

### **Response to Referee #3:**

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

This study used the FTIR spectroscopy and two-D correlation analysis to investigate the hygroscopicity of several single-component aerosols and their mixtures. The sequential order during the hydration process was discussed with the 2D-IR spectroscopic analysis. The method is new. However, as a technical note, validation of the performance of current method should be conducted in a more thorough way. I have several comments regarding current version of the manuscript and hope the authors could carefully address those before being considered for publication.

**Response:** All your comments listed below have been addressed. Please check the point by point response as follows.

### **Major comments**

Since submitted as a technical note, the authors should provide a solid and sound validation of the accuracy and stability of their technique. For instance, was your DMA calibrated?

**Response:** Yes, we have calibrated. As shown in Figure R1, the SEM-measured particle size is consistent with the DMA screening size (about 100 nm).

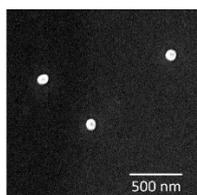
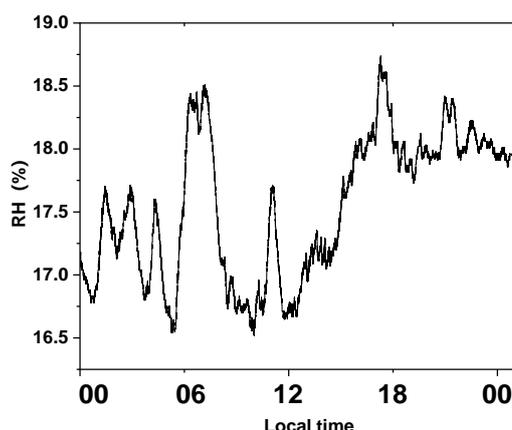


Figure R1 The SEM image of 100 nm AS particles deposited on the silicon wafer

How much did you dry your aerosols?

**Response:** As shown in Figure R2, the RH downstream of DMA was 16.52 ~ 18.74% which was below the ERH value (about ~32% RH) of AS. We have included this sentences in the revised version: The RH downstream of the DMA varies over 16.52 to 18.74% which are well below the efflorescence relative humidity (ERH) of AS (about ~32% RH) (Figure R2). As a result, the initial states of all nanoparticles are in dry

conditions.



**Figure R2** Time series of RH downstream of DMA

How many particles did you deposit onto the substrate before further measurements, would the concentration of the particles deposited influence your results?

**Response:** There were about 100 thousand particles deposited onto the substrate. The measured particles deposited onto the substrate could overlap on each other for FTIR. But the chemical composition is not changed for the 100nm nanoparticles during depositing onto the stacking state. And for the 100nm nanoparticles, its hydration characteristic mainly depends on its chemical composition and the kelvin effect is negligible. The enrichment for the nanoparticles is to improve the signal of FTIR because the hygroscopic signal of a single particle is too weak to be measured by the FTIR method. Since the chemical composition is not changed for the 100nm nanoparticles during depositing onto the stacking state, the concentration of the particles deposited does not influence our results. We have included this explanation in the revised paper.

How was the RH measured, what was its uncertainty?

**Response:** The RH was measured with a RH sensor HC2-S manufactured by Rotronic Incorporation (Switzerland), and its accuracy was  $\pm 0.8\%$  (RH range: 0 ~ 100%). We have included this description in the revised version.

Was the cell well-insulated that the RH could be maintained?

**Response:** Yes, the cell is well-insulated to maintain the RH at a constant level. A RH sensor was mounted at the inlet of the cell and the cell length is only ~ 4cm. The FTIR spectrometer starts to take absorption spectra of the samples approximately 5 min after the injection of each designated RH. This time interval is used to stabilize the RH inside the sample cell. We also measure the RH at the outlet of the cell and found that it is close to that at the inlet.

What parameters did you directly obtain from the technique and how did you interpret them? Each single part of your instrument should be described clearly.

**Response:** Done. We can directly obtain the absorbance spectroscopy under different RH condition. ① We first correct the baseline of the measured absorption spectra with the Opus 7.0 software. We then iteratively recalculate the spectra with the absorption coefficients of liquid water provided by Downing and Williams (Downing and Williams, 1975) through the non-linear least squares method till the residual between the measured spectrum and the calculated spectra are minimized. We stop the iteration and derive the liquid water content once the root mean square error (RMSE) of the residual is below 0.3%. After the deliquescence of the nanoparticles and the position of the absorption peak (referring to the wavenumber that shows the strongest absorption) of  $\text{SO}_4^{2-}$  is relative stable, we use a similar non-linear least square method to derive the mass of the sulfate ( $M_{\text{sulfate}}$ ) (Wei et al., 2019). As a result, the mass of AS ( $M_{\text{AS}}$ ), AS/SN ( $M_{\text{AS/SN}}$ ), and AS/OA ( $M_{\text{AS/OA}}$ ) can be derived with the  $M_{\text{sulfate}}$  via the following equations.

$$M_{\text{AS}} = \frac{M_{\text{sulfate}}}{96} * 132 \quad (1)$$

$$M_{\text{AS/SN}} = \frac{M_{\text{sulfate}}}{96} * 132 * 2 \quad (2)$$

$$M_{\text{AS/OA}} = \left( \frac{M_{\text{HSO}_4^-}}{97} + \frac{M_{\text{sulfate}}}{96} \right) * 132 * 2 \quad (3)$$

The mass is used to calculate the hygroscopic growth factor (GF).

② After baseline correction, the absorbance spectra are normalized into 2D-IR spectra

with the 2D Shige software which can give the Synchronous and Asynchronous correlation maps. The red and blue areas in the 2D-IR spectra indicate positive and negative correlations of the spectral intensities at  $\nu_1$  and  $\nu_2$ , respectively. In the synchronous correlation maps, the positive and negative correlations indicate simultaneous and opposite changes of the spectral intensities observed at the wavenumber pair ( $\nu_1$ ,  $\nu_2$ ), respectively. In the asynchronous correlation maps, the positive correlation indicates the spectral intensity change at  $\nu_1$  occurs predominantly before that at  $\nu_2$ , while the negative correlation indicates the spectral intensity change at  $\nu_2$  occurs predominantly before that at  $\nu_1$ .

We have added above descriptions in section 2.3.3. Please check the marked up file for details.

Second, the authors used AS to calibrate the instrument. However, the figures the authors plotted are lack of critical data points, particularly between 74% RH and 81% RH.

**Response:** Done. We have included more data points in Fig.2 and Fig. 3. Please check the marked up file for details.

The authors deposited 100 nm particles onto a substrate. These material could not represent nanoparticles anymore. The condensation of water molecules on a curved particle could be much different from that on a flat surface with deposited substances on. The author should clarify these differences and give proper discussion, emphasizing its own atmospheric relevance. A section discussing its atmospheric implications is suggested.

**Response:** The measured particles deposited onto the substrate could overlap on each other for FTIR. But the chemical composition is not changed for the 100nm nanoparticles during depositing onto the stacking state. And for the 100nm nanoparticles, its hydration characteristic mainly depends on its chemical composition and the kelvin effect is negligible. The enrichment for the nanoparticles is to improve the signal of FTIR because the hygroscopic signal of a single particle is too weak to be measured by the FTIR method. Since the chemical composition is not changed for the 100nm nanoparticles during depositing onto the stacking state, the concentration of the particles deposited does not influence our results. Lee et al., concluded that, for particles

with volume equivalent diameter of greater than 100nm, their critical hydration characteristics are essentially independent of the particle size, which is similar to the condensation of water on the flat surface (Lee et al., 1998) . In the revised version, we have given the explanation, Please check the marked up file for details.

The authors stated in their abstract as well as in the intro part that: “current techniques are also difficult to identify the intermolecular chemical interactions of phase transition micro-dynamics during nanoparticle deliquescence process because their limited temporal resolutions are unable to capture the complex femtosecond-level intermediate states”. I am curious from current results you presented did not show a higher temporal resolutions and femtosecond-level intermediate states were not displayed, either. Otherwise, please clarify.

**Response:** Done. In our manuscript, the femtosecond-level temporal resolutions are not displayed, but the intermediate states could be indicated from the IR peaks change in the order. We have revised this sentence in the version. Please check the marked up file for details.

Based on my third comment, the author should emphasis the novelty of current technique. What are the advantages compared to traditional hygroscopicity measurements? I assume Sect 3.3 and 3.4 are quite important, contributing new insights to current understandings. However, the discussion in these parts was kind of weak and plain. Proper comparisons with other studies may help.

**Response:** Compared to traditional hygroscopicity measurements, the 2D-IR spectroscopic technique captured more complex process and the intermediate state during the hygroscopic growth of AS nanoparticles (Tang, et al., 1977; Tang, et al. 1994). In the revised version, we have presented proper comparisons and analysis with previous studies in section 3.3 and 3.4. Although the hygroscopic growth characteristics observed in this study are similar to those in previous study (Cruz and Pandis, 2000), the 2D-IR spectroscopic technique captured more complex process and the intermediate state during the hygroscopic growth of AS nanoparticles. Please check section 3.3 and 3.4 in the revised version for details.

**Minor comments:**

Line 90: AN or SN? Similar in line 96.

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

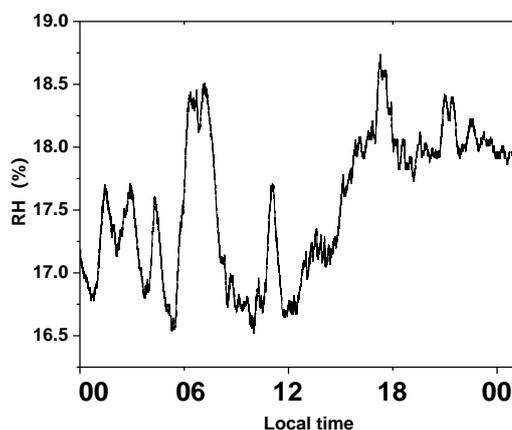
Line 102: Current work is of great significance, not only for the haze control across China, but also for the whole atmospheric community. There remains huge gaps and requires significant efforts for the haze control across China using current results.

Consider rephrase the sentence or extend the content.

**Response:** We have tempered this description in the revised version. Please check the marked up file for details.

Line 108: How much you dried your aerosols? For instance, to which RH condition?

**Response:** We have measured the RH downstream of DMA and found they varied over 16.52 to 18.74%, which are all below the ERH value (about ~32% RH) of AS . We have included this description in the revision: The RH downstream of the DMA varies over 16.52 to 18.74% which are well below the efflorescence relative humidity (ERH) of AS (about ~32% RH) (Figure R2). As a result, the initial states of all nanoparticles are in dry conditions. Please check the marked up file for detail.



**Figure R3** Time series of RH downstream of DMA

Line 110: How many particles you deposited onto the substrate? Will they overlap on each other?

**Response:** There were about 100 thousand particles deposited onto the substrate, and they could overlap on each other. But the chemical composition is not changed for the 100nm nanoparticles in the stacking state. And for the 100nm nanoparticles, its hydration character depends on mainly its chemical composition, and the kelvin effect is negligible. The enrichment for the nanoparticles is to improve the signal of FTIR because the hygroscopic signal of a single particle is too weak to be measured by the FTIR method. We have included this description in the revision. Please check the marked up file for detail.

Line 151-160: Even though you described our instrumentation, I am still confused how you measure or derive  $D_{wet}$ .

**Response:** The  $D_{wet}$  was not measure directly. It was calculated through the increased water mass and  $D_0$ .  $D_0$  (cm) is the mean initial diameter of the dry particles which was 100nm. When the RH varies from 50% to 95%. The total water mass could be calculated in different RH conditions. For example, for pure AS, we can calculate the initial mass of the dry AS particles through the simple procedure base on the sulfate IR absorbance. The simple procedure is non-linear least squares algorithm. It means that a measured spectrum is fitted by iteratively recalculating the spectrum until the mean-squared residual between the measured spectrum and calculated spectra is minimized. The calculated spectra are the standard absorption spectrum of liquid water and AS. So from the  $V_0$  and  $V_{wet}$  can be calculated via equations (1) and (2). So the  $D_{wet}$  could be derived vis equations (1) to (4).

$$V_{water} = \frac{M_{water}}{\rho_{water}} \quad (1)$$

$$V_0 = \frac{M_{AS}}{\rho_{AS}} \quad (2)$$

$$V_{wet} = V_0 + V_{water} \quad (3)$$

$$D_{wet} = \left( \frac{3V_{wet}}{4\pi} \right)^{1/3} \quad (4)$$

Where  $V_0$  (cm<sup>3</sup>) is the initial volume of the dry nanoparticle at approximately 25°C, and  $V_{water}$  (cm<sup>3</sup>) is the water volume contained in the nanoparticle at the designated RH;

$M_{water}$  (g) and  $M_{AS}$  (g) are the calculated water mass and the pure AS component mass at the designated RH, respectively;  $\rho_{water}$  (g/cm<sup>3</sup>) (approximately 1 g/cm<sup>3</sup>) and  $\rho_{AS}$  (g/cm<sup>3</sup>) are the densities of water and the pure AS component, respectively.

We have included above detailed descriptions in the revised version.

Line 193: What do you mean by “area of OH”?

**Response:** “area of OH” mean the area of the OH absorption peak at 3250 cm<sup>-1</sup>. We have included this interpretation in the revised version. Please check the marked up file for details.

Line 211: Your DRH value for small particles is similar to that of large ones from other studies. But this is not enough to prove the accuracy of your method, as GF value of AS at a certain RH is also a necessity and it varies between small particles and large ones. Rephrase the sentence and make thorough comparison.

**Response:** Our method and the size of particle are different from previous studies, but we obtained a consistent DRH (about 79%±0.8%) to those in Tang et al. (1982), Cruz and Pandis (2000), and Estillore et al. (2016) who measured a DHR for AS was 79%±1% and 80%±0.4%. Though the particle size (~100 nm) in this study is smaller than those in previous studies, its hydration characteristic depends on mainly its chemical composition and the kelvin effect is negligible. Moreover, Lee et al. (1998) concluded that, for particles with diameter greater than 100nm, their critical hydration characteristics are essentially independent of the particle size, which is similar to the condensation of water on the flat surface. We have included above description in the revision. Please check the marked up file for details.

Line 211, also for Fig.2 and Fig. 3: Moreover, I observed that you performed the measurements at 74% RH and at 81% RH. At 81% RH, you observed deliquescence and you reported this value as DRH. This is not sound, it could be any values between 74% and 81% RH, please consider add more data points between these two RHs, specifically for your Fig.2 and Fig. 3. Before you add more data points at those RHs, I cannot be convinced.

**Response:** Done. We have included more data points in Fig.2 and Fig. 3. Please check

the marked up file for details.

Line 218: What do you mean by ‘nanoparticle volume increases but its mass keeps constant’? Please clarify.

**Response:** We mean that the nanoparticle volume increases as the increase in liquid water mass, but the AS mass keeps constant. We have changed this sentence to “ 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  $\text{SO}_4^{2-}$  concentration. As a result, we observe a decrease in the area of  $\text{SO}_4^{2-}$  absorption peak starting from  $\sim 83\%$  RH.” in the revised version. Please check the marked up file for details.

Line 223: When you referred the calculation to previous section, for instance,  $M_{\text{water}}$  and  $M_0$ , you should specify all of these quantities in previous part. I am quite confused that how you obtained  $M_{\text{water}}$ ,  $M_{\text{wet-Mo}}$ ?

**Response:** In the revised version, we have included detailed quantitative analysis for  $M_{\text{water}}$ ,  $M_0$  in section 2.3.1. we also analyze the RMSE for the quantitative method.

Line 228: Please add comparison with other studies, especially 100 nm particles of oxalic acid. Boreddy et al. (2018) measured the GF of oxalic acid using a HTDMA and they found that oxalic acid started to absorb water at  $\text{RH} < 45\%$  and the GF of oxalic acid was 1.47 at 90% RH. Please consider giving proper discussion.

**Response:** Several previous measurements using the H-TDMA found substantial growth of oxalic acid particles under low RH, which was 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 could lead to a growth of size with the GF of around 1.17 during the transform. Thus, if the initial particles prepared could 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 of OA particles

are easy to find in bulk studies. Moreover, theoretical prediction and bulk measurements indicate 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  $3250\text{cm}^{-1}$  peak intensity will increase continually. In the revised version, we have given the detailed description. Please check the marked up file for details.

Line 236: I suggest you add the results for sodium nitrate (SN) particles before you discuss the results for mixtures. Again, it should be SN but not AN, isn't it? Also in Fig. 5, what does NN stand for?

**Response:** Done. We have changed the abbreviation of sodium nitrate to SN and increase the FTIR spectral characteristics of the SN nanoparticles under humidity conditions from 55% to 85% (RH) in Supplement. Please check the marked up file for details.

Line 254-259: Similarly, add more data points for GF at RH between 74% and 81% to complete your validation. And the content of this paragraph was well known by hygroscopicity community, you don't have to repeat it, but give detailed description of your DRH value as well as corresponding GF and compare with other studies.

**Response:** We have included the more data points in Fig.2 and Fig. 3. Furthermore, we have given detailed description of our DRH value as well as corresponding GF and compared with other studies. Please check the marked up file for details.

Line 260-265, also for Fig. 6: At RH between 70% to 85%, your results for mixtures deviate from the predictions. Give proper explanations. You cannot just state that they are in good agreement with other studies without presenting their data points.

**Response:** Done. We have included more explanation in the revised version. Please check the marked up file for details.

Line 269: What does absorption peak mean? Please clarify.

**Response:** Absorption peak refers to the wavenumber that shows the strongest absorption by a chemical sample which is used to identify specific radicals or compounds.

Line 271: Since 2D-IR spectroscopic technique is a major instrument for your results, you should describe it in a more detailed way. For instance, in Sect2.1. The description was too simplified and should be extended. Give possible examples and emphasize its significance. I do think line 267-277 should go to the experiment section. And please further explain “Synchronous correlation maps” and “asynchronous correlation maps”, give examples and how we use these results, what do these results indicate or how we interpret them.

**Response:** Done. We have interpreted them in section2.3.3. Please check the marked up file for details.

Line 310: So all the auto-peaks were all the same during all the RH conditions?

Similar questions to the asynchronous correlation maps.

**Response:** The 2D-IR spectra represent the perturbation-induced variations of a series of spectral intensity observed during the interval of external variable RH. In present work, the red and blue areas in the 2D-IR spectra indicate positive and negative correlations of the spectral intensities at  $\nu_1$  and  $\nu_2$ , respectively. In the synchronous correlation maps, the positive and negative correlations indicate simultaneous and opposite changes of the spectral intensities observed at the wavenumber pair ( $\nu_1$ ,  $\nu_2$ ), respectively. In the asynchronous correlation maps, the positive correlation indicates the spectral intensity change at  $\nu_1$  occurs predominantly before that at  $\nu_2$ , while the negative correlation indicates the spectral intensity change at  $\nu_2$  occurs predominantly before that at  $\nu_1$ .

In the revised version, we have given the detailed description in section2.3.3, section 3.3 and section 3.4. Please check the marked up file for details.

Line 341-345: Too long sentence, please rephrase it.

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

**Reference:**

Yuh-Lang Lee, Wen-Sheng Chou, Liang-Huei Chen, surface science, 1998, 414, 363-373