

Response to Reviewer #2

Overall, the work is new and the method to apply multiple-charging corrections for the BS2-CCN instrumentation has not been done before. The work extends on previously published works (e.g., the kernel function is added to the Kim et al 2021 multiple charge correction) with the BS2-CCN data. In general, the main concern is that multiple factors affect CCN measurement (aerosol shape, aerosol aggregation, viscosity, volatility, solubility, surface activity) and these effects are confounded; it is difficult to isolate the effects of multiple charging alone. However, the data collected from the BS2-CCN counter and subsequent analysis will be important for understanding CCN spectra of atmospheric aerosol and thus the work warrants publication. The following questions and comments address ideas that maybe unclear to the reader in the manuscript.

A: We thank the reviewer for encouraging and helpful comments on our manuscript. We believe that the quality of our manuscript is improved as we reflect the reviewer's comments. Below each of the questions/comments is written with the *Italic font* and then our response is followed with the normal font.

Comments

Q1: Composition of aerosols does not affect the probability of multiple charging. However, the morphology of the aerosols changes the probability of charging. Are the ambient aerosols spherical?

A: We assumed that ambient aerosols are spherical in this study. We added sentence of this assumption in the text (Line 201-202).

“As in Section 4.1, the measured aerosol number concentration data were fitted to the log-normal distribution for calculation and the aerosols are assumed to be spherical”

Q2: Was there any contribution from other physical factors (e.g., mixing state surface activity, viscosity, non-spherical morphology) on the uncertainties in? Did the authors take any measures to control the contribution from the aforementioned and other sources of uncertainty in?

A: As reviewer commented, CCN activation is affected by combined physical factors including mixing state, surface activity, viscosity and particle morphology. Also, these physical factors themselves can influence the CCN activation by multiply charged particles. In other words, other physical factors can contribute uncertainties of CCN activation. For example, particle morphology can influence in determining the diameter corresponding to the centroid mobility of each size bin. Altaf (2018) explored the effect of size-dependent morphology on CCN activity using aerosol particles composed of organic compounds and salts. The difference in activation can be explained by a homogeneous and phase-separated morphology. In this study, we focus on the effect of multiply charged particles on CCN activation. For laboratory experiment, we consider the particle morphology by applying the particle shape factor when calculating κ values. For examining the uncertainties of activation fraction by morphology, we calculate relative uncertainties (=absolute error / measured value). It does not exceed 1% when applying the shape factor of

ammonium sulfate ($\chi=1.02$) and sodium chloride ($\chi=1.08$). Unlike calibration experiment, other physical factors cannot be controlled during the ambient aerosol measurement. For the BS2-CCN system, aerosol and sheath flow, and supersaturation in the CCNC are fixed during the particle size scan process of the CCN activation curve, uncertainties in CCN activation due to changes in flow rate and supersaturation can be minimized. Figure R1 showed exemplary D_p scan (20-100nm) of lab generated ammonium sulfate. When scanning the D_p , absolute deviation of F_{act} was mostly less than 0.05 except the first 10 seconds of each scan and F_{act} value is higher than 0.85. We minimize the uncertainty by defining the first 10 seconds of each D_p scan as a stabilization time and excluding it when calculating the F_{act} value.

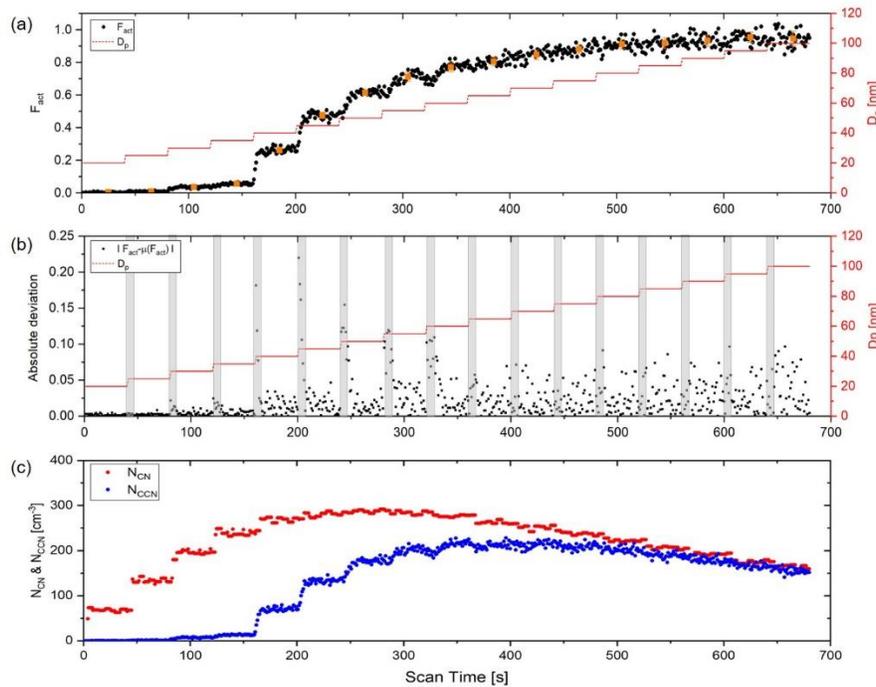


Figure R 1. Exemplary D_p scan (20-100 nm) of lab generated ammonium sulfate. (a) 1 second data of activated fraction (F_{act}), marked in black dot (left ordinate), particle diameter (red line, right ordinate). Average and standard deviation of each diameter (30-second average data except for 10 seconds of stabilization) are presented in orange square with bar. (b) Absolute deviation of F_{act} (black dot, left ordinate) and particle diameter (red line, right ordinate): The grey shaded box indicates the stabilization time (~10 seconds) of each particle diameter. (c) Particle number concentration (N_{CN} , red dot) and CCN number concentration (N_{CCN} , blue dot). Time resolution of each data point is 1 second and the particle diameter is changed every 40 seconds. S_{max} is set to be 10 K (0.8%). Reprinted from Kim et al. (2021) under the Creative Commons Attribution 4.0 License.

We added the sentences to explain possible uncertainties including combined physical factor that reviewer mentioned (Line 241-251).

“In addition to the effect of multiply charged particles on CCN activation, there are other possible

uncertainties of CCN activation in the BS2-CCN system. It can be affected by combined physical factors including mixing state, surface activity, viscosity and particle morphology. For example, CCN number concentration can be underestimated in the ultrafine mode with a high organic mass fraction due to the lower water surface tension. Particle morphology can affect CCN activity as it can influence in determining the diameter corresponding to the centroid mobility of each size bin. Altaf et al. (2018) explored the effect of size-dependent morphology on CCN activity using aerosol particles composed of organic compounds and salts. For calibration experiment, particle morphology is considered by applying the particle shape factor when deriving κ values. The relative uncertainties, the ratio between absolute error and measured value, do not exceed 1% for calibration aerosols. However, the relative uncertainties could be higher in ambient aerosols due to the non-sphericity. For BS2-CCN system, the absolute deviation of F_{act} was mostly less than 0.05 except for the stabilization time, the first 10 seconds for each D_p scan and the F_{act} value that is higher than 0.85 (Kim et al. 2021).”

Q3: Page 4 – The authors did a good job of describing the formulation of the new kernel function for multiple charge correction in the CN and CCN number concentrations measured using the DMA 3080. Traditionally, the charge correction for the CN and CCN measurements from the DMA 3080 is done using the Wiedensohler (1988) method in the SMCA. Was any significant difference observed between the number concentrations obtained from the 2 charge correction methods? On Line 79, Is charging theory - Wiedensohler 1988 applied? Some clarification on this part of the text could elucidate differences and similarities in theories applied.

A: In this study, we adopted methods of Wiedensohler (1988) and, Gunn and Woessner (1956) for charge correction. The Kernel function is the same with traditional methods but the main difference of our method is calculation of CCN number concentration inside the algorithm. Here, we calculated CCN number concentration by doubly/triply charged particles using the F_{act} function, $h(x, \varphi, D_p^*)$. we added more detailed description in the algorithm part in section 2.3 and sentence in the text to describe charge correction (Line 101-102).

“The particle charge distribution at each size can be calculated according to the Wiedensohler (1988) and, Gunn and Woessner (1956).”

Q4: How much is the overall improvement in the size-resolved activation ratio of the aerosol compared to the traditional SMCA approach and is this difference statistically significant?

A: Our method cannot be directly compared to a traditional SMCA. The reasons are presented in the introduction part: 1) BS2-CCN system uses multiple and continuous supersaturations in the chamber, not a single supersaturation used in commercial DMT-CCNC. 2) The size-resolved F_{act} value is directly used to derive κ value, whereas traditional methods including SMCA aim at finding a critical diameter or supersaturation. The improvement in the size-resolved activation ratio by algorithm is shown in Fig. 7 which presents the deviation (original value – corrected value) F_{act} of two cases of ambient aerosols.

Q5: Page 6 line 160 – The authors mention that calibration results obtained using the charge correction algorithm may be closely replicated with a minimized influence of multiply charged particles, if

“experimental control is performed well”. What does that mean? Were the experimental conditions varied across different calibration procedures? What type of experimental control would be required to obtain high quality calibration without the use of charge correction algorithms?

A: Kim et al. (2021) examined the effect of multiply charged aerosols on calibration curve through CCN activation model and experiments. The CCN activation model describes the CCNC response to the transferred polydisperse charge-equilibrated particles through an ideal DMA and calculates an idealized CCN instruments response with an assumed lognormal particle size distribution. The F_{act} by doubly charged particles not only increases as the value of D_g increases, but also σ_g increases as the increases even if the is the same (Fig. R1). Therefore, when generating calibration aerosols, small D_g and σ_g in number size distribution are recommended to minimize the effect of multiply charged particles on the calibration curve. These effects can also be seen in the calibration experiment using sodium chloride. Both calculation and experiment results imply that the number size distribution of the generated particles should be considered and it is recommended to generate aerosols with D_{peak} corresponding to an F_{act} less than 0.5. The number size distribution of generated calibration aerosols can be controlled by adjusting the particle concentration. We added the sentence to clarify experimental control part (Line 185-187).

“Kim et al. (2021) examined the effect of multiply charged aerosols on calibration curve through CCN activation model and experiments. By adjusting the particle number concentrations, number size distribution with a small D_g and σ_g could be generated to minimize the influence of multiply charged particles.”

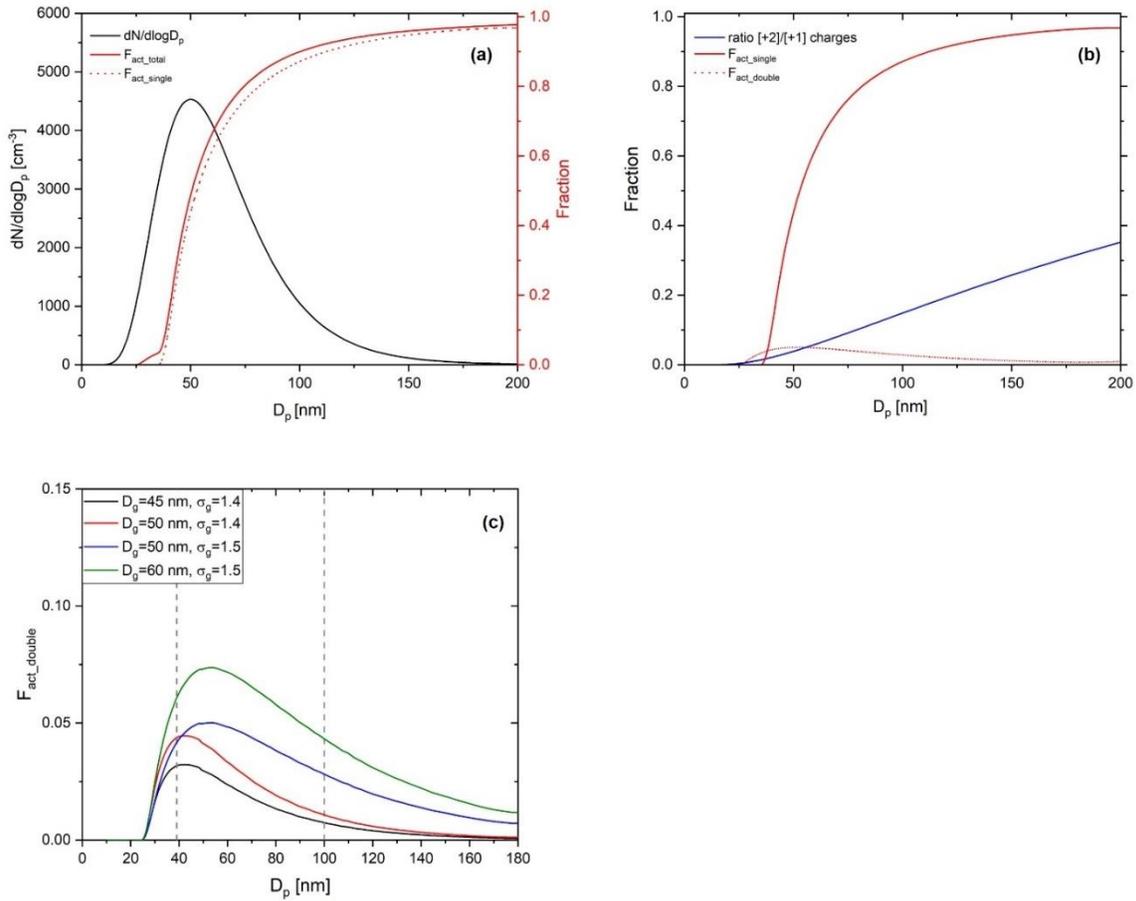


Figure R 2. Calculated ideal activation fraction for log-normally distributed, charge-equilibrated particles transmitted BS2-CCNC system. Shown are (a) assumed log-normal particle size distribution (black solid line, left ordinate, $N = 2000 \text{ cm}^{-3}$, $D_g = 50 \text{ nm}$, and $\sigma_g = 1.5$), total activation fraction (red solid line), activation fractions by singly charged particles (red dashed line), (b) activation fraction by singly charged particle (red solid line) and doubly charged particles (red dashed line), and the ratio of [+2]/[+1] charges (blue solid line), which refers to $f(D, n = +2)/f(D, n = +1)$ with mobility diameter at charge equilibrium. $f(D, n)$ is the fraction of particle carrying n charges at charge equilibrium by Wiedensohler (1988) and (c) activation fractions by doubly charged particles (F_{act_double}) for variant particle size distributions. Information of each particle size distribution is presented in the legend of the figure. Reprinted from Kim et al. (2021) under the Creative Commons Attribution 4.0 License.

Q6: The authors mention that the hygroscopicity parameter was derived from the formulation given by Petters and Kreidenweis (2007). This suggests that the uncertainties in the at the point of activation (which result from there being multiply charged particles in the population corresponding to the dry activation ratio) will directly relate to the uncertainties in. Moreover, the uncertainties due to different multiply charged particles will likely have different magnitude. How do these uncertainties in the size-resolved activation ratio translate to the uncertainties in the aerosol? Furthermore, is there any correlation between the uncertainties due to specific multiply charge particles and the charge that they

carry?

A: Uncertainties of size-resolved activation ratio connected to κ can be explained by Fig.R3 and Fig. R4. Figure R3 presents the κ distribution which corresponds to the F_{act} values of a particle ranged from 50 nm to 150 nm. Figure R4 shows the distribution of the absolute deviation of κ when there is a 0.05 difference from the original F_{act} value. As the D_p increases and the F_{act} value increases, the deviation of κ becomes larger.

And, it can be sized that there is a correlation between the uncertainties caused by specific multiply charged particles and the charge that they carry. The uncertainty by particle morphology could be an example. As mentioned above, particle morphology could affect the determination of particle size in DMA and particle diameter corresponding to the doubly and triply charges can be affected accordingly. Depending on the particle number size distribution, the activation fraction induced by multiply charged particles can be different. These are described in the Fig.2 and Section 4.

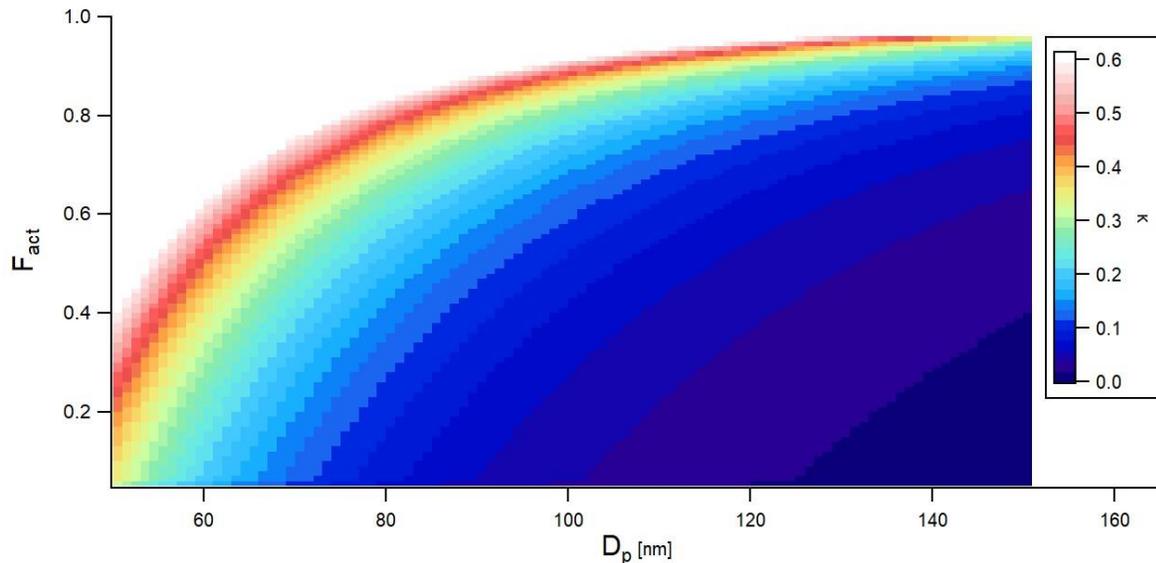


Figure R 3. κ distribution which corresponds to the F_{act} values of a particle ranged from 50 nm to 150 nm. It is calculated from the fitting curve of $F_{act} - S_{aerosol}$ relation for $dT=8$ K condition. Reprinted from Kim et al. (2021) under the Creative Commons Attribution 4.0 License.

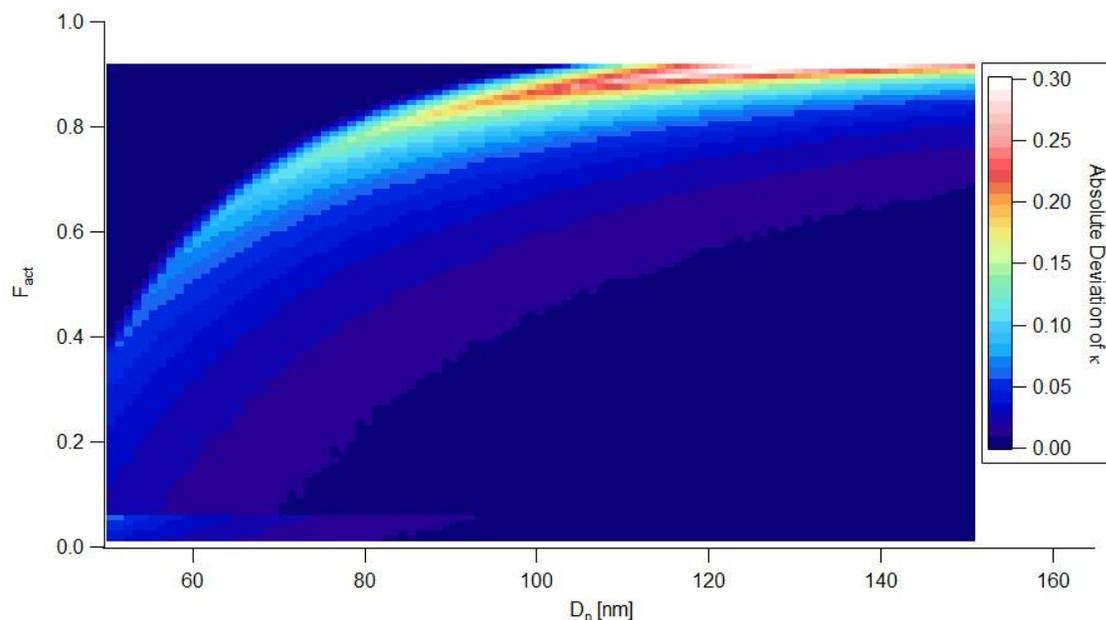


Figure R 4. Distribution of absolute deviation of κ when there is a 0.05 difference from the original F_{act} value. The same fitting curve of $F_{act} - S_{aerosol}$ relation for $dT=8$ K condition used in Fig.R3 is applied for the calculation.

Q7: For the test on the ambient aerosols – What was the chemical composition of the ambient aerosols which were analyzed using the new algorithm? The quantified uncertainties in was helpful, however did the authors verify what proportion of these uncertainties in were due to the multiple charging problem?

A: We measured the mass concentration of PM1 chemical composition (organics, sulfate, nitrate, ammonium and chloride) using aerosol chemical speciation monitor (ACSM). For Case I, organics occupied about 50.4% among the composition followed by sulfate (26.8%), ammonium (12.3%), nitrate (10.0%) and chloride (0.5%) whereas sulfate accounted for the highest percentage (43.0%) followed by organics (33.0%), ammonium (18.0%), nitrate (5.0%) and chloride (1.0%). For quantifying the proportion of uncertainties by possible factors including multiply charged problem, we need additional experiments. Especially, size-resolved chemical composition data which is not available in this study is necessary. Instead, we add the description of possible uncertainties and calculate the relative uncertainty of CCN activation by the particle morphology which can also affect the CCN activation by multiply charged particles.

Q8: Figure 2(b) is confusing. What are the sizes of the particles that carrying doubly and triply charges? Are they the particles with the same mobility of the singly charged particles, or the probability of the size of the particles being doubly or triply charged? Are the doubly and triply charged particle sizes in the 95% of the Gaussian distribution? It is suggested to mention that fraction of doubly and triply charged particles depends on the number concentration of the larger particles.

A: Thanks for your suggestion. Particle number fraction at each charge in Fig. 2b is calculated with Kernel function (Fig. 1) and particle number size distribution. Specifically, number fractions of singly and doubly

charged particles are 0.88 and 0.11, respectively, when particle diameter (i.e., DMA set size) is set to be 70.6 nm (Fig.2b). According to Fig.1, peak diameters of Kernel function for double and triple charging particle are about 103.8 nm 131.4 nm that are within the 95% of the confidence interval when DMA set size is 70 nm. It is noted that particle number size distribution is assumed to be log-normal distribution. As you suggested, we added the sentence in the revised manuscript (Line 153-154)

“And, the number fraction of doubly and triply charged particles depends on the number concentration of the larger particles”