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 a 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). The values of size, uncertainty of nano-DMA voltage and sheath flow rates, and calculated size uncertainty.

Size (nm)	Uncertainty (V, 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: "Sizing accuracy of sub-100 nm aerosol nanoparticles, as discussed in Sec. 2.2.1, is even impossible to verify using PSL nanoparticles. Duplissy et al. (2009) and Wiedensohler et al. (2012) suggested that sizing accuracy of sub-100 nm nanoparticles could be test by a DMA transfer function. The theoretical DMA transfer function (see SI. 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. Thence, for nanoparticles with diameter smaller than 100 nm, 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. According to the error propagation formula (see SI. Eq. (S5)) (Taylor and Taylor, 1997). The calculated uncertainty in sizing of 6-100 nm nanoparticles increases as size decreases, which is roughly consistent with measured sizing accuracy and sizing offset of two nano-DMAs (see SI. Table S5). However, the calculated sizing accuracy is smaller than measured sizing accuracy. This suggested uncertainties of slip correction, DMA dimensions (inner and outer radius, length), temperature, pressure, and viscosity of air could affect the sizing accuracy according to Eq. (S4) (Kinney et al., 1991). Besides DMA transform function, Wiedensohler et al. (2012) suggested that the possible sources of uncertainty of sizing are particle losses, the size- and material-dependent CPC counting efficiency, which results in a bigger sizing deviation of nanoparticle during the measurements compared to the estimated sizing accuracy according to theory."

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.

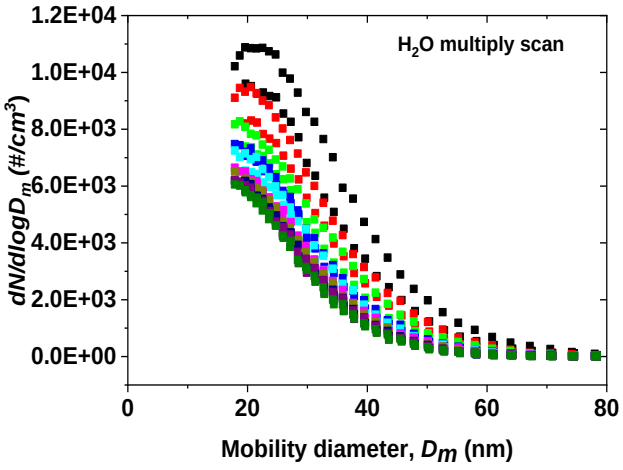

Figure R1. Number concentration scanned for water nanoparticles by the nano-DMA2 at RH below 5 % at 298 K.

Page 13 line 305, we add: "Uncertainties in the sheath flow rates and nan-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.