

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

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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. Droplets of a dilute aqueous ammonium sulfate  
9 solution with an average radius of 21.6  $\mu\text{m}$  fall freely into a chamber and collide with sub-  
10 micrometer Polystyrene Latex Sphere (PSL) particles of known sizes and concentrations. Two  
11 Relative Humidity (RH) conditions,  $15\pm 3\%$  and  $88\pm 3\%$ , hereafter termed ‘Low’ and ‘High’,  
12 respectively, were varied with different particles sizes and concentrations. After passing through  
13 the chamber, the droplets and aerosol particles were sent to the Particle Analysis by Laser Mass  
14 Spectrometry (PALMS) instrument to determine chemical compositions on a single droplet  
15 basis. “Coagulated droplets” (droplets that collected aerosols) had mass spectra that contained  
16 signatures from both an aerosol particle and a droplet residual. CE values range from  $2.0\times 10^{-1}$  to  
17  $1.6$  for the Low RH and from  $1.5\times 10^{-2}$  to  $9.0\times 10^{-2}$  for the High RH cases. CE values were, within  
18 experimental uncertainty, independent of the aerosol concentrations. CE values in this study  
19 were found to be in agreement with previous experimental and theoretical studies. To our  
20 knowledge, this is the first collection experiment performed on a single droplet basis with  
21 atmospherically relevant conditions such as droplets sizes, droplets charges and flow.

22  
23 **1. Introduction**

24 The interplay between aerosol particles and water droplets in the atmosphere, especially in  
25 clouds, influences both aerosol and cloud properties. The major uncertainty in our understanding  
26 of climate arises from this interplay: the ability of an aerosol to affect cloud formation and,  
27 consequently, alter the global radiative balance (IPCC, 2007). When an aerosol particle comes in  
28 contact with a water droplet, the interaction can result in a collision followed by coalescence of  
29 the two. This process is known as “collection” or “coagulation”. The collection process is  
30 considered an important mechanism that can “scavenge”, and thereby remove, aerosol particles  
31 from the atmosphere (Starr and Mason, 1966; Owe Berg et al., 1970; Hampl and Kerker, 1972;

1 Pranesha and Kamra, 1996). Collection can also affect cloud dynamics, the precipitation process  
2 and cloud lifetime, and thereby change the global radiation budget (Rasch et al., 2000; Croft et  
3 al., 2009).

4  
5 In supercooled clouds, where droplets are present at temperatures below 0°C, the collection  
6 process can have an effect on precipitation when the contacting aerosol initiates ice nucleation.  
7 The result is the creation of an ice crystal, a process known as “contact nucleation” (Vali, 1996).  
8 Contact can influence cloud lifetime and precipitation formation in mixed-phase clouds, which  
9 will also affect the global radiation budget. In order to understand the contact freezing process, it  
10 is important to determine the efficiencies at which the aerosol particles collide with a liquid  
11 droplet within a cloud.

12  
13 Collection efficiency (CE) is the ability of a droplet to coagulate with the aerosol particles within  
14 the volume swept out as it falls. Several mechanisms and forces can affect the collection process.  
15 These include inertial impaction, Brownian diffusion, interception, electrical and other phoretic  
16 forces (See Fig. 1). Inertial impaction is defined as the impaction of particles that have sufficient  
17 inertia that they do not follow their original streamline around the droplet but instead travel close  
18 enough to the surface to result in a collision. Brownian diffusion refers to the movement of the  
19 particle due to collisions with air molecules. In this context it results in a “random walk” into the  
20 droplet surface. Interception is the impaction of particles that follow a streamline that approaches  
21 the droplet within a distance equivalent to the particle radius. Electrical forces, also commonly  
22 termed electro-scavenging or electrophoresis, occur when opposite electrical charges are present  
23 on the droplet and the particle resulting in an attraction between the two. Other phoretic forces  
24 occur when a droplet evaporates or grows. These phoretic forces include thermophoresis and  
25 diffusiohoresis. Thermophoresis takes place when there is a temperature gradient between a  
26 droplet and its surroundings. When a droplet evaporates, its surface can become colder and  
27 aerosols will be drawn towards it. Diffusiohoresis, a counterforce to thermophoresis, occurs  
28 when there is a concentration gradient in water vapor, as is the case near an evaporating droplet.  
29 Higher water vapor concentration surrounding the droplet “pushes” particles outward. A review  
30 of the phoretic forces can be found in Pruppacher and Klett (1997).

31

1 The mechanisms described above are dependent on the size of the aerosol particle being  
2 collected. Whereas for large particles (radius  $> 1 \mu\text{m}$ ) inertial effects dominate the collection  
3 process, small particle (radius  $< 0.1 \mu\text{m}$ ) motion is dominated by Brownian diffusion and electro-  
4 scavenging (Wang and Pruppacher, 1977), where the effects of the latter is higher (Tinsley et al.,  
5 2001). Phoretic forces have a larger impact on particles in the intermediate size range (Wang and  
6 Pruppacher, 1977). This intermediate range,  $0.1 - 1 \mu\text{m}$ , is normally termed the “Greenfield gap”,  
7 and coincides with an observed minimum in CE (Greenfield, 1957). The particle radius of the  
8 Greenfield gap has also been observed to vary with the collecting droplet size (Tinsley et al.,  
9 2001).

10

11 Many factors, besides particle size, have been observed to affect CE (Byrne and Jennings,  
12 1993). These include particle density (Chate and Kamra, 1997), turbulence (Grover and  
13 Pruppacher, 1985) and RH. Lower RH has been observed to correlate with higher CE values,  
14 apparently due to phoretic forces (Grover et al., 1977; Tinsley et al., 2001). Droplet size can  
15 impact CE, where lower values correlate with larger droplets (Lai et al., 1978; Pranesha and  
16 Kamra, 1996). Higher charge also correlates with higher CE, indicative of greater electrical  
17 force (Beard, 1974; Wang and Pruppacher, 1977; Lai et al., 1978; Barlow and Latham, 1983;  
18 Pranesha and Kamra, 1997a,b; Tinsley et al., 2000). It should be noted that the number of  
19 elementary charges used in previous work was often motivated by atmospheric observations: a  
20 few tens to hundreds elementary charges for altostratus and stratocumulus clouds (Phillips and  
21 Kinzer, 1958; Beard et al., 2004) and hundreds to thousands elementary charges in  
22 cumulonimbus clouds (Thomson and Iribarne, 1978; Marshall and Winn, 1982).

23

24 To date, there have been numerous experimental and theoretical studies of the collection process  
25 (Beard, 1974; Grover et al., 1977; Pranesha and Kamra, 1996; Parker et al., 2005; Tinsley et al.,  
26 2006). Most of the experimental studies have focused on drizzle and rain drop sizes (Hampl and  
27 Kerker, 1972; Deshler, 1985; Pranesha and Kamra, 1997a,b) while few used smaller cloud  
28 droplets (Ladino et al., 2011). A list of these studies is provided in Table 1. Note that only a few  
29 of the experiments reported aerosol concentrations and none mentioned if different  
30 concentrations were compared.

31

1 Previous studies have relied on bulk collection of coagulated droplets followed by off-line  
2 analysis to assess CE (Hampl et al., 1971; Deshler, 1985; Pranisha and Kamra, 1993; Chate and  
3 Kamra, 1997). Off-line analytical instruments include mass spectrometry (Ladino et al., 2011),  
4 atomic absorption spectroscopy (Barlow and Latham, 1983; Pranisha and Kamra, 1996),  
5 fluorescence spectrometry (Byrne and Jennings, 1993) and neutron activation analysis (Beard,  
6 1974). The efficiency determined from bulk collection of droplets results in a signal to noise  
7 issue where minimal collection events can fall below instrumental detection limits. The inability  
8 to determine multiple collection events by single droplets is another possible source of error. To  
9 our knowledge, no previous study allowed for determination of collection on a single droplet  
10 basis with atmospherically relevant conditions of droplets size, droplets charge and flow, which  
11 are a key to many cloud processes, including contact nucleation. Another limitation of these bulk  
12 analytical methods lies in the aerosol type. Since each technique relies on certain property of the  
13 aerosol particles (such as fluorescence, radioactivity or atomic absorption), these experiments  
14 were restricted to a specific particle type exhibiting that property. These constraints often limit  
15 the atmospheric applicability of the results.

16  
17 Theoretical calculations of CE in a cloud environment have been the subject of many studies,  
18 driven by the necessity to explain aspects of both warm and cold precipitations. An experimental  
19 validation of the theoretical knowledge related to CE, particularly for droplet–aerosol collisions,  
20 is difficult and far from complete (Ladino, 2011). According to Santachiara et al. (2012),  
21 significant discrepancies between theoretical and experimental studies have been found for sub-  
22 micrometer particles in the “Greenfield gap”, and the measured values can be one to two orders  
23 of magnitude higher than predicted. According to Wang et al. (2010), this disagreement could be  
24 because some physical processes considered in theoretical models are neglected, difficult to  
25 represent or hard to control in experimental studies.

26  
27 The goal of this study was to determine the CE of sub-micrometer aerosol particles by cloud  
28 droplets. This study was conducted on a single droplet basis with sensitivity to one or more  
29 collection events.

30  
31 **2. Experimental Methods**

## 1 2.1. Experimental Setup

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

9  
10 Polystyrene Latex Spheres (PSL) with radius 0.025, 0.125, 0.25 and 0.475  $\mu\text{m}$  were used in the  
11 experiments. PSLs were wet generated using a Brechtel Manufacturing, Inc. (BMI, Hayward,  
12 CA) Model 9203 Aerosol Generation System. Condensed-phase water was removed by in-line  
13 dryers. Large particle (diameter  $> 0.35 \mu\text{m}$ ) and residual concentrations were measured by an  
14 Optical Particle Sizer (OPS; TSI, Inc., Shoreview, MN Model 3330). Particles below diameter of  
15  $0.35 \mu\text{m}$  were measured using a Scanning Mobility Particle Sizer (SMPS) consisting of a  
16 Differential Mobility Analyzer (DMA; BMI, Inc. Model 2002) and a condensation particle  
17 counter (CPC; BMI, Inc. MCPC Model 1710). Similar concentrations were observed in the  
18 overlapping sensitivity region of both instruments. Two aerosol concentrations were used in the  
19 experiments: 50 and  $100 \text{ cm}^{-3}$ . Particle losses were calculated by measuring the particle  
20 concentration at the entrance and at the bottom of the chamber (i.e., before PALMS). Particle  
21 losses were  $14 \pm 10\%$ .

22  
23  
24 After the particles were generated, but before they entered the chamber, the particle flow either  
25 passed directly over a RH sensor (Omega EE08) in a Low RH experiment or through a  
26 humidifier and then over the RH sensor in a High RH experiment. The humidifier, a mixing  
27 volume containing Milli-Q 18.2 M $\Omega$  cm water, was used to increase the RH of the airflow to  
28  $88 \pm 3\%$ . Two additional RH sensors were placed at the chamber top and bottom to monitor the  
29 temperatures and RH profiles. Valves were placed in-line to either block or admit particles  
30 depending on the experimental phase described in the following paragraphs.

31

1 The overall length of the MIT-CEC is 160 cm. The chamber was constructed of glass with  
2 stainless steel and aluminum ports for connections to the dryers, aerosol and droplet inputs. The  
3 upper part of the chamber, termed the Droplet Generator and Neutralizer (DGN) unit, is a 21 cm  
4 long 5 cm diameter stainless steel cylinder. This section contains a commercial droplet generator,  
5 a charge neutralizer, and ports for aerosol injection. A mesh grid is used to straighten the particle  
6 flow. Droplets are injected vertically downward through a tube to avoid contact with the aerosol  
7 particles until the lower portion of the DGN. A neutralizer, containing two Polonium-210 strips  
8 (0.64 cm thickness and 15 cm long), is placed in the lower part of the DGN. The lower part of  
9 the DGN is connected directly to the main chamber, a single-jacketed glass column with an inner  
10 diameter of 5 cm. The length of the jacketed area is 140 cm. An aluminum cone reducer, 4 cm in  
11 length, is attached to the bottom of the main chamber in order to focus the flow into a variable  
12 length dryer used for condensed phase water removal prior to analysis with PALMS.

13  
14 A Microdrop Technologies Dispenser Systems (Microdrop Technologies Norderstedt, Germany  
15 Model MD-K-130) was used to generate droplets. This Droplet Generator (DG), based on piezo-  
16 driven inkjet printing technology, generates droplets with an average radius of  $21.6 \pm 0.8 \mu\text{m}$ . A  
17 Microdrop CCD camera (Model MD-O-538-85) and imaging system, with a total magnification  
18 of 120x, was used to determine droplet size on a daily basis before the generator was set atop the  
19 chamber. The size differed slightly for the Low and High RH experiments, 21.9 and 21.4  $\mu\text{m}$ ,  
20 respectively. Due to the position of the camera, droplet size could not be monitored during an  
21 experiment or within the chamber. Droplet size was, however, measured before and after the  
22 experiment, and the size was constant within the quoted uncertainty. Droplets size during  
23 experiments was also verified by the residual size after the droplets evaporated. Droplets were  
24 generated at 30Hz. This is a frequency much lower than previously used in other experimental  
25 works using cloud droplets (e.g., 1000Hz in Ladino et al., 2011) where analysis was performed  
26 on a bulk basis. This rate yielded both a collection signal with PALMS and minimized possible  
27 droplet-droplet collisions inside the chamber.

28  
29 As mentioned in the previous section, droplet and aerosol charge affect electro-scavenging forces  
30 and can therefore impact the collection rate. To determine the droplet charge, we utilized an  
31 electrometer (Liu and Pui, 1974) which was connected to the DG. Using the electrometer, we

1 determined that  $\sim 10^4$  elementary charges are imparted to each droplet upon production from the  
2 generator. The neutralizer reduces this charge to  $400 \pm 400$  elementary charges. Aerosol charge  
3 distribution was assumed to be a Boltzmann distribution after neutralization where the most  
4 common charge state other than neutral is a single charge (Wiedensohler, 1988; Hinds, 1999).

5  
6 The droplets were produced from a dilute ammonium sulfate  $((\text{NH}_4)_2\text{SO}_4$ ; hereafter AS) solution,  
7  $0.08 \text{ gL}^{-1}$ . Dilute AS was used due to its atmospheric relevance as a condensation nucleus and in  
8 order to provide a chemically distinct signature for detection of droplets residuals with PALMS.  
9 Based on the original droplet size and solution concentration, and as verified by PALMS sizing,  
10 a single effloresced residual was  $0.75 \mu\text{m}$  radius.

11  
12 The PALMS instrument determines size and chemical composition of a single particle basis.  
13 A detailed description of the PALMS instrument has been published previously (Murphy and  
14 Thomson, 1995; Cziczo et al., 2006). In brief, particles enter an aerodynamic inlet, which  
15 focuses the particle stream. The particles then enter the source region where they pass through  
16 two 532 nm Nd:YAG laser beams which yields scattering signals that are used to trigger an  
17 excimer laser beam (193 nm). The time difference between the two scattering signals provides an  
18 aerodynamic size of the particle (Cziczo et al., 2006). The excimer laser ablates and ionizes the  
19 particle. The ions from each detected particle are ejected into a reflectron mass spectrometer and  
20 detected on a micro-channel plate (MCP), thus providing a mass spectrum of the particle.

## 21 22 **2.2. Data Analysis**

23 Droplet residuals, PSL particles and coagulated droplets had a distinct sizes and mass spectrum  
24 (Fig. 3). In positive ion mode PSL particles had distinct signatures of their carbon chains at mass  
25 to charge ratio (M/C) 12 ( $\text{C}_1$ ), 24 ( $\text{C}_2$ ), 36 ( $\text{C}_3$ ) and 48 ( $\text{C}_4$ ); in many cases the carbons were  
26 associated with hydrogen. Droplets residuals had a signature at M/C 18 ( $\text{NH}_4$ ) and 30 (NO). It  
27 should be noted that the PSLs did not contain the droplet signature nor did the droplets contain a  
28 PSL signature. Coagulated droplets, on the other hand, exhibited mass spectra with signatures  
29 from both the droplet residuals and the PSL particles (Fig. 3, Panel C). In order to determine the  
30 presence or absence of a collection event, a Coagulated Index (CI) was developed:

$$31 \quad \text{CI} = \frac{\text{carbon signal}}{\text{amonium sulfate signal}} \quad (1)$$

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

$$9 \quad \text{ECR} = \frac{\text{number of droplets that coagulated}}{\text{total number of droplets}} \quad (2)$$

10 For this experiment, 5 out of the 1189 droplets experienced collection, yielding an ECR of  
 11  $4.2 \times 10^{-3}$ . It should be noted that an experiment of PSL with AS residual (from the evaporated  
 12 droplet) was performed. Several thousand spectra were examined with PALMS but no collection  
 13 event was observed.

14  
 15 A CE value, normalized by the number of particles contained within the volume swept out by a  
 16 falling droplet, was also calculated. This calculation takes into account a droplet's cross section,  
 17 the aerosol concentration, and the effective interaction length of the chamber so that comparisons  
 18 can be drawn between these data and previous experiments:

$$19 \quad \text{CE} = \frac{\text{ECR}}{\pi(R_d + R_a)^2 L A_c} \quad (3)$$

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

$$22 \quad L = \frac{V_d l}{V_d + V_a} \quad (4)$$

23 where  $V_d$  and  $V_a$  are the droplet terminal (settling) velocity and the velocity of the air carrying  
 24 the particles, respectively, and  $l$  is the length of the chamber before the droplets evaporate.

25

### 26 **2.3. Theoretical CE Models**

27 Previous studies have theoretically determined the CE between droplets and aerosol particles  
 28 (Slinn and Shen, 1970; Beard, 1974; Grover et al., 1977; Davenport and Peterst, 1978; Wang et  
 29 al., 1978; Park et al., 2005; Tinsley et al., 2000; Chate, 2005; Tinsley et al., 2006; Andronache et  
 30 al., 2006; Feng, 2007; Croft et al., 2009; Tinsley, 2010; Wang et al., 2010; Tinsley and Leddon,



1 2013). In order to understand our experimental data, we compare them to a theoretical treatment  
 2 of CE. This treatment includes Brownian diffusion, interception, inertial impaction,  
 3 thermophoresis, diffusiophoresis and electro-scavenging. The total CE is the sum of these  
 4 processes. The CE due to Brownian diffusion, interception and inertial impaction are based on  
 5 Park et al. (2005) which expands on Jung and Lee (1998). Thermophoresis, diffusiophoresis and  
 6 electro-scavenging are based on Wang et al. (2010) which expands on Andronache et al. (2006)  
 7 and Davenport and Peterst (1978). The efficiencies used here are:

$$8 \quad E_{Bdiff} = 2 \left( \frac{\pi\sqrt{3}}{4P_e} \right)^{2/3} \left[ \frac{(1-\alpha)(3\frac{\mu_w}{\mu_a}+4)}{(1-\frac{6}{5}\alpha^{1/3}+\frac{1}{5}\alpha^2)+\frac{\mu_w}{\mu_a}(1-\frac{9}{5}\alpha^{1/3}+\frac{1}{5}\alpha^2+\alpha)} \right]^{1/3} \quad (5)$$

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

$$10 \quad E_{imp} = \left( \frac{Stk}{Stk+0.35} \right)^2 \quad (7)$$

$$11 \quad E_{th} = \frac{4 \left[ \frac{2Cc \left( K_a + 5\frac{\lambda}{D_d} K_p \right) K_a}{5P \left( 1 + 6\frac{\lambda}{D_d} \right) \left( 2K_a + K_p + 10\frac{\lambda}{D_d} K_p \right)} \right] (2 + 0.6R_e^{1/2} P_r^{1/3}) (T_a - T_d)}{D_d V_d} \quad (8)$$

$$12 \quad E_{df} = \frac{4 \left[ \frac{T_a D_w}{P} \left( \frac{M_w}{M_a} \right)^{1/2} \right] (2 + 0.6R_e^{1/2} P_r^{1/3}) \left( \frac{\rho_a - \rho_d}{T_a - T_d} \right)}{D_d V_d} \quad (9)$$

$$13 \quad E_{ec} = \frac{16 C_c k_{ec} Q_r q_r}{3\pi\mu_a D_p^2 D_d V_d} \quad (10)$$

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

21

### 22 3. Result and Discussion

23 A total of 16 collection experiments were performed. The collection experiments were for four  
 24 different aerosol sizes (with radius 0.025, 0.125, 0.25 and 0.475  $\mu\text{m}$ ), each at two different  
 25 concentrations (50 and 100  $\text{cm}^{-3}$ ) and two different RH conditions ( $15\pm 3\%$  and  $88\pm 3\%$ ). A full

1 description of the experiments is summarized in Table 3. All experiments were conducted at  
2 room temperature ( $22.5 \pm 1.3^\circ\text{C}$ ). Droplet radius was  $21.6 \pm 0.8 \mu\text{m}$ . Terminal (settling) velocity  
3 was calculated based on the experimental temperature and droplet size. The terminal velocity  
4 varied from  $4.7 \text{ cm s}^{-1}$  to  $5.8 \text{ cm s}^{-1}$ . Total droplet evaporation time (i.e., residence in the  
5 generator section and experimental chamber) was calculated based on the average droplet size  
6 and the RH condition: 2.1 and 16.6 seconds for the Low and High RH cases, respectively. The  
7 droplets residence time in the chamber was 0.7 and 6.1 seconds, for the Low and High RH cases,  
8 respectively. Calculations of Reynolds number were performed using the experimental  
9 conditions and chamber geometry. Reynolds numbers from 0.12 to 0.16 were calculated and,  
10 based on this, we assume the aerosol particles and droplets interact in flow condition close to  
11 laminar throughout the chamber.

12

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

20

21 CE value was calculated for each experiment, based on the average droplet size measured from  
22 each experiment and when similar RH, aerosol size and concentration conditions were used. CE  
23 values, normalized to aerosol concentration and time, ranged from  $2.0 \times 10^{-1}$  to 1.6 for the Low  
24 RH experiments and from  $1.5 \times 10^{-2}$  to  $9.0 \times 10^{-2}$  for the High RH experiments (see Fig. 5). These  
25 values are in a similar range to that found by previous works (Wang and Pruppacher, 1977; Lai  
26 et al., 1978). Shown in Fig. 5, no significant difference in CE values between the two aerosol  
27 concentrations ( $50$  and  $100 \text{ cm}^{-3}$ ) was observed. Most previous experiments did not specify what  
28 aerosol concentration were used during their collection experiments (Hampl et al., 1971; Lei et  
29 al., 1978; Prodi et al., 2014). Those who did specify had a higher aerosol concentration, in most  
30 cases above atmospheric relevance except within polluted boundary layers (above  $1000 \text{ cm}^{-3}$ ;  
31 Beard, 1974; Wang and Pruppacher, 1977; Barlow and Latham, 1983; Deshler, 1985; Ladino et

1 al., 2011). The use of these high aerosol concentrations was likely due to the limitation of bulk  
2 analysis methods, as discussed in the Introduction, which required a high concentration for  
3 adequate signal.

4  
5 It has been shown theoretically by Wang et al. (1978), Grover and Pruppacher (1985) and Ladino  
6 et al. (2011), and experimentally by Grover et al. (1977) that CE increases with decreasing RH.  
7 This is because a lower RH leads to an increase of the evaporation rate of the droplet, which  
8 strengthens the phoretic forces. Two RH conditions were measured in this experimental work,  
9 Low ( $15\pm 3\%$ ) and High ( $88\pm 3\%$ ). Consistent with these previous works, we find a higher CE  
10 values for the Low RH experiments, by as much as one order of magnitude, when compared to  
11 otherwise similar High RH experiments.

12  
13 In the previous experimental studies of collection, many considered significantly larger droplets  
14 (of drizzle or rain size; Leong et al., 1982; Pranesha and Kamra, 1993; Chate and Kamra, 1997)  
15 and particle sizes (super-micrometer; Owe Berg et al., 1970; Hampl and Kerker, 1972). For these  
16 reasons, we do not believe a direct comparison to our data is valid. This lack of comparison  
17 holds for other studies using aerosol in a similar size range but with much larger droplets (Hampl  
18 et al.; 1971; Deshler, 1985; Vohl et al., 2001). The droplets used in the current work were  
19 significantly smaller, >15 times, than those used in the aforementioned experiments. Those  
20 studies reported lower CE values than measured here, in some cases by an order of magnitude. It  
21 has been shown in previous experimental and theoretical studies that the CE decreases with  
22 increasing droplet size (Davenport and Peterst, 1978; Wang et al., 1978; Leong et al., 1982;  
23 Pranesha and Kamra, 1993). It is likely that some of the differences in CE are also a result of  
24 different experimental conditions, such as droplets and/or particle charge.

25  
26 Two experimental studies, Wang and Pruppacher (1977) and Lai et al. (1978), are roughly  
27 similar to our study and both exhibit CE values slightly lower than the values from our  
28 measurements. A comparison is provided in Fig. 6. The differences in CE values could be a  
29 result of the different experimental conditions. For example, Wang and Pruppacher (1977) and  
30 Lai et al. (1978) used somewhat larger droplets (of 170-340  $\mu\text{m}$  and 620  $\mu\text{m}$ , respectively), with  
31 higher charges than those used in the current work,  $5\times 10^5$ - $7.1\times 10^6$  elementary charges in Wang

1 and Pruppacher (1977) and  $6.6 \times 10^8$ - $1.9 \times 10^9$  elementary charges in Lai et al. (1978). The larger  
2 droplets and higher droplets charges used by Wang and Pruppacher (1977) and by Lai et al.  
3 (1978) could explain the differences between these works and ours, as will be discussed further  
4 in subsequent sections. Lai et al. (1978) did not mention the aerosol concentrations or RH  
5 conditions used in their work. Wang and Pruppacher (1977) used a RH condition similar to the  
6 low RH used in this study but with higher aerosol concentrations. It is expected that a higher  
7 aerosol concentration will increase the chance of collision between particles and droplets, which  
8 will increase the value of ECR, but will not affect CE, which is normalized.

9

10 The most similar experimental conditions to ours are those of Ladino et al. (2011). Ladino et al.  
11 used similar droplets (radius of 12.8-20  $\mu\text{m}$ ) and particle sizes (radius of 0.05-0.33  $\mu\text{m}$ ).  
12 Experiments were conducted at RH conditions similar to our High RH experiments ( $88 \pm 2\%$ ).  
13 Although most of the experimental conditions were similar, there are noteworthy differences  
14 between the CE values of Ladino et al. and those measured in this study, which are lower overall  
15 (Fig. 6). The main difference between the two studies is the droplet charge, which has a stronger  
16 impact on the electro-scavenging force. Ladino et al. used droplets with high charges,  $5 \times 10^4$   
17 elementary charges per droplet (Claudia Marcolli, personal communication, 2014), which are  
18 two orders of magnitude higher than the one used in this study. The higher droplet charge  
19 explains the higher CE values compared to those determined in this study.

20

21 In order to compare our experimental work with theoretical studies, a set of calculations  
22 combining six different forces, as described in section 2.3, was conducted. Examples of  
23 theoretical forces and CE are given in Fig. 7. The properties used in these calculations included  
24 an air temperature of  $22.5^\circ\text{C}$ , a pressure of 981 mb, RH of 50%, PSL particles with a density of  
25  $1000 \text{ Kg m}^{-3}$  of different sizes matching the experiments, a thermal conductivity of  $0.1 \text{ Kg m s}^{-3}$   
26  $\text{K}^{-1}$  (Romay et al., 1998), and a constant droplet radius of 21.6  $\mu\text{m}$ . Droplets were assumed to  
27 have 400 elementary charges, the average value determined by the electrometer experiments (see  
28 section 2.1). These calculations were made for charged particles that contained one elementary  
29 charge per particle. Most particles in a Boltzmann distribution contain no charges and will  
30 therefore not be affected by electro-scavenging forces. The most common charge state other than  
31 neutral is a single charge, about 10% of particles, and this forms the basis of our calculation

1 (Hinds, 1999). This is further supported by a decreasing effect of multiple charges when  
2 considering the effect on CE (Fig. 8).

3  
4 From Fig. 7, the total CE varies for different particle sizes. The contribution of Brownian  
5 diffusion decreases rapidly as particle size increases while the contribution of inertial impaction  
6 increases rapidly as particle size increases. Interception forces also increase as particle size  
7 increases, but its effect is smaller than that of inertial impaction. The contribution of  
8 diffusiophoresis is smaller than that of thermophoresis for particles below  $0.05\mu\text{m}$ . The  
9 Greenfield gap is evident in this figure, as the local minimum between the diffusion- and  
10 impaction-dominated regimes. This corresponds to a minimum at a particle size of  $0.15\ \mu\text{m}$ . In  
11 Fig. 7, electro-scavenging have a significant impact on the curves. Previous work by Wang et al.  
12 (1978), Byrne and Jennings (1993) and Tinsley et al. (2000) showed the presence of charge on  
13 droplets and aerosol can increase the CE throughout the Greenfield gap. Moreover, as described  
14 by Tinsley et al. (2001), the electrical effect is more important for smaller particle sizes ( $< 0.1$   
15  $\mu\text{m}$ ) than Brownian diffusion. This could explain why the Greenfield Gap is highly pronounced  
16 in the data in Fig. 6, while it is more pronounced in the data of Lai et al. (1978) and Ladino et al.  
17 (2011).

18  
19 In order to directly compare theoretical and measured CE, two cases were calculated: (1) droplet  
20 radius  $21.4\ \mu\text{m}$  and Low RH and (2)  $21.9\ \mu\text{m}$  and High RH. In both calculations 0, 400 and 800  
21 elementary charges were assumed per droplet; the range of values determined in the electrometer  
22 experiments. The result of this comparison is shown in Fig. 9, where the points represent the  
23 experimental work and the lines represent the theoretical CE. Overall, the experimental work  
24 presents higher CE values compared to the theoretical CE. Differences between theoretical and  
25 measured CE may be considered a result of conditions not modeled theoretically or difficult to  
26 constrain experimentally. Possibilities include rare multiply charged particles, aerosol droplet  
27 electric interaction that are not fully considered (such as the induced dipole force), the  
28 evaporation rate of the droplets, variable terminal settling velocity due to changes in droplet size,  
29 and the present of solute in the droplets.

30

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

14  
15 It is known that droplets carrying higher electric charge have higher CE (Barlow and Latham,  
16 1983; Byrne and Jennings, 1993; Pranesha and Kamra, 1997a,b; Tinsley and Leddon, 2013;  
17 Tinsley et al., 2000; Tinsley, 2010), and this is consistent with our data in Fig 9. Droplets size  
18 also affects CE, where smaller droplets have higher CE values (Lai et al., 1978; Pranesha and  
19 Kamra, 1996). Fig. 11 shows a calculation of CE based on different droplet charges and sizes.  
20 Two droplets sizes were used: 20  $\mu\text{m}$ , which is similar to the size used in this study and by  
21 Ladino et al. (2011) and 200  $\mu\text{m}$ , which is the size used by Wang and Pruppacher (1977). Three  
22 different droplet charges were considered: 400 elementary charges, as used in this study,  $5 \times 10^4$   
23 elementary charges, used by Ladino et al. (2011) and  $5 \times 10^5$  elementary charges, the lower limit  
24 of charges used by Wang and Pruppacher (1977). Shown in Fig. 11, CE values increase as  
25 droplet charge increases. Droplets size and charge conditions can counteract each other in the  
26 case of larger droplets (lower CE) with higher charge (higher CE). We suggest this may explain  
27 the agreement found between the CE values measured in this study and those of Wang and  
28 Pruppacher (1977) and the disagreement between our values and those of Ladino et al. (2011). It  
29 should be noted that the experimental CE values fall within the region of the 20  $\mu\text{m}$  case. The CE  
30 values of the small particles ( $<0.1 \mu\text{m}$ ) match the theoretical CE, while for larger particles ( $>0.1$

1  $\mu\text{m}$ ) they are slightly higher. These differences could be a result of some conditions not modeled  
2 theoretically or conditions difficult to constrain experimentally, as discussed above.

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

5 An experimental setup has been constructed to measure the CE of 21.6  $\mu\text{m}$  radius water droplets  
6 with sub-micrometer PSL particles of 0.025, 0.125, 0.25 and 0.475  $\mu\text{m}$  radius and concentrations  
7 of 50 and 100  $\text{cm}^{-3}$ . Two RH conditions,  $15\pm 3\%$  and  $88\pm 3\%$ , were used. Coagulated droplets  
8 were identified on a single-droplet basis using a single particle mass spectrometer. CE values  
9 ranged from  $2.0\times 10^{-1}$  to 1.6 for the Low RH and from  $1.5\times 10^{-2}$  to  $9.0\times 10^{-2}$  for the High RH cases.

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

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

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31 which greatly helped improve the paper.

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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	$<100$

2

1 Table 2: Definition of acronyms and relevant units.

Parameter	Definitions	units
Cc	Cunningham slip correction factor	[-]
CE	Collection Efficiency	[-]
D <sub>a</sub>	Aerosol particles diameter	[m]
D <sub>d</sub>	Droplets diameter	[m]
E <sub>Bdiff</sub>	Brownian diffusion efficiency	[-]
ECR	Experimental collection ratio	[-]
E <sub>ec</sub>	Electric charges efficiency	[-]
E <sub>df</sub>	Diffusiophoresis efficiency	[-]
E <sub>imp</sub>	Inertial impaction efficiency	[-]
E <sub>int</sub>	Interception efficiency	[-]
E <sub>th</sub>	Thermophoresis efficiency	[-]
K <sub>a</sub>	Thermal conductivity of moist air	[Kg m s <sup>-3</sup> K <sup>-1</sup> ]
K <sub>p</sub>	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 <sub>ec</sub>	K constant for E <sub>ec</sub> calculations equal to 9x10 <sup>9</sup>	[Nm <sup>2</sup> C <sup>-2</sup> ]
Mw	Molecular weight of water	[Kg mol <sup>-1</sup> ]
P	Atmospheric pressure	[Pa]
P <sub>e</sub>	Peclet number	[-]
P <sub>r</sub>	Prandtl number of air	[-]
q <sub>r</sub>	Mean charge on aerosol particles	[Coulomb, C]
Q <sub>r</sub>	Mean charge on droplets	[Coulomb, C]
R <sub>a</sub>	Aerosol radius	[m]
R <sub>d</sub>	Droplets radius	[m]
R <sub>e</sub>	Reynolds number	[-]
Stk	Stokes number	[-]
T <sub>a</sub>	Temperature of air	[K]
T <sub>d</sub>	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 7
$\rho_d$	Water vapor of water temperature at droplets surface	$[Pa]$ 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	20.0±2.2	1966	2.4E-03
2	0.025±0.005	96±8	11	20.0±2.2	2578	8.6E-03
3	0.025±0.005	56±13	85±1	22.2±2.2	3778	1.5E-03
4	0.025±0.005	100±6	83	22.2±2.2	2446	1.6E-03
5	0.125±0.01	49±5	13±2	22.2±2.2	1923	2.0E-03
6	0.125±0.01	88±20	15±1	22.2±2.2	2025	4.9E-03
7	0.125±0.01	50±3	87	22.2±2.2	4598	2.6E-03
8	0.125±0.01	102±9	88	22.2±2.2	2831	2.5E-03
9	0.25±0.02	49±2	17±1	21.7±0.8	1039	6.5E-04
10	0.25±0.02	92±4	16±1	21.7±0.8	3282	1.9E-03
11	0.25±0.02	51±2	94±3	22.2±2.9	1530	9.6E-04
12	0.25±0.02	101±18	90±3	22.2±2.9	1554	3.0E-03
13	0.475±0.02	52±3	17	21.7±0.8	1050	1.4E-03
14	0.475±0.02	98±11	20±3	21.7±0.8	1232	2.9E-03
15	0.475±0.02	48±10	87±2	20.9±0.9	1473	1.9E-03
16	0.475±0.02	99±16	88±1	20.9±0.9	1049	4.9E-03

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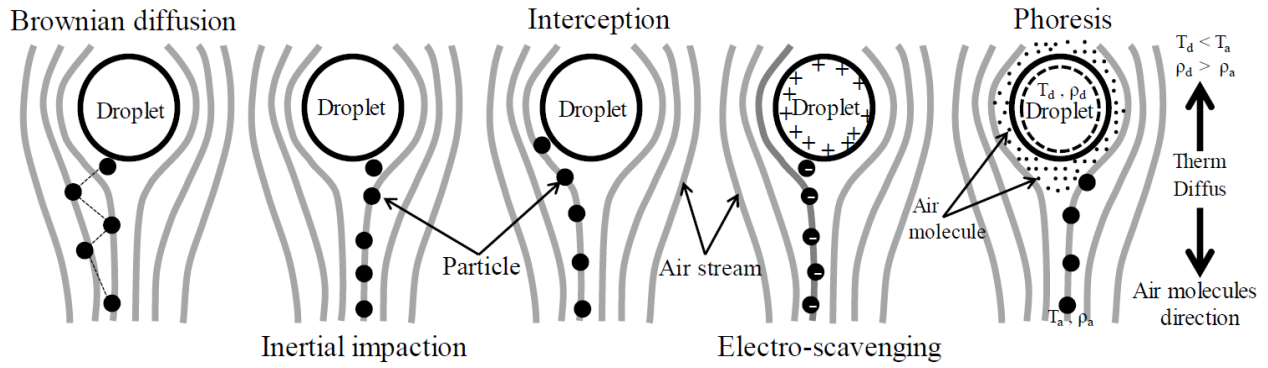
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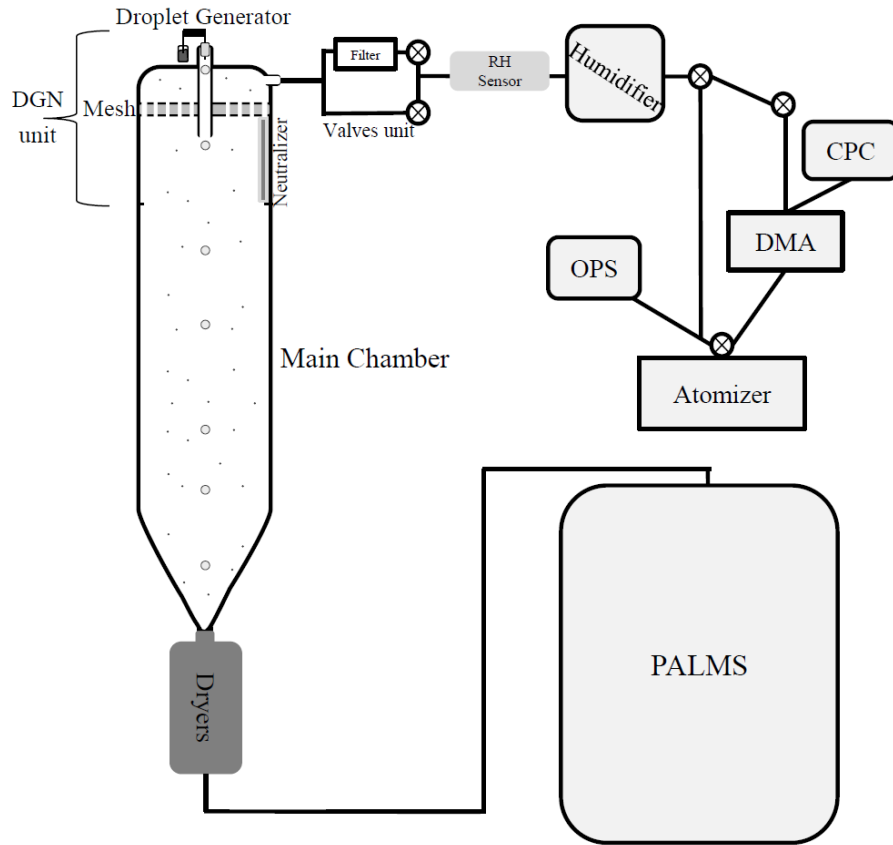




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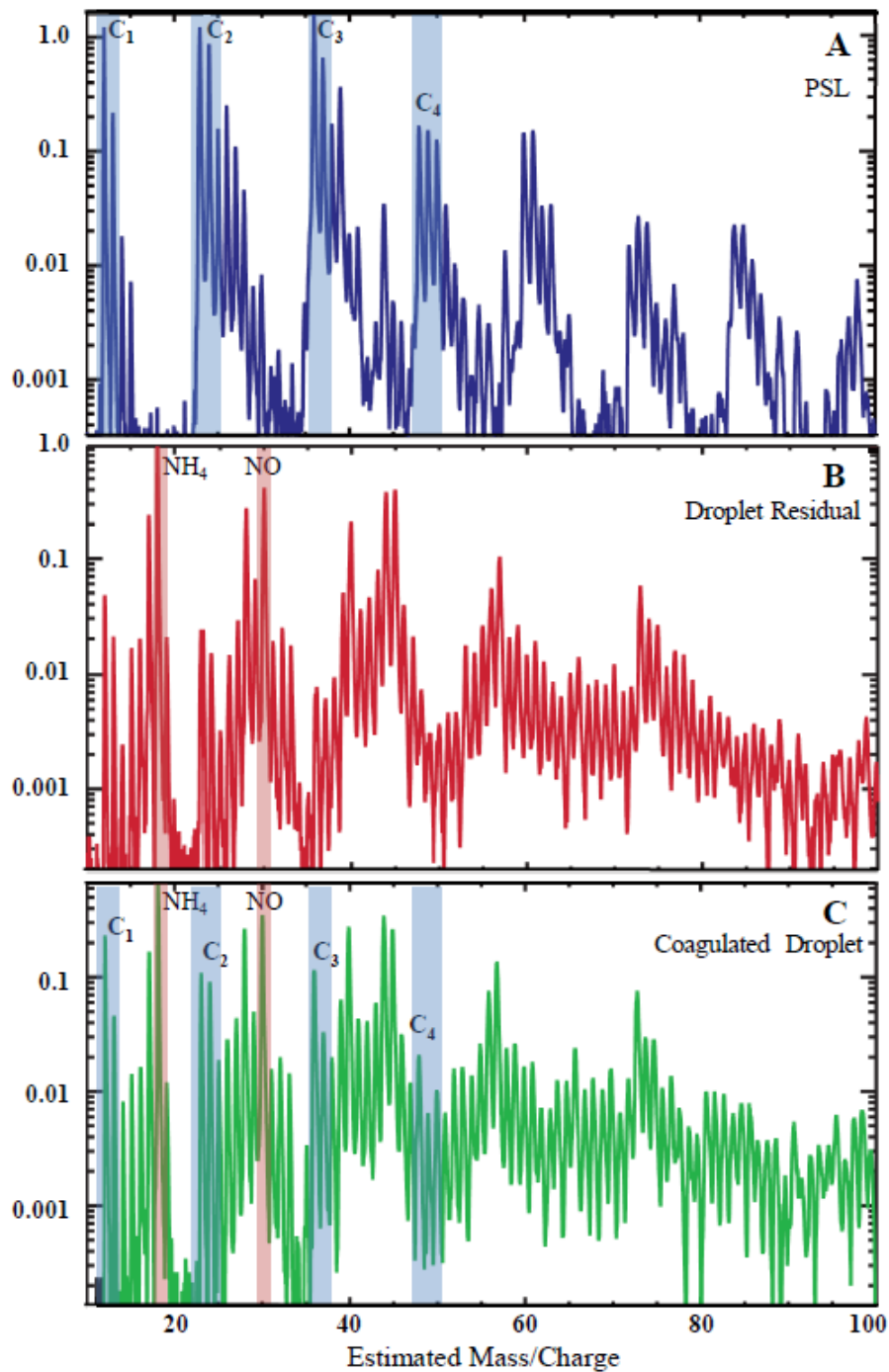
3 Figure 1: Mechanisms that affect the collection process of aerosol particles by water droplets.  
 4 The mechanisms, from left to right, are Brownian diffusion, inertial impaction, interception,  
 5 electro-scavenging and phoresis.  $T_d$  and  $\rho_d$  are the temperature and water molecule density 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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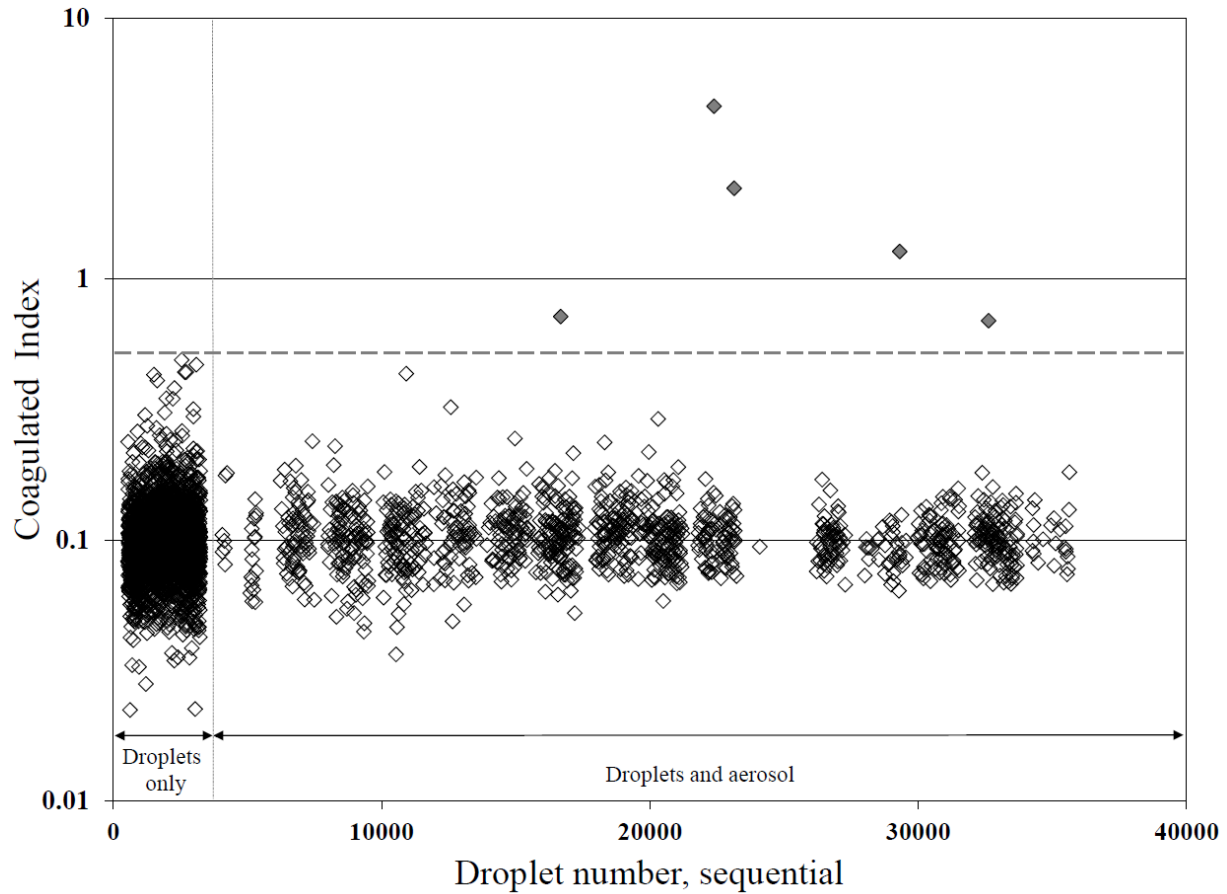
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Figure 2: Experimental setup. DGN denotes the Droplet Generation Unit. Additional description is provided in the text.



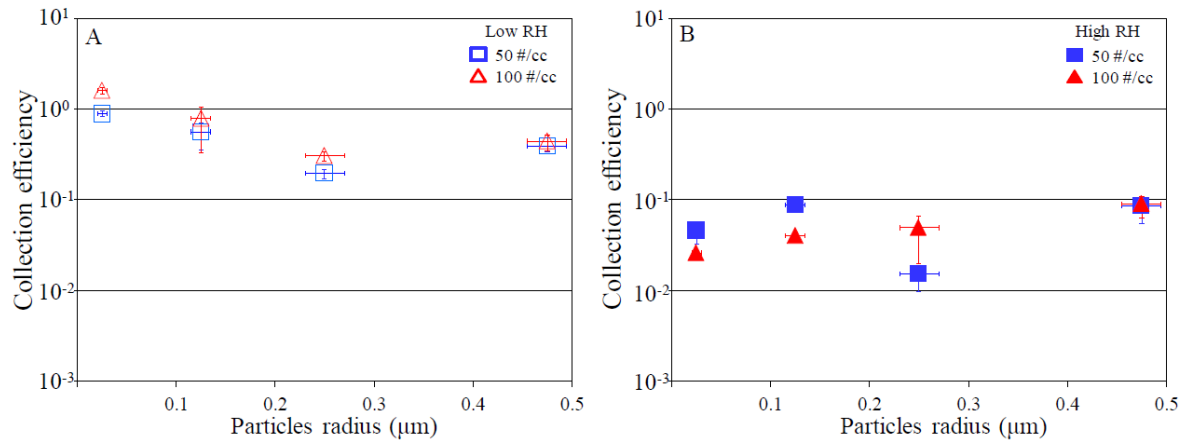
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Figure 3: Mass spectra of a PSL particle (panel A), an evaporated droplet composed of dilute AS, termed a droplet residual (panel B), and a coagulated and evaporated droplet that contained both a PSL particle and residual AS (panel C).



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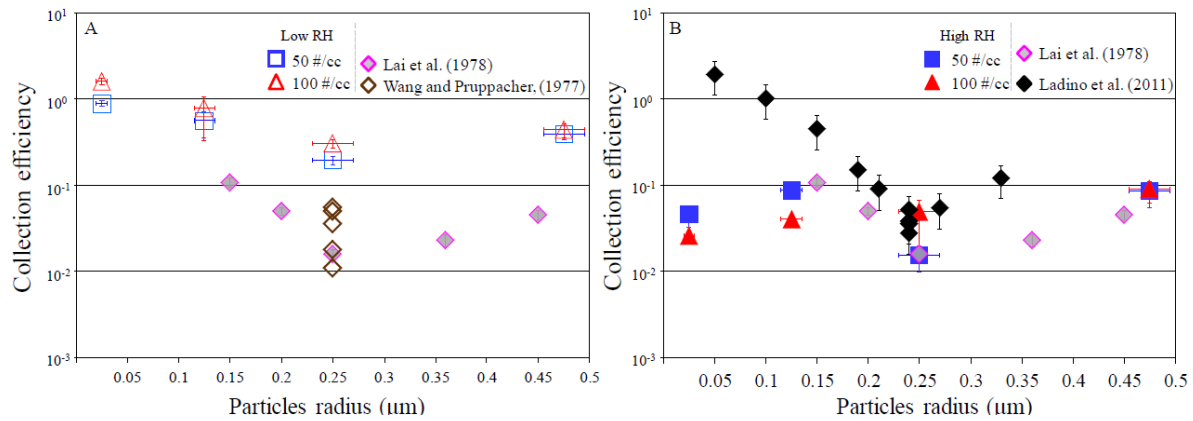
Figure 4: Coagulated Index (CI), the ratio of PSL (aerosol) to AS (droplet residual) signal in a mass spectrum, for a typical experiment. In this experiment the RH was 15%, droplet radius was 20  $\mu\text{m}$ , PSL particles were 0.125  $\mu\text{m}$  radius with a concentration of 100  $\text{cm}^{-3}$ . The X axis represents the sequential analysis of 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 events. There are 5 collection events during this experimental period.



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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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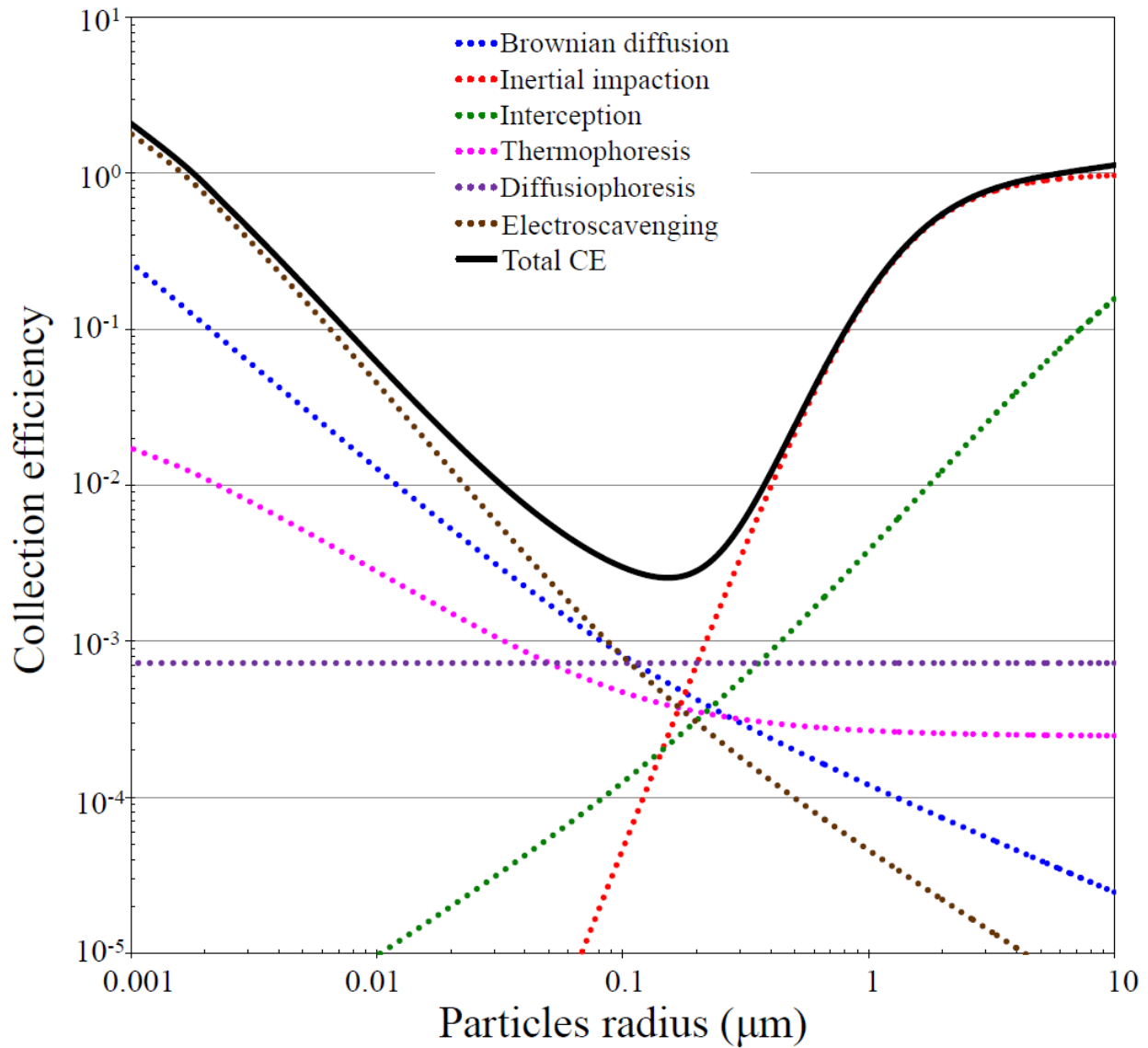
4 Figure 6: Comparison of CE from this study to previous experimental work. Panel A: Low RH  
5 experiments. Panel B: High RH experiments. Shapes (square and triangle) represent different  
6 aerosol concentrations. Diamond shapes represent previous experimental work. Black diamonds  
7 are from Ladino et al. (2011), RH 88±2% with aerosol concentration 2000 cm<sup>-3</sup> and droplets size  
8 of 12.8-20.0 μm. Brown diamonds represent are from Wang and Pruppacher (1977), RH of  
9 23±2% with aerosol concentration of about 10<sup>17</sup> cm<sup>-3</sup> and droplets size of 170-340 μm. Pink  
10 diamonds are from Lai et at. (1978), when 620 μm droplets were used; there was no information  
11 provided regarding the RH or aerosol concentration.

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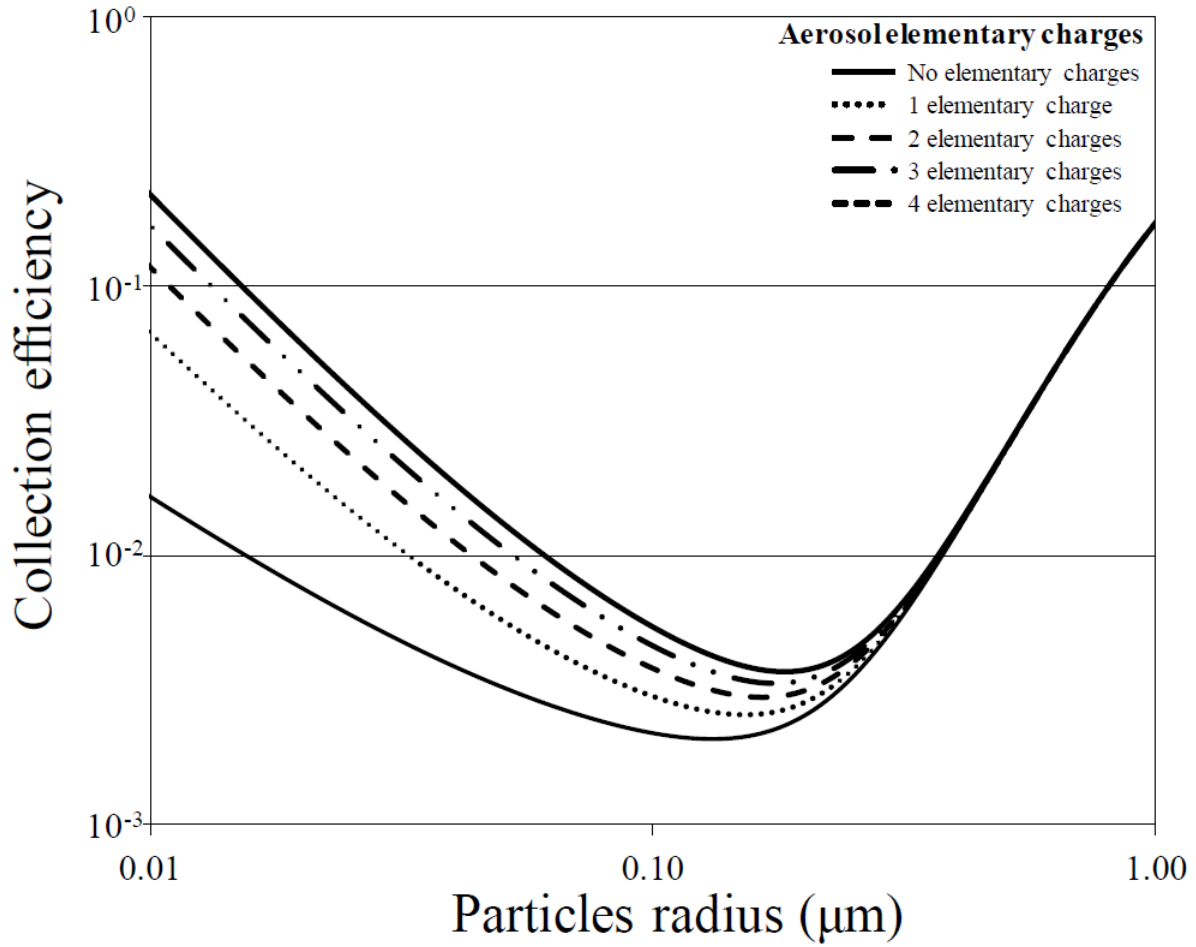
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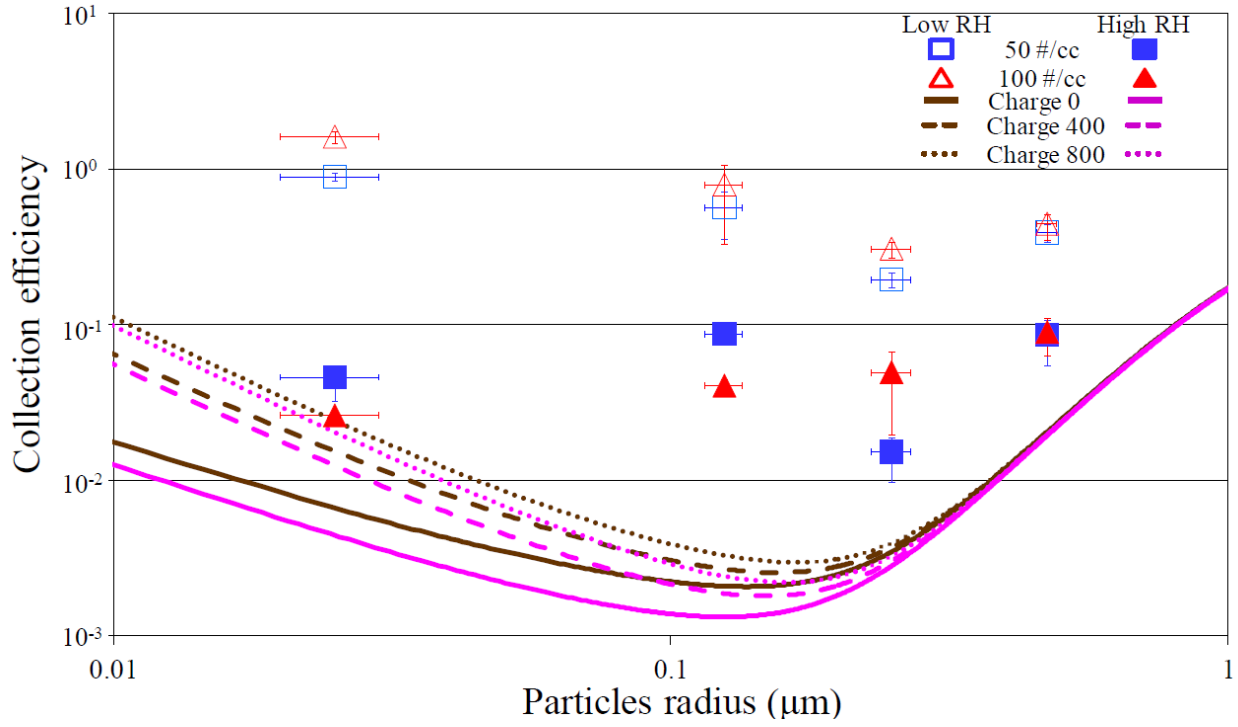
Figure 7: Theoretical CE and the individual contribution of each force. Calculation details are provided in the text. Experimental conditions of 400 elementary charges per droplets and one elementary charge per particle are used for a variable aerosol size, a droplet radius of 21.6 μm, a RH of 50% and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



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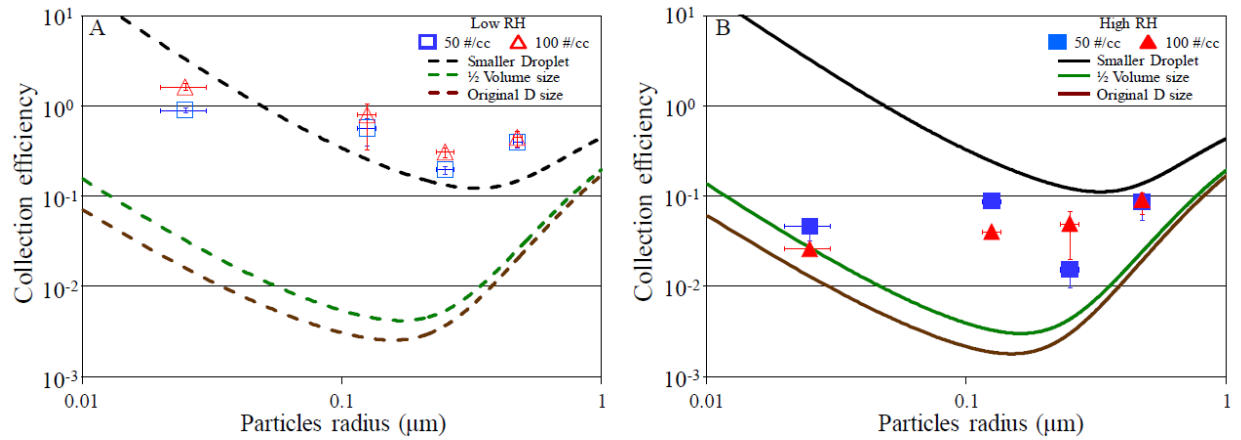
Figure 8: CE values for 50% RH and 400 elementary charges per droplets with different particles elementary charge for a droplet radius of 21.6  $\mu\text{m}$  and room temperature.





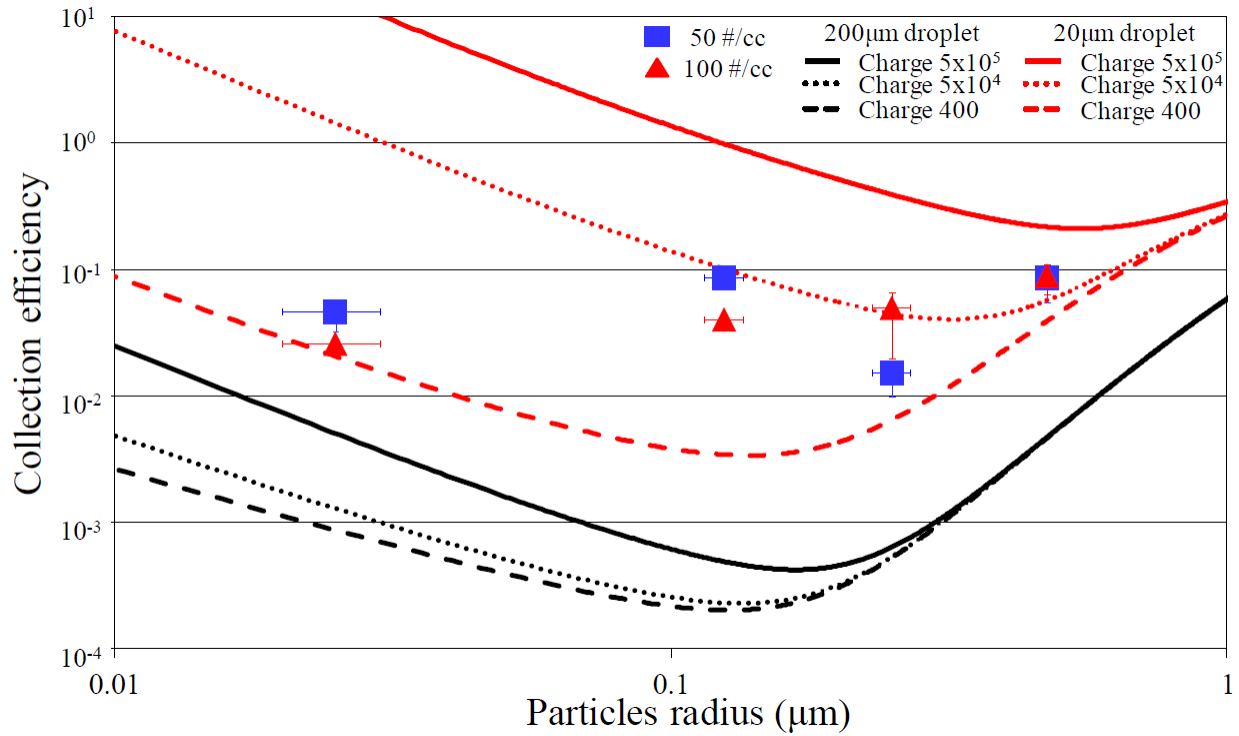
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Figure 9: Comparison of CE experimentally determined in this study (points) with theoretical calculations (lines) where the charge number is elementary charge units per droplet (i.e., the lines span the range of measured droplet charge) and particles are singly charged.



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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.



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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.