***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 is to compare with literature studies, which are the most abundant (especially for 100 nm) and also is 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 for 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 sizes (e.g., 6, 8, 10 nm) selected by the nano-DMA1 were 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 rate 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 of ammonium sulfate.

**Page 19 line 428, we add**: "Due to the water adsorption on the surface of nanoparticles, the morphology of particles may change and further 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 generation conditions (e.g., chemical composition, solution concentration) and drying process."

**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% |

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%. Also, a slight difference in hygroscopic growth factor of 20-nm NaCl aerosol nanoparticles is observed in previous study using the different generation methods (Biskos et al., 2006a). Figure R1b shows the results of 20-nm sodium chloride nanoparticles using an electrospray and a vaporization-condensation method (Biskos et al., 2006a), respectively. 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.

**Page 19 line 432, we add**: "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 sizes (e.g., 6, 8, 10 nm) selected by the nano-DMA1 were 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.

Also, we used an electrospray and an atomizer to generate 20-nm ammonium sulfate, respectively, and then compared their hygroscopic growth factors prior to deliquescence. Figure S13a 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%, which is similar to a slight difference in hygroscopic growth factor of 20-nm NaCl aerosol nanoparticles as observed in Fig S13b in Biskos et al. (2006a) using the different generation methods. Besides different generation conditions, the drying rate is mainly dependent on drying flow rate 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."

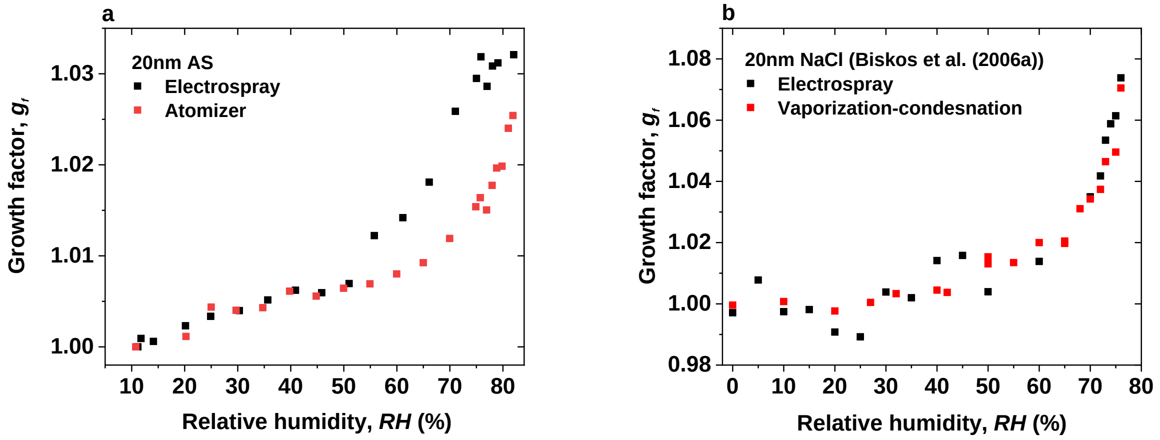

**Figure R1 (new Figure S13 in revised SI)**. Hygroscopic growth factors of 20-nm **(a)** ammonium sulfate (AS) nanoparticles and **(b)** sodium chloride (NaCl) nanoparticles from Biskos et al. (2006a) using the different generation methods prior to deliquescence.

*(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 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 there is more water adsorption onto 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 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.

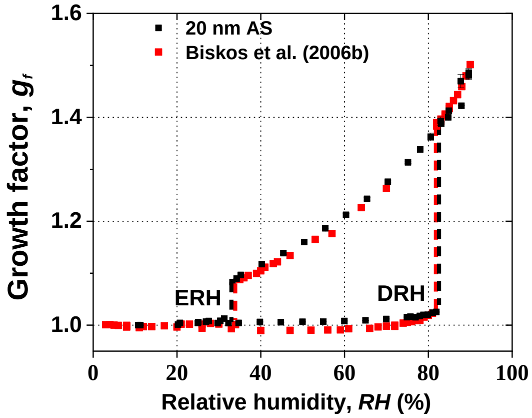

**Figure R2**. Comparison of the hygroscopic behavior of 20-nm ammonium sulfate (AS) with Biskos et al. (2006b).

**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:**

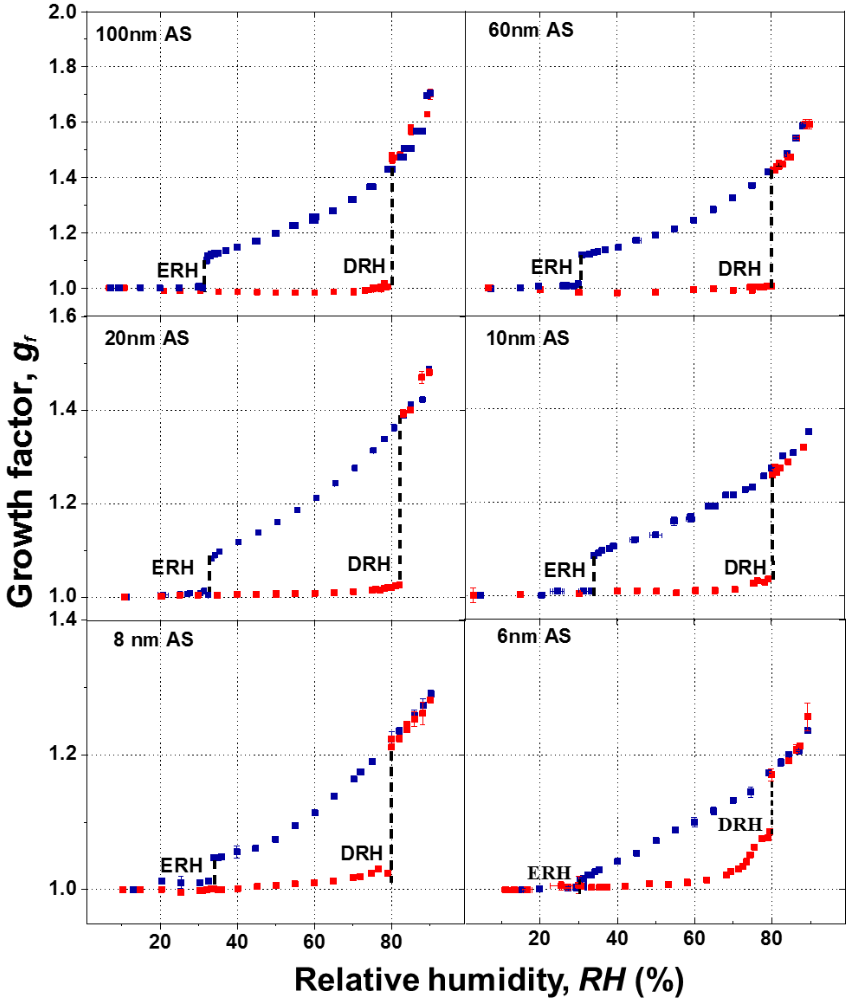

**Figure 7.** Mobility-diameter hygroscopic growth factors ($g_f$) of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 6 to 100 nm in the deliquescence mode (red square and error bar) and the efflorescence mode (royal square and error bar). Deliquescence, and efflorescence 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.

No significant size effect on the DRH and ERH of 6-100 nm ammonium sulfate nanoparticles is mainly due to the strong non-ideality of aqueous ammonium sulfate solution property (Cheng et al. 2015). The different responses of DRH and ERH of sodium chloride and ammonium sulfate on changing particle size have been theoretically studied and explained by Cheng et al. (2015). They show that, as presented in Fig. R3, the main reason for this phenomenon is that the stronger increase in solute molality of ammonium sulfate is required for the same change of solute activity than that of sodium chloride, although the different solute-liquid surface tension may also play a role. The phase transition concentration (deliquescence and crystallization concentration) of ammonium sulfate is thus more sensitive to the size range from 6 to 100 nm compared to that of sodium chloride. This leads to the almost unchanged DRH and ERH of ammonium sulfate nanoparticles (Cheng et al., 2015).

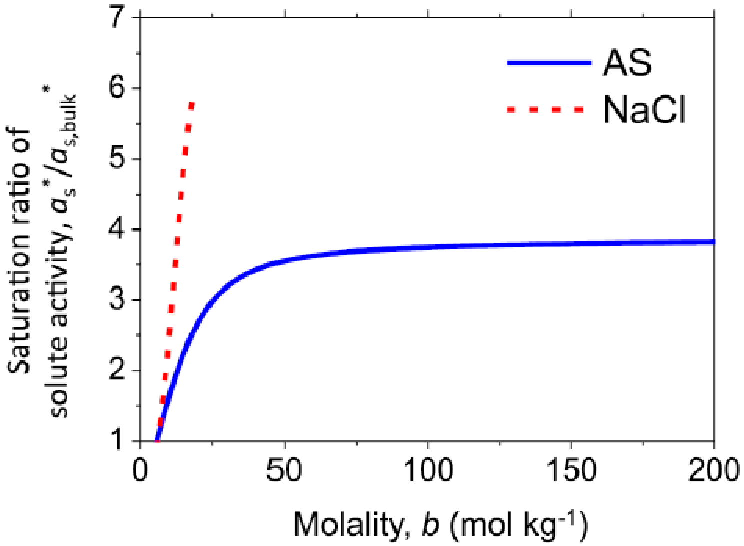

**Figure R3**. Saturation ratio of solute activity ($a_s^*/a_{s,bulk}^*$) as a function of molality $b$ for ammonium sulfate (AS) and sodium chloride (NaCl). Reprinted with permission by Cheng et al. (2015).

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.

**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 no significant size effect on the DRH and ERH was observed, there is a strong size effect of DRH and ERH of sodium sulfate with diameter down to 6 nm. The different responses of DRH and ERH of sodium chloride and ammonium sulfate on changing particle size have been theoretically studied and explained by Cheng et al. (2015). They explained that the main reason for this phenomenon is that the stronger increase in solute molality of ammonium sulfate is required for the same change of solute activity than that of sodium chloride, although the different solute-liquid surface tension may also play a role. The phase transition concentration (deliquescence and crystallization concentration) of ammonium sulfate is thus more sensitive to the size range from 6 to 100 nm compared to that of sodium chloride. This leads 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, the 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:** "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 sensitive 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)."

*(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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