Response to comments by anonymous referee #1:

In the work submitted, Lei et al. presented the design, construction, calibration and validation of a nano-HTDMA apparatus, which can be used to measure hygroscopic growth of aerosol particles down to < 10 nm. The technique they developed is very important, and they also carried out calibration and validation experiments very comprehensively. The paper is also well-written, and I only have a few comments.

Response: We are grateful to referee #1 for her/his comments and suggestions to improve our manuscript. We have implemented changes based on these comments in the revised manuscript. We repeat the specific points raised by the reviewer in italic font, followed by our response. The pages numbers and lines mentioned are with respect to the Atmospheric Measurement Techniques Discussions (AMTD) version.

General comments:

(1) Compared to "sizing accuracy", "sizing offset" may better describe the actual content of Section 3.1.1. Sections 2.2.1 and Section 3.1.1: I think both sizing accuracy (difference between actual size and the size measured using a DMA) and sizing offset (i.e. measured difference between the two DMAs) are important for H-TDMA. While sizing offset has been carefully characterized (Section 3.1.1) for particles down to a few nm, not much information has been provided for the sizing accuracy for <100 nm particles. Although experiments to determine size accuracy for <100 nm particles seem to be impossible, as discussed in Section 2.2.1, could the author estimate the sizing accuracy from a theoretical view?

Response: Good comment, and thanks. Yes, the reviewer is right, it is not possible to determine size accuracy for < 100 nm particles, and sub-20 nm PSL is even not available. Following the reviewer's suggestion, here we try to estimate the sizing accuracy in this size range through error propagation by using differential mobility analysis (DMA) transfer function and the uncertainties of its input parameters (Duplissy et al., 2009; Wiedensohler et al., 2012). According to Knutson and Whitby (1975), sizing of DMA transfer function mainly depends on sheath flow rates and high voltage (HV) applied to the DMA as follows:

$$z_p^* = \frac{Q_{sh} ln\frac{r_2}{r_1}}{2\pi LV} \quad \text{(R1)}$$

$$z_p^* = \frac{neC_c}{3\pi\mu d_p^*} \quad \text{(R2)}$$

$$d_p^* = \frac{2VLneC_c}{3\mu Q_{sh} ln\frac{r_2}{r_1}} \quad \text{(R3)}$$

where z_p^* is the central electrical mobility, Q_{sh} is the sheath flow rate, V is the applied voltage, L is the length of the classification region within the DMA, and r_1 and r_2 are the inner and outer radii of the DMA annulus, respectively. n is the number of elementary charges of particles. e is the elementary charges. C_c is the slip correction. μ is the flow viscosity. d_p^* is the mean particle mobility diameter.

According to Eq. (R3) above, we use the following error propagation formula (Eq. (R4)) (Taylor and Taylor, 1997) to calculate the uncertainties in sizing of nanoparticles. In our study, the flow accuracy of mass flow meter (TSI series 4000) is within ±2%. The deviation of voltage applied to the nano-DMAs (0-12500 V, 0-350 V) varies around the set value when test with voltage power supply (HCE 0-12500, HCE 0-350, Fug Electronic) shown in Table R1. Thence, the sizing accuracy is obtained using Eq. (R5) as shown in Table R1.

$$\delta z = \sqrt{\left(\frac{\partial z}{\partial x}\right)^2 (\delta x)^2 + \left(\frac{\partial z}{\partial y}\right)^2 (\delta y)^2} \quad \text{(R4)}$$

$$\frac{\delta d}{d} = \sqrt{\left(\frac{\delta V}{V}\right)^2 + \left(\frac{\delta Q_{sh}}{Q_{sh}}\right)^2} \quad \text{(R5)}$$

Table R1 (new Table S5 in revised SI). Uncertainties of nano-DMA voltage (V) and sheath flow rates (Q_{sh}), and calculated size uncertainty.

Size (nm)	Uncertainties in V and Q_{sh}	Uncertainty (Sizing accuracy)
100	2648.2±0.02592 V, 10±0.02 L/min	0.2000%
60	1063.0±0.02686 V, 10±0.02 L/min	0.2000%
20	131.1±0.01519 V, 10±0.02L/min	0.2003%
10	33.7±0.02435 V, 10±0.02 L/min	0.2127%
8	21.6±0.03725 V, 10±0.02 L/min	0.2641%
6	12.2±0.06920 V, 10±0.02 L/min	0.6014%

Related additions and changes included in the revised manuscript:

Page 13 line 299, we add: "As discussed in Sec. 2.2.1, it is difficult to verify the sizing accuracy of sub-100 nm aerosol nanoparticles using PSL nanoparticles. Duplissy et al. (2009) and Wiedensohler et al. (2012) suggested to estimate the sizing accuracy of sub-100 nm nanoparticles through DMA transfer function. The theoretical DMA transfer function (see SI. S2. Eq. (S2-S4)) was proposed by Knutson and Whitby (1975) and they noted that sizing is crucially dependent on flow rates and high voltage (HV) applied to the DMA. In our study, the flow accuracy calibrated by the mass flow meter (TSI series 4000) is within ±2%. The variation of voltage applied to the nano-DMAs (0-12500 V, 0-350 V) around the set value were measured with voltage power supply (HCE 0-12500, HCE 0-350, Fug Electronic) and summarized in Table S5. According to the error propagation formula (see SI. S2. Eq. (S5)) (Taylor and Taylor, 1997), the calculated uncertainty in sizing of 6-100 nm nanoparticles increases as size decreases (Table S5).The estimated sizing accuracy is slightly smaller than the sizing offset of two nano-DMAs, but in principle they are still consistent with each other. This suggests that uncertainties of slip correction, DMA dimensions (inner and outer radius, length), temperature, pressure, and viscosity of air may also affect the sizing accuracy (see SI. S2. Eq. (S4), Kinney et al., 1991). Besides, Wiedensohler et al. (2012) also suggested that particle losses, the size- and material-dependent CPC counting efficiency can affect the size accuracy of DMAs."

Related additions included in the supplementary information:

Line 156, we add:

S2. Calculation of sizing accuracy of sub-100 nanoparticles

Knutson and Whitby (1975) proposed the following theoretical differential mobility analyzer (DMA) transfer function and showed that sizing is crucially dependent on sheath flow rates and high voltage (HV) applied to the DMA.

$$z_p^* = \frac{Q_{sh} ln\frac{r_2}{r_1}}{2\pi LV} \quad \text{(S2)}$$

$$z_p^* = \frac{neC_c}{3\pi\mu d_p^*} \quad \text{(S3)}$$

$$d_p^* = \frac{2VLneC_c}{3\mu Q_{sh} ln\frac{r_2}{r_1}} \quad \text{(S4)}$$

where z_p^* is the central electrical mobility, Q_{sh} is the sheath flow rate, V is the applied voltage, L is the length of the classification region within the DMA, and r_1 and r_2 are the inner and outer radii

of the DMA annulus, respectively. n is the number of elementary charges of particles. e is the elementary charges. C_c is the slip correction. μ is the flow viscosity. d_p^* is the mean particle mobility diameter.

According to Eq. (S4) above, we use the following error propagation formula ((Taylor and Taylor, 1997) to calculate the uncertainties in sizing of nanoparticles. In our study, the flow accuracy of mass flow meter (TSI series 4000) is within ±2%. The deviation of voltage applied to the nano-DMAs (0-12500 V, 0-350 V) varies around the set value when test with voltage power supply (HCE 0-12500, HCE 0-350, Fug Electronic) shown in Table S5. Thence, the uncertainties in sizing of nanoparticles are obtained based on the following Eq. (S5) as shown in Table S5.

$$\frac{\delta d}{d} = \sqrt{\left(\frac{\delta V}{V}\right)^2 + \left(\frac{\delta Q_{sh}}{Q_{sh}}\right)^2} \quad \text{(S5)}$$

(2) Line 300-305: It is interesting to find that sizing offset (<0.9%) is smallest at 8 and 10 nm, smaller than that at smaller diameter (6 nm) and at larger diameter (20 nm or larger). Is there any explanation.

Response: Thanks for the comment. Uncertainties in the sheath flow rates and nano-DMA voltages will increase as size decreases, which results in a larger size offset of 6-nm nanoparticles compared with other sizes. However, we observed that the peak diameter of number size distribution of the generated pure water is ~20-30 nm (Figure R1), which is more likely due to presence of impurities in the water. This interferes the accurate measurement of 20-nm nanoparticles.

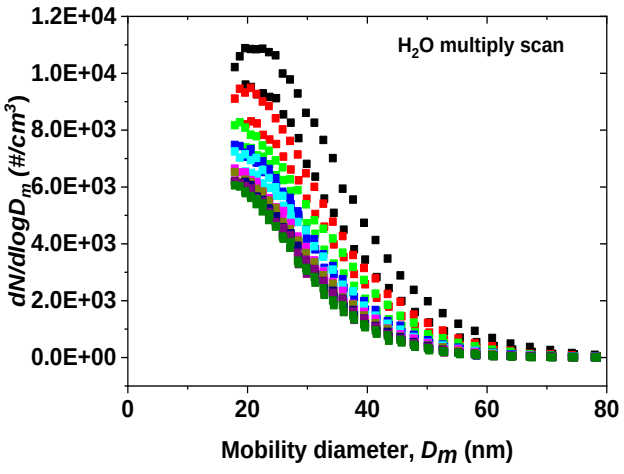

Figure R1. Number concentration scanned for water nanoparticles by the nano-DMA2 at RH below 5 % at 298 K.

Page 13 line 305, we add: "As discussed above, uncertainties in the sheath flow rates and nano-DMA voltages will increase as size decreases, which results in a larger sizing offset of 6-nm nanoparticles compared with other sizes."

Technical comments:

(1) Line 57: change "challenge" to "challenging".

Response: Many thanks. We have revised in the following sentence and now they read as:

Page 3 line 55-57: "In addition, by knowing the hygroscopicity of newly formed nanoparticle, one can infer the involving chemical species (e.g., organic ratio) in particle formation and initial growth (Wang et al., 2010), which is otherwise difficult and highly challenging to measure directly (Wang et al., 2010; Ehn et al., 2014)."

(2) Line 349-353: I am not sure Wikipedia is a reliable source for physical/chemical constants. I would recommend textbooks/handbooks instead.

Response: Thanks for your suggestions. We have cited Atkins et al. (2006) in the following sentence:

Page 15 line 349-353: "It may due to the heat produced from the inner electrode of nano-DMA2, which we estimated to be ~0.08 W ($Q = mdTC_{p,}$) by considering the density and heating capacity of air, and aerosol and sheath air flow rate (ρ=1.2041kg/m^3; C_p=1.859kJ/kg°C) (Atkins et al., 2006)."

Reference:

Atkins, P., De Paula, J., and Walters, V.: Physical Chemistry, W. H. Freeman, 2006.

Kinney, P. D., Pui, D. Y. H., Mullholland, G. W. & Bryner, N. P. Use of the Electrostatic Classification Method to Size 0.1 μm SRM Particles—A Feasibility Study. Journal of Research of the National Institute of Standards and Technology, 96, 147, 1991.

Knutson, E. O. and Whitby, K. T.: Aerosol classification by electric mobility: apparatus, theory, and applications, Journal of Aerosol Science, 6, 443-451, 1975.

Taylor, J. R. and Taylor, S. L. L. J. R.: Introduction To Error Analysis: The Study of Uncertainties in Physical Measurements, University Science Books, 1997.

Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjäraa, A. M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J. A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Hüglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Grüning, C., Faloon, K., Beddows, D., Harrison, R., Monahan, C., Jennings, S. G., O'Dowd, C. D., Marinoni, A., Horn, H. G., Keck, L., Jiang, J., Scheckman, J., McMurry, P. H., Deng, Z., Zhao, C. S., Moerman, M., Henzing, B., de Leeuw, G., Löschau, G., and Bastian, S.: Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions, Atmos. Meas. Tech., 5, 657-685, 2012.

Response to comments by anonymous referee #2:

This manuscript "Nano-hygroscopicity tandem differential mobility analyzer (nano-HTDMA) for investigating hygroscopic properties of sub-10 nm aerosol nanoparticles" presents a design of a HTDMA to measure the hygroscopicity particle down to ~6 nm. The performance and the methods to calibrate and validate the setup were also reported. This setup was shown to have low sizing offset (<1.4% for 100 nm particle). High accuracy for flow rates of aerosol and sheath flow (±1%) and high accuracy for voltages applied to DMA (±0.1%) were found to be crucial to achieve the low sizing offset. Also the DMA2 and humidification system were designed to be placed in housing with stable temperate (±0.1K). The RH of sheath flow was set to the same as RH of aerosol flow to prevent the pre-deliquescence. Using this setup, the authors measured the deliquescence and the efflorescence RH as well as the growth factors of ammonium sulfate and sodium sulfate. For ammonium sulfate, no significant size dependence of DRH and ERH was observed while clear size dependence was observed. Determining the hygroscopicity of nano-particles is important to understand aerosol-water interaction and provides constraints on the chemical composition of nano-particles. This nano-HTDMA has excellent performance and will be useful to measure hygroscopictiy of atmospheric nano-particles. The manuscript is well-written and fit well the scope of AMT. I recommendation its publication in AMT after addressing the following minor comments.

Response: We are grateful to referee #2 for the comments and the constructive suggestions. We address in the following the comments and suggestions by referee #2 and provide improvements based on these clarify the questioned issues in the revised manuscript. The pages numbers and lines mentioned are with respect to the Atmospheric Measurement Techniques Discussions (AMTD) version.

Minor comments:

(1) What is the smallest particle size that the HTDMA can measure?

The title "Nano-hygroscopicity tandem differential mobility analyzer (nano-HTDMA) for investigating hygroscopic properties of sub-10 nm aerosol nanoparticles" reads a little redundant for me. In addition, the manuscript discusses many experiments for particle >10 nm. I suggest optimizing the title.

Response: Thanks for the comment. At the moment, the smallest size that we can measure is 6 nm. The main purpose of the instrument development is to have a device that is able to measure hygroscopic growth of sub-10 nm nanoparticles. We discussed that the results of 20 nm and 100 nm are to compare with literature studies, which are the most abundant (especially for 100 nm) and also are to demonstrate the differences between measuring hygroscopic growth of sub-10 nm nanoparticles and larger ones. Following the suggestion, we revised the tittle as "Nano-HTDMA for investigating hygroscopic properties of sub-10 nm aerosol nanoparticles".

Related additions and changes included in the revised manuscript:

Page 1 line 1-2: "Nano-HTDMA for investigating hygroscopic properties of sub-10 nm aerosol nanoparticles".

(2) Line 428-434, and Fig. 8d, the same method, electrospray was used to generate aerosol <20 nm in this study and the study by Biskos et al. 2006. But the results (growth factors) are still different. Can the authors discuss the difference? Is it possible to generate particles of the same size, i.e. 20 nm with different methods and compare the GF?

Response: Thanks for the comment.

The morphology of particles may affect their hygroscopic behavior (Mikhailov et al., 2004, 2009). Iskandar et al. (2003) and Wang et al. (2019) show that the morphology of the aerosol particles mainly depends on initial properties of droplets (e.g., chemical composition and solution concentration) and drying process. In Table 1, we compared the generation conditions with Biskos et al. 2006b for 6-10 nm ammonium sulfate nanoparticles using an electrospray. Different from generation conditions in Biskos et al. (2006b) for 6-10 nm ammonium sulfate nanoparticles, in our study, in order to minimize the multiple charged nanoparticles, three different concentrations are used so that the size (e.g., 6, 8, 10 nm) selected by the nano-DMA1 was always slight larger than peak of the number size distribution of the generated nanoparticles by the electrospray. This is to ensure that we could have as many as nanoparticles as possible to compensate the strong nanoparticle losses in the nano-HTDMA system. Besides different generation conditions shown in Table R1, the drying rate is mainly dependent on drying flow rates in the HTDMA system (Wang et al., 2019). The RH of dried ammonium sulfate aerosol nanoparticles varies due to the different aerosol/sheath flow rates employed in Biskos et al. (2006b) and this study, respectively. These

differences may lead to the small difference in growth factor of ammonium sulfate nanoparticles prior to the deliquescence.

Following reviewer's suggestion, we used an electrospray and an atomizer to generate 20-nm ammonium sulfate aerosol nanoparticles, respectively. We then compared their hygroscopic growth factors prior to deliquescence. Figure R1a shows a ~ 0.1 higher growth factor of 20-nm ammonium sulfate generated by an electrospray than that using an atomizer in the RH range from 55% to 82%. Figure R1b shows the results of 20-nm sodium chloride nanoparticles using an electrospray and a vaporization-condensation method (Biskos et al., 2006a), respectively. Also, There is a slight difference in the growth factor of 20-nm sodium chloride at RH between 20% and 60% using the different generation methods.

Table R1. Comparison of generation of ammonium sulfate (AS) nanoparticles with diameter from 6-10 nm with Biskos et al. (2006b) using an electrospray

Generation of 6-10 nm AS nanoparticles	AS concentration (mM)	Size of capillary	Flow rates	RH of generated AS nanoparticles
Biskos et al. (2006b)	10	40 μm	2 l/min dry air	0.1%
This study	1, 5, 20	20 μm	1 l/min dry N_2	2%

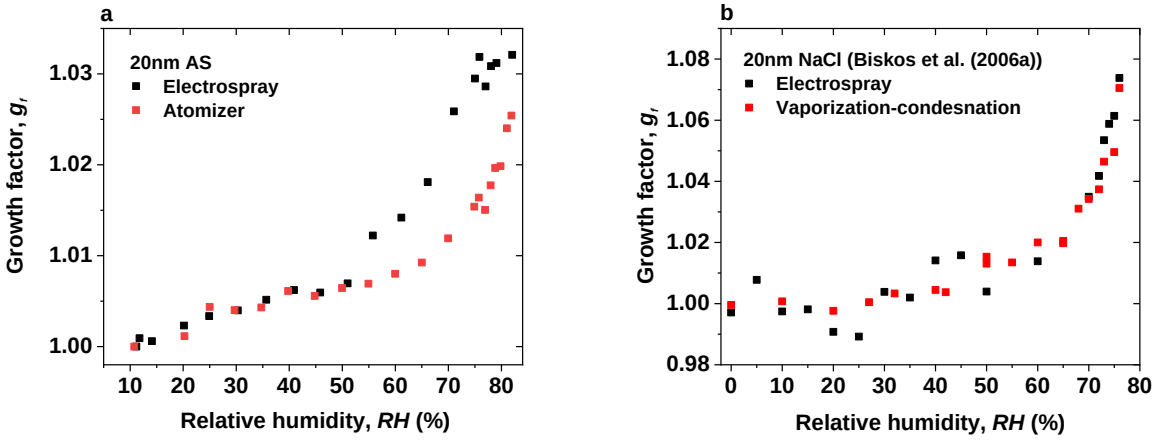

Figure R1 (new Figure S12 in revised SI). Hygroscopic growth factors of 20-nm **(a)** ammonium sulfate from our study (AS) nanoparticles and **(b)** sodium chloride (NaCl) nanoparticles from Biskos et al. (2006a) using the different generation methods prior to deliquescence.

Page 19 line 432, we add: "Different from generation conditions of for 6-10 nm ammonium sulfate nanoparticles in Biskos et al. (2006b), in our study, in order to minimize the multiple charged

nanoparticles, three different concentrations are used so that the size selected by the nano-DMA1 (i.e., 6, 8, 10 nm) was always slight larger than peak of the number size distribution of the generated nanoparticles by the electrospray. This also helps us to have as many as nanoparticles as possible to compensate the strong nanoparticle losses in the nano-HTDMA system. In addition, we used both electrospray and atomizer to generate 20-nm ammonium sulfate, and compared their hygroscopic growth factors prior to deliquescence. Figure S12a shows a ~ 0.1 higher growth factor of 20-nm ammonium sulfate generated by the electrospray than that using the atomizer in the RH range from 55% to 82%, which is similar to the difference in hygroscopic growth factor of 20-nm NaCl aerosol nanoparticles using the different generation methods as observed in Fig S12b in Biskos et al. (2006a). Besides different generation conditions, the morphology of dried ammonium sulfate particles may also differ slightly between our study and Biskos et al. (2006) because of different dying rates, as drying flow rates and RH of the dried ammonium sulfate in the two HTDMA systems are different too."

(3) Fig. 5 and Fig. 7, can the author discuss why the 6 nm AS showed a slight increase with increasing RH.

Response: Thanks for the comments. Yes, a slight increase in hygroscopic growth factor of 6-nm ammonium sulfate nanoparticles was observed in the RH range from 65 to 79% RH before deliquesces. This is attributed to water adsorption onto the surfaces of these nanoparticles. It seems that there is more water adsorption onto the small nanoparticles than that of large nanoparticles. Similar phenomenon has also observed by Hämeri et al. (2000, 2001), Romakkaniemi et al. (2001), Biskos et al. (2006a, b, 2007), and Giamarelou et al. (2018). The reason for such enhanced adsorption at smaller sizes is still to be investigated.

Page 19 line 428, we added: "For example, a slight increase in hygroscopic growth factor of 6-nm ammonium sulfate nanoparticles is observed in the RH range from 65 to 79% RH before deliquescence. This is attributed to water adsorption onto the surfaces of these nanoparticles. It seems that smaller nanoparticles have a stronger tendency of adsorbing water when approaching the DRH than the larger ones. Similar phenomenon has also observed by Hämeri et al. (2000, 2001), Romakkaniemi et al. (2001), Biskos et al. (2006a, b, 2007), and Giamarelou et al. (2018). The reason for such enhanced adsorption at smaller sizes is still to be investigated."

(4) Fig.7, why the DRH for 20 nm AS is different from others (the dashed line)? Also the coloring of efflorescence and deliquescence in this panel contradicts the caption.

Response: Thanks for the comment. The DRH of 20-nm ammonium sulfate is slightly different from that at other sizes. Also, the similar phenomenon was observed for 20-nm ammonium sulfate nanoparticles from Biskos et al. (2006b) shown in Fig. R2, which shows in agreement with our study. To my knowledge, we observed that the peak diameter of number size distribution of pure water is ~20-30 nm (Figure S2a), which is more likely due to presence of impurities in the water. This interferes the accurate measurement of 20-nm nanoparticles.

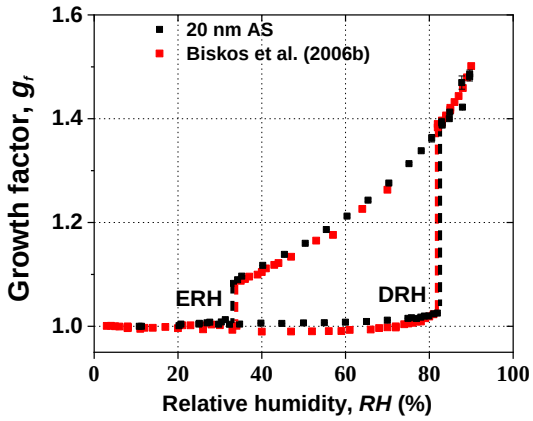

Figure R2. Comparison of the hygroscopic behavior of 20-nm ammonium sulfate (AS) with Biskos et al. (2006b).

Page 45 line 917, we revised the color of 20-nm ammonium sulfate in both deliquescence and efflorescence measurement modes and made the color consistent with citation:

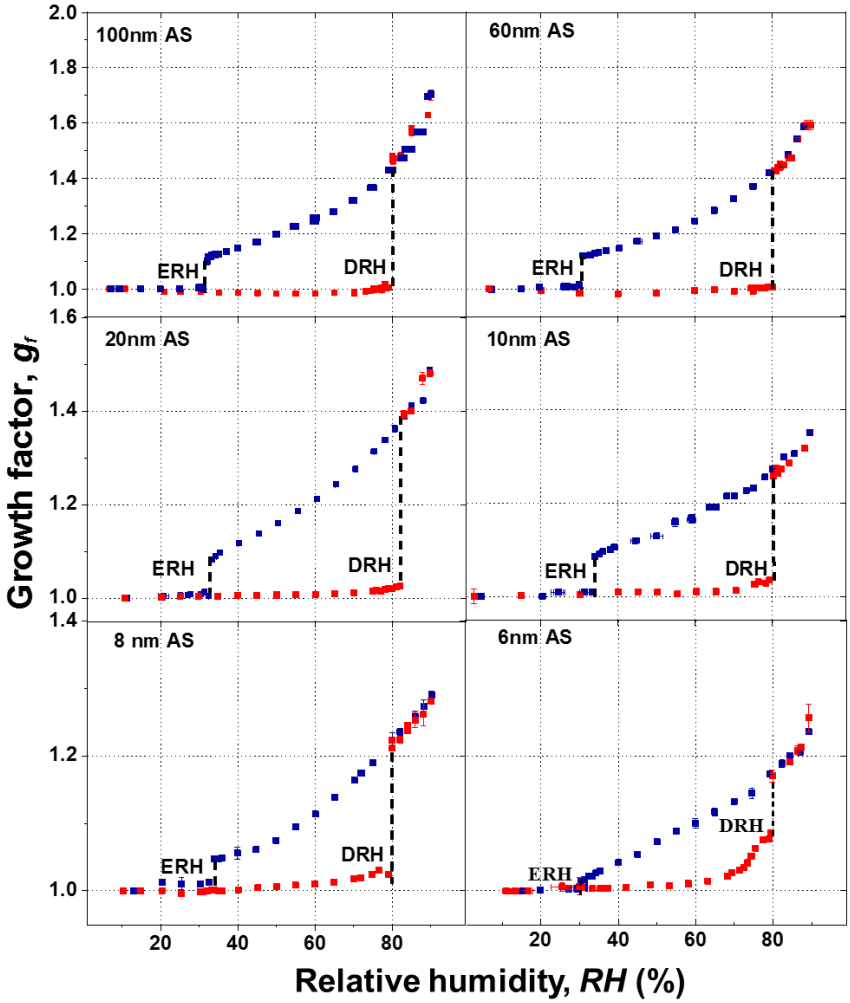

Figure 7. Mobility-diameter hygroscopic growth factors (g_f) of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 6 to 100 nm in the deliquescence mode (red square and error bar) and the efflorescence mode (royal square and error bar). Deliquescence, and efflorescence relative humidity (DRH&ERH, black dashed line) of ammonium sulfate (AS) nanoparticles with dry mobility diameter from 6 to 100 nm.

(5) Line 375-376, "double-mode phenomenon was not observed 375 for 8 and 6 nm ammonium sulfate nanoparticles". Is this because of the slower mass transfer of water vapor for larger particles?

Response: Many thanks. No, this is not because of the slower mass transfer of water vapor for larger sulfate nanoparticles. Double-mode phenomenon was observed for 99-nm sodium chloride in Mikhailov et al. (2004) and for 10-nm ammonium sulfate and sodium chloride in Biskos et al. (2006b, 2007) in the deliquescence measurement mode, respectively. They attributed this to the co-existence of solid and liquid phase of aerosol nanoparticles due to the slight inhomogeneity of RH within nano-DMA2. Bezantakos et al. (2016) have shown the difference of RH for sheath flow and aerosol flow upstream of DMA2 and temperature gradient within DMA2 can result in RH non-uniformities within DMA2. In our study, we also observed this double-mode phenomenon for ammonium sulfate nanoparticles with diameters (e.g., 100, 60, 20, 10 nm) but not for 8 and 6 nm ammonium sulfate nanoparticles. Because this phenomenon is an essentially stochastic process.

(6) Line 472-474, why does DRH/ERH of sodium sulfate show a clear size dependence while ammonium sulfate does not?

Response: Many thanks.

Different from ammonium sulfate, of which DRH and ERH shows no significant size dependence, there is a strong size-dependence of DRH and ERH of sodium sulfate according to our observations down to 6 nm. The different size dependence of DRH and ERH between sodium chloride and ammonium sulfate have been theoretically studied and explained by Cheng et al. (2015). The main reason is the different concentration dependence of solute activities and the different solute-liquid surface tension, e.g., the same change in solute molality leads to a larger change in the solute activity of sodium chloride than that of ammonium sulfate shown in Fig. R3. The phase transition concentration (deliquescence and crystallization concentration) of ammonium sulfate is thus more sensitive to the size change compared to that of sodium chloride, leading to the almost unchanged DRH and ERH of ammonium sulfate nanoparticles (Cheng et al., 2015). For the size dependence of phase transition of sodium sulfate, there is a clear size effect on DRH and ERH similar to that of sodium chloride but different from that of ammonium sulfate in the size range from 6 to 20 nm, suggesting that non-ideality of solution property is close to that of sodium chloride but weaker than that of ammonium sulfate.

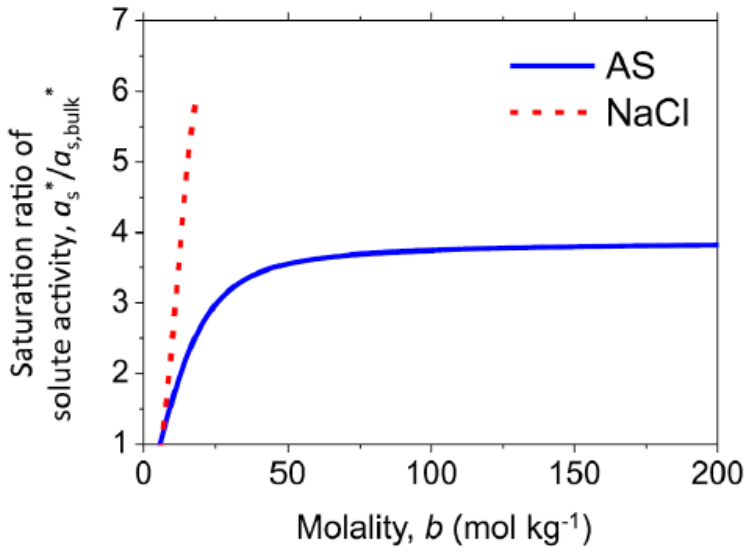

Figure R3. Saturation ratio of solute activity ($a_s^*/a_{s,bulk}^*$) as a function of molality b for ammonium sulfate (AS) and sodium chloride (NaCl). Reprinted with permission by Cheng et al. (2015).

Page 20 line 466-477, we revised: "The strong size-effect on the DRH and ERH of sodium chloride and on hygroscopic growth factors of ammonium sulfate have been observed by Biskos et al. (2006a, b, 2007) and theoretically studied and explained by Cheng et al. (2015). Owning to the strong non-ideality of aqueous ammonium sulfate solution, the phase transition concentration (deliquescence and crystallization concentration) of ammonium sulfate is much more sensitivity to the size changes from 60 nm to 6 nm than that of sodium chloride, leading to the almost unchanged DRH and ERH of ammonium sulfate nanoparticles (Cheng et al., 2015). Compared the three compounds, the size-dependent hygroscopicity of sodium sulfate nanoparticles from 20 nm to 6 nm is similar to that of sodium chloride, but different to that of ammonium sulfate, where no significant change in DRH and ERH was observed. However, in this size range, the increase of the ERH and the decrease of growth factor upon decreasing size seems to be stronger for sodium sulfate than sodium chloride, although no significant change in DRH was observed from micrometer size particles down to 20 nm." **as**

"Different from ammonium sulfate, of which DRH and ERH shows no significant size dependence, there is a strong size-dependence of DRH and ERH of sodium sulfate according to our observations down to 6 nm. The different size dependence of DRH and ERH between sodium chloride and ammonium sulfate have been theoretically studied and explained by Cheng et al. (2015). The main reason is the different concentration dependence of solute activities and the different solute-liquid

surface tension, e.g., the same change in solute molality leads to a larger change in the solute activity of sodium chloride than that of ammonium sulfate. The phase transition concentration (deliquescence and crystallization concentration) of ammonium sulfate is thus more sensitive to the size change compared to that of sodium chloride, leading to the almost unchanged DRH and ERH of ammonium sulfate nanoparticles (Cheng et al., 2015). For the size dependence of phase transition of sodium sulfate, a strong size effect on DRH and ERH is similar to that of sodium chloride but different from that of ammonium sulfate in the size range from 6 to 20 nm, suggesting that non-ideality of solution property is close to that of sodium chloride but weaker than that of ammonium sulfate."

Technical comments:

(1). Line 347, "excuses air" or "excess air"?

Response: Many thanks. We have carefully checked and revised the whole of manuscript and supplement information, including grammar, wording, and sentence structure.

Page 15 line 347-349: "we monitored that the sheath flow temperature at the inlet of nano-DMA2 is slightly lower (less than ~0.2 K) than that at the outlet, i.e., the RHs at the inlet of nano-DMA2 is slightly higher (~ 1%) than the RH of the excess air at the outlet."

(2). Line 427, "continues" should be "continuous".

Response: Many thanks. We have revised in the following sentence and now they read as:

Page 18 line 426-428: "There seems to be continuous water adsorption and the adsorbed water layers (Romakkaniemi et al., 2001) become significantly thicker when RH closer to the DRH (i.e, RH > 70%)."

(3). Line 470, "sensitivity" should be "sensitive".

Response: Many thanks. We have revised in the following sentence and now they read as:

Page 20 line 468-472: "The phase transition concentration (deliquescence and crystallization concentration) of ammonium sulfate is thus more sensitive to the size change compared to that of sodium chloride, leading to the almost unchanged DRH and ERH of ammonium sulfate nanoparticles (Cheng et al., 2015)."

(4). Fig. 5 and 6, I suggest explaining the red and blue lines in the captions, although they were explained in the main text.

Response: Many thanks. We add explanations of the red and blue lines in the all captions in the manuscript and supplement information, respectively.

Page 44 line 907-909: "Figure 5. Deliquescence-mode measurements of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 20-6nm. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively. The RH history in each measurement is 5% → X%, where X is the RH value given in each panel."

Page 45 line 912-914: "Figure 6. Efflorescence-mode measurements of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 20-6nm. The measured (black circle) and fitted (solid lines) normalized size distribution are shown for increasing RH. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively. The RH history in each measurement is 5%→97%→X%, where X is the RH value given in each panel."

Related additions and changes included in the revised supplement information:

Line 44-47: "Figure S4. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 100-nm ammonium sulfate (AS) aerosol nanoparticles. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively."

Line 52-55: "Figure S5. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 60-nm ammonium sulfate (AS) aerosol nanoparticles. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively."

Line 59-62: "Figure S6. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 8-nm ammonium sulfate (AS) aerosol nanoparticles. The measured (black square) and fitted (solid lines, single-mode log-normal fit) normalized size

distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively."

Line 95-100: "Figure S9. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 20-nm sodium sulfate aerosol nanoparticles. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. Red/blue solid line is fitted by a single-mode log-normal fit. Red, blue, and black lines are fitted by a double-mode log-normal fit. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively. The voltage applied to the nano-DMAs (0-12500 V) is kept within ±1% around the set value shown in the voltage meter."

Line 104-109: "Figure S10. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 6-nm sodium sulfate aerosol nanoparticles. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. Red/blue solid line is fitted by a single-mode log-normal fit. Red, blue, and black lines are fitted by a double-mode log-normal fit. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively. The voltage applied to the nano-DMAs (0-350 V) is kept within ±1% around the set value shown in the voltage meter."

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Nano-HTDMA for investigating hygroscopic properties of sub-10 nm aerosol nanoparticles

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Abstract. Interactions between water and nanoparticles are relevant for atmospheric multiphase processes, physical chemistry, and materials science. Current knowledge of the hygroscopic and related physico-chemical properties of nanoparticles, however, is restricted by limitations of the available measurement techniques. Here, we present the design and performance of a nano-hygroscopicity tandem differential mobility analyzer (nano-HTDMA) apparatus that enables high accuracy and precision in hygroscopic growth measurements of aerosol nanoparticles with diameters less than 10 nm. Detailed methods of calibration and validation are provided. Beside maintaining accurate and stable sheath/aerosol flow rates (±1%), high accuracy of DMA voltage (±0.1%) in the range of ~0-50 V is crucial to achieve accurate sizing and small sizing offsets between the two DMAs (<1.4%). To maintain a stable relative humidity (RH), the

humidification system and the second DMA are placed in a well-insulated and air conditioner housing (±0.1K). We also tested and discussed different ways of preventing pre-deliquescence in the second DMA. Our measurement results for ammonium sulfate nanoparticles are in good agreement with Biskos et al. (2006b), with no significant size-effect on the deliquescence and efflorescence relative humidity (DRH, ERH) at diameters down to 6 nm. For sodium sulfate nanoparticles, however, we find a pronounced size-dependence of DRH and ERH between 20 and 6 nm nanoparticles.

1 Introduction

The climatic effects of aerosol nanoparticles have attracted increasing interests in recent years (Wang et al., 2016; Andreae et al., 2018; Fan et al., 2018). Interactions between water and nanoparticles are relevant for atmospheric multiphase processes, physical chemistry, and materials science (Zheng et al., 2015; Cheng et al., 2015, 2016). Aerosol nanoparticles in the atmosphere are mostly originating from new particle formation, and a fraction of these nanoparticles could potentially grow into sizes to efficiently act as cloud condensation nuclei and thus to change the contributions of aerosol nanoparticles to climate forcing (Lihavainen 2003; Wiedensohler et al., 2009; Sihto et al., 2011; Kirkby et al., 2011; Keskinen et al., 2013; Dunne et al., 2016; Kim et al., 2016). These processes strongly depend on the chemical composition and physico-chemical properties of these nanoparticles (Köhler, 1936; Su et al., 2010; Wang et al., 2015; Cheng et al., 2015). One of the most important physico-chemical properties of nanoparticles is their hygroscopic behavior that describes their ability to take up water, and it can differ significantly from that of larger particles (Hämeri et al., 2000, 2001; Gao et al., 2006; Biskos et al., 2006a, b, 2007; Cheng et al., 2015).

To understand and predict hygroscopic properties of nanoparticles, current thermodynamic models mostly rely on the concentration-dependent thermodynamic properties (such as water activity and interfacial energy) derived from the measurements of large aerosol particles or even bulk samples (Tang and Munkelwitz, 1994; Tang 1996; Pruppacher and Klett, 1997; Clegg et al., 1998). They are thus difficult or

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impossible to be applied to describe the hygroscopic behavior of sub-10 nm nanoparticles which can be often supersaturated in concentration compared to bulk solutions (Cheng et al., 2015). Furthermore, the nanosize effect on these properties may also need to be considered (Cheng et al., 2015). The lack of such data hinders the understanding and an accurate simulation of the interaction of water vapor and atmospheric nanoparticles. In addition, by knowing the hygroscopicity of newly formed nanoparticle, one can infer the involving chemical species (e.g., organic ratio) in particle formation and initial growth (Wang et al., 2010), which is otherwise difficult and highly challenging to measure directly (Wang et al., 2010; Ehn et al., 2014). Hence, to measure the hygroscopicity of nanoparticles is essential to improve our understandings of aerosol formation, transformation, and their climate effects.

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Different techniques have been employed to characterize the hygroscopic properties of aerosol particles in different sizes (Fig. S1) (Tang et al., 2019), such as Fourier transform infrared spectrometer (FT-IR) (Zhao et al., 2006), Raman spectroscopy (Dong et al, 2009), electrodynamic balance (EDB) (Chan and Chan, 2003, 2005; Chan et al., 2008), optical tweezers (Reid et al., 2011; Rickards et al., 2013), hygroscopicity tandem differential mobility analyzer (HTDMA) (e.g., Rader and McMurry, 1986; Mikhailov et al., 2004; 2008; 2009; Biskos et al., 2006a, b, 2007; Cheng et al., 2008, 2009; Eichler et al., 2008; Stock et al., 2011; Hong et al., 2014, 2015; Lei et al., 2014; 2018; Mikhailov and Vlasenko, 2019), and atomic force microscopy (AFM) (Estillore et al., 2017). Using these techniques, most of the early lab studies focus on the hygroscopic behavior of particles in accumulation modes and super-micron size range, including deliquescence, efflorescence of pure components and the effect of organics on the change or suppression of deliquescence and efflorescence of these inorganic components in mixtures.

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For nanoparticles with diameters down to sub-10 nm, there are, however, only very few studies attempting to investigate their interactions with water molecules, which mainly utilized the setup with humidified tandem DMAs (Hämeri et al., 2000, 2001; Sakurai et al., 2005; Biskos et al., 2006a, b, 2007; Giamarelou et al., 2018). In Table S1, we summarized the measured DRH and ERH of ammonium sulfate nanoparticles

in the size range from 6 to 100 nm using HTDMAs. In these studies, the results of the observed deliquescence and efflorescence relative humidity (respective DRH and ERH) and prompt or non-prompt phase transitions of ammonium sulfate nanoparticles, however, do not show universal agreement. The technical challenges in HTDMA measurements, especially in the sub-10 nm size range, mainly lie on: (1) accurate sizing and small sizing offset of the two DMAs, (2) highly stable measurement conditions in the whole system. Large sizing offset between the two DMAs may lead to significant error in the measured growth factor based on error propagation (Mochida and Kawamura, 2004). Massling et al. (2011) and Zhang et al. (2016) suggested that to achieve good hygroscopic growth factor of nanoparticles, the sizing offset of the two DMAs should be within ±2-3%, which is however very difficult to maintain for the sub-10 nm size range. To accurately measure phase transition (e.g., DRH and ERH), a highly stable measurement condition is essential, especially maintaining a small temperature perturbation in the humidification system and inside the second DMA to prevent pre-deliquesce. For example, a 0.8 K fluctuation of the experimental temperature during the measurement can result in a 4% difference in RH (0-90%) inside the humidified DMA (Hämeri et al., 2000), leading to an inaccurate determination of the phase transition. Another problem is the prompt versus non-prompt phase transition. Although effects of impurities on the phase transition of aerosol nanoparticles (Biskos et al., 2006a; Russell and Ming, 2002) may be one possible reason of the previously observed non-prompt phase transitions (e.g., Hämeri et al., 2000), the apparent non-prompt phase transition of aerosol nanoparticles has been thought to be mainly due to the inhomogeneity of RH and temperature in the humidified DMA during measurements (Biskos et al., 2006b; Bezantakos et al., 2016). Moreover, the hygroscopic measurements are in general difficult for nanoparticles with diameters below 20 nm due to high diffusion losses of nanoparticles (Seinfeld and Pandis, 2006).

In this study, we present a design of nano-HTDMA setup that enables high accuracy and precision in hygroscopic growth measurements of aerosol nanoparticles with diameters less than 10 nm. Detailed methods of calibration and validation are provided. We discuss in detail how to maintain the good

performance of the system by minimizing uncertainties associated with the stability and accuracy of RH, temperature, voltage for nanoparticle classification, and sheath and aerosol flows in the DMA systems. We then apply the nano-HTDMA system to study the size dependence of the deliquescence and the efflorescence of aerosol nanoparticles of two specific inorganic compounds (e.g., ammonium sulfate and sodium sulfate) for sizes down to 6 nm.

2. Methods

2.1 Nano-HTDMA system

A nano-HTDMA system is built up to measure the aerosol nanoparticle hygroscopic growth factor (g_f), especially aiming for accurate measurement of phase transition and hygroscopic growth factor for nanoparticles in the sub-10 nm size range. Here, g_f is defined as the ratio of mobility diameters of nanoparticles after humidification ($D_m(RH)$) to that at dry condition ($D_m(< 10\%$ RH)) (see SI. S1. Eq. (S1)). As presented in Fig. 1, the nano-HTDMA composes three main components, including two nano-differential mobility analyzers (nano-DMA, TROPOS Model Vienna-type short DMA; Birmili et al., 1997), an ultrafine condensation particle counter (CPC, TSI Model 3776), and a humidification system. Table 1 shows the technical specification, where the DMA system, humidification system, and temperature system of the three HTDMAs setup are compared among the systems of Biskos et al. (2006b), Hämeri et al. (2000) and this study.

In our setup (Fig. 1), the first nano-DMA (nano-DMA1) is used to produce quasi-monodisperse nanoparticles at a desired dry diameter. The flow rate of the closed-loop sheath flow in the nano-DMA1 is maintained at 10 l/min. The ratio of sheath flow to aerosol flow is 10:1.5. The sheath flow is dried to RH below 10% by two custom-built Nafion dryers (TROPOS Model ND.070) in parallel. The quasi-monodisperse nanoparticles produced by nano-DMA1 then enter the humidification system, which can be

set to deliquescence mode (from low RH to high RH for measuring deliquescence) or efflorescence mode (from high RH to low RH for measuring efflorescence). In the deliquescence mode, dry nanoparticles are humidified by a Nafion humidifier (NH-1, TROPOS Model ND.070, L. 24″) to a target RH. In the efflorescence mode, nanoparticles are first exposed to a high RH condition (~97% RH) in a Nafion humidifier (NH-2, Perma Pure Model MH-110, L. 12″) and then dried to a target RH through NH-1. The humid flow in the outer tube of NH-1 is a mixture of high-humidity air produced with a custom-built Gore-Tex humidifier and heater (GTHH: TROPOS Model Di. 0.6″, L. 11.8″) and dry air in variable proportions. To have a precise control of the aerosol RH, the flow rates of the humid and dry air are adjusted with a proportional-integral-derivative (PID) system, including two mass flow controllers (MFC: MKS Model MF1) and a RH sensor (Vaisala Model HMT330) downstream of NH-1.

The residence time is ~5.4 s in the NH-1for both the deliquescence and the efflorescence modes. Many groups have reported that the residence time of a few seconds is sufficient to reach equilibrium for measuring hygroscopic growth or shrink of inorganic salt particles, e.g., ammonium sulfate and chloride sodium (Chan and Chan, 2005; Duplissy et al., 2009; Lei et al., 2014, 2018; Giamarelou et al., 2018). More specifically, Kerminen (1997) estimated the time for reaching the water equilibrium to be between 8×10^{-6} s and 0.005 s for 100 nm nanoparticles at 90% RH at 25°C with accommodation coefficients from 0.001 to 1, respectively. In our study, we measured the inorganic aerosol nanoparticles with diameters from ~100 nm down to 6 nm, thus the equilibrium time should be even shorter as nanoparticle size decreases (Table. S2). In NH-2, the residence time is ~0.07 s for the deliquescence of inorganic aerosol nanoparticles at very high RH condition (~97% RH), which is much longer than the time estimated for phase transition by Duplissy et al. (2009) (in the order of a few milliseconds) and Raoux et al. (2007) (in the order of a few nanoseconds). In addition, we have tested a longer NH-2 (Perma Pure Model MH-110, L. 48″) in the efflorescence mode, and no significant difference in measured growth factors are found, indicating that the residence time in NH-1 and NH-2 should be sufficient.

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153 The number size distribution of the humidified nanoparticles is measured with a combination of the second
154 nano-DMA (nano-DMA2) and the ultrafine CPC. Similar to Biskos et al. (2016b), a multiple Nafion
155 humidifier (NH-3, Pure Model PD-100) is used in our nano-HTDMA system to rapidly adjust the RH of
156 the sheath flow of nano-DMA2. The sheath flow is fed into the outer tube of NH-3 to minimize its pressure
157 drop. The RH of humid flow in the inner tube of NH-3 is controlled with a similar PID system as that for
158 NH-1. A RH sensor (Vaisala Model HMT330) downstream of NH-3 is used to provide feedback to the PID
159 system. In our nano-HTDMA system, a dew point mirror (DPM: EDGE TECH Model MIRROR-99) is
160 placed in the excess flow line to measure the RH and temperature of excess flow of the nano-DMA2. During
161 the operation, the difference between sheath flow RH and aerosol flow RH has been maintained within
162 ±1% (see more details in Section 2.2).

163 The sheath flow is maintained to the set flow rate with a PID-controlled recirculation blower (RB:
164 AMETEK Series MINISPIRAL). Prior to every size scan, the sheath flow rate of nano-DMA2 is adjusted
165 by the PID system according to the measurement of a mass flow meter (MFM: TSI Series 4000) in the
166 sheath flow line. In order to minimize the pressure drop along the recirculating sheath flow loop, low flow
167 resistance MFM and hydrophobic filter (HF: Whatman Model 6702-3600) are used. A heat exchanger (HE,
168 Ebmpapst Model 4414FM) is installed downstream of the RB to minimize the temperature perturbation in
169 the sheath flow by the heat generated in the RB.

170 As aforementioned, temperature non-uniformity is the main contributor to the fluctuation of RH within
171 humidified DMA. Temperature difference within nano-DMA2 is unavoidable mainly due to temperature
172 difference between inner electrode and the rest of nano-DMA2 parts and/or the temperature difference
173 between aerosol and sheath flow (Duplissy et al., 2009; Bezantakos et al., 2016). As shown in Fig. 1, to
174 investigate and monitor the temperature difference within nano-DMA2 during measurements, a
175 temperature sensor (THERMO ELECTRON Model Pt100) is placed at the inlet of the sheath flow and the
176 temperature of sheath excess flow is monitored by the DPM. Note that, a DPM should be installed as close

as possible to the nano-DMA2 in the excess flow, which better represents the conditions inside the nano-DMA2, such as temperature and RH (Wiedensohler et al., 2012). In addition, the temperature of aerosol flow is monitored at the inlet of the aerosol flow of nano-DMA2.

Moreover, to maintain a stable environment that required for the growth factor measurements, nano-DMA2 with its sheath flow humidification system is placed in a well-insulated housing chamber (marked with yellow dashed lines in Fig. 1). An air conditioner (Telemeter Electro Model TEK-1004-RR-24-IP55) is installed inside the housing to maintain a constant temperature (292.15±0.1 K), which is set to be ~1 K lower than the constant laboratory temperature (293 K) in order to achieve high RH (~90%) inside nano-DMA2.

2.2 Calibration of nano-HTDMA

The purpose of this study is to design and build a nano-HTDMA system that is able to measure the hygroscopic properties of nanoparticles, especially in the sub-10 nm size range. A small perturbation in the measurement conditions may lead to large biases in the results. Hence, to provide high quality hygroscopicity measurements of nanoparticles, systematic calibration of the nano-HTDMA should be conducted regularly to ensure the accuracy and stability of the measurement conditions. Table 1 lists the possible sources of uncertainty, which could affect the performance of the HTDMAs. In our setup, nanoparticle sizing, aerosol/sheath flow rates, the high voltage (HV) applied to nano-DMAs, RH sensors, and temperature sensors are calibrated and verified independently.

Note that in the following, for calibration and/or checking of different parameters, the criteria and/or standard that the nano-HTDMA system has to meet are listed mainly according to the suggestions from Duplissy et al., (2009) and Wiedensohler et al. (2012), which are not specifically provided for accurately measuring sizes or hygroscopic growth of sub-10 nm nanoparticles. Compared with these criteria, to measure hygroscopic growth of sub-10 nm nanoparticles, we have achieved a better condition for our nano-

HTDMA system after comprehensive calibrations described as follows (more details about performance of our system see section 3).

2.2.1 Sizing accuracy

For particle diameters higher than 100 nm, the verification of sizing accuracy of DMAs can be accomplished by using certified particles of known sizes such as polystyrene latex (PSL) spheres (Hennig et al., 2005; Mulholland et al., 2006; Duplissy et al., 2009; Wiedensohler et al., 2012, 2018). The particle sizing of nano-DMA2 is checked with PSL by switching off the sheath flow and the HV supply of nano-DMA1, which actually in this case does not function as a DMA, but rather a stainless-steel tube. Sizing agreement between measured diameters and nominal diameters of PSL particles above 100 nm should be within ±3% (Wiedensohler et al., 2012). After confirming the accurate sizing of nano-DMA2, the sizing accuracy of nano-DMA1 can be in turn checked by the nano-DMA2 with a full scan of a certain size of PSL selected by the nano-DMA1. Note that, it is important to check not only the sizing accuracy of both DMAs, but also the sizing agreement between the nano-DMA1 and nano-DMA2. To achieve good hygroscopicity measurements of nanoparticles, the sizing offset of the two DMAs should be within ±2-3% (Massling et al., 2011; Zhang et al., 2016).

For nanoparticles with diameters smaller than 100 nm, the sizing accuracy is, however, difficult to check by using PSL nanoparticles. This is mainly because the size of residual material in the solution also peaks around 20 – 30 nm (Fig. S2a), resulting in an asymmetric number size distribution of generated PSL nanoparticles (Fig. S2b) (Wiedensohler et al., 2012). PSL nanoparticles with diameters below 20 nm are not commercially available (https://www.thermofisher.com/order/catalog/product/3020A), making the verification in this size range even impossible. Sizing accuracy of nanoparticles is critically determined by sheath flow rates and HV applied to the nano-DMAs. However, unlike for the 100 nm nanoparticles, a ±2-3% sizing offset between the two DMAs would be very difficult to maintain for nanoparticles with diameters smaller than 20 nm. Thence, accurate calibrations of sheath flow rates and high voltage are crucial

for constraining the uncertainty associated with sizing of nanoparticles below 100 nm. The calibrations for aerosol/sheath flow, DMA voltage, and sensors will be described in detail in the following Section 2.2.2-2.2.5.

2.2.2 Aerosol and sheath flow

Sizing accuracy of a DMA directly depends on the accuracies of aerosol and sheath flow rates. The aerosol flow rate at the inlet of the nano-DMA1 is checked by using a bubble flow meter (Gilian Model Gilibrator-2). Wiedensohler et al. (2012) recommended that the measured aerosol flow rate should not deviate more than 5% from the set flow rate during the measurements, otherwise one should check the flow rate of CPC or if there is a leakage in the system. Details about leakage checking can be found in Birmili et al. (2016).

To calibrate the sheath flow, a verified MFM (TSI Series 4000) is placed in the recirculating sheath flow close-loop upstream of the MFM. By applying a series of sheath flow rates, a calibration curve (flow rate vs. MFM analogue output) can be obtained according to the reading of the reference MFM. Maximum deviation of 2% from the sheath flow rate value of the reference MFM is recommended by Wiedensohler et al. (2012), which can keep sizing accuracy of 200 nm PSL particles within ±2%.

2.2.3 DMA voltage

The sizing of nano-DMAs is very sensitive to the accuracy and precision of the voltages applied, especially when measuring nanoparticles in the sub-10 nm diameter range. A verified reference voltage meter with voltage up to 1000 V (Prema Model 5000 DMM, accuracy 0.005%) is used to calibrate the HV supply of the nano-DMAs (0-350 V). By setting a series of analogue voltage values, the HV applied to nano-DMA can be calibrated according to the values shown in the reference voltage meter. For our nano-DMAs, sub-10 nm in particle sizes correspond to voltage below 50 V. Thence, voltage calibration should be performed with a higher resolution (smaller voltage interval) from 0 to 50 V (shown in the insert of Fig. 2).

2.2.4 RH sensor

One typical method to calibrate RH sensors in a HTDMA system is to measure the hygroscopic growth factors of ammonium sulfate (Hennig et al., 2005), although the effects of shape factors, restructuring, and impurities in the solutions may hamper a reliable RH calibration with this method (Duplissy et al., 2009). Moreover, this indirect RH sensor calibration through measurement of the hygroscopic growth factors of ammonium sulfate (usually with nanoparticle diameters around or above 100 nm) only calibrates the RH values higher than the ERH of the pure salt. Calibration of RHs below ERH of ammonium sulfate is important for the phase transition measurements. Most importantly, we are investigating the hygroscopic growth factors of ammonium sulfate nanoparticles. Hence, using ammonium sulfate nanoparticles to calibrate RH sensors in our system becomes invalid.

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Therefore, we alternatively calibrate the RH sensors by using a DPM (EDGE TECH Model MIRROR-99), which is recommended in several previous studies (Hennig et al., 2005; Duplissy et al., 2009; Biskos et al., 2006a, b, 2007). In the calibration, the DPM and RH sensors should be kept in the well-insulated chamber with constant laboratory conditions (e.g., flow rates, temperature, and pressure). By running the DPM and all the other RH sensors in parallel at various RHs (5% to 90%), a calibration curve of the RHs measured by the DPM against analogue voltages of RH sensor can be obtained.

2.2.5 Temperature sensor

Since all our temperature sensors and the high accurate DPM (EDGE TECH Model MIRROR-99) are installed in the aforementioned well-insulated chamber and the chamber temperature is maintained with air conditioner at about 292.15±0.1 K, we calibrate the temperature sensors and corrected their systematic shift by comparing the record of temperature sensors and the DPM by keeping them in parallel inside the chamber over a 12-hour time period.

2.3 Particle generation

The experiments shown in this study were conducted using laboratory generated ammonium sulfate and sodium sulfate nanoparticles. Nanoparticles with diameters of 6, 8, and 10 nm were generated by an electrospray (AG: TSI Model 3480) with 1, 5, and 20 mM aqueous solution of ammonium sulfate and sodium sulfate (Aldrich, 99.99%), respectively. The generated particles were then diluted and dried to RH below 2% by mixing with dry and filtered N_2 (1 l/min) and CO_2 (0.1 l/min). The dried polydisperse aerosol nanoparticles were subsequently neutralized by a Po^{210} neutralizer. To avoid blocking the 25-μm capillary of the electrospray with high solution concentration, we used an atomizer (AG: TSI Model 3076) to generate nanoparticles with diameters of 60-100 nm and 20 nm with 0.05 and 0.001 wt% solution of ammonium sulfate and sodium sulfate (Aldrich, 99.99%), respectively. Also, 100-nm PSL nanoparticles were atomizing a PSL solution of mixing 3 drops of 100-nm PSL with 300 mL distilled and de-ionized milli-Q water. The generated nanoparticles were subsequently dried to RH below 10% with a custom-built Nafion dryer (ND: TROPOS Model ND.070) and then neutralized by a Kr^{85} neutralizer.

The solutions used in our measurements were prepared with distilled and de-ionized milli-Q water (resistivity of 18.2 MΩ cm at 298.15 K). Note that, for 100-60 nm and 20 nm, the solution concentration was adjusted so that the sizes selected by the nano-DMA1 were always larger than the peak diameter of the number size distribution of the generated nanoparticles to minimize the influence of the multiple charged nanoparticles in hygroscopicity measurements. The influence of multiple charges on sub-10 nm particles is expected to be very small, we, however, still used different concentrations so that the sizes selected by the nano-DMA1 were always around the peak of the number size distribution of the generated nanoparticles by the electrospray (Fig. S3). This is to ensure that we could have as many particles as possible to compensate the strong loss of very small particles in the whole humidification systems.

3 Results and discussion

3.1 Performance of the nano-HTDMA

3.1.1 Sizing accuracy

In this section, we show the performance of our nano-HTDMA after a full calibration, including accuracy and stability of the aerosol/sheath flow rates, the voltage applied to the nano-DMAs, and nanoparticle-sizing accuracy. In our study, the sheath/aerosol flow rates and nano-DMA voltage supply have been calibrated every day and every two weeks, respectively. The deviations of the measured aerosol/sheath flow rates from the set-point values are less than ±1%, which is lower than the maximum variation of 2% recommended by Wiedensohler et al. (2012).

The voltage applied to the nano-DMAs (up to 350 V) is kept within ±0.1% around the set value shown in the voltage meter. As shown in Fig. 3a, when test with 100-nm PSL nanoparticles, the average peak diameter of scans from the nano-DMA2 is 100.4 nm, which matches well with the mean diameter of PSL nanoparticles (100±3 nm, Thermo Fisher Scientific Inc.). Afterwards, when using nano-DMA1 select 100 nm PSL, the scanned size distribution by nano-DMA2 has a peak diameter at 100.3 nm (Fig. 3b), indicating a good sizing accuracy of the nano-DMA1 too. As discussed in Sec. 2.2.1, it is difficult to verify the sizing accuracy of sub-100 nm aerosol nanoparticles using PSL nanoparticles. Duplissy et al. (2009) and Wiedensohler et al. (2012) suggested to estimate the sizing accuracy of sub-100 nm nanoparticles through DMA transfer function. The theoretical DMA transfer function (see SI. S2. Eq. (S2-S4)) was proposed by Knutson and Whitby (1975) and they noted that sizing is crucially dependent on flow rates and high voltage (HV) applied to the DMA. In our study, the flow accuracy calibrated by the mass flow meter (TSI series 4000) is within ±2%. The variation of voltage applied to the nano-DMAs (0-12500 V, 0-350 V) around the set value were measured with voltage power supply (HCE 0-12500, HCE 0-350, Fug Electronic) and summarized in Table S5. According to the error propagation formula (see SI. S2. Eq. (S5)) (Taylor and Taylor, 1997), the calculated uncertainty in sizing of 6-100 nm nanoparticles increases as size decreases (Table S5).The estimated sizing accuracy is slightly smaller than the sizing offset of two nano-DMAs, but in principle they are still consistent with each other. This suggests that uncertainties of slip correction, DMA

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dimensions (inner and outer radius, length), temperature, pressure, and viscosity of air may also affect the sizing accuracy (see SI. S2. Eq. (S4), Kinney et al., 1991). Besides, Wiedensohler et al. (2012) also suggested that particle losses, the size- and material-dependent CPC counting efficiency can affect the size accuracy of DMAs.

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After calibration, on average a <1.4% sizing offset between the two nano-DMAs can be achieved for ammonium sulfate nanoparticles with dry diameters of 100 nm, 60 nm and 20 nm (Fig. 3c, Fig.5, Table S3, Fig. S4, and Fig. S5), which is much better than the 2-3% criteria recommended by Massling et al. (2011) and Zhang et al. (2016). For sub-10 nm ammonium sulfate nanoparticles, our system has an average sizing offset of <0.9% for 10 and 8 nm particles and ~1.4% for 6 nm particles, respectively (Fig. 3d, Fig. 5, Table S3, and Fig. S6). As discussed above, uncertainties in the sheath flow rates and nano-DMA voltages will increase as size decreases, which results in a larger sizing offset of 6-nm nanoparticles compared with other sizes. Note that, we also tested to calibrate the DMA voltage with a voltage meter with lower accuracy of ±1%, and the DMA voltages can only be kept within ±1% around the set value. In this way, we found a much larger sizing offset for the sub-10 nm particles, i.e., 5.4% and 6.0% for 8 and 6 nm ammonium sulfate nanoparticles, respectively. These results show that maintaining an accurate sheath/aerosol flow (with ±1% around the set value) together with a careful voltage calibration (with ±0.1% around the set value, especially in low voltage range, i.e., <50 V for our system) is the key for accurate sizing of sub-10 nm nanoparticles.

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3.1.2 Preventing pre-deliquescence in the deliquescence measurement mode

Pre-deliquescence of dry nanoparticles in the deliquescence measurement mode is an important issue that needs to be resolved in order to obtain accurate DRH (Biskos et al., 2006b; Duplissy et al., 2009; Bezantakos et al., 2016; Hämeri et al., 2000). Since temperature and RH are closely linked and accurate monitoring of these two quantities in the system are critical for nano-HTDMA measurements, we calibrated all RH and T sensors regularly (every two weeks in this study). To prevent pre-deliquescence and optimize the system, we have conducted three tests using ammonium sulfate nanoparticles with a dry diameter of

100 nm. In the first test, we regulated the RH of excess flow (RH_e) and made it equal to that of the aerosol flow at the inlet of nano-DMA2 (RH_a), i.e., RH_e=RH_a, as done by previous HTDMA measurements, e.g., Villani et al. (2008). As shown in Fig. 4a, the measured growth factors of 100-nm ammonium sulfate are in good agreement with predictions of the Extended Aerosol Inorganic Model (E-AIM; Clegg et al., 1998) at RH above 80%. However, the ammonium sulfate nanoparticles deliquesce at 75% RH, which is significantly lower than the expected DRH (80%, Tang and Munkelwitz (1994)). Since our RH sensors were all well calibrated and the uncertainty of RH measurement is ±1%, it is reasonable to hypothesize that the RH upstream of nano-DMA2 has already reached the deliquesce RH of ammonium sulfate nanoparticles. When these aerosol nanoparticles move downstream of the nano-DMA2, the RH decreases back to 75%, which dehydrates the deliquesced ammonium sulfate nanoparticles. To avoid the pre-deliquescence, Hämeri et al. (2001) has suggested to set RH_a to be 3-5% lower than RH_e. In the second test, we have configured and regulated the system following this suggestion, i.e., $RH_e \geq RH_a+3\%$. In this case, the ammonium sulfate nanoparticles still deliquesce at 79% RH (Fig. 4b), even if RH_a is 6% lower than RH_e.

Previous studies (Biskos et al., 2006b; Bezantakos et al., 2016) have shown that RH non-uniformities within the nano-DMA2 can result in inaccurate measurements of phase transition and hygroscopic growth of aerosol nanoparticles. One reason for RH non-uniformities within nano-DMA2 is that the sheath flow RH is different from the aerosol flow RH at the inlet of the DMA (Hämeri et al., 2000, 2001). Another important reason is the existence of temperature gradient within nano-DMA2 (Bezantakos et al., 2016). Hence, in the third test, we moved the RH sensor from the excess flow downstream of nano-DMA2 to the sheath flow upstream of nano-DMA2 and then regulated RH of sheath flow (RH_s) the same as RH_a (shown in Fig. 1), i.e., RH_s=RH_a, as done by Kreidenweis et al. (2005), Biskos et al. (2006a, b), and Massling et al. (2011). Note that to minimize the temperature gradient within the nano-DMA2 in our system so that nanoparticles can undergo almost the same RH conditions, the nano-DMA2 with its sheath flow humidification system has been placed in a well-insulated air-conditioned chamber. The air temperature inside the chamber can

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be maintained at an almost constant level (292.15±0.1 K). In addition, a heat exchanger was installed downstream of the recirculation blower to minimize the temperature perturbation in the sheath flow by the heat generated in the RB. Unlike previously reported by Bezantakos et al. (2016) that the RH at the outlet was higher than that the inlet of the sheath air, we monitored that the sheath flow temperature at the inlet of nano-DMA2 is slightly lower (less than ~0.2 K) than that at the outlet, i.e., the RH_s at the inlet of nano-DMA2 is slightly higher (~ 1%) than the RH of the excess air at the outlet. It may due to the heat produced from the inner electrode of nano-DMA2, which we estimated to be ~0.08 W ($Q = mdTC_{p,k}$) by considering the density and heating capacity of air, and aerosol and sheath air flow rate ((ρ=1.2041kg/m^3; C_p= 1.859kJ/kg°C) (Atkins et al., 2006). Although this temperature perturbation (less than ~0.2 K between the sheath flow at the inlet and the excess flow at the outlet of the nano-DMA2) is larger than the ideal condition of less than 0.1 K that Duplissy et al. (2009) and Wiedensohler et al. (2012) suggested, our experimental results show that a prompt phase transition can be still achieved. In this case, the measured DRH of ammonium sulfate nanoparticles is almost at 80% (Fig. 4c and 4d).

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3.1.3 Prompt phase transition of ammonium sulfate

Figure 5 and 6 show the normalized particle number size distributions measured by the nano-DMA2 in the respective deliquescence and efflorescence measurement modes for ammonium sulfate nanoparticles with dry mobility diameters of 20 nm, 10 nm, and 6 nm (see Fig. S4 for 100 nm, see Fig. S5 for 60 nm, see Fig. S6 for 8 nm). In the deliquescence measurement mode (Fig. 5, Fig. S4a, and Fig. S5a), we observed the similar double-mode phenomenon as reported by Mikhailov et al. (2004) and Biskos et al. (2006b, 2007). For example, at 20 nm, there are two distinct intersecting modes of particle size distributions determined by the nano-DMA2 in the RH range from 79% to 83% RH (around the DRH of ammonium sulfate). Biskos et al. (2006b, 2007) attributed these two modes to the co-existence of solid and liquid phase nanoparticles at RH close to the DRH of ammonium sulfate, due to the slight inhomogeneity of RH in the second nano-DMA, i.e., some nanoparticles have already undergo deliquescence (liquid state) and some are not (solid).

This is evident through a double-mode log-normal fitting (red and blue modes in Fig. 5). Until RH ~82%, the peak diameter of the red mode at 82% RH is similar to that at 11% RH, indicating that these nanoparticles are still in a solid state. At 82% RH, a population of ammonium sulfate nanoparticles starts to deliquesce and exists in a distinct mode with significant larger peak diameter (blue mode), although majority of the nanoparticles remain solid (red mode). Further increase RH, the peak diameter of normalized number size distribution of the blue mode increases, indicating the continuous growth the nanoparticles after deliquescence. However, in our case the double-mode phenomenon was not observed for 8 and 6 nm ammonium sulfate nanoparticles (Fig. 5 and Fig. S6a). To have a better estimation of DRH when the double modes occurred, the peak diameter of the mode with larger number of nanoparticles was chosen for growth factor calculation (Biskos et al., 2006b, 2007). For example, for 20 nm ammonium sulfate nanoparticles, the peak diameters of normalized number size distribution of the red and blue modes are used to calculate growth factor at RH between 79% to 83%, respectively.

For the efflorescence measurement mode, we adopted the approach of Biskos et al. (2006b) and used the geometric standard deviation of number size distribution (sigma: σ) to quantify the diversity of the sizes of nanoparticles. As shown in Fig. 6, Fig. S4b, Fig. S5b, and Fig. S6b, broadening of the normalized number size distributions measured with nano-DMA2 was only observed for 20-nm ammonium sulfate nanoparticles in the RH range from 33% to 30%. There, at RH higher than 33% or lower than 30%, σ stays stably at 1.072. However, clear increases of σ (1.078-1.087) were observed for RH between 33% and 30%. The normalized number size distributions in the RH range from 33% to 30% can be further resolved by double-mode fit with fixed σ of 1.072 (the red and the blue mode in Fig. 6 for 20 nm). The ammonium sulfate nanoparticles in the red mode at RH between 33% to 30% are in solid state because the peak diameter of red mode is similar as that at 11% RH. However, within this RH range, the peak diameter of the blue mode is significantly larger, indicating that these nanoparticles are still in liquid state. Further decreasing RH (lower than 30%), only one mode has been observed and the peak diameter of the normalized number size distribution almost unchanged as RH decreases (red mode in Fig. 6 for 20nm), which means that the

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nanoparticles have been all in the solid state. Similar to the deliquescence measurement shown above and in Fig. 5, the co-existence of solid and aqueous phase nanoparticles at RH 30-33% is also very likely to stem from the slight heterogeneous RH in nano-DMA2 (Biskos et al., 2006b). To have a better estimation of ERH when the broadening phenomenon exists, the peak diameter of the mode with larger number of nanoparticles was used for growth factor calculation. After such data processing in both deliquescence and efflorescence modes, we obtained prompt deliquescence and efflorescence of 6 to 100 nm ammonium sulfate nanoparticles (more details in Section 3.1.4).

3.1.4 Size-dependent hygroscopicity of ammonium sulfate nanoparticles

Figure 7 shows the humidogram of ammonium sulfate nanoparticles measured by our nano-HTDMA system in the size (dry diameter) range of 6-100 nm. The detailed comparison between our results and Biskos et al. (2006b) during both deliquescence and efflorescence measurements are presented in Fig. 8a and b (also Fig. S7). In general, our results are in a good agreement with the measurement results of Biskos et al (2006) and the theoretical prediction by Cheng et al. (2015). First, there is a strong size dependence in the hygroscopic growth factor of ammonium sulfate nanoparticles, and smaller ammonium sulfate nanoparticles exhibit lower growth factor at a certain RH. For example, the difference of the growth factor between 6 and 100 nm nanoparticles is up to 0.28 at 80% RH (Fig. S8a). Second, there is, however, no significant size dependence in both DRH and ERH (Fig. S8b). For nanoparticles of different sizes (6-100 nm), the DRH and ERH of ammonium sulfate varies slightly from ~80-83% and ~30-34%, respectively. This variation of the DRH and ERH along the size is much smaller for ammonium sulfate nanoparticles than for sodium chloride (Biskos et al. 2006a, 2007).

Although our results in general agree well with Biskos et al. (2006b), the growth factors of 10, 8, and 6 nm ammonium sulfate nanoparticles that we measured at high RH (i.e., > ~70%) are slightly lower (~0.02 in growth factor) than that in Biskos et al. (2006b) in both deliquescence and efflorescence processes (Fig. 8b and Fig. S7). We calculated the uncertainties of growth factor of 10-nm ammonium sulfate from 80% to

90% RH for our system and Biskos et al. (2006b) system by $\sqrt{\left(\left(g_f \frac{\sqrt{2}\varepsilon_{Dp}}{D_p}\right)^2 + \left(\varepsilon_{RH} \frac{dg_f}{dRH}\right)^2,\right)}$ (Mochida and Kawamura, (2004)). Here, ε_{Dp}, ε_{RH}, and g_f are uncertainty of particle mobility diameter, uncertainty of relative humidity, and growth factor with respect to RH, respectively. The average sizing offsets of our system and Biskos et al. (2006b) for 10 nm ammonium sulfate are taken here as $\frac{\varepsilon_{Dp}}{D_p}$ (see Table 1). As shown in the insert of Fig. 8b, the discrepancies between the two systems are still within measurement uncertainty.

In addition, compared to Biskos et al. (2006b), our results show a similar re-structuring in deliquescence mode at RH between about 20% to 75% for 100, and 60 nm ammonium sulfate nanoparticles (Fig 8c). However, different than in Biskos et al. (2006b), we do not find re-structuring for smaller ammonium sulfate nanoparticles (20, 10, 8, and 6 nm) at RH below deliquescence point (Fig. 8c and Fig. 8d). There seems to be continuous water adsorption and the adsorbed water layers (Romakkaniemi et al., 2001) become significantly thicker when RH closer to the DRH (i.e, RH > 70%). For example, a slight increase in hygroscopic growth factor of 6-nm ammonium sulfate nanoparticles is observed in the RH range from 65 to 79% RH before deliquescence. This is attributed to water adsorption onto the surfaces of these nanoparticles. It seems that smaller nanoparticles have a stronger tendency of adsorbing water when approaching the DRH than the larger ones. Similar phenomenon has also observed by Hämeri et al. (2000, 2001), Romakkaniemi et al. (2001), Biskos et al. (2006a, b, 2007), and Giamarelou et al. (2018). The reason for such enhanced adsorption at smaller sizes is still to be investigated. Note that, the ammonium sulfate hygroscopic data from Biskos et al. (2006b) shown here are all generated by an electrospray, but in our experiments, only the ammonium sulfate nanoparticles with diameters smaller than 20 nm (i.e., 10, 8, and 6 nm) were generated by an electrospray, while the larger nanoparticles (i.e., 20, 60, and 100 nm) were generated by a atomizer. Different from generation conditions of for 6-10 nm ammonium sulfate nanoparticles in Biskos et al. (2006b), in our study, in order to minimize the multiple charged nanoparticles, three different concentrations are used so that the size selected by the nano-DMA1 (i.e., 6, 8, 10 nm) was

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always slight larger than peak of the number size distribution of the generated nanoparticles by the electrospray. This also helps us to have as many as nanoparticles as possible to compensate the strong nanoparticle losses in the nano-HTDMA system. In addition, we used both electrospray and atomizer to generate 20-nm ammonium sulfate, and compared their hygroscopic growth factors prior to deliquescence. Figure S12a shows a ~ 0.1 higher growth factor of 20-nm ammonium sulfate generated by the electrospray than that using the atomizer in the RH range from 55% to 82%, which is similar to the difference in hygroscopic growth factor of 20-nm NaCl aerosol nanoparticles using the different generation method as observed in Fig S12b in Biskos et al. (2006a). Besides different generation conditions, the morphology of dried ammonium sulfate particles may also differ slightly between our study and Biskos et al. (2006) because of different dying rate, as drying flow rates and RH of the dried ammonium sulfate in the two HTDMA systems are different too. This means the different generation methods and drying conditions may influence the surface structure of the nanoparticles and thus their interaction with the adsorbed water layers (Iskandar et al., 2003; Xin et al., 2019).

3.2 Size-dependent hygroscopicity of sodium sulfate nanoparticles

As a common constituent of atmospheric aerosol particles (Tang and Munkelwitz, 1993, 1994; Tang 1996; Tang et al., 2007), hygroscopicity of sodium sulfate with diameters above 20 nm particles has been investigated by a few groups (Tang et al., 2007; Xu and Schweiger, 1999; Hu et al., 2010). However, its hygroscopic behavior in the sub-10 nm size range has not been investigated yet. In this study, we applied our nano-HTDMA system to measure the hygroscopic growth factors, DRH, and ERH of sodium sulfate nanoparticles with dry size from 20 nm down to 6 nm.

Figure 9 shows the measured size-resolved hygroscopic growth factors of sodium sulfate nanoparticles. Different from the observations by Tang et al. (2007) using an electrodynamic balance (EDB), we observed prompt deliquescence and efflorescence for both 20-nm and 6-nm sodium sulfate nanoparticles. Two intersecting modes in the measured number size distribution of humidified sodium sulfate nanoparticles is

observed at RH close to the DRH (Fig. S9 and S10 in the Supplementary Information) and ERH, suggesting an externally mixed of aqueous and solid nanoparticles. As shown in Sect. 3.1.3, a similar phenomenon is also observed for ammonium sulfate, which could be attributed to the slight RH heterogeneities in nano-DMA2, which makes only part of the nanoparticles deliquesce at RH close to the DRH, while the others remain in solid state.

Together with the hygroscopic growth of 14-16 µm and 200-20 nm sodium sulfate measured previously by Tang et al. (2007) and Hu et al. (2010), we show a strong size dependence in hygroscopic growth factors of sodium sulfate nanoparticles (Fig. S11d). For example, at RH 84%, the hygroscopic growth factor of 6 nm sodium sulfate is only ~ 1.3 (in efflorescence mode), while the respective growth factors are about 1.5 and 1.8 for 20 nm and 14-16 µm particles. As shown in Fig. 9, E-AIM already agrees well with the hygroscopic growth of micrometer particles (14-16 µm) without shape correction (DeCarlo et al., 2004), i.e., shape factor (χ) of 1.0. However, to explain observation, a shape factor of ~1.16 and 1.26 would be needed for 20 nm and 6 nm sodium sulfate nanoparticles, respectively.

There is no significant change in DRH between 14-16 µm (~84%) and 20 nm (~84%) sodium sulfate particles (Fig. 9). This is consistent with Hu et al. (2010) where no change in DRH from 200 nm down to 20 nm (~82%, see Table 1 from Hu et al. (2010)) was observed. However, a significant increase of DRH occurred when further decreasing particle diameters to 6 nm (DRH = ~90%). The size dependence of ERH is stronger than that of DRH, as there is already a clear increase of ERH from micrometer 14-16 µm (~57%) to 20 nm (~62%) sodium sulfate particles. When further reducing the particle diameters to 6 nm, an almost 6% increase of DRH can be found, compared to the micrometer 14-16 µm particles (i.e., ERH increases from 57 to 82%, respectively). Different from ammonium sulfate, of which DRH and ERH shows no significant size dependence, there is a strong size-dependence of DRH and ERH of sodium sulfate according to our observations down to 6 nm. The different size dependence of DRH and ERH between sodium chloride and ammonium sulfate have been theoretically studied and explained by Cheng et al.

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(2015). The main reason is the different concentration dependence of solute activities and the different solute-liquid surface tension, e.g., the same change in solute molality leads to a larger change in the solute activity of sodium chloride than that of ammonium sulfate. The phase transition concentration (deliquescence and crystallization concentration) of ammonium sulfate is thus more sensitive to the size change compared to that of sodium chloride, leading to the almost unchanged DRH and ERH of ammonium sulfate nanoparticles (Cheng et al., 2015). For the size dependence of phase transition of sodium sulfate, a strong size effect on DRH and ERH is similar to that of sodium chloride but different from that of ammonium sulfate in the size range from 6 to 20 nm, suggesting that non-ideality of solution property is close to that of sodium chloride but weaker than that of ammonium sulfate. As different hydrates of sodium sulfate may exist during the deliquescence and efflorescence processes (Xu and Schweiger, 1999), to explain the underline mechanism of the size dependent hygroscopicity of sodium sulfate particles can be challenging.

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4 Summary and Conclusion

In this study, we presented our newly designed and self-assembled nano-HTDMA for measuring hygroscopicity of nanoparticles in the sub-10 nm diameter size range. We also introduced the comprehensive methods for system calibration and reported the performance of the system, focusing on the sizing accuracy and preventing pre-deliquescence in the deliquescence measurement mode. By comparing with previous studies on ammonium sulfate nanoparticles (Biskos et al., 2006b), we show that our system is capable of providing high quality data of the hygroscopic behavior of sub-10 nm nanoparticles. We then extended our measurements for sodium sulfate nanoparticles, of which size-dependent deliquescence and efflorescence have been clearly observed for nanoparticles down to 6 nm in size, with similar behavior as sodium chloride.

As we know, atmospheric aerosol particles consist of not only inorganic components, but also a vast number of organic components existing in the atmosphere. However, their physico-chemical properties are still not fully understood, especially when comes to the nano-scale and supersaturated concentration range. The nano-HTDMA system can be directly applicable to explore the size dependence of aerosol nanoparticles. Combing the multi-size measurements of hygroscopicity and the Differential Köhler Analyses (DKA, Cheng et al., 2015) in nano size range, we will be able characterize and parameterize the water activity and surface tension of different inorganic and organic systems. This will further help us to understand the formation and transformation of aerosol nanoparticles in the atmosphere and their interaction with water vapor.

Data availability

Readers who are interested in the data should contact Yafang Cheng (yafang.cheng@mpic.de).

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Author contributions: Y.C. and H.S. designed and led the study. N.M., T.T. and A. W. assembled the basic HTDMA system. Y.C., H.S. and T.L. modified and advanced the basic system into the nano-HTDMA for the purpose of measuring hygroscopic properties of aerosol nanoparticles in sub-10 nm size range at MPIC. T.L. performed the experiments. J.H., N.M. and X.W. supported the experiments. All co-authors discussed the results and commented on the manuscript. T.L. wrote the manuscript with input from all co-authors.

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941 ## Tables

942 **Table 1.** Accuracy, precision and sources of uncertainty associated with HTDMA measurements.

	Biskos et al. (2006b)	Hämeri et al. (2000)	Nano-HTDMA (This study)
DMA System			
Type of DMA1 & DMA2	TSI nano-DMAs	Hauke-type DMAs	Vienna-type short DMAs
Accuracy of aerosol flow in DMA2	±1% (0.3-1.5 l/min)	-	±1% (1.5 l/min)
Accuracy of sheath flow in DMA2	±1% (5-15 l/min)	-	±1% (10 l/min)
Accuracy of DMA voltage	±0.1% (0-500V)	-	±0.1% (0-350V)
Sizing accuracy of DMA2 using PSL	3%	-	0.4% (100-nm PSL)
Sizing agreement between DMAs using ammonium sulfate	3.1% (10 nm) [a]	±1% [b]	0.6% (100 nm) [c] 0.5% (60 nm) [c] 1.4% (20 nm) [c] 0.9% (10 nm) [c] -0.2% (8 nm) [c] 1.4% (6 nm) [c]
Precision of particle-sizing	<2%	-	<2% (6-200 nm) [d]

Humidification System			
Type of RH sensor	RH sensors (Omega Model HX93AV)	Dew point mirror (GE) RH sensors (Vaisala Humitter model 50Y)	Dew point mirror (Edge) RH sensors (Vaisala model HMT 330)
Accuracy of RH sensors (0-90% RH)	±2.5% RH	±3% RH [e]	±1% (RH sensor)
Position of the probe in the system	Inlet of DMA2 (RH_a sensor [f], RH_s sensor [g])	Inlet of DMA2 (RH_a sensor) & excess air (RH_s sensor, dew point mirror)	Inlet of DMA2 (RH_a sensor, RH_s sensor) & excess air (dew point mirror)
RH setting	$RH_a=RH_s$	$RH_s \geqslant RH_a+3\%$	$RH_a=RH_s$
Temperature Control System			
Temperature control type	Thermally isolated environment (humidification+DMA2)[h]	Thermally isolated environment (DMA2)	Box T regulated (humidification+DMA2)
Difference in T between inlet and outlet of DMA2	-	-	<0.2°C

- Not reported.
[a] According to the scans of the second DMA for the hygroscopic growth of 10 nm ammonium sulfate and the growth factors at different RHs provided by Biskos et al. (2006b), we retrieved an average sizing offset of Biskos et al. (2006b) system to be ~3.1% at 10 nm (see SI, S1).
[b] Size range not given.
[c] See Table S2 in supporting information.
[d] Value calculated according to the relative standard derivation.
[e] From Vaisala Humitter model 50Y manual.
[f] RH_a: the RH of aerosol flow.
[g] RH_s: the RH of sheath flow.
[h] Bezantakos et al. (2016).

Figures

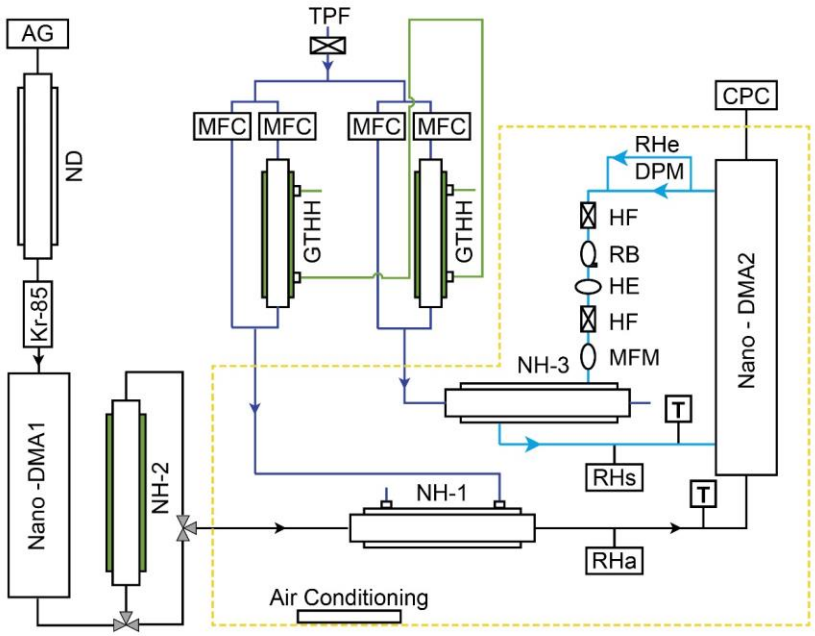

Figure 1. Experimental setup of the nano-HTDMA. Here, AG: aerosol generator (aerosol atomizer or electrospray); ND: nafion dryer; Kr-85: Krypton source aerosol neutralizer; Nano-DMA: nano differential mobility analyzer; TPF: total particle filter; HF: hydrophobic filter; MFC: mass flow controller; MFM: mass flow meter; RB: recirculation blower; DPM: dew point mirror; GTHH: Gore-Tex humidifier and heater; NH: nafion humidifier; HE: heat exchanger; CPC: condensation particle counter; Black line: aerosol line; Blue line: sheath line; Royal blue line: humidified air; Green line: MilliQ water (resistivity of 18.2 MΩ cm at 298.15 K). RH_a and RH_s (measured by RH sensors) represent the RH of aerosol and sheath flow in the inlet of nano-DMA2, respectively. RH_e (measured by dew point) represents the RH of excess air. T represent the temperature of aerosol and sheath flow in the inlet of nano-DMA2, respectively.

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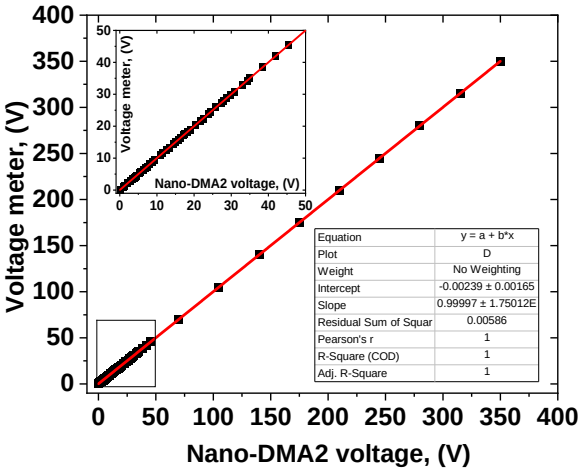

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967 **Figure 2.** An example of voltage calibration of the nano-DMA2.

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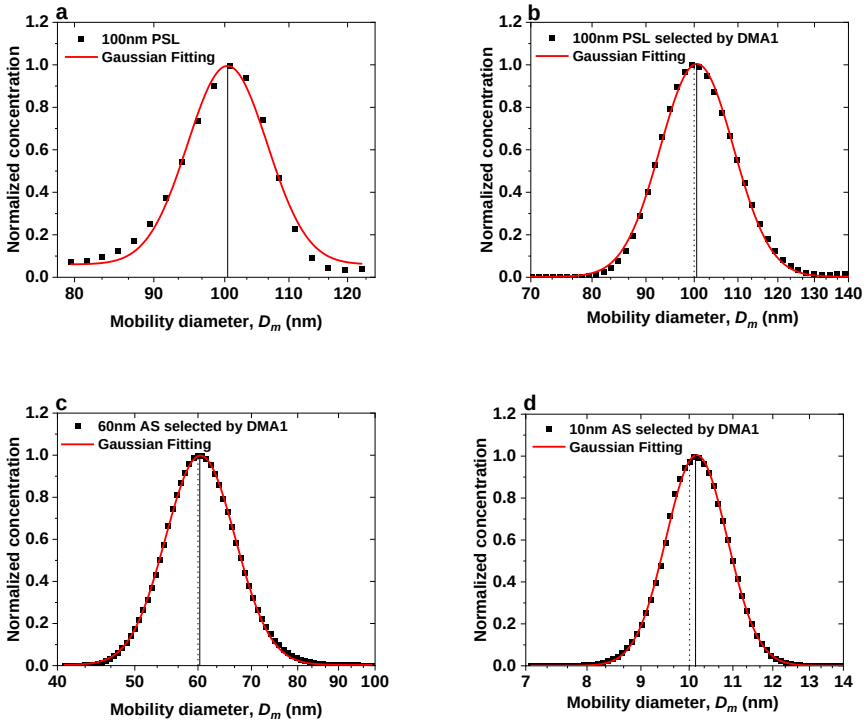

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977 **Figure 3**. Sizing accuracy and sizing offset of nano-DMAs after calibration. **(a)** Normalized number size distribution
978 scanned by the nano-DMA2 for 100-nm PSL nanoparticles (black solid square). The black solid line marks peak
979 diameter from the Gaussian fits for the scan (red curve). Normalized number size distributions scanned by the nano-
980 DMA2 for 100-nm PSL nanoparticles **(b)**, 60-nm **(c)**, and 10-nm **(d)** ammonium sulfate (AS) selected by the nano-
981 DMA1 at RH below 5% at 298 K (black solid square). The dotted lines mark the diameters of the monodispersed
982 nanoparticles selected by the nano-DMA1, i.e., 100 nm in **(b)**, 60 nm in **(c)** and 10 nm in **(d)**. The black solid lines
983 mark the peak diameters from the Gaussian fits (red curve).

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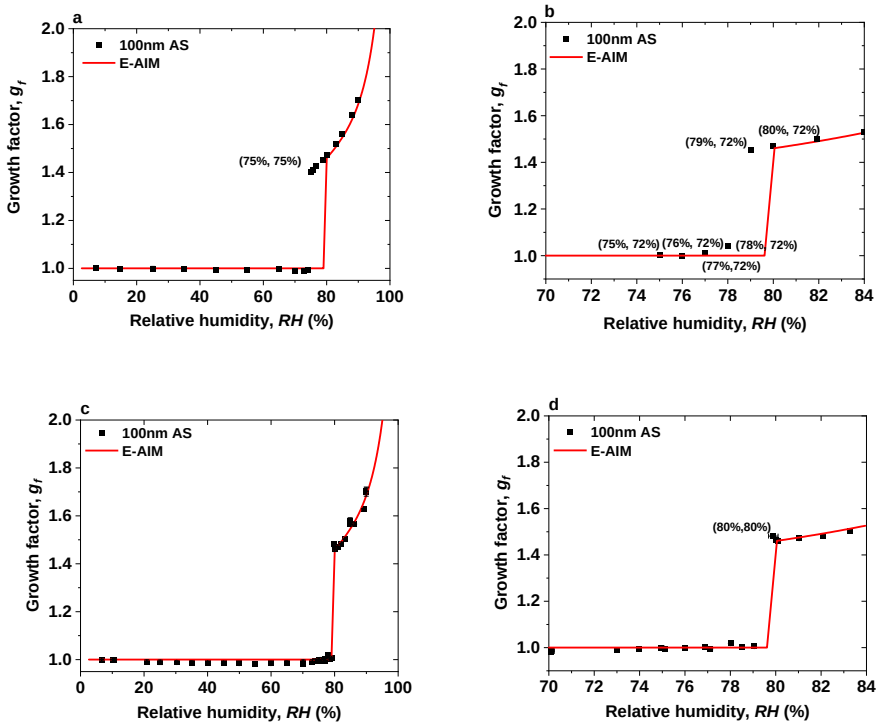

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987 **Figure 4.** Mobility-diameter hygroscopic growth factors (g_f) of 100-nm ammonium sulfate (AS) nanoparticles at 298
988 K measured in deliquescence mode. In comparison, the E-AIM model predicted growth factors of ammonium sulfate
989 nanoparticles at 100 nm. **(a) RH_e=RH_a**, (75%, 75%) represents the (RH_e, RH_a), **(b) $RH_e \geq RH_a$+3%**, (75%, 72%)
990 represents the (RH_e, RH_a), and **(c) RH_s = RH_a**. (**d)** The enlarged view of the RH range of 70% to 84% in Fig. 4c. (80%,
991 80%) represents the (RH_s, RH_a). RH_s and RH_e are the RH of sheath flow in the inlet of nano-DMA2 and in the excess
992 air line, respectively; RH_a is the RH of aerosol flow in the inlet of nano-DMA2.

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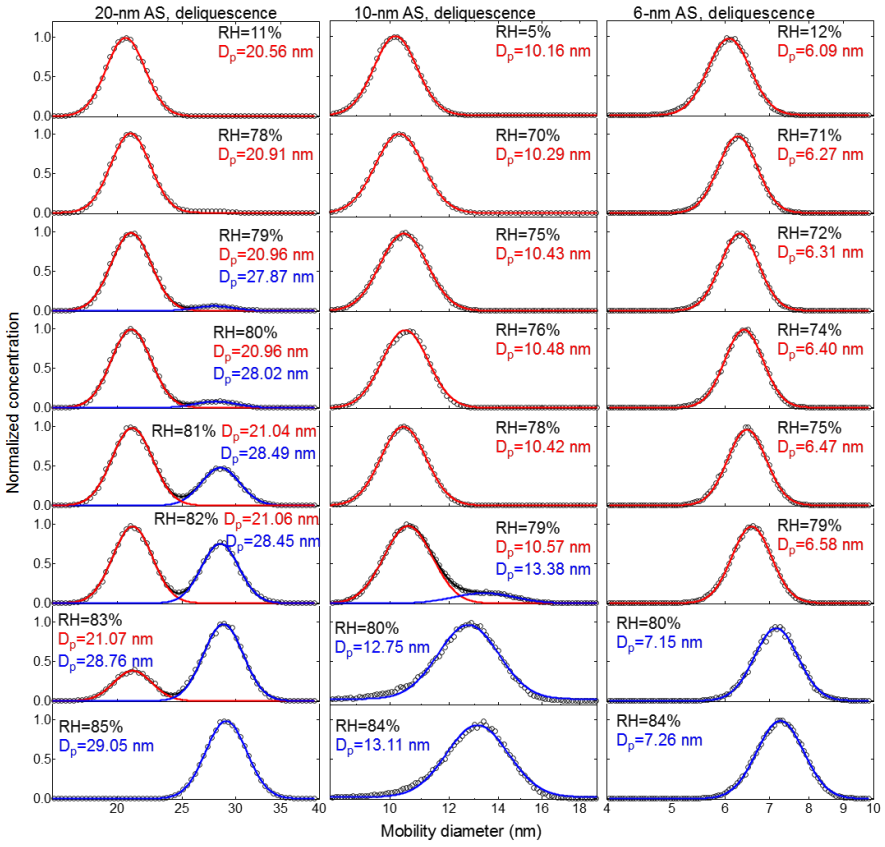

Figure 5. Deliquescence-mode measurements of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 20-6nm. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively. The RH history in each measurement is 5% → X%, where X is the RH value given in each panel.

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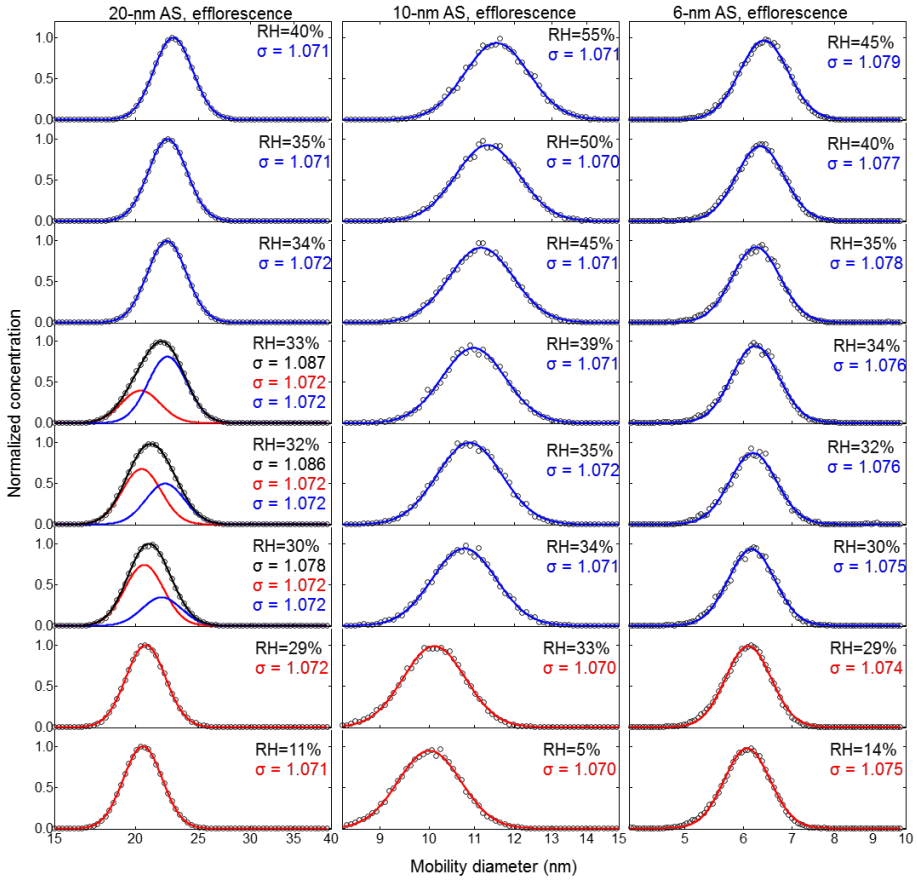

Figure 6. Efflorescence-mode measurements of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 20-6nm. The measured (black circle) and fitted (solid lines) normalized size distribution are shown for increasing RH. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively. The RH history in each measurement is 5%→97%→X%, where X is the RH value given in each panel.

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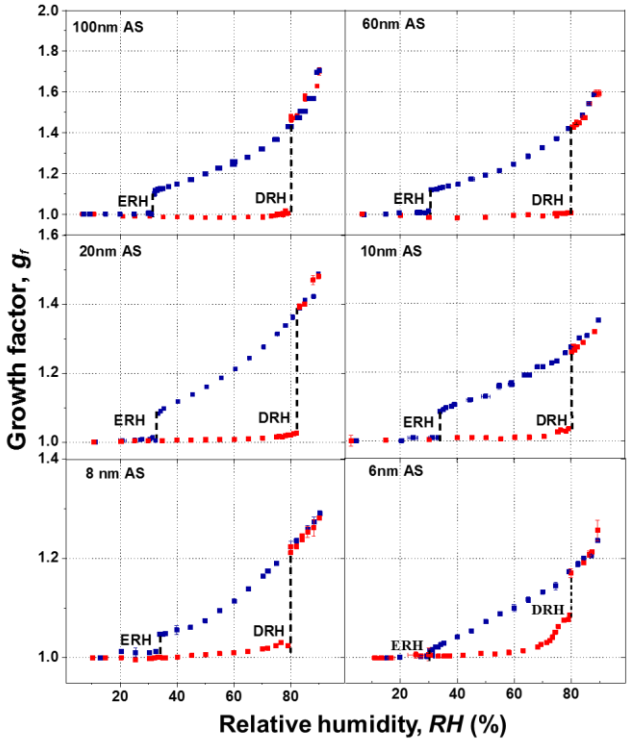

Figure 7. Mobility-diameter hygroscopic growth factors (g_f) of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 6 to 100 nm in the deliquescence mode (red square and error bar) and the efflorescence mode (royal square and error bar). Deliquescence, and efflorescence relative humidity (DRH&ERH, black dashed line) of ammonium sulfate (AS) nanoparticles with dry mobility diameter from 6 to 100 nm.

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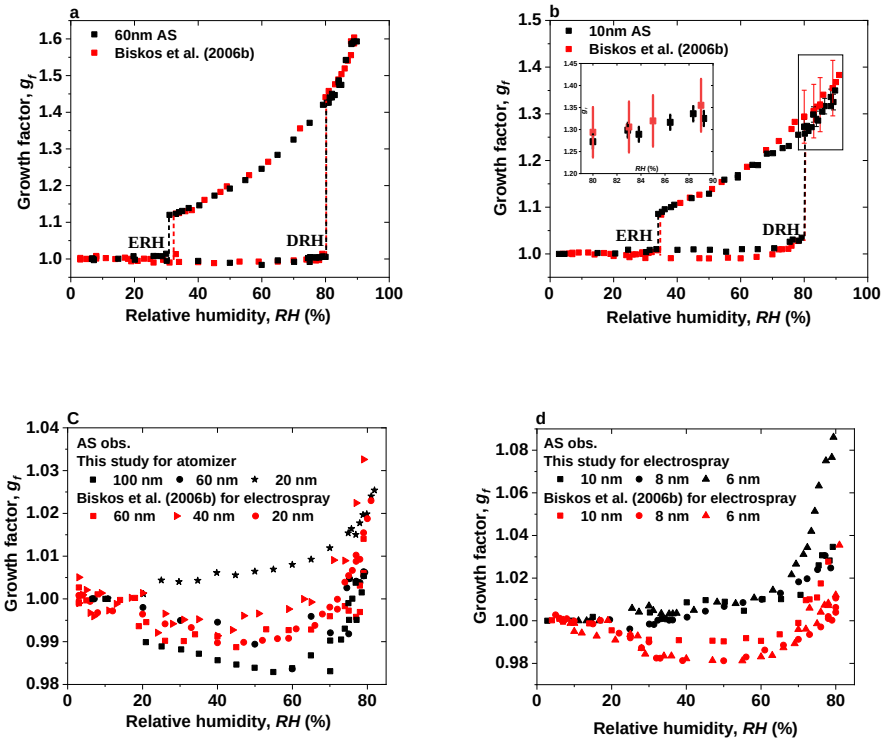

Figure 8. **(a-b)** Mobility-diameter hygroscopic growth factors (g_f, black squares), deliquescence and efflorescence relative humidity (DRH&ERH, black dashed lines) of ammonium sulfate (AS) nanoparticles with dry diameter 60 and 10 nm, respectively. Red squares and dashed lines show the respective results from Biskos et al. (2006b), respectively. Black and red uncertainties of growth factors at certain RH are calculated by $\sqrt{\left(\left(g_f \frac{\sqrt{2}\varepsilon_{Dp}}{D_p}\right)^2 + \left(\varepsilon_{RH}\frac{dg_f}{dRH}\right)^2\right)}$, where ε_{Dp}, ε_{RH}, and g_f are uncertainty of particle mobility diameter, uncertainty of relative humidity, and growth factor with respect to RH, respectively (Mochida and Kawamura 2004). **(c-d)** Comparison of growth factors of ammonium sulfate (AS) nanoparticles with dry diameter range from 6 to 100 nm with Biskos et al. (2006b) prior to deliquescence of ammonium sulfate nanoparticles.

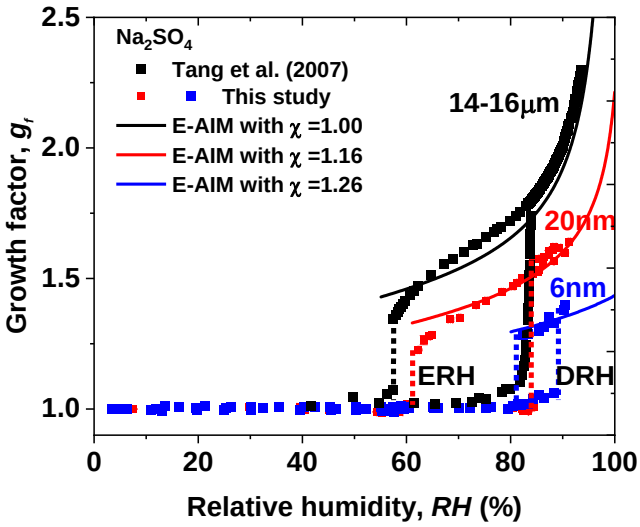

Figure 9. Mobility-diameter hygroscopic growth factors (g_l), deliquescence and efflorescence relative humidity (DRH&ERH, red and blue dashed lines) of sodium sulfate nanoparticles with dry diameter 20 (red square) and 6 (blue square) nm, respectively. Black squares and dashed lines show the respective results from Tang et al. (2007) with electrodynamic balance (EDB), respectively. In this study, the black, red, and blue curves show E-AIM predictions, including the Kelvin effect and shape factors (χ).

Table S1: Deliquescence and efflorescence relative humidity of ammonium sulfate below 100 nm reported by difference studies in temperature ranging from 290-300K

Deliquescence relative humidity (DRH)	Efflorescence relative humidity (ERH)	Technique (initial particle size)	Reference
80-86%* (8 nm) 80-85%* (10 nm) 80-90%* (15 nm) 78-80%* (30 nm) 76-79%* (50 nm)		HTDMA (8.10,15,30,50 nm)	Hämeri et al. (2000) (cf. Figure 2a, 2b, 2c, 2d, and 2e)
76-80%*	65%*	HTDMA (100 nm)	Gysel et al. (2002) (cf. Figure 2)
82% (6 nm) 81% (8 nm) 80% (10 nm) 82% (20 nm) 80% (40 nm) 80% (60 nm)	34% (6 nm) 33% (8 nm) 35% (10 nm) 35% (20 nm) 36% (40 nm) 33% (6 nm)	HTDMA (6,8,10,20,40,60 nm)	Biskos et al. (2006b)
-	27-31%* (43.7 nm) 21-30.7%* (47 nm)	HTDMA (43.7,47 nm)	Gao et al. (2006) (cf. Figure 5)
78-81%*	-	HTDMA (100 nm)	Duplissy et al. (2009) (cf. Figure 4)
77-78%*	-	HTDMA	Duplissy et al. (2009)

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		(100 nm)	(cf. Figure 4)
78-80%*	29-34%*	HTDMA (100 nm)	Mikhailov et al. (2009) (cf. Fig4)
77-78%	-	HTDMA (100 nm)	Wu et al. (2011)

-: Not reported

*: Data retrieved from figures in the references

80-86%: Non-prompt deliquescence of 8-nm ammonium sulfate from 80% to 86% RH

27-31%: Non-prompt efflorescence of 43.7-nm ammonium sulfate from 31% to 27% RH

82%: Prompt deliquescence of 6-nm ammonium sulfate at 82% RH

Table S2. Residence time (s) for the water equilibrium for particles with diameter ranging from 6 to 100 nm particles at RH=90% at 25°C

χ	1	0.1	0.01	0.001
100nm	6.26×10^{-6}	3.55×10^{-5}	3.12×10^{-4}	0.0031
60nm	6.04×10^{-6}	3.34×10^{-5}	3.07×10^{-4}	0.0030
20nm	6.03×10^{-7}	5.17×10^{-6}	5.08×10^{-5}	5.07×10^{-4}
10nm	1.88×10^{-7}	1.74×10^{-6}	1.73×10^{-5}	1.72×10^{-4}
8nm	3.10×10^{-8}	1.93×10^{-7}	1.82×10^{-6}	1.81×10^{-5}
6nm	1.48×10^{-8}	1.08×10^{-7}	1.04×10^{-6}	1.03×10^{-5}

Table S3. Average sizing offset between nano-DMAs in the nano-HTDMA system at RH below 10%

	Average sizing offset (nm)[a]	Size agreement between nano-DMA1 and nano-DMA2[b]
100-nm $(NH_4)_2SO_4$	0.619318	0.619318%
60-nm $(NH_4)_2SO_4$	0.298691	0.4978%
20-nm $(NH_4)_2SO_4$_	0.278311	1.3916%
10-nm $(NH_4)_2SO_4$	0.089647	0.8965%
8-nm $(NH_4)_2SO_4$	-0.01598	-0.19975%
6-nm $(NH_4)_2SO_4$_	0.083965	1.3994 %

[a] Calculation from $(\overline{D}_{measured\ by\ nano-DMA2} - D_{selected\ by\ nano-DMA1})$

[b] Calculation from $[(\overline{D}_{measured\ by\ nano-DMA2} - D_{selected\ by\ nano-DMA1}) / D_{selected\ by\ nano-DMA1}] \times 100\%$

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Table S4. The values of D_m, g_f, and D_m (< 5% RH) of 10-nm ammonium sulfate of Biskos et al. (2006b) system in the different RHs.

Relative humidity	D_m	g_f	D_m (<5 % RH)
25%	10.3982439	0.992914120	10.47245043
76%	10.38867117	1.017488426	10.21011237
78%	10.54314064	1.027692308	10.25904404
80%	13.31036607	1.293796610	10.28783502
44%	11.56059002	1.120463542	10.31768513
35%	11.24527292	1.084064417	10.37325157
34%	10.59107394	1.007786565	10.50924304
32%	10.24542551	1.003831854	10.20631639
31%	10.20845456	1.001920937	10.18888236
30%	10.38101934	1.001441750	10.36607405
29%	10.27755951	1.003183756	10.2779752
24%	10.26077112	0.997295121	10.28860053

Table S5. Uncertainties of nano-DMA voltage (V) and sheath flow rates (Q_{sh}), and calculated size uncertainty.

Size (nm)	Uncertainties in V and Q_{sh}	Uncertainty (Sizing accuracy)
100	2648.2±0.02592* V, 10±0.02* L/min	0.2000%
60	1063.0±0.02686 V, 10±0.02 L/min	0.2000%
20	131.1±0.01519 V, 10±0.02L/min	0.2003%
10	33.7±0.02435 V, 10±0.02 L/min	0.2127%
8	21.6±0.03725 V, 10±0.02 L/min	0.2641%
6	12.2±0.06920 V, 10±0.02 L/min	0.6014%

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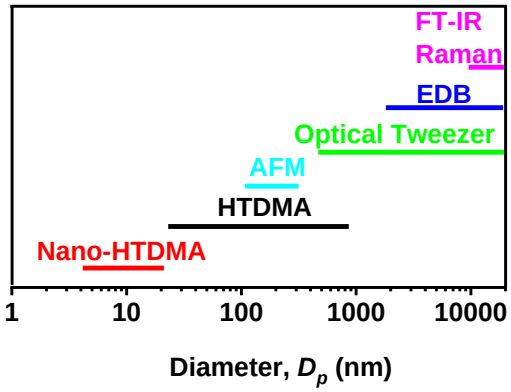

Figure S1. Methods for measuring hygroscopicity of atmospheric aerosol particles in different size (D_p).

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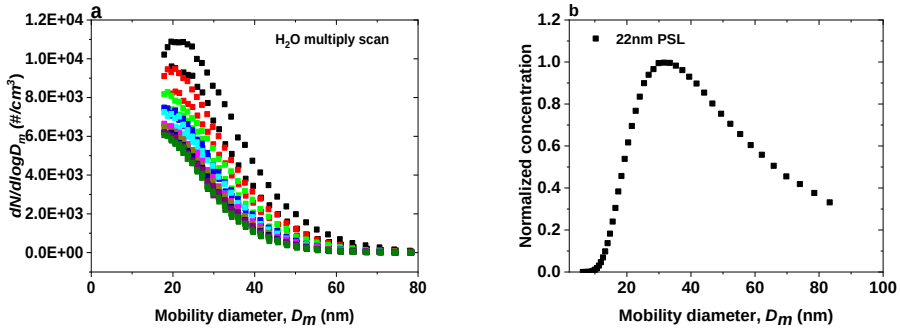

Figure S2. (a) Number concentration scanned for water nanoparticles by the nano-DMA2 at RH below 5 % at 298 K.

(b) Normalized number size distribution scanned for 22-nm PSL nanoparticles by nano-DMA2 after calibration.

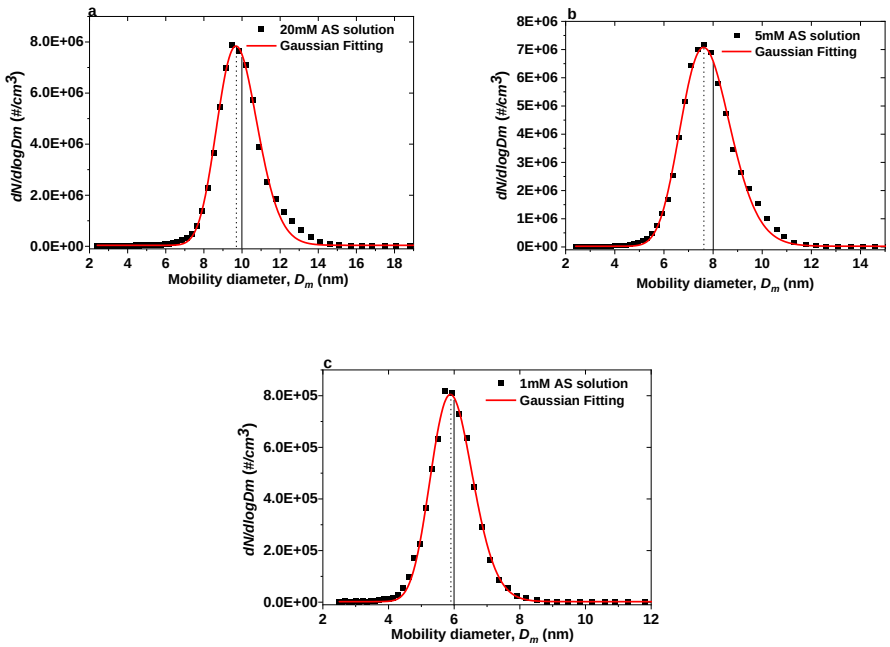

Figure S3. Number size distribution of ammonium sulfate (AS) nanoparticles (black solid square) generated by the electrospray. **(a)** 20mM, **(b)** 5mM, and **(c)** 1mM AS solution. The dotted line marks peak diameter from the Gaussian fits for the scan (red curve). The black solid lines mark the diameters of the monodispersed nanoparticles selected by the nano-DMA1.

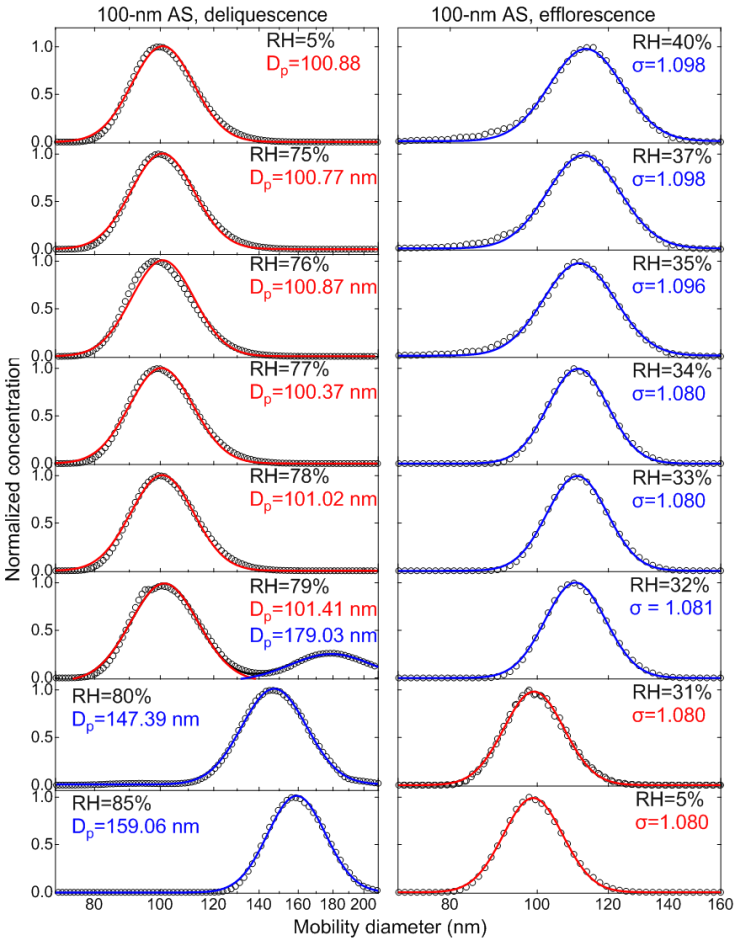

Figure S4. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 100-nm ammonium sulfate (AS) aerosol nanoparticles. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively.

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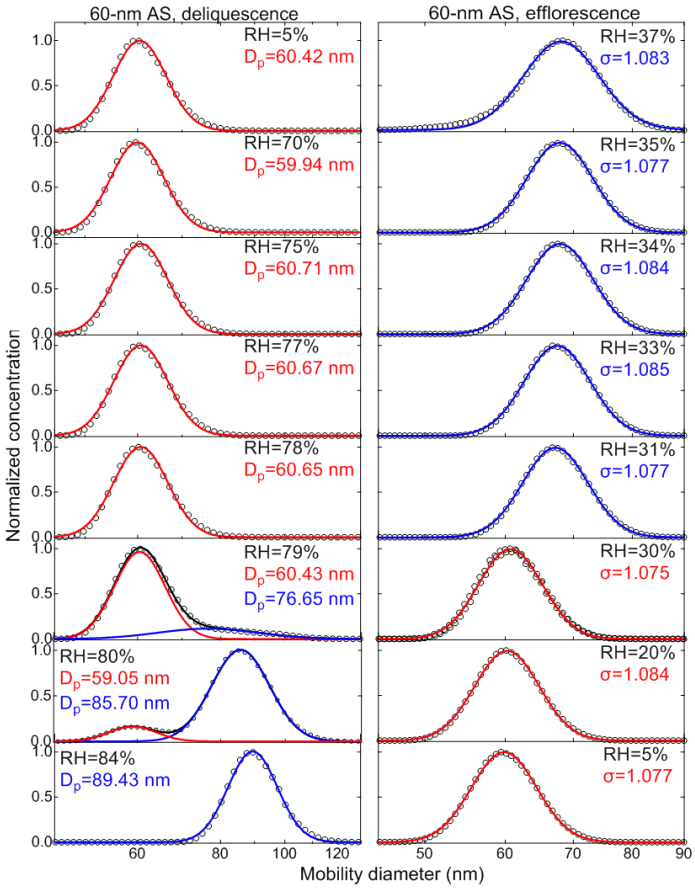

Figure S5. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 60-nm ammonium sulfate (AS) aerosol nanoparticles. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively.

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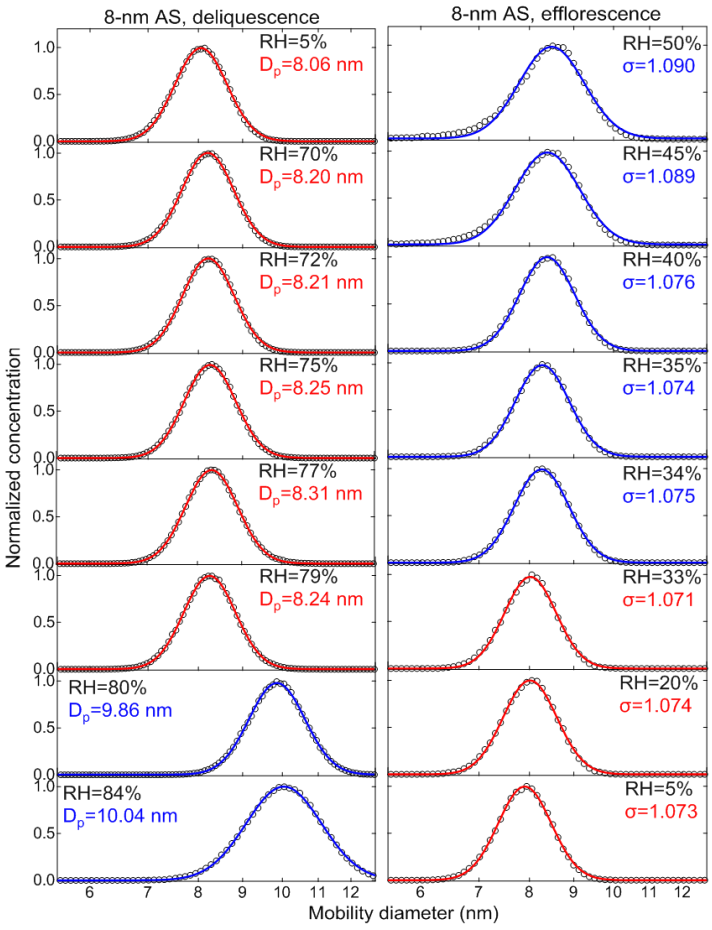

Figure S6. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 8-nm ammonium sulfate (AS) aerosol nanoparticles. The measured (black square) and fitted (solid lines, single-mode log-normal fit) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively.

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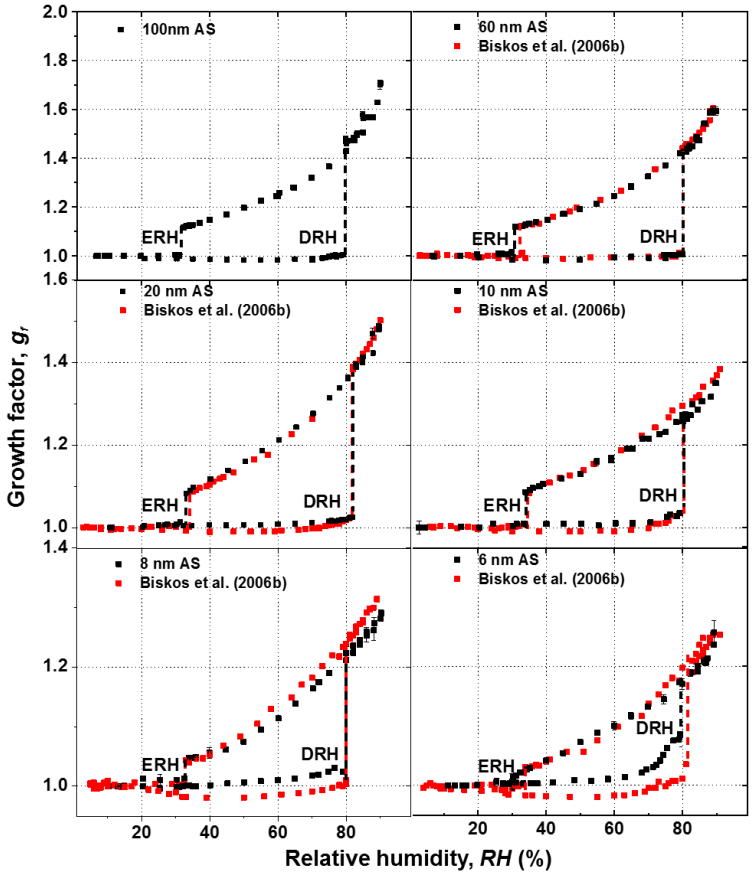

Figure S7. Mobility-diameter hygroscopic growth factors (g_f, black squares), deliquescence and efflorescence relative humidity (DRH&ERH, black dashed lines) of ammonium sulfate (AS) nanoparticles with dry diameter from 6 to 100 nm, respectively. Red squares and dashed lines show the respective results from Biskos et al. (2006b).

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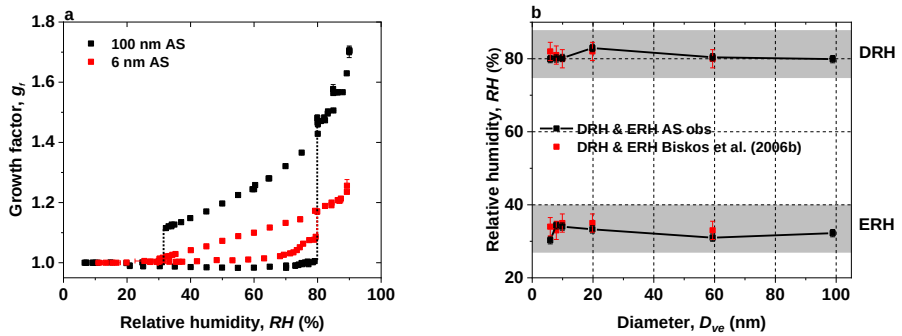

Figure S8. (a) Comparison of mobility-diameter hygroscopic growth factors (g_f) of 100-nm (black square) with 6-nm (red square) ammonium sulfate (AS) nanoparticles. **(b)** Dependence of deliquescence and efflorescence relative humidity (DRH&ERH) of ammonium sulfate (AS) on dry volume equivalent diameter (D_{ve}). The measured DRH and ERH of ammonium sulfate within RH uncertainty (black line + black square) compared with data from Biskos et al. (2006b) (red square) in the volume equivalent diameter with shape factor (χ=1.02) range from 5 to 100 nm.

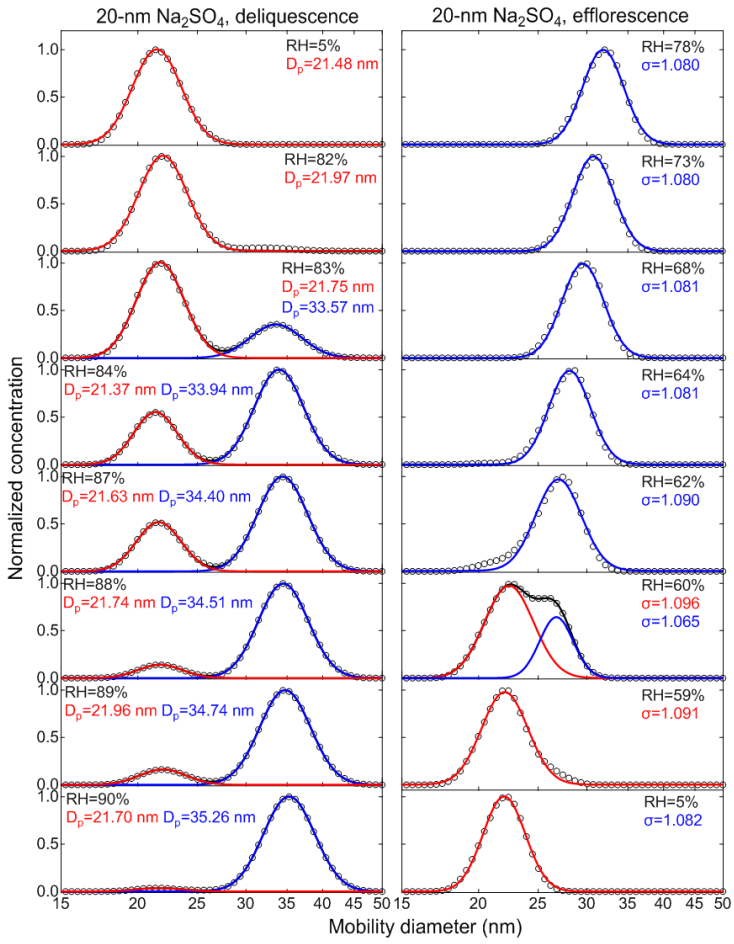

Figure S9. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 20-nm sodium sulfate aerosol nanoparticles. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. Red/blue solid line is fitted by a single-mode log-normal fit. Red, blue, and black lines are fitted by a double-mode log-normal fit. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively. The voltage applied to the nano-DMAs (0-12500 V) is kept within ±1% around the set value shown in the voltage meter.

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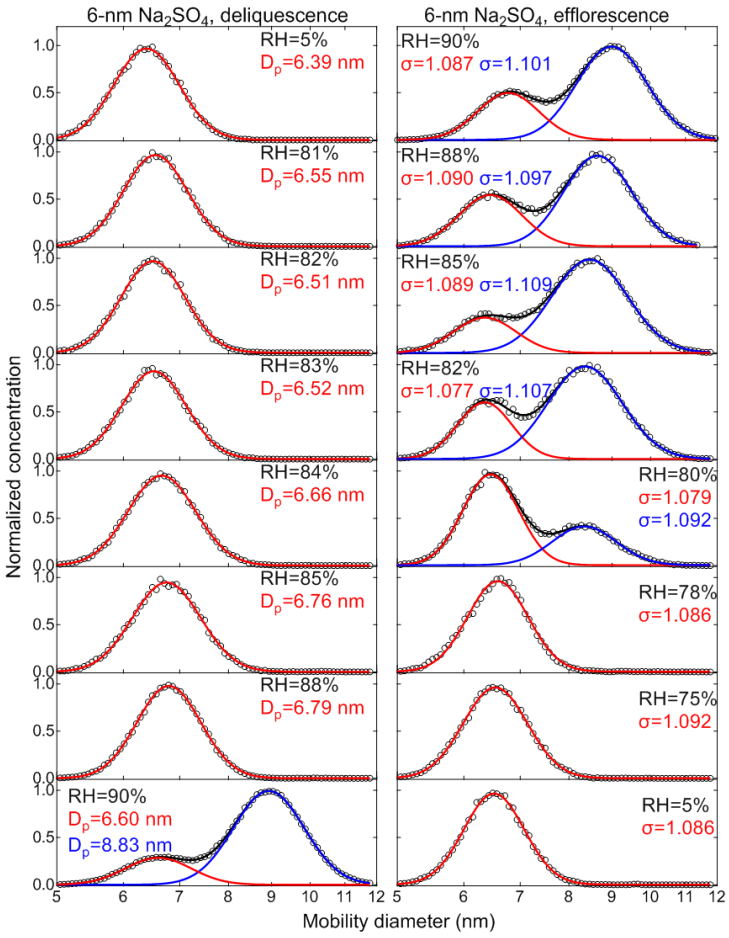

Figure S10. Deliquescence-mode **(a)** and efflorescence-mode **(b)** of 6-nm sodium sulfate aerosol nanoparticles. The measured (black square) and fitted (solid lines) normalized size distribution are shown for increasing RH (5%→X%, where X is the RH value given in each panel) and decreasing RH (5%→97%→X%, where X is the RH value given in each panel), respectively. Red/blue solid line is fitted by a single-mode log-normal fit. Red, blue, and black lines are fitted by a double-mode log-normal fit. The red and blue lines represent the aerosol nanoparticles in the solid and liquid state, respectively. The voltage applied to the nano-DMAs (0-350 V) is kept within ±1% around the set value shown in the voltage meter.

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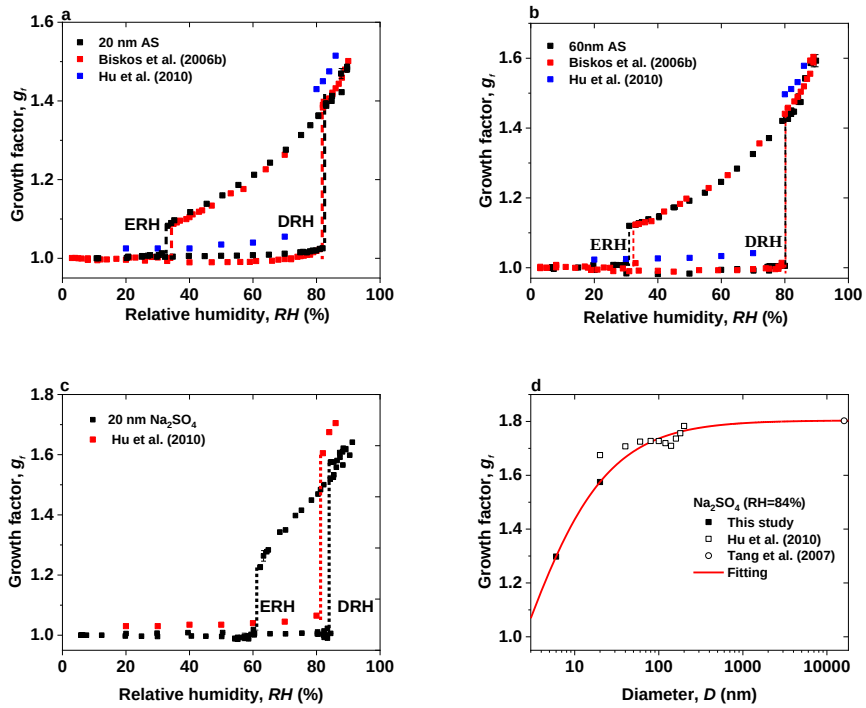

Figure S11. (a) Comparison of mobility-diameter hygroscopic growth factors (g_f) of 20-nm **(a)** and 60-nm **(b)** ammonium sulfate (AS) nanoparticles with Biskos et al. (2006b) and Hu et al. (2010). (black squares: in this study; red square: Biskos et al. (2006b); blue square: Hu et al. (2010)). **(c)** Comparison of mobility-diameter hygroscopic growth factors of 20-nm Na_2SO_4 nanoparticles with Hu et al. (2010). (black squares: in this study; red square: Hu et al. (2010)). **(d)** Mobility-diameter hygroscopic growth factors of Na_2SO_4 nanoparticles with diameter from 6 nm to 14~16 um at 84% RH (black solid squares: in this study; black open square: Hu et al. (2010); black open cycle: Tang et al. (2007)). A fitting equation ($g_f = \frac{1.804}{1+(0.5267*D)^{-0.8194}}$) based on this study at 6-nm, 20-nm Na_2SO_4, and 14~16 um data from Tang et al. (2007).

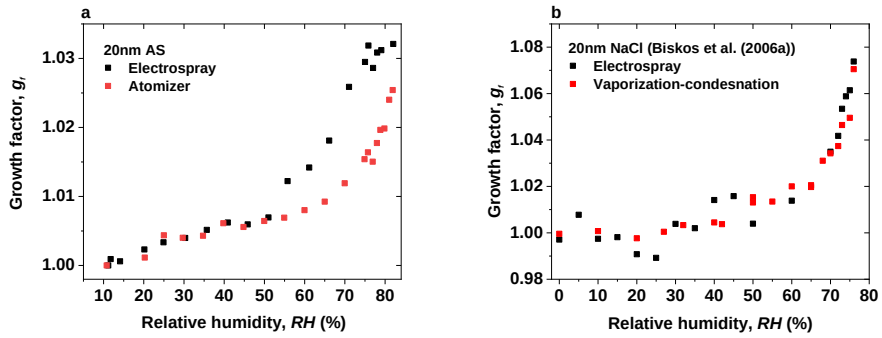

Figure S12. Hygroscopic growth factors of 20-nm **(a)** ammonium sulfate (AS) nanoparticles from our study and **(b)** sodium chloride (NaCl) nanoparticles from Biskos et al. (2006a) using the different generation methods prior to deliquescence of ammonium sulfate.

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S1. Calculation of sizing offset of 10-nm AS

The mobility growth factor (g_f) is given by:

$$g_f = \frac{D_m(RH)}{D_m(<10\ \%\ RH)} \quad \text{(S1)}$$

g_f was from the data of Biskos et al. (2006b) in the different RHs (see the SI. Fig.5). D_m was retrieved the data of Biskos et al. (2006b) in the different RHs (see the SI. Fig.2) as follows:

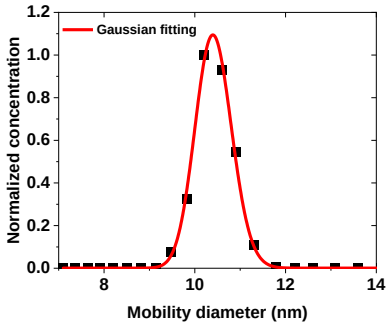

Figure S1. Measured (black square) and fitted (red solid line) normalized number size distributions are show for ammonium sulfate aerosol particles at 25% RH. The black square symbols show the data of Biskos et al. (2006b) (see the S1. Fig. 2).

Therefore, the initial dry mobility diameter (D_m (< 5% RH)) was obtained using Eq. (S1) based on values of g_f and D_m in the different RHs (see SI. Table S4). We further calculated the average sizing offset of 10-nm ammonium sulfate of Biskos et al. (2006b) system based on the values of D_m (< 5% RH). The average sizing offset of 10-nm was ~3.1%.

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Deleted: **Table S4.** The values of D_m, g_f, and D_m (< 5% RH) of 10-nm ammonium sulfate of Biskos et al. (2006b) system in the different RHs.¶
Relative humidity ...

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S2. Calculation of sizing accuracy of sub-100 nanoparticles

Knutson and Whitby (1975) proposed the following theoretical differential mobility analyzer (DMA) transfer function and showed that sizing is crucially depend on sheath flow rates and high voltage (HV) applied to the DMA.

$$z_p^* = \frac{Q_{sh} ln\frac{r_2}{r_1}}{2\pi LV} \quad \text{(S2)}$$

$$z_p^* = \frac{neC_c}{3\pi\mu d_p^*} \quad \text{(S3)}$$

$$d_p^* = \frac{2VLneC_c}{3\mu Q_{sh} ln\frac{r_2}{r_1}} \quad \text{(S4)}$$

where z_p^* is the central electrical mobility, Q_{sh} is the sheath flow rate, V is the applied voltage, L is the length of the classification region within the DMA, and r_1 and r_2 are the inner and outer radii of the DMA annulus, respectively. n is the number of elementary charges of particles. e is the elementary charges. C_c is the slip correction. μ is the flow viscosity. d_p^* is the mean particle mobility diameter.

According to Eq. (S4) above, we use the following error propagation formula ((Taylor and Taylor, 1997) to calculate the uncertainties in sizing of nanoparticles. In our study, the flow accuracy of mass flow meter (TSI series 4000) is within ±2%. The deviation of voltage applied to the nano-DMAs (0-12500 V, 0-350 V) varies around the set value when test with voltage power supply (HCE 0-12500, HCE 0-350, Fug Electronic) shown in Table S5. Thence, the uncertainties in sizing of nanoparticles are obtained based on the following Eq. (S5) as shown in Table S5.

$$\frac{\delta d}{d} = \sqrt{\left(\frac{\delta V}{V}\right)^2 + \left(\frac{\delta Q_{sh}}{Q_{sh}}\right)^2} \quad \text{(S5)}$$

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