Response to Referee #1:

Thanks very much for your comments, suggestions and recommendation with respect to improve this paper. The response to all your comments are listed below.

In this manuscript, the authors present the hygroscopic study of 100 nm ammonium sulfate and ammonium sulfate mixed with sodium nitrate/oxalic acid nanoparticles using Fourier transform infrared (FTIR). The aerosol liquid water content was obtained using the FTIR spectral, and further the hygroscopic growth factor was calculated. The GF measurements are neither better nor worse than those of previous studies. The sequential order during the deliquescence process was also discussed with the 2D-IR spectroscopic analysis. From this point, the method is quite meaningful to better understand the intermolecular interaction within the phase transition.

The work is laboratory-based but has relevance to modeling. The topic of the manuscript fits into the scope of ACP. However, there are still some small mistakes in the manuscript. More discussion could be addressed before publication. I have several comments and suggestions for the authors below.

Major comments:

1. The authors mentioned the nanoparticle with approximately 100 nm is the electrical mobility diameter (line 25). Later the diameter of 100 nm was described as volume equivalent diameter in the experiment description section. The authors better describe clearly. For spherical particles, assuming that the particle and its mobility equivalent sphere have the same charge, then Dem=Dve. For non-spherical particles, the shape factor and slip correction factor should be considered.

Response: In our paper, we used a differential mobility analyzer (DMA) to sort the diameter of the nanoparticle. The diameter of 100 nm in the experiment description section should also be electrical mobility diameter. In the revised version, we have changed "volume equivalent diameter" to "electrical mobility diameter" in the experiment description in section 2.1. In section 2.3.2, we have proved that the Dem is close to Dve. Yan et al. (2020) have compared the D_{ve} and the D_{em} of AS sorted by the identical DMA of this study, which is shown in the figure R1. A good agreement between D_{em} and D_{ve} for ~100 nm AS was observed by Yan et al. (2020). As a result, in present work, we use D_{em} the same as the D_{ve}. For the AS with an electrical mobility diameter of ~100 nm, its volume equivalent diameter is ~ 94 nm. Please check the marked up file for details.

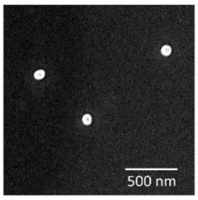

Figure R1 The SEM image of 100 nm AS particles deposited on the silicon wafer

2. The authors stressed several times that the nanoparticle shape is one of the large uncertainties for the hygroscopicity study. Because normally the nanoparticle is assumed to have a spherical shape. Actually, the authors also supposed spherical particles when calculating the growth factor in this study, even the particles were deposited on the substrate. Since this is not a shape factor study, I would recommend do not emphasize this point.

Response: We have followed your suggestion and don’t emphasize this point. We have changed some sentences in the abstract. Please check the marked up file for details.

3. About RH:

1). The authors claim the accuracy of RH measurement for the sample cell is 0.1% (Line 117). Is this 0.1% available for the whole studied RH range? Which sensor or instrument was employed? Normally the uncertainly will get larger when the RH increases (Mikhailov and Vlasenko, 2020). And 0.1% RH is extremely precise.

Response: This is a typing mistake. The sensor for RH measurement is HC2-S manufactured by Rotronic Incorporation (Switzerland), and its accuracy is ±0.8% (RH range: 0 ～ 100%). In the revised version, we have corrected this mistake. Please check the marked up file for details.

2). The initial RH is 45% for AS measurement and there is an OH stretching vibration peak at 3250 cm^{-1} for all RH below DRH in Figure 2. Can authors explain why? I am considering whether the RH downstream of diffusion dryer (or DMA) was below the ERH value of AS. If not, then the particle is a droplet at the initial 45% RH.

Response: Since the FTIR instrument was not working under vacuum condition, OH stretching vibration peak at 3250 cm^{-1} for all RH below DRH in Figure 2 could be attributed to the liquid water in the ambient atmosphere and not the peak for NH_4^+ which locates at about 3000cm^{-1}. Moreover, we found that the liquid water mass calculated from these peaks was constant, which further consolidate our deduction. In the revised version, we eliminated the interference of OH stretching vibration peak at 3250 cm^{-1} by subtracting the background and added more data points in Fig.2. As shown in Figure R2, the RH downstream of DMA was 16.52 ～ 18.74% which is below the ERH value (about ~32% RH) of AS.

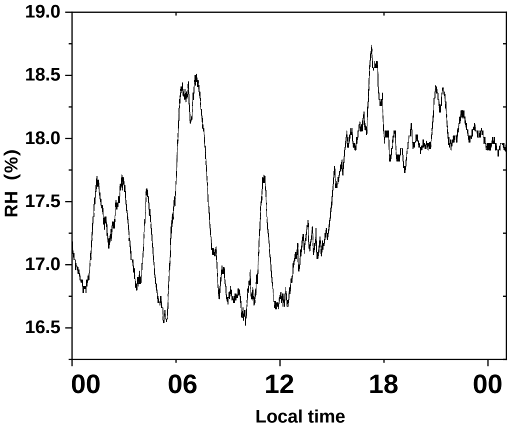

Figure R2 Time series of RH downstream of DMA

4. The authors mentioned the mass of nanoparticles was quantified using a simple procedure. Could authors prove more details? And it would be nice to add some discussions about the uncertainty of mass and GF. Actually, there are error bars shown in some figures. But there is no description in the main text.

Response: We have included a new section, i.e., section 2.3.1, to present how we quantify the mass of nanoparticles and estimate the uncertainty. Briefly, the procedure is based on a non-linear least squares algorithm. It fits a measured spectrum by iteratively recalculating the spectrum until the mean-squared residual between the measured spectrum and calculated spectra are minimized. The calculated spectra are then the standard absorption spectra of liquid water. We also described the error bars in all figures. Please check the marked up file for details.

5. The authors illustrated the OA does not absorb water in the RH between 40% to 90%

in Figure 4. However, some previous studies demonstrated that oxalic acid dihydrate could form which will absorb water continually (Wang et al., 2017; Ma et al., 2019; Prenni et al., 2001). Since the FTIR could identify the hydration interactions, any explanations?

Response: Several previous measurements through the H-TDMA have found substantial growth of oxalic acid particles under low RH, which is mainly due to its amorphous state. In addition, it was reported that anhydrous oxalic acid particles could transform into oxalic acid dihydrate between 10 and 30% RH which can lead to a growth of size with the GF of around 1.17 during the transform. As a result, if the initial particles prepared can be in the form of oxalic acid dihydrate or nonstoichiometric hydrates containing about two water molecules per oxalic acid molecule, oxalic acid particles have no significant increase in the GF below 90% RH. Most stable dihydrate OA particles are easy to find in bulk studies but the OA particles in this study could be crystalline. Moreover, theoretical prediction and bulk measurements indicate that the deliquescence point of OA is greater than 97%RH (Peng et al., 2001).

In our paper, the initial OA particles prepared was in the form of oxalic acid dihydrate and there was no significant increase in the GF observed below 90% RH. If OA absorb water continually, the 3250cm^{-1} peak intensity will increase continually. We have included this interpretation in the revised version. Please check the marked up file for details.

6. The DRH point in both AS/NA and AS/OA systems is lower than the pure AS. According to 2D-IR results, the hydrolysis reaction mechanism of AS/OA is different from AS/NA. Also considering OA does not absorb water, then why the DRH value gets smaller?

Response: We have included the following interpretation in the revised version.

Although OA particle does not absorb water, OA and AS in the AS/OA aqueous solution can react with each other via the following pathway (Minambres et al., 2013):

$$(NH_4)_2SO_4 + H_2C_2O_4 \rightarrow NH_4HSO_4 + NH_4HC_2O_4$$

This reaction can be identified in Figure S5, where the absorption peak at 1245cm^{-1} is the stretching vibration peak of HSO_4^-. As a result, a lower DRH for the mixed nanoparticles relative to the pure AS can be due to the formation of NH_4HSO_4 which has a lower DRH (about 40%) than the pure AS (80%) (Tang and Munkelwitz, 1994).

Minor comments

According to the detailed description of manuscript type in ACP (https://www.atmosphericchemistry- and-physics.net/about/manuscript_types.html), I would recommend Research articles instead of Technical notes.

Response: We have included many description, comparison, analysis, and discussion in the revised version. As we have followed your recommendation and change it to a research article.

Line 38, "but only AN can change the hydrolysis reaction mechanism for AS in AS/AN and AS/OA mixtures." Is there AS/AN and AS/OA mixture experiment?

Response: Yes, in the experiments for AS/SN and AS/OA mixture, we found AN can change the occurrence sequential order for AS, but OA can not. We have added this explanation in the revised version. Please check the marked up file for details.

Line 42, "… between nanoparticle and medium", medium size particle? Please rewrite this sentence. Same Line 102

Response: Done. Please check the marked up file for details.

Line 47, "Nanoparticles have long atmospheric lifetimes of weeks to months". Any references?

Response: Done. We have included a reference for this description. Please check the marked up file for details.

Line 80, "the hygroscopic growth process of a single aerosol with particle diameter of less than 100 nm" maybe become "the hygroscopic growth process of a single particle with a diameter of less than 100 nm". Please rewrite this sentence.

Response: Done. Please check the marked up file for details.

Line 155, "room temperature is assumed to be 25 °C". What does this mean? No temperature sensor could measure the room temperature? Since the temperature has an influence on the RH, is there any temperature monitoring inside the sample cell?

Response: The air conditioner was run uninterruptedly to keep the laboratory under constant temperature. We put a temperature sensor in the room and the room temperature is a 25 °C. We thought the sample cell has the same temperature. There is no temperature monitoring inside the sample cell. We have included this description in the revised version. Please check the marked up file for details.

Line 156, the authors described the RH varies from 50% to 95% in the present work. But in AS study, the initial RH is 45%. In the OA study, the initial RH is 40%.

Response: Starting the initial RH from 40%, 45% or 50% does not affect the deliquescence point and deliquescence process because all of them are below the deliquescence point. To uniform the description, in all cases, we have changed the RH from 50% to 95% in the revised version. Please check the marked up file for details.

Line 209, "the nanoparticle volume increases but its mass keeps constant." Quite misleading, its means sulfate not nanoparticle, right?

Response: We mean that " As a further increase in RH, the volume of AS nanoparticles increases due to the increase in liquid water content, but the mass of AS nanoparticles keeps constant, resulting in a decrease in SO_4^{2-} concentration. As a result, we observe a decrease in the area of SO_4^{2-} absorption peak starting from ~ 83% RH.". We have changed this sentence in the revised version. Please check the marked up file for details**.**

Line 255, "at the RH of 79.9 ± 0.10%", is this RH measurement from this study? And how do the authors obtain this value? Since the FTIR measurement is a real-time method. Why authors don't provide more data points between 74% and 81% RH?

Response: We have included more data points between 74% and 81% RH (at a 2% RH interval) using FTIR measurement with different spectral resolution and repeat times. In this paper, more data could provide more information to understand the intermolecular interaction within the phase transition. "at the RH of 79.9 ± 0.10%", should be at the RH of 79 ± 0.80%, which is the measurement from this study. We have revised accordingly in the revised version.

Line 282, what does the 1097 cm-1 stand for? NH4+? It seems hard to see a peak at 1097 cm-1 from Figure 2.

Response: Generally, 1097 cm^{-1} stands for sulfate in the aqueous phase. For NH_4^+, its peak shows in about 1442cm^{-1}, and the strong peak of H_2O (gas) show in 1350-1850 cm^{-1}. So in the FTIR spectroscopy, we could not distinguish the NH_4^+ peak.

Line 310, what does the 1320 cm^{-1} stand for? I would recommend the authors provide all FTIR spectral figures (OA, AS/NA, and AS/OA) at least in the supplement. Table1, I would recommend adding the reference (or data source) for density and solubility.

Response: The 1320 cm^{-1} stands for the absorption of NO_3^- hidden by the H_2O (gas) peaks in 1300-1900 cm^{-1}. The NO_3^- peak in 1320cm^{-1} would change but the water (gas) peaks in 1300-1900 cm^{-1} keep roughly unchanged with the increase in RH. The 2D-IR analysis method can provide detailed information about the dynamic deliquescence processes of NO_3^- peak.

We have provided all FTIR spectral figures (OA, AS/NA, and AS/OA) in the supplement. And we have added the data source for density and solubility in Table1. Please check the marked up file for details.

Technical corrections

Unified abbreviation. Line 33 & 37, Sodium nitrate (SN); Line 38 & 90, sodium nitrate (AN); In the Figure 5&6, NN.

Response: Done. Please check the marked up file for details.

Line 52, “is” not are

Response: Done. Please check the marked up file for details.

Line 68, “the” nanoscale

Response: Done. Please check the marked up file for details.

Line 73, “the” nanoparticle

Response: Done. Please check the marked up file for details.

Line 92, “in” real time, not on real time; also other places

Response: Done. Please check the marked up file for details.

Line 93, “the” molecular scale

Response: Done. Please check the marked up file for details.

Line 209, “large” size particles, not big

Response: Done. Please check the marked up file for details.

Line 212, “the” Kelvin effect

Response: Done. Please check the marked up file for details.

Line 238, “behavior” not behavior

Response: Done. Please check the marked up file for details.

Line 247, “via direct measurement of the aerosol diameter”

Response: Done. Please check the marked up file for details.

Line 259, “increasing”

Response: Done. Please check the marked up file for details.

Line 263, “the” FTIR measurement

Response: Done. Please check the marked up file for details.

Line 349 & 359, “the” 2D-IR spectroscopic

Response: Done. Please check the marked up file for details.

Line 362, “a” better understanding

Response: Done. Please check the marked up file for details.

Ma, Q., Zhong, C., Liu, C., Liu, J., Ma, J., Wu, L., and He, H.: A Comprehensive Study about the Hygroscopic Behavior of Mixtures of Oxalic Acid and Nitrate Salts: Implication for the Occurrence of Atmospheric Metal Oxalate Complex, ACS Earth and Space Chemistry, 3, 1216-1225, 10.1021/acsearthspacechem.9b00077, 2019.

Mikhailov, E. F., and Vlasenko, S. S.: High-humidity tandem differential mobility analyzer for accurate determination of aerosol hygroscopic growth, microstructure, and activity coefficients over a wide range of relative humidity, Atmos Meas Tech, 13, 2035-2056, 10.5194/amt-13-2035-2020, 2020.

Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E., Russell, L. M., and Ming, Y.: The Effects of Low Molecular Weight Dicarboxylic Acids on Cloud Formation, J. Phys. Chem. A, 105, 11240-11248, 10.1021/jp012427d, 2001