier, the droplets evaporated completely while in the chamber at both RH conditions. Since droplet size could not be determined precisely at the moment when collection occurred in the chamber, calculations of theoretical CE were performed for three relevant droplets sizes: The first was the original droplet size as measured from the droplet generator (21.4 and 21.9  $\mu\text{m}$ , for Low and High RH conditions, respectively) for the full droplet lifetime. The second, droplet size with half the volume of the original droplet (radius of 17 and 17.4  $\mu\text{m}$ , for Low and High RH conditions, respectively) over the full lifetime. For the third an extreme case was considered, droplets with a radius of 5  $\mu\text{m}$  for the full droplet lifetime. The results of these calculations are presented in Fig. 10. Overall, as droplet size decreases, CE values increases. In the extreme 5  $\mu\text{m}$  case, CE values increases by more than an order of magnitude. For the Low RH case the best agreement is with the 5  $\mu\text{m}$  case, which logically follows from the rapid evaporation of these droplets. In the High RH case the experimental CE values fall nearest the half volume case, which again logically follows since these droplets more slowly evaporate.*

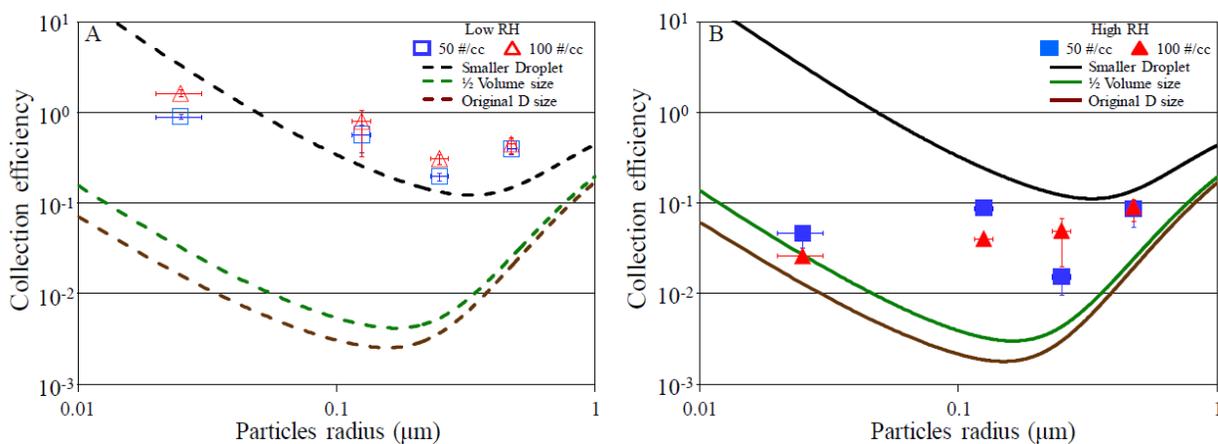


Figure 10: CE as a function of particle radius at Low and High RH (Panel A and B, respectively). CE experimentally determined in this study (points) with theoretical calculations (lines). The lines

*represent calculation with different droplets sizes: the measured droplet size (brown), droplets with half the volume (green) and 5  $\mu\text{m}$  droplets (black). See text for details.*

**5. Ladino et al. (2011) showed the high variability in measuring collection efficiencies from the bulk collection of coagulated particle-droplets. Does this also apply to the single droplet basis analysis? How reproducible are your coagulation experiments? If I interpret Table 3 correctly, each coagulation experiment was conducted only once.**

By definition in a single particle experiment, each droplet residual is a sample. We believe this is a noteworthy advantage of this type of experiment and it should not be compared with the different off-line analysis results. Instead, each ‘experiment’ in this work contains more than 1000 droplets evaluated on a single droplet basis. For clarity, Table 3 summarizes all measurements per experimental condition.

**6. I think that the atmospheric relevance of your results needs to be clearly stated in the conclusions. This is currently missing.**

**7. What did we learn from the single particle basis analysis compared to the bulk analysis? Is it better to use the single particle basis approach? Why?**

Based on Dr. Ladino’s suggestion the following was added to the conclusions section: *This technique overcomes some of the limitations inherent in previous studies which required a bulk collection of material. The analytical methods employed were limited by issues such as signal to noise and an inability to observe multiple collection events on single droplets. Moreover, very few experimental works have been performed with atmospherically relevant particles sizes (Radke et al., 1980; Andronache et al., 2006), another advantage of this technique. The droplet size and charge state used here are also consistent with atmospheric conditions.*

**8. How were the CE uncertainties calculated? What is the meaning of the error-bars reported in Figures 5, 6 and 8.**

CE uncertainties calculations are based on droplet size, aerosol size and aerosol number concentrations, which were measured in each experiment. This information was added to Fig. 5 caption: *CE calculated as a function of particle radius. Shapes represent different aerosol concentrations. CE error bars based on droplets size, aerosol size and aerosol number concentration measured from each experiment as describe in Eq. 3.*

**Minor comments:**

**1. Brownian motion is very effective at promoting collisions of aerosol particles cloud droplets at aerosol particle sizes smaller than 0.25  $\mu\text{m}$  as shown experimentally by Lai et al. (1978) and Ladino et al. (2011); however, this was not observed in this study. Can the authors discuss this? Why do you think you were unable to clearly see the theoretically predicted Greenfield Gap? Why this was experimentally observed by Lai et al. (1978) and Ladino et al. (2011) and not in the present study?**

An explanation about this difference was added to the paper under the result and discussion section: *Moreover, as described by Tinsley et al. (2001), the electrical effect is more important for smaller particle sizes ( $< 0.1 \mu\text{m}$ ) than Brownian diffusion. This could explain why the Greenfield Gap is highly pronounced in the data in Fig. 6, while it is more pronounced in the data of Lai et al. (1978) and Ladino et al. (2011).*

**2. I am wondering why the aerosol particle concentration was measured with two different instruments. It is clear that the OPC has a lower operational limit higher than the smallest studied particles; however, the CPC has the capability to count/measure particles with sizes similar to those used in this study. Why you did not use the CPC for the whole set of experiments? Are the uncertainties from the CPC and OPC comparable? Why did you size select the small particles (0.025  $\mu\text{m}$ , 0.125  $\mu\text{m}$ ) and not the large ones (0.25  $\mu\text{m}$  and 0.475  $\mu\text{m}$ )? PSL spheres are supposed to hold a specific size (that is the reason they are used as standards for calibration). What was the motivation to size select them?**

The SMPS is optimal for sizes smaller than 1 $\mu\text{m}$  radius while the OPS is optimal for particles larger than ~0.35 micrometers. The OPS is also able to identify the aerosol size distribution more rapidly

and is sensitive in the range of the droplet residuals, the latter of which cannot be detected with the CPC.

Explanation was added to the text: *Large particle (diameter >0.35  $\mu\text{m}$ ) and residual concentrations were measured by an Optical Particle Sizer (OPS; TSI, Inc., Shoreview, MN Model 3330). Particles, below diameter of 0.35  $\mu\text{m}$  were measured using a Scanning Mobility Particle Sizer (SMPS) consisting of a Differential Mobility Analyzer (DMA; BMI, Inc. Model 2002) and a condensation particle counter (CPC; BMI, Inc. MCPC Model 1710). Similar concentrations were observed in the overlapping sensitivity region of both instruments.*

**3. Which was the motivation to choose these theoretical models to inter-compare the experimentally obtained collection efficiencies? The used theoretical models were developed for below-cloud scavenging where rain drops are included instead of the small droplets used in this study.**

Information was added to the paper under the Theoretical CE Models section: *These theoretical models include the known forces that affect CE values and which were measured or constrained by data in the experimental measurements presented here. It should be noted that although these theoretical models were developed for large droplets they have been used to calculate CE for sizes relevant to this work (Ladino, 2011).*

**4. The authors showed that there was not any difference in the CE values when the aerosol concentration was increased from 50 to 100  $\text{cm}^{-3}$ . Why would you expect to see a difference here? The CEs are normalized by the total particle concentration; therefore, there should not be any effect. “Wang and Pruppacher (1977) used RH condition similar to that used in this work but with a higher aerosol concentrations”. Why would a higher concentration result in higher CEs?**

We thank Dr. Ladino for this comment and we agree with the reviewer that CE is normalized. Based on the comment we clarify the sentence: *Wang and Pruppacher (1977) used a RH condition similar to that used in this study but with a higher aerosol concentrations. It is expected that a higher aerosol*

concentration will increase the chance of collision between particles and droplets, which will increase the value of ECR, but will not affect CE, which is normalized.

**5. On page 6219, lines 11-12 it is written: “it is possible the size and charge conditions offset each other, lending to the comparison to our data.” In order to confirm this hypothesis, can the authors infer from your calculations how much the CE will increase/decrease when the droplet size is increased from 20 to 200  $\mu\text{m}$  or when the charges are increased from 400 to  $5 \times 10^5$ ?**

As requested by Dr. Ladino, calculations of CE values were made for droplets sizes of 20  $\mu\text{m}$  and 200  $\mu\text{m}$  with droplets charges of 400 and  $5 \times 10^5$  elementary charges. These calculations were added to the result and discussion part of the paper: *It is known that droplets carrying higher electric charge have higher CE (Barlow and Latham, 1983; Byrne and Jennings, 1993; Pranesha and Kamra, 1997a,b; Tinsley and Leddon, 2013; Tinsley et al., 2000; Tinsley, 2010), and this is consistent with our data in Fig 9. Droplets size also affects CE, where smaller droplets have higher CE values (Lai et al., 1978; Pranesha and Kamra, 1996). Fig. 11 shows a calculation of CE based on different droplet charges and sizes. Two droplets sizes were used: 20  $\mu\text{m}$ , which is similar to the size used in this study and by Ladino et al. (2011) and 200  $\mu\text{m}$ , which is the size used by Wang and Pruppacher (1977). Three different droplet charges were considered: 400 elementary charges, as used in this study,  $5 \times 10^4$  elementary charges, used by Ladino et al. (2011) and  $5 \times 10^5$  elementary charges, the lower limit of charges used by Wang and Pruppacher (1977). Shown in Fig. 11, CE values increase as droplet charge increases. Droplets size and charge conditions can counteract each other in the case of larger droplets (lower CE) with higher charge (higher CE). We suggest this may explain the agreement found between the CE values measured in this study and those of Wang and Pruppacher (1977) and the disagreement between our values and those of Ladino et al. (2011). It should be noted that the experimental CE values fall within the region of the 20  $\mu\text{m}$  case. The CE values of the small particles ( $<0.1 \mu\text{m}$ ) match the theoretical CE, while for larger particles ( $>0.1 \mu\text{m}$ ) they are slightly higher. These differences could be a result of some conditions not modeled theoretically or conditions difficult to constrain experimentally, as discussed above.*

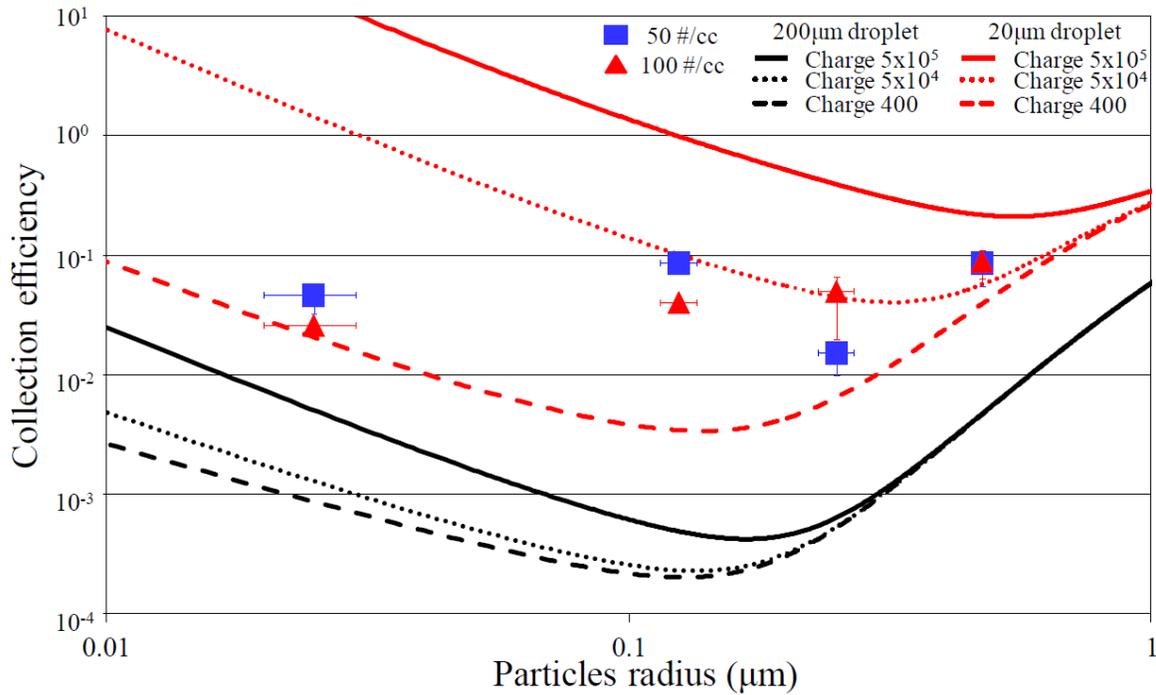


Figure 11: CE as a function of particle radius at High RH condition. CE experimentally determined in this study (points) with theoretical calculations (lines), where the charge number is in elementary charge units per droplet. Black lines are for CE of 200  $\mu\text{m}$  droplet size and red for 20  $\mu\text{m}$  droplet size.

**6. Fig. 6 and its corresponding discussion: The Wang and Pruppacher (1977) data needs to be used with caution. They used different droplet sizes but this is neither mentioned in the figure nor in the text. This needs to be clearly stated because in its current form it seems like they run different experiments with one droplet size only and 0.25  $\mu\text{m}$  aerosol particles. I suggest to only use one data point from the Wang and Pruppacher (1977) study (i.e., CE for 0.25  $\mu\text{m}$  aerosol particles and 150  $\mu\text{m}$  droplets)**

Note the information about Wang and Pruppacher (1977) droplets sizes is mentioned in the paper under the result and discussion section: *For example, Wang and Pruppacher (1977) and Lai et al. (1978) used somewhat larger droplets (of 170-340  $\mu\text{m}$  and 620  $\mu\text{m}$ , respectively).*

In order to clarify this point we added the droplets sizes to Fig. 6 caption: *Black diamonds are from Ladino et al. (2011), RH 88 $\pm$ 2% with aerosol concentration 2000  $\text{cm}^{-3}$  and droplets size of 12.8-20.0*

*µm. Brown diamonds represent are from Wang and Pruppacher (1977), RH of 23±2% with aerosol concentration of about 10<sup>17</sup> cm<sup>-3</sup> and droplets size of 170-340 µm. Pink diamonds are from Lai et al. (1978), when 620 µm droplets were used; there was no information provided regarding the RH or aerosol concentration.*

### **Technical comments**

**1. In some cases the droplet size is said to be “~20 µm” but on page 6217 line 7 it is said that the size is 22 µm.**

Based on the reviewer technical comments 1 and 6 changes have been made, droplet size was written as 21.6 µm.

**2. Page 6208, line 22: It should be IPCC**

We thank the reviewer for this correction ICCP was changed to IPCC.

**3. Coagulation and collection are used throughout the text. I suggest sticking to one of them.**

Changes have been made; the term collection was used throughout the paper.

**4. The term “coagulated droplets” is used in several places. I am not sure if this will be clear for readers. Can the authors use a different term?**

We believe that the definition “coagulated droplets” describes the process clearly, based on this comment we add an explanation to this term: *“Coagulated droplets” (droplets that collected aerosols) had mass spectra that contain signatures from both an aerosol particle and a droplet residual.*

**5. Brownian motion and Brownian diffusion are used throughout the text.**

Changes were made, the term Brownian diffusion was used throughout the paper.

**6. In many places either ~20  $\mu\text{m}$  or ~80% are used when referring to the droplet size and the relative humidity. The authors measure the size of the droplets and the RH quantitatively. What is the need to use the approximation symbol (i.e., “~”)?**

Changes were made, the symbol ~ was removed from the paper and quantitative values (such as 21.6  $\mu\text{m}$  and 88%) were used throughout the paper.

**7. Page 6209, line 2: I think Ladino et al. (2011) is not the best reference here. I suggest to replace it with a more appropriate reference (e.g., Rasch et al. (2000) and Croft et al. (2009))**

We thank the Dr. Ladino for this suggestion changes were made accordingly.

We would like to thank anonymous reviewer 2, for the helpful comments and suggestions. In line with the comments and suggestions, we revised the manuscript. Below are all the comments (in bold) followed by the replies. The parts that are in italic are corrections that are included in the revised version of the paper:

**1. The authors should provide a motivation why there is a need to develop a new technique to measure CE. Are there discrepancies in previous results? Or the present technique can provide information that cannot be offered by previous researches? One of the papers they may want to refer to is Radke et al. (1980, J. Appl. Meteor., 19, 715) where discrepancies between CE measured in labs and derived from field observations are described. Also, the single-drop technique can potentially differentiate different factors influencing the CE which cannot be done by previous methods. The authors should give a more detailed description on this point.**

We would like to thank the reviewer for this important point, which was also raised by the first reviewer. The suggested reference was added to the paper. We emphasize these suggestions in a new paragraph that was added to the conclusions section: *This technique overcomes some of the limitations inherent in previous studies which required a bulk collection of material. The analytical methods employed were limited by issues such as signal to noise and an inability to observe multiple collection events on single droplets. Moreover, very few experimental works have been performed with atmospherically relevant particles sizes (Radke et al., 1980; Andronache et al., 2006), another advantage of this technique. The droplet size and charge state used here are also consistent with atmospheric conditions.*

**2. One of the possible error sources of the CE results reported here is the droplet size which seems to be assumed constant. Given that the RH is very low, the evaporation and hence the change of drop size can be very quick, and this will affect the results of CE calculations. The authors should make estimates of the drop size during the aerosol collection and report errors.**

Based on the reviewer comment we added standard deviation values to the droplets sizes in Table 2. The variations in droplets sizes were taken into account and they are represented by the error bar of CE values in Fig. 5. With these suggestions and those made by reviewer 1, we added an explanation

in the caption of Fig. 5: *CE calculated as a function of particle radius. Shapes represent different aerosol concentrations. CE error bars based on droplets size, aerosol size and aerosol number concentration measured from each experiment as describe in Eq. 3.*

We agree with the reviewer that evaporation may change the droplet size, which may affect CE values. Since all three reviewers asked about the droplet sizes due to evaporation and the effect it has on the CE, we decided to change our CE calculation in order to include the fact that droplets evaporate in the chamber. In addition, we include a new paragraph on the subject in the result and discussion section. The droplet size at the time that collection occurred is not measured in our system; therefore, we used different droplets sizes that corresponded to the range of evaporation times in the system in order to calculate theoretical CE values. The following was added to the paper in the result and discussion: *As noted earlier, the droplets evaporated completely while in the chamber at both RH conditions. Since droplet size could not be determined precisely at the moment when collection occurred in the chamber, calculations of theoretical CE were performed for three relevant droplets sizes: The first was the original droplet size as measured from the droplet generator (21.4 and 21.9  $\mu\text{m}$ , for Low and High RH conditions, respectively) for the full droplet lifetime. The second, droplet size with half the volume of the original droplet (radius of 17 and 17.4  $\mu\text{m}$ , for Low and High RH conditions, respectively) over the full lifetime. For the third an extreme case was considered, droplets with a radius of 5  $\mu\text{m}$  for the full droplet lifetime. The results of these calculations are presented in Fig. 10. Overall, as droplet size decreases, CE values increases. In the extreme 5  $\mu\text{m}$  case, CE values increases by more than an order of magnitude. For the Low RH case the best agreement is with the 5  $\mu\text{m}$  case, which logically follows from the rapid evaporation of these droplets. In the High RH case the experimental CE values fall nearest the half volume case, which again logically follows since these droplets more slowly evaporate.*

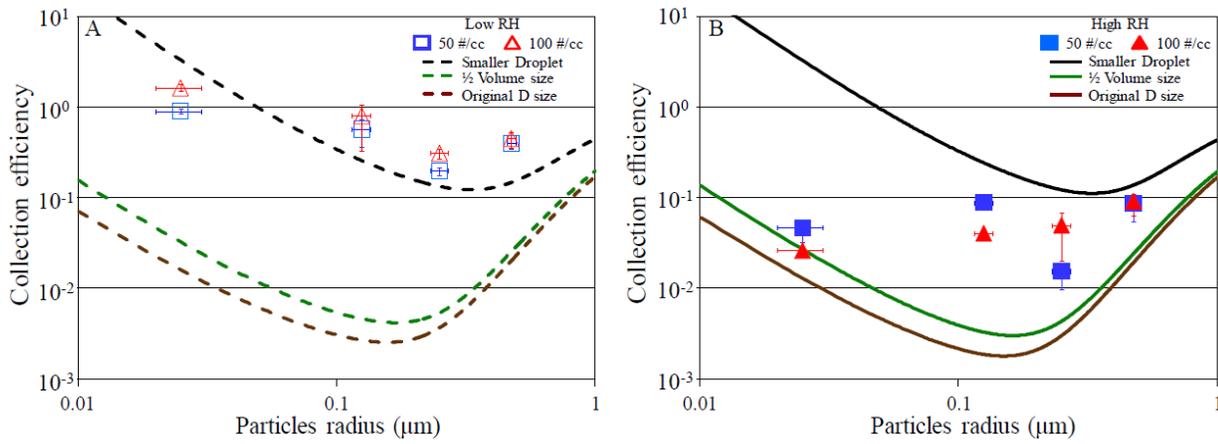


Figure 10: CE as a function of particle radius at Low and High RH (Panel A and B, respectively). CE experimentally determined in this study (points) with theoretical calculations (lines). The lines represent calculation with different droplets sizes: the measured droplet size (brown), droplets with half the volume (green) and 5 μm droplets (black). See text for details.

We would like to thank reviewer 3, Dr. Alexei Kiselev, for the helpful comments and suggestions. In line with the comments and suggestions, we revised the manuscript. Below are all the comments (in bold) followed by the replies. The parts that are in italic are corrections that are included in the revised version of the paper:

### **Specific comments:**

#### **Introduction:**

**1. The motivation of this research is not completely clear from the introduction. Scavenging of the aerosol particles by cloud droplets is a part of aerosol and cloud interaction process and as such undoubtedly contributes to cloud dynamics (including precipitation) and radiative properties. The questions remains, however, what is the contribution of the uncertainty associated with the scavenging efficiency into the overall uncertainty of radiative forcing due to the indirect aerosol effect? To justify the necessity of a sophisticated experiment aimed to quantify the collection efficiency (CE) this connection has to be discussed at least briefly.**

We would like to thank Dr. Kiselev for this suggestion. We made several changes in the introduction section: *The interplay between aerosol particles and water droplets in the atmosphere, especially in clouds, influences both aerosol and cloud properties. The major uncertainty in our understanding of climate arises from this interplay: the ability of an aerosol to affect cloud formation and, consequently, alter the global radiative balance (IPCC, 2007). When an aerosol particle comes in contact with a water droplet, the interaction can result in a collision followed by coalescence of the two. This process is known as “collection” or “coagulation”. The collection process is considered an important mechanism that can “scavenge”, and thereby remove, aerosol particles from the atmosphere (Starr and Mason, 1966; Owe Berg et al., 1970; Hampl and Kerker, 1972; Praneshia and Kamra, 1996). Collection can also affect cloud dynamisc, the precipitation process and cloud lifetime, and thereby change the global radiation budget (Rasch et al., 2000; Croft et al., 2009).*

*In supercooled clouds, where droplets are present at temperatures below 0°C, the collection process can have an effect on precipitation when the contacting aerosol initiates ice nucleation. The result is the creation of an ice crystal, a process known as “contact nucleation” (Vali, 1996). Contact can influence cloud lifetime and precipitation formation in mixed-phase clouds, which will also affect the*

global radiation budget. In order to understand the contact freezing process, it is important to determine the efficiencies at which the aerosol particles collide with a liquid droplet within a cloud.

**2. Although numerous theoretical and experimental studies of the aerosol scavenging are listed in the introduction, it remains unclear what is the status quo in this research field? Is the theory insufficient to describe the CE in most cases? Were previously reported experimental results very far from the theoretically predicted values? Are there any specific cases where observed collection efficiency could not be explained by accurate consideration of all droplet-particle interaction mechanisms?**

Based on the reviewer comment a new paragraph was added to the paper under the introduction section: *Theoretical calculations of CE in a cloud environment have been the subject of many studies, driven by the necessity to explain aspects of both warm and cold precipitations. An experimental validation of the theoretical knowledge related to CE, particularly for droplet–aerosol collisions, is difficult and far from complete (Ladino, 2011). According to Santachiara et al. (2012), significant discrepancies between theoretical and experimental studies have been found for sub-micrometer particles in the “Greenfield gap”, and the measured values can be one to two orders of magnitude higher than predicted. According to Wang et al. (2010), this disagreement could be because some physical processes considered in theoretical models are neglected, difficult to represent or hard to control in experimental studies.*

Additional information about this comparison was also added to the result and discussion section: *Differences between theoretical and measured CE may be considered a result of conditions not modeled theoretically or difficult to constrain experimentally. Possibilities include rare multiply charged particles, aerosol droplet electric interaction that are not fully considered (such as the induced dipole force), the evaporation rate of the droplets, variable terminal settling velocity due to changes in droplet size, and the present of solute in the droplets.*

**3. The authors put a special stress on the statement that the presented work is the first experimental study of CE “on a single droplets basis”. I believe this is not exactly so: (Hoffmann et al., 2013) has reported the determination of the collection efficiency measured for**

**the individual droplets levitated in the electrodynamic balance. Though dominated by electrostatic forces, the experimental CE was in a good agreement with theoretical predictions and the multiple collection events have been explicitly taken into account.**

A correction was added to the paper under in abstract and the Introduction sections:

*To our knowledge, this is the first collection experiment performed on a single droplet basis with atmospherically relevant conditions such as droplets sizes, droplets charges and flow.*

*To our knowledge, no previous study allowed for determination of collection on a single droplet basis with atmospherically relevant conditions of droplets size, droplets charge and flow, which are a key to many cloud processes, including contact nucleation.*

#### **Experimental methods**

**4. If I interpret the figure 2 correctly, both droplets AND aerosol particles are passing the neutralizer at the lower end of DGN section! In this case, the initially single charged aerosol particles should assume Boltzmann distribution centered on zero charge. The free path of alpha particles produced by Po-210 source (5 to 7 cm in air) is sufficient to produce homogeneous concentration of ions inside the DGN section for that. It seems that the authors are aware of this effect (see also comment 10). If so, the question arises if the true charge distribution for aerosol particles after the neutralizer has been taken into account for the calculation of theoretical CE?**

Dr. Kislev is correct, the particles will experience a Boltzmann distribution, where most particles have zero charges and most charged particles have  $\pm 1$  elementary charge. Per Dr. Kislev comment, an explanation and correction was added to the paper under the result and discussion section: *These calculations were made for charged particles that contained one elementary charge per particle. Most particles in a Boltzmann distribution contain no charges and will therefore not be affected by electro-scavenging forces. The most common charge state other than neutral is a single charge, about 10% of particles, and this forms the basis of our calculation (Hinds, 1999). This is further supported by a decreasing effect of multiple charges when considering the effect on CE, (Fig 8).*

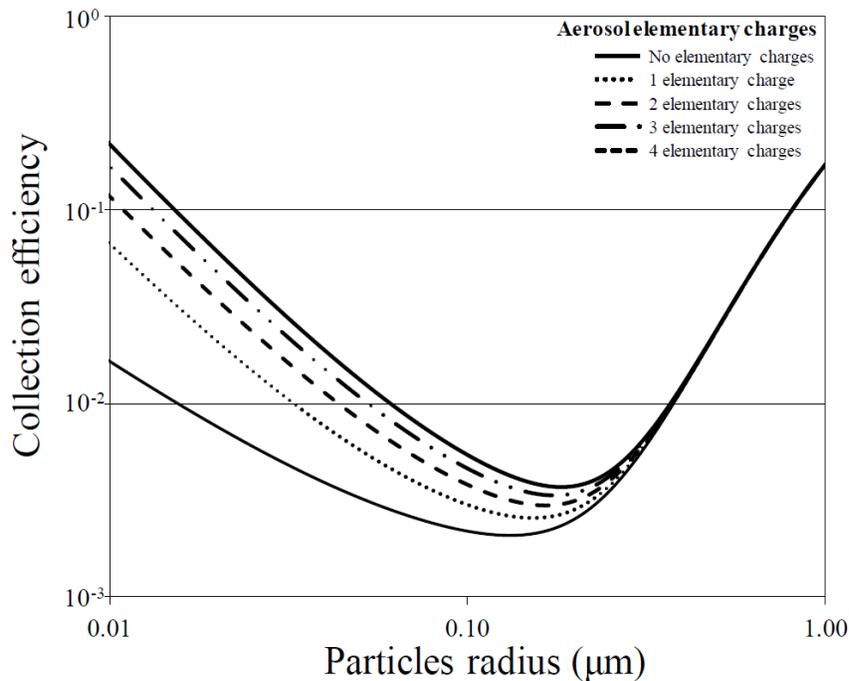


Figure 8: CE values for 50% RH and 400 elementary charges per droplets with different particles elementary charge for a droplet radius of 21.6  $\mu\text{m}$  and room temperature.

## Data Analysis

**5. The calculation of the CE (equation 3) is done under assumption of constant droplet size during the droplet fall through the chamber. However, the evaporation time of the droplets is obviously shorter than the residence time (which I was unable to determine exactly because the flow rate in the chamber is not given). The experimental values of CE cannot be correct if the droplet size is reduced by factor 10 or more after travelling just a few centimeters! How this reduction of the droplet diameter is taken into account in the theoretical calculation?**

Per Dr. Kislev's comment, Information on the flow rate and droplets residence time were added to the paper under the result and discussion section.

Since all three reviewers asked about the droplet sizes due to evaporation and the effect it has on the CE, we decided to change our CE calculation in order to include the fact that droplets evaporate in the chamber. In addition, we include a new paragraph on the subject in the result and discussion section. The droplet size at the time that collection occurred is not measured in our system; therefore, we used different droplets sizes that corresponded to the range of evaporation times in the system in

order to calculate theoretical CE values. The following was added to the paper in the result and discussion: *As noted earlier, the droplets evaporated completely while in the chamber at both RH conditions. Since droplet size could not be determined precisely at the moment when collection occurred in the chamber, calculations of theoretical CE were performed for three relevant droplets sizes: The first was the original droplet size as measured from the droplet generator (21.4 and 21.9  $\mu\text{m}$ , for Low and High RH conditions, respectively) for the full droplet lifetime. The second, droplet size with half the volume of the original droplet (radius of 17 and 17.4  $\mu\text{m}$ , for Low and High RH conditions, respectively) over the full lifetime. For the third an extreme case was considered, droplets with a radius of 5  $\mu\text{m}$  for the full droplet lifetime. The results of these calculations are presented in Fig. 10. Overall, as droplet size decreases, CE values increases. In the extreme 5  $\mu\text{m}$  case, CE values increases by more than an order of magnitude. For the Low RH case the best agreement is with the 5  $\mu\text{m}$  case, which logically follows from the rapid evaporation of these droplets. In the High RH case the experimental CE values fall nearest the half volume case, which again logically follows since these droplets more slowly evaporate.*

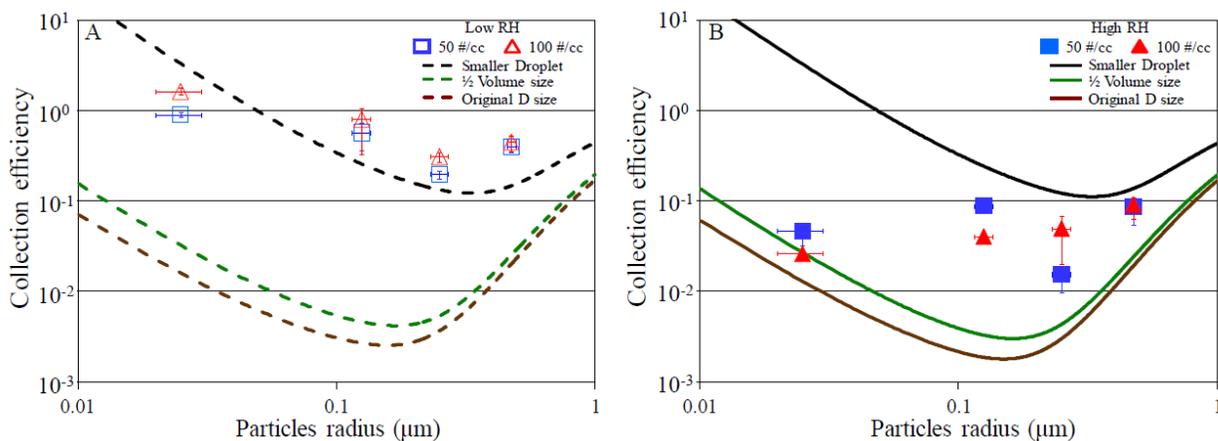


Figure 10: CE as a function of particle radius at Low and High RH (Panel A and B, respectively). CE experimentally determined in this study (points) with theoretical calculations (lines). The lines represent calculation with different droplets sizes: the measured droplet size (brown), droplets with half the volume (green) and 5  $\mu\text{m}$  droplets (black). See text for details.

## Result and discussion

**6. The evaporation time of the droplet (page 6217 line 10) is given for pure water (at least I obtain the same values if calculating the evaporation time for pure water droplets using the**

formula in (Hinds, 1999). However, droplets of aqueous ammonium sulfate solution have been used, meaning that the Raoult term has to be taken into account. Under “high-RH” conditions droplet would not evaporate completely (efflorescence RH is not reached) so that the solute droplet of approximately 1.3  $\mu\text{m}$  diameter (corresponding to the equilibrium saturation ratio of 0.88) is left. Note that this droplet will have the same charge so that the electrostatic interaction with aerosol particles would be completely different (see discussion of the electrostatic interaction). The same considerations apply to the dry residual of the ammonium sulfate left by evaporating droplet under “low-RH” conditions.

We agree with Dr. Kislev that the residual presented at the end of the chamber (based on OPS distribution) was at about 1.3 $\mu\text{m}$ . A collection experiment of PSL with AS residual (evaporated droplet), with similar sizes as mentioned by the reviewer, were performed. Several thousand spectra were examined with PALMS with no coagulation event observed. This information was added to the paper under the experimental setup section: *It should be noted that an experiment of PSL with AS residual (from the evaporated droplet) was performed. Several thousand spectra were examined with PALMS but no collection event was observed.*

**7. The number of elementary charges carried by the droplet in the study of (Lai et al., 1978) cannot be as high as  $10^n$  (page 6219, line 5). I assume the authors used the charge of the droplet given in the table 2 of (Lai et al., 1978) where the minus sign in the exponent is erroneously omitted (“...Average charge  $\times 10^{10}\text{C}$  ...”).**

We would like to thank the reviewer for finding this mistake, the values were corrected accordingly, and they are now  $6.6 \times 10^8$ - $1.9 \times 10^9$  elementary charges.

#### **Theoretical CE models**

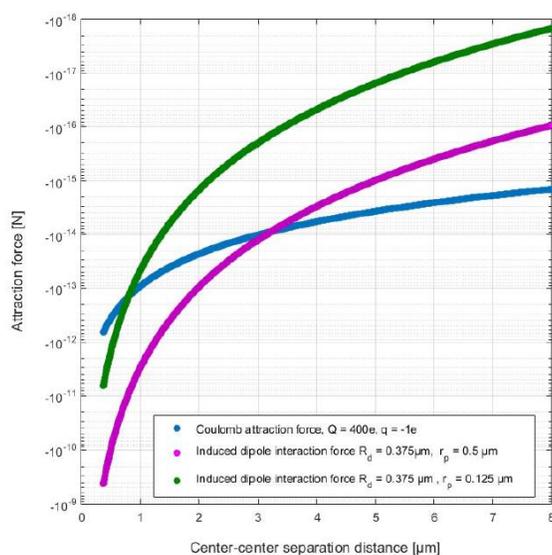
**8. More details should be provided on the theoretical calculations. Is the terminal settling velocity kept constant together with the size? Is the presence of solute (ammonium sulfate) is taken into account in the calculations of phoretic forces? Is the true charge distribution of aerosol particles taken into account for calculations of electrostatic interaction? I believe that**

**taking into account all these effects together with careful consideration of droplet evaporation would allow for much better agreement between measured and calculated values of CE.**

This comment is related to earlier point 5. Please see response to point 5 above and the figure addition to the paper.

In addition, information on parameters that could not taken into account for the theoretical calculation were added to the paper: *Differences between theoretical and measured CE may be considered a result of conditions not modeled theoretically or difficult to constrain experimentally. Possibilities include rare multiply charged particles, aerosol droplet electric interaction that are not fully considered (such as the induced dipole force), the evaporation rate of the droplets, variable terminal settling velocity due to changes in droplet size, and the present of solute in the droplets.*

**9. I wonder if the effect of electric charge should be considered more thoroughly for the theoretical calculation of CE. The long-range electrostatic interaction between the charged droplet and the aerosol particles is correctly identified as Coulomb attraction (equation 9 of the manuscript). However, at short distances comparable to the size of evaporated droplet, the induced dipole interaction has to be considered (equation 13 in Hoffmann et al., 2013; Tinsley, 2010; Tinsley et al., 2000). For small droplets carrying strong charge (on the order of 500 elementary charges), this interaction force dominates all others and can significantly increase collection efficiency. In the figure below, I illustrate my point comparing Coulomb and induced dipole interaction forces between the droplet residual particle (0.75  $\mu\text{m}$ , 400e) and single charged PSL particle of 1  $\mu\text{m}$  (magenta curve) and 0.25 $\mu\text{m}$  (green curve) as a function of distance between the centers of the particles. The negative sign of the force denotes attraction between the particles. Note that for larger PSL particle at short separation distances (below 3  $\mu\text{m}$  from center to center) the induced dipole interaction force is much stronger than the Coulomb attraction force (blue curve), potentially increasing the coagulation probability between PSL and residual particle.**



Dr Kislev raised a very interesting point here. It is clear that induced dipole interaction is a stronger force than Coulomb attraction force that could increase the electro-scavenging force and the CE values. Unfortunately, our experimental work and the theoretical calculation could not examine such small-scale separation between the droplets and PSL, therefore such information could not be included in the paper. Indeed, to our knowledge, these types of theoretical models are not used for this length scale of effect in the models used in this paper. The problem is that inclusion of a new force at this scale is beyond the scope of this paper and would also not allow for direct comparison with previous calculations which is fundamental to this work. We agree with the importance and, based on Dr. Kislev's comment, we included the following: *Differences between theoretical and measured CE may be considered a result of conditions not modeled theoretically or difficult to constrain experimentally. Possibilities include rare multiply charged particles, aerosol droplet electric interaction that are not fully considered (such as the induced dipole force), the evaporation rate of the droplets, variable terminal settling velocity due to changes in droplet size, and the present of solute in the droplets.*

**10. Page 6220 line 20: “One elementary charge was used for the particles, consistent with a Boltzmann distribution imparted by the neutralizer”.** Again, a Boltzmann distribution is centered around the zero charge, not single charge of any sign. For particles of 0.01 μm (radius) 90% of all particles would have no charge, whereas for particles of 5μm 70% of all particles will carry more than 3 elementary charges (of any sign) (see Chapter 15.7 in Hinds, 1999, sec. ed.).

Dr. Kislev is correct, per Dr. Kislev comment, an explanation and corrections were added to the paper, see our reply to comment 4. For this paper it should be noted the aerosol would not extend to the super-micrometer size so 10% is the likely value to consider here.

1 **Laboratory Studies of Collection Efficiency of Sub-micrometer Aerosol Particles by Cloud**  
2 **Droplets on a Single Droplet ~~basis~~Basis**

3 Karin Ardon-Dryer, Yi-wen Huang and Daniel J. Cziczo

4 *Dept. of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology*

5  
6 **Abstract**

7 An experimental setup has been constructed to measure the Collection Efficiency (CE) of sub-  
8 micrometer aerosol particles by cloud droplets. ~~Water droplets~~ Droplets of a dilute aqueous  
9 ammonium sulfate solution with an average radius of ~~~2221.6~~  $\mu\text{m}$  fall freely into a chamber and  
10 collide with sub-micrometer Polystyrene Latex Sphere (PSL) particles of ~~variable~~ known sizes  
11 and concentrations. Two Relative Humidity (RH) conditions, 15±3% and 88±3%, ~~~15% and~~  
12 ~~~88%~~, hereafter termed ‘Low’ and ‘High’, respectively, were varied with different particles sizes  
13 and concentrations. After passing through the chamber, the droplets and aerosol particles were  
14 sent to the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument to determine  
15 chemical compositions on a single ~~particle-droplet~~ basis. “Coagulated droplets” (droplets that  
16 collected aerosols) had mass spectra that contained signatures from both an aerosol particle and a  
17 droplet residual. CE values range from  $2.0 \times 10^{-1}$   ~~$5.7 \times 10^{-3}$~~  to  $1.64 \cdot 6 \times 10^{-2}$  for the Low RH and from  
18  ~~$6.4 \times 10^{-3}$~~   $1.5 \times 10^{-2}$  to  ~~$2.2 \times 10^{-2}$~~   $9.0 \times 10^{-2}$  for the High RH cases. CE values were, within  
19 experimental uncertainty, independent of the aerosol concentrations. CE values in this ~~work~~  
20 study were found to be in agreement with previous experimental and theoretical studies. To our  
21 knowledge, this is the first ~~collection~~ coagulation experiment performed on a single droplet basis  
22 with atmospherically relevant conditions such as droplets sizes, droplets charges and flow.

23  
24 **1. Introduction**

25 The interplay between aerosol particles and water droplets in the atmosphere, especially in  
26 clouds, influences both aerosol and cloud properties. The major uncertainty in our understanding  
27 of climate arises from this interplay: the ability of an aerosol to affect cloud formation and,  
28 consequently, alter the global radiative balance (IPCC, 2007). When an aerosol particle comes in  
29 contact with a water droplet, the interaction can result in a collision followed by coalescence of  
30 the two. This process is known as “collection” or “coagulation”. The collection process is  
31 considered an important mechanism that can “scavenge”, and thereby remove, aerosol particles

1 from the atmosphere (Starr and Mason, 1966; Owe Berg et al., 1970; Hampl and Kerker, 1972;  
2 Pranisha and Kamra, 1996). Collection can also affect cloud dynamics, the precipitation process  
3 and cloud lifetime, and thereby change the global radiation budget (Rasch et al., 2000; Croft et  
4 al., 2009).

5  
6 In supercooled clouds, where droplets are present at temperatures below 0°C, the collection  
7 process can have an effect on precipitation when the contacting aerosol initiates ice nucleation.  
8 The result is the creation of an ice crystal, a process known as “contact nucleation” (Vali, 1996).  
9 Contact can influence cloud lifetime and precipitation formation in mixed-phase clouds, which  
10 will also affect the global radiation budget. In order to understand the contact freezing process, it  
11 is important to determine the efficiencies at which the aerosol particles collide with a liquid  
12 droplet within a cloud.

13 ~~The interplay between aerosol particles and water droplets in the atmosphere, especially in~~  
14 ~~clouds, influences both aerosol and cloud properties. The major uncertainty in our understanding~~  
15 ~~of climate arises from the indirect effect of aerosol particles: their ability to affect cloud~~  
16 ~~formation and, consequently, alter the global radiative balance (ICCP, 2007). When an aerosol~~  
17 ~~particle comes in contact with a water droplet the interaction can result in a collision followed by~~  
18 ~~coalescence of the two. This process is known as “collection” or “coagulation”. The collection~~  
19 ~~process is considered an important mechanism that can “scavenge”, and thereby remove, aerosol~~  
20 ~~particles from the atmosphere (Starr and Mason, 1966; Owe Berg et al., 1970; Hampl and~~  
21 ~~Kerker, 1972; Pranisha and Kamra, 1996). This process can also influence aerosol and cloud~~  
22 ~~lifetime and thereby affect the global radiation budget (Ladino et al., 2011). In supercooled~~  
23 ~~clouds, where droplets are present at temperatures below 0°C, the collection process can have an~~  
24 ~~effect on precipitation when the contacting aerosol initiates ice nucleation. The result is the~~  
25 ~~creation of an ice crystal, a process known as “contact nucleation” (Vali, 1996).~~

26  
27 Collection efficiency (CE) is the ability of a droplet to coagulate with the aerosol particles within  
28 the volume swept out as it falls. Several mechanisms and forces can affect the collection process.  
29 These include inertial impaction, Brownian diffusion, interception, electrical and other phoretic  
30 forces (See Fig. 1). Inertial impaction is defined as the impaction of particles, ~~those of that have~~  
31 sufficient inertia that they do not follow their original streamline around the droplet but instead

1 | travel close enough to the surface to result in a collision. Brownian ~~diffusion motion~~ refers to the  
2 | movement of the particle due to collisions with air molecules, ~~in~~ In this context it results in a  
3 | “random walk” into the droplet surface. Interception is the impaction of particles that follow a  
4 | streamline that approaches the droplet within a distance ~~equivalent to~~ the particle radius.  
5 | Electrical forces, also commonly termed electro-scavenging or electrophoresis, occur when  
6 | opposite electrical charges are present on the droplet and the particle resulting in an attraction  
7 | between the two. Other phoretic forces occur when a droplet evaporates or grows. These phoretic  
8 | forces include thermophoresis and diffusiohoresis. Thermophoresis takes place when there is a  
9 | temperature gradient between a droplet and its surroundings. When a droplet evaporates, its  
10 | surface can become colder and aerosols will be drawn ~~inward~~ towards it. Diffusiohoresis, a  
11 | counterforce to thermophoresis, occurs when there is a concentration gradient in water vapor, as  
12 | is the case near an evaporating droplet. Higher water vapor concentration surrounding the droplet  
13 | “pushes” particles outward. A review of the phoretic forces can be found in Pruppacher and Klett  
14 | (1997).

15 |  
16 | The mechanisms described above are dependent on the size of the aerosol particle being  
17 | collected. Whereas for large particles (radius > 1  $\mu\text{m}$ ) inertial effects dominate the collection  
18 | process, small particle (radius < 0.1  $\mu\text{m}$ ) motion is dominated by Brownian diffusion and electro-  
19 | scavenging (Wang and Pruppacher, 1977), where the effects of the latter is higher (Tinsley et al.,  
20 | 2001). Phoretic ~~and electrical effects have forces have~~ a larger ~~relative~~ impact on particles in ~~an~~  
21 | the intermediate size range (Wang and Pruppacher, 1977). This intermediate range, ~~~0.1  $\mu\text{m}$  -~~ 1  
22 |  $\mu\text{m}$ , is normally termed the “Greenfield gap”, and coincides with an observed minimum in CE  
23 | (Greenfield, 1957). The particle radius of the Greenfield gap has also been observed to vary with  
24 | the collecting droplets size (Tinsley et al., 2001).

25 |  
26 | Many factors, besides particle size, have been observed to affect CE (Byrne and Jennings,  
27 | 1993). These include particle density (Chate and Kamra, 1997), turbulence (Grover and  
28 | Pruppacher, 1985) and RH. Lower RH has been observed to correlate with higher CE values,  
29 | apparently due to phoretic forces (Grover et al., 1977; Tinsley et al., 2001). Droplet size can  
30 | impact CE, where lower values correlate with larger droplets (Lai et al., 1978; Pranesha and  
31 | Kamra, 1996). Higher charge also correlates with higher CE, indicative of greater electrical

1 force (Beard, 1974; Wang and Pruppacher, 1977; Lai et al., 1978; Barlow and Latham, 1983;  
2 Pranesha and Kamra, 1997a,b; Tinsley et al., 2000). It should be noted that the number of  
3 ~~elementaryelemental~~ charges used in previous work was often motivated by atmospheric  
4 observations: a few tens to hundreds elementary charges for altostratus and stratocumulus  
5 clouds (Phillips and Kinzer, 1958; Beard et al., 2004) and hundreds to thousands elementary  
6 charges in cumulonimbus clouds (Thomson and Iribarne, 1978; Marshall and Winn, 1982).

7  
8 To date, there have been numerous experimental and theoretical studies of the collection process  
9 (Beard, 1974; Grover et al., 1977; Pranesha and Kamra, 1996; Parker et al., 2005; Tinsley et al.,  
10 2006). Most of the experimental studies have focused on drizzle and rain drop sizes (Hampl and  
11 Kerker, 1972; Deshler, 1985; Pranesha and Kamra, 1997a,b) while few used smaller cloud  
12 droplets (Ladino et al., 2011). A list of these studies is provided in Table 1. Note that only a few  
13 of the experiments reported aerosol concentrations and none mentioned if different  
14 concentrations were compared.

15  
16 Previous studies have relied on bulk collection of coagulated droplets followed by off-line  
17 analysis to assess CE (Hampl et al., 1971; Deshler, 1985; Pranesha and Kamra, 1993; Chate and  
18 Kamra, 1997). Off-line analytical instruments include mass spectrometry (Ladino et al., 2011),  
19 atomic absorption spectroscopy (Barlow and Latham, 1983; Pranesha and Kamra, 1996),  
20 fluorescence spectrometry (Byrne and Jennings, 1993) and neutron activation analysis (Beard,  
21 1974). The efficiency determined from bulk collection of droplets results in a signal to noise  
22 issue where minimal ~~collection~~coagulation events can fall below instrumental detection limits.  
23 The inability to determine multiple collection events by single droplets is another possible source  
24 of error. To our knowledge, no previous study allowed for determination of collection  
25 ~~coagulation~~ on a single droplets basis with atmospherically relevant conditions of droplets size,  
26 droplets charge and flow, which ~~is there a key to~~ relevant condition for many cloud processes,  
27 ~~among these~~including contact nucleation. Another limitation of these bulk analytical methods  
28 lies in the aerosol type. Since each technique relies on certain property of the aerosol particles  
29 (such as fluorescence, radioactivity or atomic absorption), these experiments were restricted to a  
30 specific particle type exhibiting that property. These ~~constraints~~ limitations often limit the  
31 atmospheric applicability of the results.

1  
2 Theoretical calculations of CE in a cloud environment have been the subject of many studies,  
3 driven by the necessity to explain aspects of both warm and cold precipitations. An experimental  
4 validation of the theoretical knowledge related to CE, particularly for droplet–aerosol collisions,  
5 is difficult and far from complete (Ladino, 2011). According to Santachiara et al. (2012),  
6 significant discrepancies between theoretical and experimental studies have been found for sub-  
7 micrometer particles in the “Greenfield gap”, and the measured values can be one to two orders  
8 of magnitude higher than predicted. According to Wang et al. (2010), this disagreement could be  
9 because some physical processes considered in theoretical models are neglected, difficult to  
10 represent or hard to control in experimental studies.

11  
12 The goal of this study was to determine the CE of sub-micrometer aerosol particles by cloud  
13 droplets. This study was conducted on a single droplet basis with sensitivity to one or more  
14 collection coagulation-events.

## 15 16 **2. Experimental Methods**

### 17 **2.1. Experimental Setup**

18 The CE experiments were performed in the new Massachusetts Institute of Technology  
19 Collection Efficiency Chamber (MIT-CEC). A schematic of the system is shown in Fig. 2.  
20 Aerosol particles and droplets were generated and separately passed into the MIT-CEC chamber  
21 where they could fall, in a 0.48 l/m flow, and interact in the laminar flow environment of the  
22 chamber. Condensed phase water was removed in dryers after the chamber, and the flow  
23 containing aerosol particles and droplet residuals was directed to the Particle Analysis by Laser  
24 Mass Spectrometry (PALMS) instrument for single particle analysis.

25  
26 Polystyrene Latex Spheres (PSL) with radius 0.025, 0.125, 0.25 and 0.475  $\mu\text{m}$  were used in the  
27 experiments. PSLs were wet generated using a Brechtel Manufacturing, Inc. (BMI, Hayward,  
28 CA) Model 9203 Aerosol Generation System. ~~Condensed-Condensed~~-phase water was removed  
29 by ~~in-in~~-line dryers. Large particle (diameter > 0.35  $\mu\text{m}$ ) (0.25 and 0.475  $\mu\text{m}$ ) and residual  
30 concentrations were measured by an Optical Particle Sizer (OPS; TSI, Inc., Shoreview, MN  
31 Model 3330). ~~Smaller particles~~Particles, below ~~the OPC detection threshold~~diameter of 0.35

1 μm, were ~~size selected~~ measured using a Scanning Mobility Particle Sizer (SMPS) consisting of  
2 a Differential Mobility Analyzer (DMA; BMI, Inc. Model 2002)~~and their concentrations~~  
3 ~~monitored by and~~ a condensation particle counter (CPC; BMI, Inc. MCPC Model 1710). Similar  
4 concentrations were observed in the overlapping sensitivity region of both instruments. Two  
5 aerosol concentrations were used in the experiments:  $\sim 50$  and  $100 \text{ cm}^{-3}$ . Particle losses were  
6 calculated by measuring the particle concentration at the entrance and at the bottom of the  
7 chamber (i.e., before PALMS). Particle losses were  $14 \pm 10\%$ .

8  
9  
10 After the particles were generated, but before they entered the chamber, the particle flow either  
11 passed directly over a RH sensor (Omega EE08) in a Low RH experiment or through a  
12 humidifier and then over the RH sensor in a High RH experiment. The humidifier, a mixing  
13 volume containing Milli-Q 18.2 MΩ cm water, was used to increase the RH of the airflow to  
14  ~~$88 \pm 3$~~   $88\%$ . Two additional RH sensors were placed at the chamber top and bottom to monitor  
15 the temperatures and RH profiles. Valves were placed in-line to either block or admit particles  
16 depending on the experimental phase described in the following paragraphs.

17  
18 The overall length of the MIT-CEC is ~~1.60~~ 1.40 cm. The chamber was constructed of glass with  
19 stainless steel and aluminum ports for connections to the dryers, aerosol and droplet inputs. The  
20 upper part of the chamber, termed the Droplet Generator and Neutralizer (DGN) unit, is a 21 cm  
21 long 5 cm diameter stainless steel cylinder. This section contains a commercial droplet generator,  
22 a charge neutralizer, and ports for aerosol injection. A mesh grid is used to straighten the particle  
23 flow. Droplets are injected vertically downward through a tube ~~to avoid contact so they do not~~  
24 ~~come in contact~~ with the aerosol particles until ~~they reach~~ the lower portion of the DGN. A  
25 neutralizer, containing two Polonium-210 strips (0.64 cm thickness and 15 cm long) ~~in length~~, is  
26 placed in the lower part of the DGN. The lower part of the DGN is ~~then~~ connected directly to the  
27 main chamber, a single-jacketed glass column with an inner diameter of 5 cm. The length of the  
28 jacketed area is ~~1.40~~ 1.40 cm. An aluminum cone reducer, 4 cm in length, is attached to the bottom of  
29 the main chamber in order to focus the flow into a variable length dryer used for condensed  
30 phase water removal prior to analysis with PALMS.

31

1 A Microdrop Technologies Dispenser Systems (Microdrop Technologies Norderstedt, Germany  
2 Model MD-K-130) was used to generate droplets. This ~~Droplet generator~~Generator (DG), based  
3 on piezo-driven inkjet printing technology, generates droplets with an average radius of  
4 ~~~22~~21.6±0.8 ~~μm radius~~. A Microdrop CCD camera (Model MD-O-538-85) ~~coupled to and~~  
5 imaging ~~optiessystem~~, ~~yielding with~~ a total magnification of 120x, was used to determine droplet  
6 size on a daily basis before the generator was set atop the chamber. The size differed slightly for  
7 the Low and High RH experiments, 21.9 and 21.4 μm, respectively. Due to the position of the  
8 camera, droplet size could not be monitored during an experiment or within the chamber. Droplet  
9 size was, however, measured before and after the experiment, and the size was constant within  
10 the quoted uncertainty. Droplets size during experiments was also verified by the residual size  
11 after the droplets evaporated. Droplets were generated at 30Hz. This is a frequency much lower  
12 than previously used in other previous experimental works using cloud droplets (e.g., 1000Hz in  
13 Ladino et al., 2011) ~~since detection was accomplished on a single droplet, not bulk, basis where~~  
14 analysis was performed on a bulk basis. This rate yielded both a ~~collection~~coagulation signal  
15 with PALMS and minimized possible droplet-droplet collisions inside the chamber.

16  
17 As mentioned in the previous section, droplet and aerosol charge affect electro-scavenging forces  
18 and can therefore impact the ~~collection~~ coagulation rate. To determine the droplets charge, we  
19 utilized an electrometer (Liu and Pui, 1974) which was connected to the DG. Using the  
20 electrometer, we determined that  $\sim 10^4$  ~~elementary~~elemental charges are imparted to each droplet  
21 upon production from the generator. The neutralizer reduces this charge to  $400 \pm 400$   
22 ~~elementary~~elemental charges. Aerosol charge distribution was assumed to be a Boltzmann  
23 distribution after neutralization where the most common charge state other than neutral is a  
24 single charge (Wiedensohler, 1988; Hinds, 1999).

25  
26 The droplets were produced from a dilute ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; hereafter AS) solution,  
27 0.08 gL<sup>-1</sup>. Dilute AS was used due to its atmospheric relevance as a condensation nucleus and in  
28 order to provide a chemically distinct signature for detection of droplets residuals with PALMS.  
29 Based on the original droplet size and solution concentration, and as verified by PALMS sizing,  
30 a single effloresced residual ~~particle~~ was ~~~~~0.75 μm radius.

31

1 | The PALMS instrument determines size and chemical composition of ~~a single an individual~~  
2 | ~~aerosol~~-particle basis. A detailed description of the PALMS instrument has been published  
3 | previously (Murphy and Thomson, 1995; Cziczo et al., 2006). In brief, particles enter an  
4 | aerodynamic inlet, which focuses the particle stream. ~~The p~~Particles then enter ~~a-the~~ source  
5 | region where they pass through two 532 nm Nd:YAG laser beams which yields scattering signals  
6 | that are used to trigger an excimer laser beam (193 nm). The time difference between the two  
7 | scattering signals provides an aerodynamic size of the particle (Cziczo et al., 2006). The excimer  
8 | laser ablates and ionizes the particle. The ions from each detected particle are ejected into a  
9 | reflectron mass spectrometer and detected ~~at-on~~ a micro-channel plate (MCP), thus providing a  
10 | mass spectrum of the particle.

11

## 12 | 2.2. Data Analysis

13 | Droplet residuals, PSL particles and coagulated droplets ~~each exhibit~~had a distinct sizes PALMS  
14 | and mass ~~spectrum~~-spectrum (Fig. 3). In positive ion mode PSL particles had distinct signatures  
15 | of their carbon chains at mass to charge ratio (M/C) ~~of~~ 12 (C<sub>1</sub>), 24 (C<sub>2</sub>), 36 (C<sub>3</sub>) and 48 (C<sub>4</sub>); in  
16 | many cases the carbons were associated with hydrogen. Droplets residuals had a signature at  
17 | M/C 18 (NH<sub>4</sub>) and 30 (NO). It should be noted that the PSLs did not contain the droplet  
18 | signature nor did the droplets contain a PSL signature. Coagulated droplets, on the other hand,  
19 | exhibited mass spectra with signatures from both the droplet residuals and the PSL particles (Fig.  
20 | 3, Panel C). In order to determine the presence or absence of a collection ~~coagulation~~-event, a  
21 | Coagulated Index (CI) was developed:

$$22 | \quad \text{CI} = \frac{\text{carbon signal}}{\text{amonium sulfate signal}} \quad (1)$$

23 | Each experiment started by passing only droplets through the chamber. This allowed for a  
24 | reference case of maximum CI without collection ~~coagulation~~-based on >1000 droplets analyzed.  
25 | After the reference spectra were obtained, aerosol particles were added to the chamber by  
26 | opening the in-line valves. Each collection ~~coagulation~~-experiment contained at least 1000  
27 | analyzed droplets with a CI value greater than the baseline obtained from the droplet-only phase.  
28 | CI for each droplet during a typical experiment is plotted in Fig. 4. The leftmost data is the  
29 | baseline CI, in this case for >2500 droplets. The collection ~~coagulation~~-experiment is on the right  
30 | where 5 collection ~~coagulation~~-events were observed. Using these data an Experimental  
31 | Collection Ratio (ECR) was calculated:

$$ECR = \frac{\text{number of droplets that coagulated}}{\text{total number of droplets}} \quad (2)$$

For this experiment, 5 out of the 1189 droplets experienced ~~collection~~ coagulation, yielding an ECR of  $4.2 \times 10^{-3}$ . It should be noted that an experiment of PSL with AS residual (from the evaporated droplet) was performed. Several thousand spectra were examined with PALMS but no collection event was observed.

A CE value, normalized by the number of particles contained within the volume swept out by a falling droplet, was also calculated. This calculation takes into account a droplet's cross section, the aerosol concentration, and the effective interaction length of the chamber so that comparisons can be drawn between these data and previous experiments ~~using different setups~~:

$$CE = \frac{ECR}{\pi(R_d + R_a)^2 L A_c} \quad (3)$$

~~Where~~ where  $R_d$  is the droplet radius,  $R_a$  is the aerosol radius,  $A_c$  is the aerosol number concentration and  $L$  is the effective interaction length of the chamber, which defined as:

$$L = \frac{V_d \cdot l}{V_d + V_a} \quad (4)$$

where  $V_d$  and  $V_a$  are the droplet terminal (settling) velocity and the velocity of the air carrying the particles, respectively, and  $l$  is the length of the chamber before the droplets evaporate. ~~length of the chamber and  $A_c$  is the aerosol number concentration.~~

### 2.3. Theoretical CE Models

Previous studies have theoretically determined the CE between droplets and aerosol particles (Slinn and Shen, 1970; Beard, 1974; ~~Wang and Pruppacher, 1977~~; Grover et al., 1977; Davenport and Peterst, 1978; Wang et al., 1978; Park et al., 2005; Tinsley et al., 2000; Chate, 2005; Tinsley et al., 2006; Andronache et al., 2006; Feng, 2007; Croft et al., 2009; Tinsley, 2010; Wang et al., 2010; Tinsley and Leddon, 2013). In order to understand our experimental data, we compare them to a theoretical treatment of CE. This treatment includes Brownian diffusion, interception, inertial impaction, thermophoresis, diffusiophoresis and electro-scavenging. The total CE is the sum of these processes. The CE due to Brownian diffusion, interception and inertial impaction are based on Park et al. (2005) which, ~~in turn~~, expands on Jung and Lee (1998). Thermophoresis, diffusiophoresis and electro-scavenging are based on Wang et al.

1 | (2010) which expands on [Andronache et al. \(2006\)](#) and Davenport and Peterst (1978). The  
2 | efficiencies used here are:

$$3 \quad E_{Bdiff} = 2 \left( \frac{\pi\sqrt{3}}{4P_e} \right)^{2/3} \left[ \frac{(1-\alpha)(3\frac{\mu_w}{\mu_a}+4)}{(1-\frac{6}{5}\alpha^{1/3}+\frac{1}{5}\alpha^2)+\frac{\mu_w}{\mu_a}(1-\frac{9}{5}\alpha^{1/3}+\frac{1}{5}\alpha^2+\alpha)} \right]^{1/3}$$

4 | (45)

$$5 \quad E_{int} = \left[ \frac{1-\alpha}{(1-\frac{6}{5}\alpha^{1/3}+\frac{1}{5}\alpha^2)+\frac{\mu_w}{\mu_a}(1-\frac{9}{5}\alpha^{1/3}+\frac{1}{5}\alpha^2+\alpha)} \right] \left[ \frac{(D_a/D_d)}{1+(D_a/D_d)} + \frac{1}{2} \left( \frac{(D_a/D_d)}{1+(D_a/D_d)} \right)^2 \left( 3 \frac{\mu_w}{\mu_a} + 4 \right) \right]$$

6 | (56)

$$7 \quad E_{imp} = \left( \frac{Stk}{Stk+0.35} \right)^2$$

8 | (67)

$$9 \quad E_{th} = \frac{4 \left[ \frac{2Cc \left( K_a + 5 \frac{\lambda}{D_d} - K_p \right) K_a}{5P \left( 1 + 6 \frac{\lambda}{D_d} \right) \left( 2K_a + K_p + 10 \frac{\lambda}{D_d} - K_p \right)} \right] (2 + 0.6R_e^{1/2} P_r^{1/3}) (T_a - T_d)}{D_d V_d}$$

10 | (78)

$$11 \quad E_{df} = \frac{4 \left[ \frac{T_a D_w (M_w)}{P (M_a)} \right]^{1/2} (2 + 0.6R_e^{1/2} P_r^{1/3}) \left( \frac{\rho_a - \rho_d}{T_a - T_d} \right)}{D_d V_d}$$

12 | (89)

$$13 \quad E_{ec} = \frac{16C_c k_{ec} Q_r q_r}{3\pi\mu_a D_p^2 D_d V_d}$$

14 | (910)

15 | Wherewhere,  $E_{Bdiff}$ ,  $E_{int}$ ,  $E_{imp}$ ,  $E_{th}$ ,  $E_{df}$  and  $E_{es}$  are Brownian diffusion, interception, inertial  
16 | impaction, thermophoresis, diffusiphoresis and electro-scavenging efficiencies, respectively. A  
17 | full definition of all variables is provided in Table 2. These theoretical models include the known  
18 | forces that affect CE values and which were measured or constrained by data in the experimental  
19 | measurements presented here. It should be noted that although these theoretical models were  
20 | developed for large droplets they have been used to calculate CE for sizes relevant to this work  
21 | (Ladino, 2011).

### 23 | 3. Result and Discussion

24 | A total of 16 collection coagulation experiments were performed. The collection coagulation  
25 | experiments contained were for four different aerosol sizes (with radius 0.025, 0.125, 0.25 and

1 0.475  $\mu\text{m}$ ), each at two different concentrations (50 and 100  $\text{cm}^{-3}$ ) and ~~at~~ two different RH  
2 conditions (15 $\pm$ 13% and 88 $\pm$ 13%). A full description of the experiments is summarized in Table  
3 3. All experiments were conducted at room temperature (22.5 $\pm$ 1.3 $^{\circ}\text{C}$ ). Droplet radius was 21.6 $\pm$ 1  
4 0.8  $\mu\text{m}$ . Terminal (settling) velocity was calculated based on the experimental temperature and  
5 droplet size. The terminal velocity varied from 4.7  $\text{cm s}^{-1}$  to 5.8  $\text{cm s}^{-1}$ . ~~Average\_droplet~~Total  
6 droplet evaporation time (i.e., residence in the generator section and experimental chamber) was  
7 calculated based on the average droplet size and the RH condition: 2.1 and 14.716.6 seconds for  
8 the Low and High RH cases, respectively. The droplets residence time in the chamber was 0.7  
9 and 6.1 seconds, for the Low and High RH cases, respectively.:- Calculations of Reynolds  
10 number were performed using the experimental conditions and chamber geometry. Reynolds  
11 numbers from 0.12 to 0.16 were calculated and, based on this, we assume the aerosol particles  
12 and droplets interact in flow condition close to laminar throughout the chamber.  
13

14 Each ~~collection coagulation~~ experiment incorporated between 1039 ~~to~~ and 4598 droplets. The  
15 droplets that coagulated were identified based on their CI as described in section 2.2. ECRs were  
16 based on the ratio between the number of coagulated droplets to the total number of droplets per  
17 experiment and these values varied from 6.5 $\times 10^{-4}$  to 8.6 $\times 10^{-3}$  for the Low RH experiments and  
18 from 9.6 $\times 10^{-4}$  to 4.9 $\times 10^{-3}$  for the High RH experiments. ECR was higher for the higher aerosol  
19 concentration experiments for most particles sizes; this is consistent with higher aerosol  
20 concentration increasing the chances for particles to coagulate with droplets.  
21

22 CE value was calculated for each experiment, ~~based on the average droplet size measured from~~  
23 each experiment and when similar RH, aerosol size and concentration conditions were used. CE  
24 values, normalized to ~~experimental conditions aerosol concentration and time~~, ranged from  
25 2.0 $\times 10^{-1}$  to 1.6 5.7 $\times 10^{-3}$  to 4.6 $\times 10^{-2}$  for the Low RH experiments and from 6.4 $\times 10^{-3}$  to 2.2 $\times 10^{-2}$   
26 1.5 $\times 10^{-2}$  to 9.0 $\times 10^{-2}$  for the High RH experiments (see Fig. 5). These values are in a similar range  
27 to that found by previous works (Wang and Pruppacher, 1977; Lai et al., 1978). Shown in Fig. 5,  
28 ~~a~~ no significant difference in CE values between the two aerosol concentrations (50 and 100  $\text{cm}^{-3}$ )  
29 was ~~not~~ observed. Most previous experiments did not specify what aerosol concentration were  
30 used during their ~~collection coagulation~~ experiments (Hampl et al., 1971; Lei et al., 1978; Prodi  
31 et al., 2014). Those who did specify had a higher aerosol concentration, in most cases above

1 | atmospheric relevance ~~outside~~except within polluted boundary layers (above  $1000 \text{ cm}^{-3}$ ; Beard,  
2 | 1974; Wang and Pruppacher, 1977; Barlow and Latham, 1983; Deshler, 1985; Ladino et al.,  
3 | 2011). The use of these high aerosol concentrations was likely due to the limitation of bulk  
4 | analysis methods, as discussed in the Introduction, which required a high concentration for  
5 | adequate signal.

6 |  
7 | It has been shown theoretically by Wang et al. (1978), Grover and Pruppacher (1985) and Ladino  
8 | et al. (2011), and experimentally by Grover et al. (1977) that ~~the~~ CE increases with decreasing  
9 | RH ~~value~~. This is because a lower RH leads to an increase of the evaporation rate of the droplet,  
10 | which strengthens the phoretic forces ~~that increases the CE~~. Two RH conditions were measured  
11 | in this experimental work, Low ( $\sim 15 \pm 3\%$ ) and High ( $\sim 88 \pm 3\%$ ). ~~The two point RH trend here is~~  
12 | ~~weak, possibly due to relatively fast evaporation. Higher~~Consistent with these previous works,  
13 | we find a higher CE values ~~were found~~ for the Low RH experiments, by as much at a particle  
14 | size of  $0.025 \mu\text{m}$  as one order of magnitude, when compared to the otherwise similar High RH  
15 | experiments. We suggest that for these small particles Brownian diffusion effects are stronger  
16 | than phoretic forces.

17 |  
18 | In the previous experimental studies of ~~collection~~coagulation, many considered significantly  
19 | larger droplets (of drizzle or rain size; Leong et al., 1982; Pranesha and Kamra, 1993; Chate and  
20 | Kamra, 1997) and particle sizes (super-micrometer; Owe Berg et al., 1970; Hampl and Kerker,  
21 | 1972). For these reasons, we do not believe a direct comparison to our data is valid. This lack of  
22 | comparison holds for other studies, using aerosol in a similar size range but with much larger  
23 | droplets (Hampl et al.; 1971; Deshler, 1985; Vohl et al., 2001). The droplets used in the current  
24 | work were significantly smaller,  $>15$  times, than those used in the aforementioned experiments.  
25 | Those studies reported lower CE values than measured here, in some cases by an order of  
26 | magnitude. It has been shown in previous experimental and theoretical studies that the CE  
27 | decreases with increasing droplet sizes (Davenport and Peterst, 1978; Wang et al., 1978; Leong  
28 | et al., 1982; Pranesha and Kamra, 1993). It is likely that some of the differences in CE are also a  
29 | result of different experimental conditions, such as droplets and/or particle charge.

1 Two experimental studies, Wang and Pruppacher (1977) and Lai et al. (1978), are roughly  
2 similar to our study and both exhibit CE values slightly lower than the values from our  
3 measurements. A comparison is provided in Fig. 6. The differences in CE values could be a  
4 result of the different experimental conditions. For example, Wang and Pruppacher (1977) and  
5 Lai et al. (1978) used somewhat larger droplets (of 170-340  $\mu\text{m}$  and 620  $\mu\text{m}$ , respectively), with  
6 higher charges than those used in the current work,  $5 \times 10^5$ - $7.1 \times 10^6$  elementary charges in Wang  
7 and Pruppacher (1977) and  $6.6 \times 10^8$ - $1.9 \times 10^9$  elementary charges in Lai et al. (1978). The larger  
8 droplets and higher droplets charges used by Wang and Pruppacher (1977) and by Lai et al.  
9 (1978) could explain the differences between these works and ours, as will be discussed further  
10 in subsequent sections. Lai et al. (1978) did not mention the aerosol concentrations or RH  
11 conditions used in their work. Wang and Pruppacher (1977) used a RH condition similar to the  
12 low RH used in this study but with higher aerosol concentrations. It is expected that a higher  
13 aerosol concentration will increase the chance of collision between particles and droplets, which  
14 will increase the value of ECR, but will not affect CE, which is normalized.

15 ~~Two experimental studies, Wang and Pruppacher (1977) and Lai et al. (1978), are comparable to~~  
16 ~~our study and both exhibit CE values in a range similar to our measurements. A comparison is~~  
17 ~~provided in Fig. 6. While difference in CE values appears at some of the measures particles~~  
18 ~~sizes, overall most had a similar range of CE values. It is noteworthy that similar CE values were~~  
19 ~~measured despite different experimental conditions. For example, Wang and Pruppacher (1977)~~  
20 ~~and by Lai et al. (1978) used somewhat larger droplets in their experiments (of 170-340  $\mu\text{m}$  and~~  
21 ~~620  $\mu\text{m}$ , respectively). In addition, both works used droplets with higher charges than those used~~  
22 ~~in the current work,  $5 \times 10^5$ - $7.1 \times 10^6$  elementary charges in Wang and Pruppacher (1977) and~~  
23  ~~$6.6 \times 10^{28}$ - $2 \times 10^{29}$  elementary charges in Lai et al. (1978). Since it is known that droplets carrying~~  
24 ~~electric charges will have higher CE (Barlow and Latham, 1983; Byrne and Jennings, 1993;~~  
25 ~~Pranisha and Kamra, 1997a,b; Tinsley and Leddon, 2013; Tinsley et al., 2000; Tinsley, 2010) it~~  
26 ~~possible the size and charge conditions offset each other, lending to the comparison to our data.~~  
27 ~~Lai et al. (1978) did not mention the aerosol concentrations or RH conditions used in their work.~~  
28 ~~Wang and Pruppacher (1977) used RH condition similar to that used in this work but with a~~  
29 ~~higher aerosol concentrations.~~

30 The most similar experimental conditions to ours are those of Ladino et al. (2011). Ladino et al.  
31 used similar droplets (radius of 12.8-20  $\mu\text{m}$ ) and particle sizes (radius of 0.05-0.33  $\mu\text{m}$ ).

1 Experiments were conducted at RH conditions similar to our High RH experiments (88±2%).  
2 Although most of the experimental conditions were similar, there are noteworthy differences  
3 between the CE values of Ladino et al. and those measured in this study, which are lower overall  
4 (Fig. 6). The main difference between the two studies is the droplet charge, which has a stronger  
5 impact on the electro-scavenging force. Ladino et al. used droplets with high charges,  $\sim 5 \times 10^4$   
6 elementary charges per droplet (Claudia Marcolli, personal communication, 2014), which are  
7 two orders of magnitude higher than the one used in this study. The higher droplet charge  
8 explains the higher CE values compared to those determined in this ~~work~~ study.

9  
10 In order to compare our experimental work with theoretical studies, a set of calculations  
11 combining six different forces, as described in section 2.3, ~~combining six different forces~~ was  
12 conducted. Examples of theoretical forces and CE are given in Fig. 7. The properties used in  
13 these calculations included an air temperature of 22.5°C, a pressure of 981 mb, RH of 50%, PSL  
14 particles with a density of 1000 Kg m<sup>-3</sup> of different sizes matching the experiments, a thermal  
15 conductivity of 0.1 Kg m s<sup>-3</sup> K<sup>-1</sup> (Romay et al., 1998), and a constant droplet radius of 21.6 μm.  
16 Droplets were assumed to have 400 elementary charges, the average value determined by the  
17 electrometer experiments (see section 2.1). These calculations were made for charged particles  
18 that contained one elementary charge per particle. Most particles in a Boltzmann distribution  
19 contain no charges and will therefore not be affected by electro-scavenging forces. The most  
20 common charge state other than neutral is a single charge, about 10% of particles, and this forms  
21 the basis of our calculation (Hinds, 1999). This is further supported by a decreasing effect of  
22 multiple charges when considering the effect on CE (Fig. 8).

23  
24 From Fig. 7, the total CE varies for different particle sizes. The contribution of Brownian  
25 diffusion decreases rapidly as particle size increases while the contribution of inertial impaction  
26 increases rapidly as particle size increases. Interception forces also increase as particle size  
27 increases, but its effect is smaller than that of inertial impaction. The contribution of  
28 diffusiophoresis is smaller than that of thermophoresis for particles below 0.05 μm. The  
29 Greenfield gap is evident in this figure, as the local minimum between the diffusion- and  
30 impaction-dominated regimes. This corresponds to a minimum at a particle size of  $\sim 0.15$  μm.  
31 ~~From In~~ Fig. 7, ~~one can see that~~ electro-scavenging have a significant impact on the curves.

1 Previous work by Wang et al. (1978), Byrne and Jennings (1993) and Tinsley et al. (2000)  
2 showed the presence of charge on droplets and aerosol can increase the CE throughout the  
3 Greenfield gap. Moreover, as described by Tinsley et al. (2001), the electrical effect is more  
4 important for smaller particle sizes ( $< 0.1 \mu\text{m}$ ) than Brownian diffusion. This could explain why  
5 the Greenfield Gap is highly pronounced in the data in Fig. 6, while it is more pronounced in the  
6 data of Lai et al. (1978) and Ladino et al. (2011).

7  
8 In order to directly compare theoretical and measured CE, two cases were calculated: (1) droplet  
9 radius  $21.4 \mu\text{m}$  and ~~the Low RH value~~ and (2)  $21.9 \mu\text{m}$  and ~~the High RH value~~. In both  
10 calculations 0, 400 and 800 elementary charges were assumed per droplet; the range of values  
11 determined in the electrometer experiments. ~~One elementary charge was used for the particles,~~  
12 ~~consistent with a Boltzmann distribution imparted by the neutralizer.~~ The result of this  
13 comparison is shown in Fig. 8, where the points represent the experimental work and the lines  
14 represent the theoretical CE. Overall, ~~there is an agreement between~~ the experimental work  
15 ~~presents higher CE values compared to the theoretical CE and the total CE within this droplet~~  
16 ~~charge regime.~~ Differences between theoretical and measured CE may be considered a result of  
17 conditions not modeled theoretically or difficult to constrain experimentally. Possibilities include  
18 rare multiply charged particles, aerosol doublet and triplet charging aerosol droplet electric  
19 interaction that are not fully considered (such as the induced dipole force), and the evaporation  
20 rate of the droplets, variable terminal settling velocity due to changes in droplet size, and the  
21 present of solute in the droplets. Regarding the comparison to Ladino et al. (2011), a simulation  
22 ~~with a higher elementary charge ( $5 \times 10^4$  per droplet) was also calculated. This calculation~~  
23 ~~exhibits higher CE values, by an order a magnitude, than the simulated CE lines which appear~~  
24 ~~for our charge conditions (Fig. 8).~~

25  
26 As noted earlier, the droplets evaporated completely while in the chamber at both RH conditions.  
27 Since droplet size could not be determined precisely at the moment when collection occurred in  
28 the chamber, calculations of theoretical CE were performed for three relevant droplets sizes: The  
29 first was the original droplet size as measured from the droplet generator ( $21.4$  and  $21.9 \mu\text{m}$ , for  
30 Low and High RH conditions, respectively) for the full droplet lifetime. The second, droplet size  
31 with half the volume of the original droplet (radius of  $17$  and  $17.4 \mu\text{m}$ , for Low and High RH

1 conditions, respectively) over the full lifetime. For the third an extreme case was considered,  
2 droplets with a radius of 5  $\mu\text{m}$  for the full droplet lifetime. The results of these calculations are  
3 presented in Fig. 10. Overall, as droplet size decreases, CE values increases. In the extreme 5  $\mu\text{m}$   
4 case, CE values increases by more than an order of magnitude. For the Low RH case the best  
5 agreement is with the 5  $\mu\text{m}$  case, which logically follows from the rapid evaporation of these  
6 droplets. In the High RH case the experimental CE values fall nearest the half volume case,  
7 which again logically follows since these droplets more slowly evaporate.

8  
9 It is known that droplets carrying higher electric charge have higher CE (Barlow and Latham,  
10 1983; Byrne and Jennings, 1993; Pranesha and Kamra, 1997a,b; Tinsley and Leddon, 2013;  
11 Tinsley et al., 2000; Tinsley, 2010), and this is consistent with our data in Fig 9. Droplets size  
12 also affects CE, where smaller droplets have higher CE values (Lai et al., 1978; Pranesha and  
13 Kamra, 1996). Fig. 11 shows a calculation of CE based on different droplet charges and sizes.  
14 Two droplets sizes were used: 20  $\mu\text{m}$ , which is similar to the size used in this study and by  
15 Ladino et al. (2011) and 200  $\mu\text{m}$ , which is the size used by Wang and Pruppacher (1977). Three  
16 different droplet charges were considered: 400 elementary charges, as used in this study,  $5 \times 10^4$   
17 elementary charges, used by Ladino et al. (2011) and  $5 \times 10^5$  elementary charges, the lower limit  
18 of charges used by Wang and Pruppacher (1977). Shown in Fig. 11, CE values increase as  
19 droplet charge increases. Droplets size and charge conditions can counteract each other in the  
20 case of larger droplets (lower CE) with higher charge (higher CE). We suggest this may explain  
21 the agreement found between the CE values measured in this study and those of Wang and  
22 Pruppacher (1977) and the disagreement between our values and those of Ladino et al. (2011). It  
23 should be noted that the experimental CE values fall within the region of the 20  $\mu\text{m}$  case. The CE  
24 values of the small particles ( $<0.1 \mu\text{m}$ ) match the theoretical CE, while for larger particles ( $>0.1$   
25  $\mu\text{m}$ ) they are slightly higher. These differences could be a result of some conditions not modeled  
26 theoretically or conditions difficult to constrain experimentally, as discussed above.

#### 28 **4. Conclusions**

29 An experimental setup has been constructed to measure the CE of  $\sim 2221.6 \mu\text{m}$  radius water  
30 droplets with sub-micrometer PSL particles of 0.025, 0.125, 0.25 and 0.475  $\mu\text{m}$  radius and  
31 concentrations of 50 and 100  $\text{cm}^{-3}$ . Two RH conditions,  $15 \pm 4\%$  and  $88 \pm 4\%$ , were used.

1 Coagulated droplets were identified on a single-droplets basis using a single particle mass  
2 ~~spectrometers~~spectrometry. CE values ranged from  $2.0 \times 10^{-1}$  to  $1.6$   ~~$5.7 \times 10^{-3}$  to  $4.6 \times 10^{-2}$~~  for the  
3 Low RH and from  $1.5 \times 10^{-2}$  to  $9.0 \times 10^{-2}$   ~~$6.4 \times 10^{-3}$  to  $2.2 \times 10^{-2}$~~  for the High RH cases. ~~CE values~~  
4 ~~were not significantly different from one another in the conditions employed in this work.~~

5  
6 The CEs measured here were found to be in agreement with previous experimental studies on  
7 droplets and aerosol particles of roughly similar sizes. Differences in measurements appear to be  
8 a result of variable (and sometimes undefined) aerosol and droplet charge, which has been  
9 theoretically shown to play an important role in CE. This finding highlights the need for explicit  
10 determination of droplet and aerosol charges when presenting results of collection coagulation  
11 experiments.

12  
13 This technique overcomes some of the limitations inherent in previous studies which required a  
14 bulk collection of material. The analytical methods employed were limited by issues such as  
15 signal to noise and an inability to observe multiple collection events on single droplets.  
16 Moreover, very few experimental works have been performed with atmospherically relevant  
17 particles sizes (Radke et al., 1980; Andronache et al., 2006), another advantage of this technique.  
18 The droplet size and charge state used here are also consistent with atmospheric conditions.

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1 Table 1: Experimental results from previous studies of CE.

Reference	Droplets radius ( $\mu\text{m}$ )	Aerosol radius ( $\mu\text{m}$ )	Aerosol type	Aerosol concentration ( $\text{cm}^{-3}$ )	RH
Starr and Mason (1966)	100-1000	2.25, 2.5, 6.4	Spores, various	Not Given	Not Given
Owe Berg et al (1970)	1210-1305	7.5-15	PSL	Not Given	Not Given
Hampl et al (1971)	710-2540	0.2-0.5	AgCl	Not Given	Not Given
Hampl and Kerker (1972)	2540	53-2000	AgCl	Not Given	Not Given
Beard (1974)	200-425	0.35-0.44	$\text{In}(\text{C}_5\text{H}_7\text{O}_2)_3$	$5 \times 10^4$	97-99
Kerker and Hampl (1974)	940-2540	0.15-0.6	AgCl	Not Given	Not Given
Wang and Pruppacher (1977)	150-2500	$0.25 \pm 0.03$	$\text{In}(\text{C}_5\text{H}_7\text{O}_2)_3$	$10^{17}-10^{18}$	$23 \pm 2$
Lai et al. (1978)	620, 820, 980	0.15- 0.45	AgCl	Not Given	Not Given
Leong et al. (1982)	56-93	0.58-3.2	$\text{MnO}_4\text{P}_2$	Not Given	$\sim 30$
Barlow and Latham (1983)	270-600	0.2-1	Not Given	$>1000$	50-70
Deshler (1985)	1200-1300	0.03,0.06, 0.13	Not Given	$2 \times 10^4 - 1.4 \times 10^5$	60-97
Byrne and Jennings (1993)	400- 550	0.35-0.88	Not Given	Not Given	50-80
Pranisha and Kamra (1993)	1800, 2100, 2400	0.95, 1.9, 3.2	NaCl	Not Given	Not Given
Pranisha and Kamra (1996)	1800, 2100, 2400	0.95, 1.9, 3.2	NaCl	Not Given	35-50
Pranisha and Kamra (1997a)	1800, 2100, 2400	0.95, 1.9, 3.2	NaCl	Not Given	35-50
Chate and Kamra (1997)	1800, 2100, 2400	1.5, 2 , 3	$\text{MgSO}_4$ & $\text{MnCl}_2$	Not Given	35-50
Vohl et al. (2001)	346, 1680, 2880	0.16-0.24	$\text{In}(\text{C}_5\text{H}_7\text{O}_2)_3$	Not Given	40
Ladino et al. (2011) & Ladino (2011)	12.8, 15, 18.2, 20	0.05-0.33	$\text{LiBO}_2$	$2 \times 10^3$	$88 \pm 2$
Prodi et al (2014)	240-1075	0.2-1	NaCl	Not Given	$<100$

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1 Table 2: Definition of acronyms and relevant units.

Parameter	Definitions	units
$C_c$	Cunningham slip correction factor	[-]
CE	Collection Efficiency	[-]
$D_a$	Aerosol particles diameter	[m]
$D_d$	Droplets diameter	[m]
$E_{Bdiff}$	Brownian diffusion -efficiency	[-]
ECR	Experimental collection ratio	[-]
$E_{ec}$	Electric charges -efficiency	[-]
$E_{df}$	Diffusiophoresis -efficiency	[-]
$E_{imp}$	Inertial impaction -efficiency	[-]
$E_{int}$	Interception -efficiency	[-]
$E_{th}$	Thermophoresis -efficiency	[-]
$K_a$	Thermal conductivity of moist air	[Kg m s <sup>-3</sup> K <sup>-1</sup> ]
$K_p$	Thermal conductivity of particles	[Kg m s <sup>-3</sup> K <sup>-1</sup> ]
Ma	Molecular weight of air	[Kg mol <sup>-1</sup> ]
$k_{ec}$	K constant for $E_{ec}$ calculations equal to $9 \times 10^9$	[Nm <sup>2</sup> C <sup>-2</sup> ]
Mw	Molecular weight of water	[Kg mol <sup>-1</sup> ]
P	Atmospheric pressure	[Pa]
$P_e$	Peclet number	[-]
$P_r$	Prandtl number of air	[-]
$q_r$	Mean charge on aerosol particles	[Coulomb, C]
$Q_r$	Mean charge on droplets	[Coulomb, C]
$R_a$	Aerosol radius	[m]
$R_d$	Droplets radius	[m]
$R_e$	Reynolds number	[-]
Stk	Stokes number	[-]
$T_a$	Temperature of air	[K]
$T_d$	Temperature at droplets surface	[K]

$V_d$	Droplets terminal velocity	$[m\ s^{-1}]$ 1 2
$\mu_w$	Water viscosity	$[Kg\ m^{-1}s^{-1}]$ 3
$\mu_a$	Air viscosity	$[Kg\ m^{-1}s^{-1}]$ 4 5
$\rho_a$	Water vapor of water at air temperature	$[Pa]$ 6
$\rho_d$	Water vapor of water temperature at droplets surface	$[Pa]$ 7 8
$\lambda$	Mean free path length of air molecules	$[m]$ 9 10
$\alpha$	Packing density of drops	$[m^3]$ 11

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1 Table 3: Particle size and concentration, RH, droplets size and total analyzed and Experimental  
 2 Collection Ratio (ECR; see text for details) for this study.

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Experiment	Particle radius (μm)	Particle concentration (cm <sup>-3</sup> )	RH (%)	Droplet radius (μm)	Total number of droplets	ECR
1	0.025±0.005	48±3	11± <del>0.1</del>	20.0± <del>2.2</del>	1966	2.4E-03
2	0.025±0.005	96±8	11	20.0± <del>2.2</del>	2578	8.6E-03
3	0.025±0.005	56±13	85± <del>0.91</del>	22.2± <del>2.2</del>	3778	1.5E-03
4	0.025±0.005	100±6	83± <del>0.1</del>	22.2± <del>2.2</del>	2446	1.6E-03
5	0.125±0.01	49±5	13± <del>1.92</del>	22.2± <del>2.2</del>	1923	2.0E-03
6	0.125±0.01	88±20	15± <del>1.41</del>	22.2± <del>2.2</del>	2025	4.9E-03
7	0.125±0.01	50±3	87± <del>0.4</del>	22.2± <del>2.2</del>	4598	2.6E-03
8	0.125±0.01	102±9	88± <del>0.2</del>	22.2± <del>2.2</del>	2831	2.5E-03
9	0.25±0.02	49±2	17± <del>1.21</del>	21.7± <del>0.8</del>	1039	6.5E-04
10	0.25±0.02	92±4	16± <del>1.31</del>	21.7± <del>0.8</del>	3282	1.9E-03
11	0.25±0.02	51±2	94± <del>2.73</del>	22.2± <del>2.9</del>	1530	9.6E-04
12	0.25±0.02	101±18	90± <del>3.43</del>	22.2± <del>2.9</del>	1554	3.0E-03
13	0.475±0.02	52±3	17± <del>0.3</del>	21.7± <del>0.8</del>	1050	1.4E-03
14	0.475±0.02	98±11	20± <del>2.53</del>	21.7± <del>0.8</del>	1232	2.9E-03
15	0.475±0.02	48±10	87± <del>2.32</del>	20.9± <del>0.9</del>	1473	1.9E-03
16	0.475±0.02	99±16	88± <del>0.61</del>	20.9± <del>0.9</del>	1049	4.9E-03

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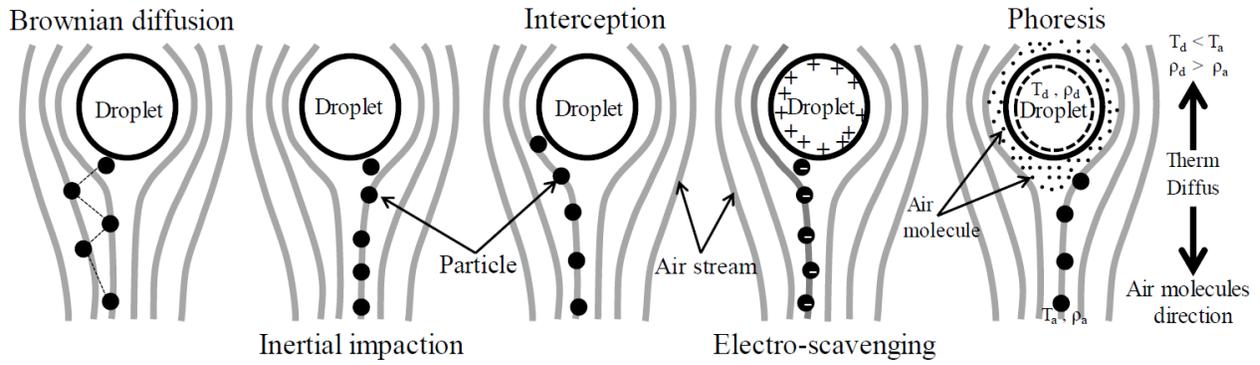
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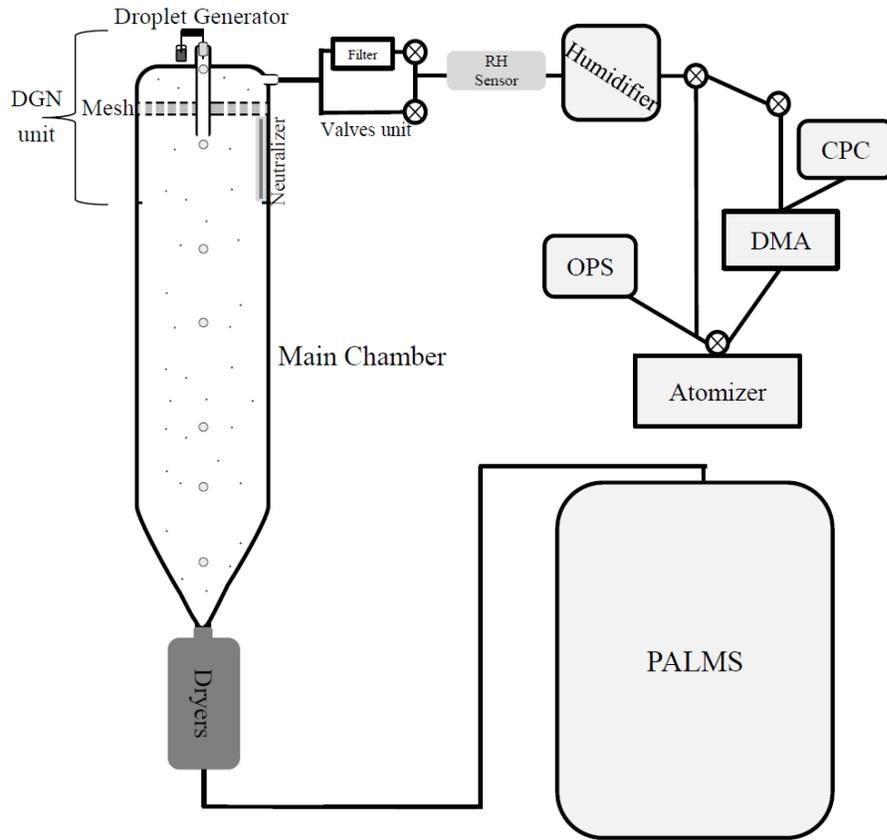
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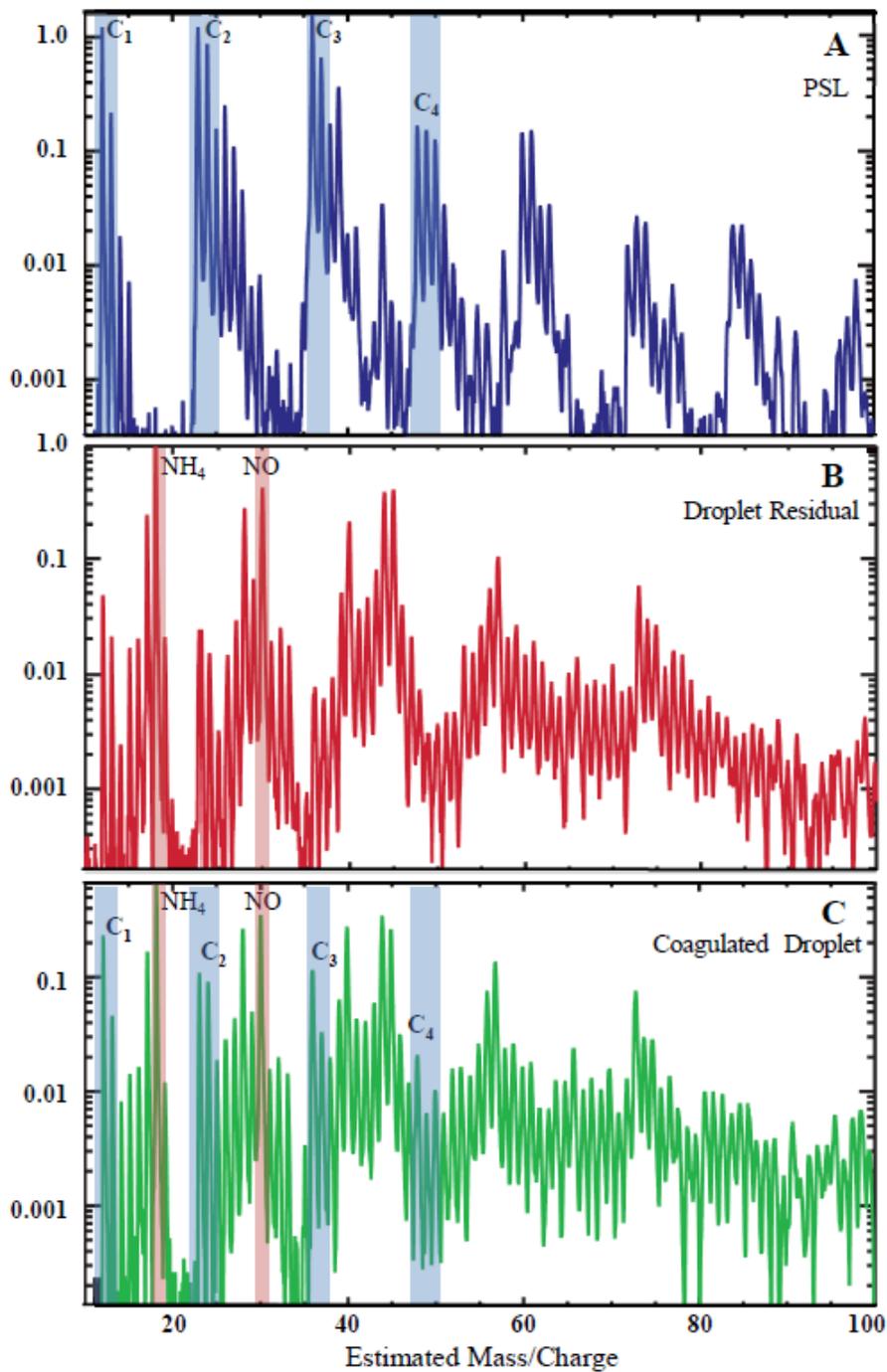
3 Figure 1: Mechanisms that affect the collection process of aerosol particles by water droplets.  
 4 The mechanisms, from left to right, are Brownian diffusion, inertial impaction, interception,  
 5 | electro-scavenging and phoresis.  $T_d$  and  $\rho_d$  are the temperature and water molecule density at the  
 6 droplet surface while  $T_a$  and  $\rho_a$  are the ambient temperature and water molecule density. See text  
 7 for additional description. Figure based on Ladino, 2011.

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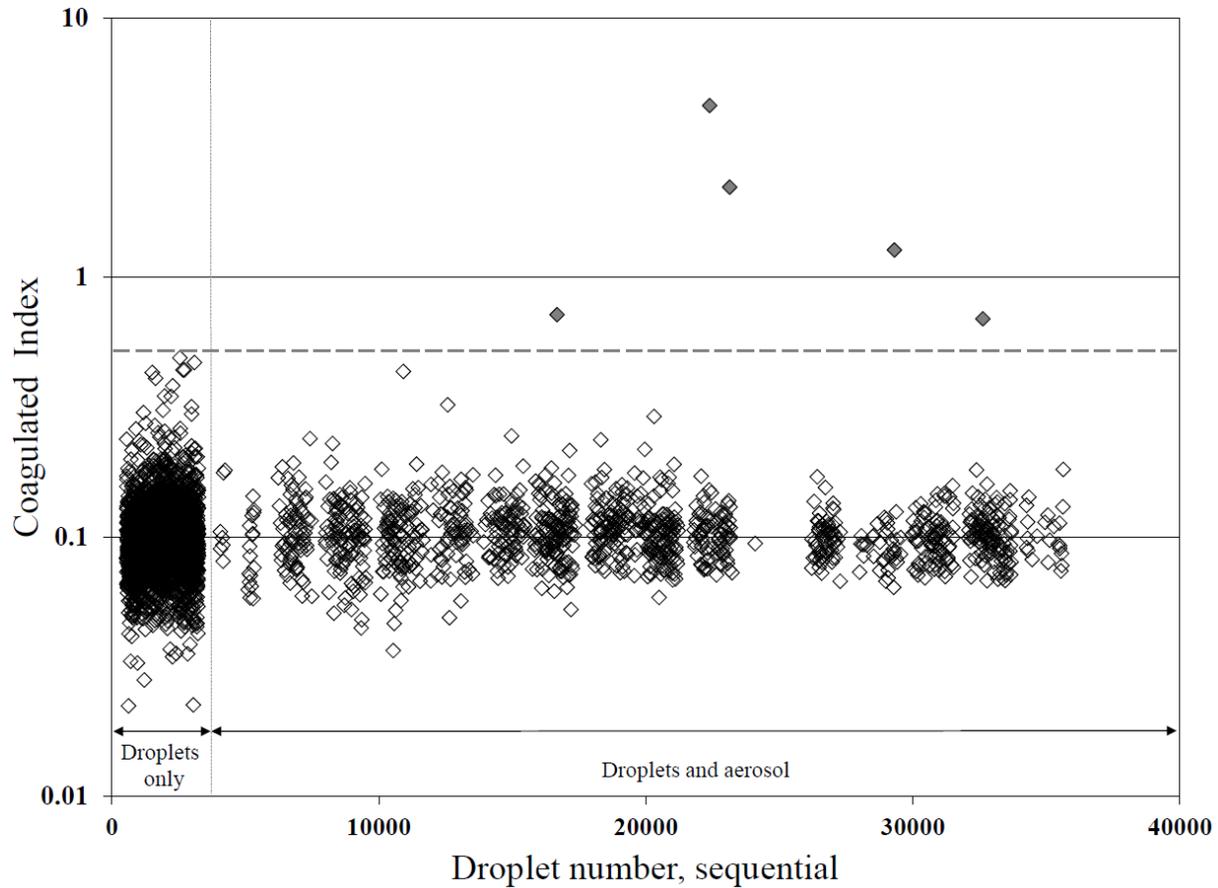
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Figure 2: Experimental setup. DGN denotes the Droplet Generation Unit. Additional description is provided in the text.



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Figure 3: Mass ~~spectraspectrum~~ spectrum of a PSL particle (panel A), an evaporated droplet composed of dilute AS, termed a droplet residual (panel B), and a coagulated and evaporated droplet that contained both a PSL particle and residual AS (panel C).



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Figure 4: Coagulated Index (CI), the ratio of PSL (aerosol) to AS (droplet residual) signal in a mass spectrum, for a typical experiment. In this experiment the RH was  $15 \pm 1\%$ , droplet radius was  $20 \mu\text{m}$ , PSL particles were  $0.125 \mu\text{m}$  radius with a concentration of  $100 \text{ cm}^{-3}$ . Each data point, the units on the X axis, represents the sequential analysis of a single droplet residuals over the course of the experiment. Particles which exceed the ratio found when only droplets are analyzed (dashed line; the ‘Droplets Only’ data acquired at the start of each experiment) are considered collection coagulation-events. There are 5 collection coagulation-events during this experimental period.

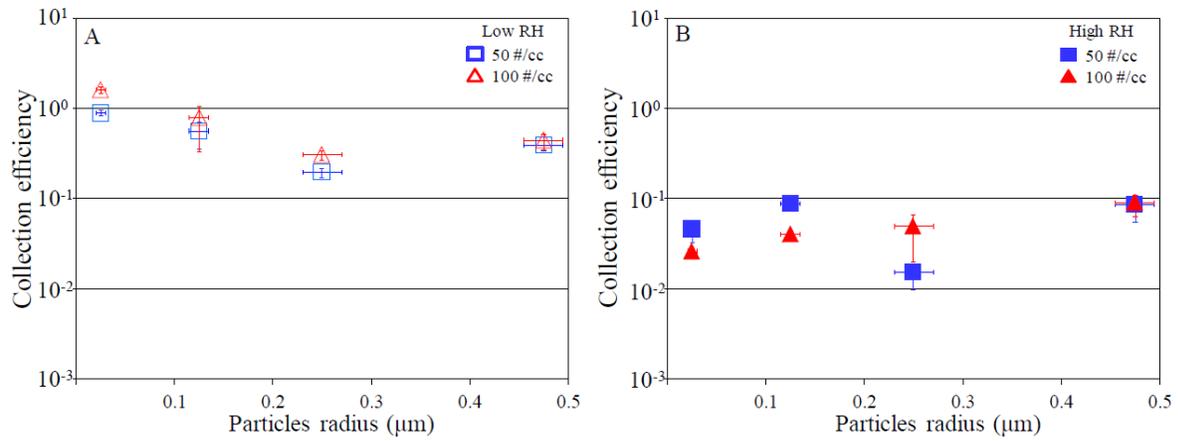
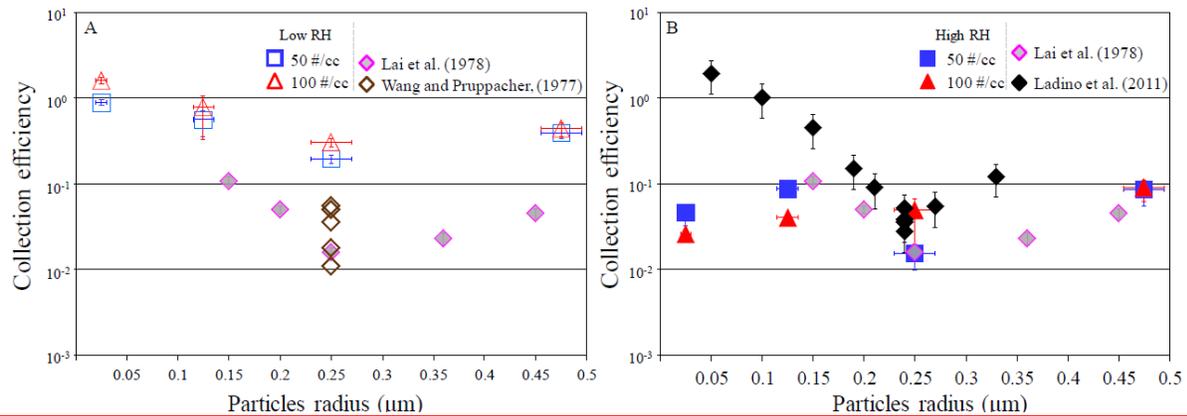


Figure 5: CE calculated as a function of particle radius. Shapes represent different aerosol concentrations. CE error bars based on droplets size, aerosol size and aerosol number concentration measured from each experiment as describe in Eq. 3. Panel A: Low RH experiments. Panel B: High RH experiments.

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4 Figure 6: Comparison of CE from this study to previous experimental work. **Panel A: Low RH**

5 **experiments. Panel B: High RH experiments.** Shapes (square and triangle) represent different

6 aerosol concentrations ~~and the hollow and filled points represent Low and High RH conditions,~~

7 **respectively.** Diamond shapes represent previous experimental work. Black diamonds are from

8 Ladino et al. (2011), RH 88±2% with aerosol concentration 2000 cm<sup>-3</sup> and droplets size of 12.8-

9 20.0 μm. Brown diamonds represent are from Wang and Pruppacher (1977), RH of 23±2% with

10 aerosol concentration ~of about 10<sup>17</sup> cm<sup>-3</sup> and droplets size of 170-340 μm. Pink diamonds are

11 from Lai et at. (1978), when 620 μm droplets were used; there was no information provided

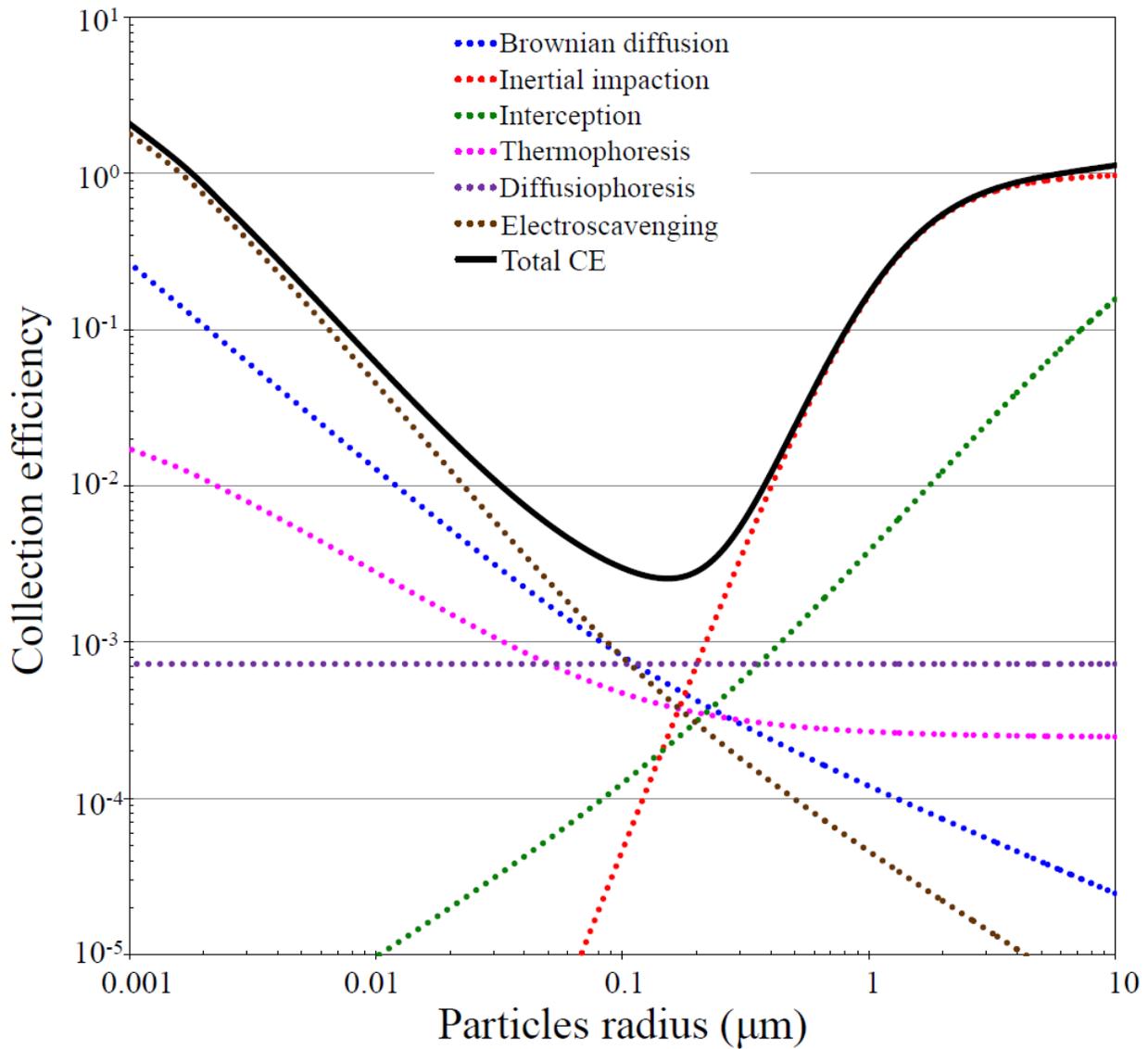
12 regarding the RH or aerosol concentration.

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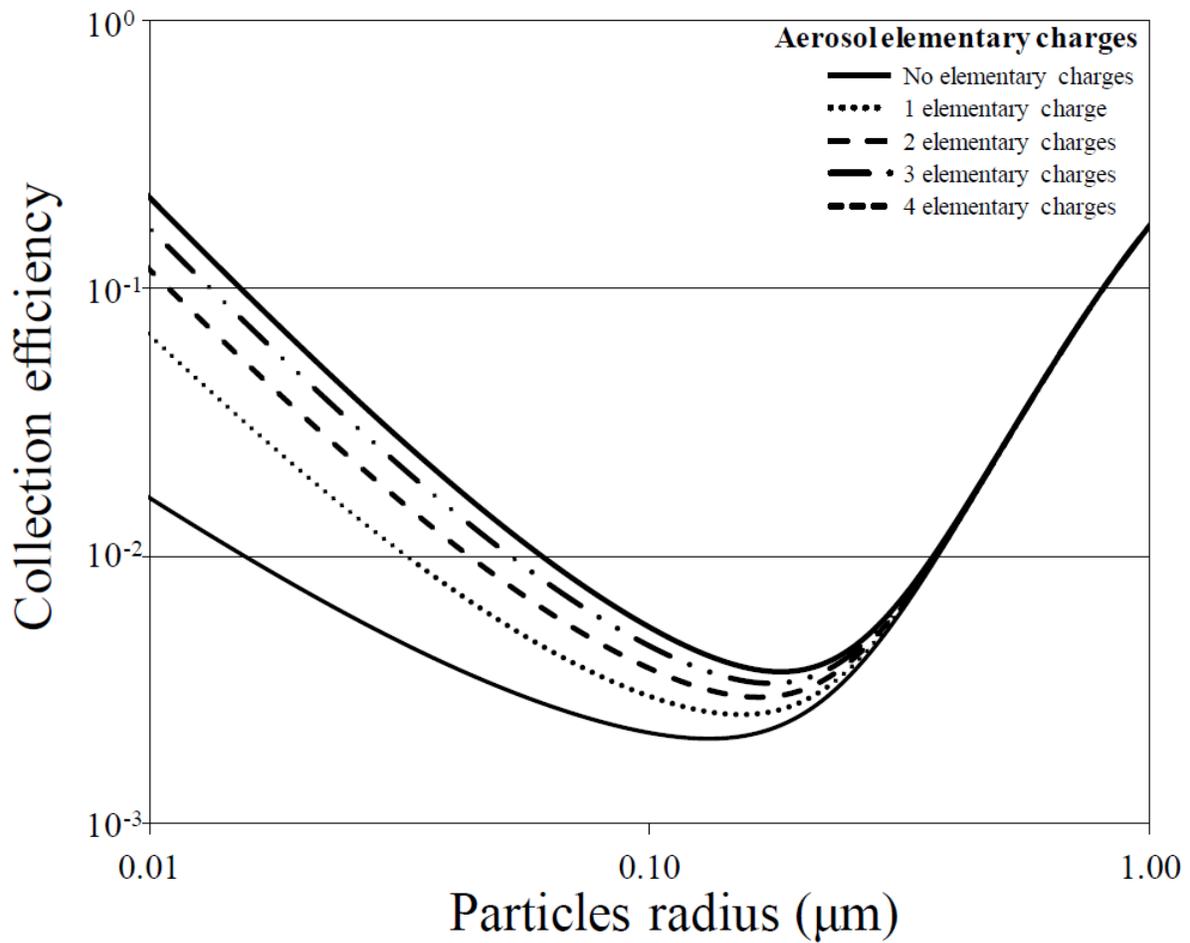
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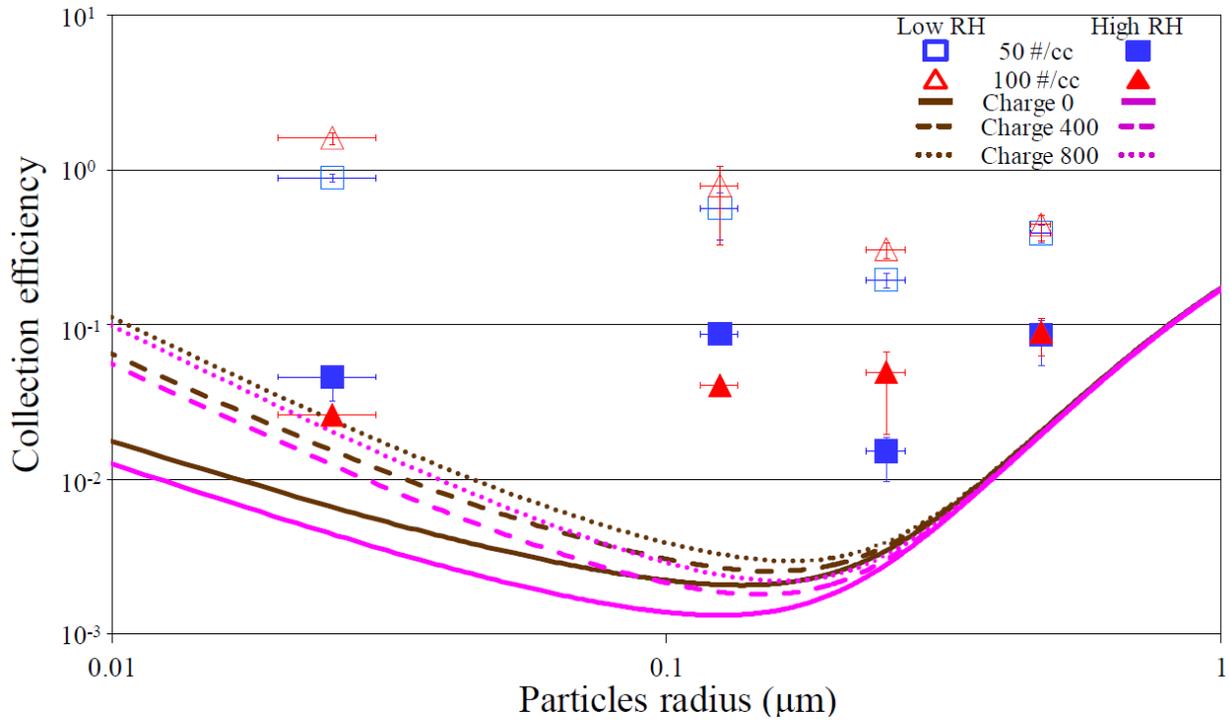
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Figure 7: Theoretical CE and the individual contribution of each force. Calculation details are provided in the text. Experimental conditions of 400 elementary charges per droplets and one elementary charge per particle are used for a variable aerosol size, a droplet radius of 21.6 μm, a RH of 50% and room temperature.



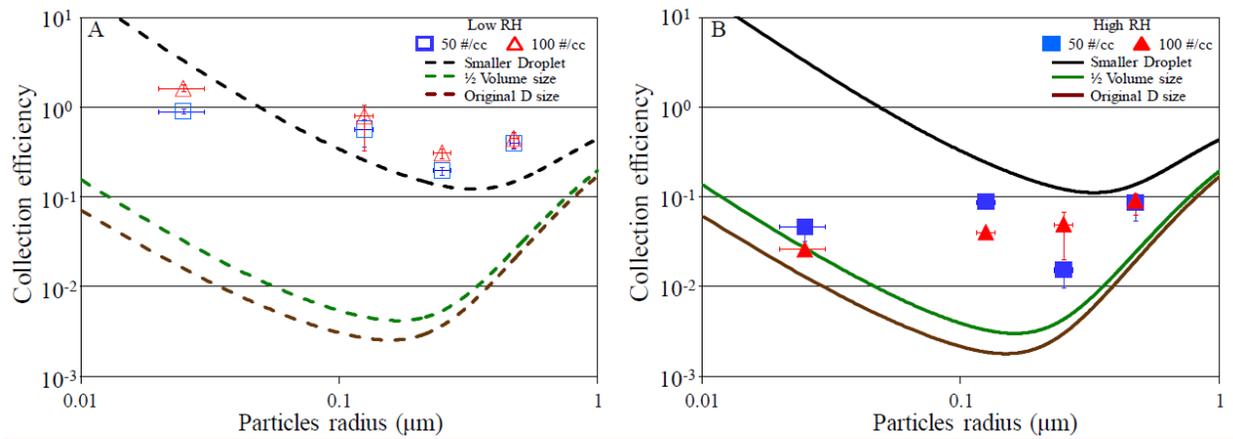
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Figure 8: CE values for 50% RH and 400 elementary charges per droplets with different particles elementary charge for a droplet radius of 21.6  $\mu\text{m}$  and room temperature.



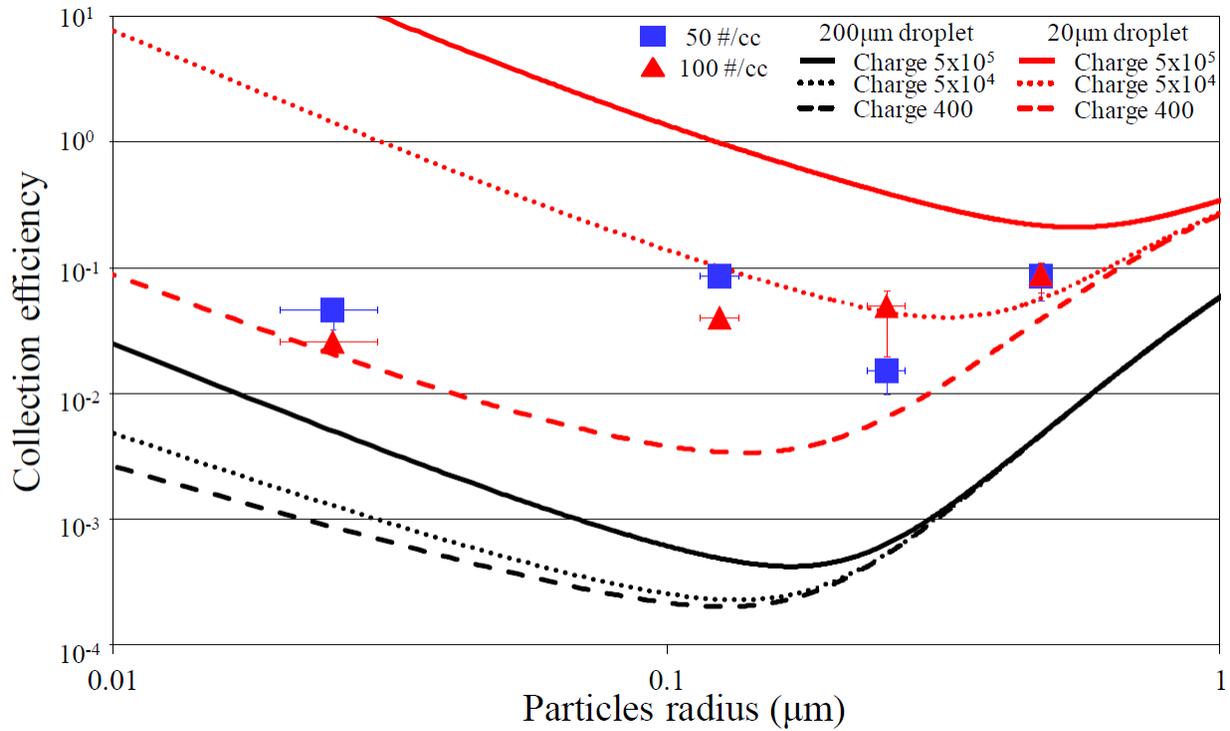
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Figure 89: Comparison of CE experimentally determined in this study (points) with theoretical calculations (lines) where the charge number is elementary charge units per droplet (i.e., the lines span the range of measured droplet charge) and particles are singly charged.



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3 Figure 10: CE as a function of particle radius at Low and High RH (Panel A and B, respectively).  
4 CE experimentally determined in this study (points) with theoretical calculations (lines). The  
5 lines represent calculation with different droplets sizes: the measured droplet size (brown),  
6 droplets with half the volume (green) and 5 μm droplets (black). See text for details.

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Figure 11: CE as a function of particle radius at High RH condition. CE experimentally determined in this study (points) with theoretical calculations (lines), where the charge number is in elementary charge units per droplet. Black lines are for CE of 200  $\mu\text{m}$  droplet size and red for 20  $\mu\text{m}$  droplet size.