Author's Response

Response to Referee #3:

We are grateful for the reviewer's comments. Those comments are all valuable and helpful for improving our paper. Our response to the comments and changes to the manuscript are included below. We repeat the specific points raised by the reviewer in bold font, followed by our response in italic font. The pages numbers and lines mentioned below are consistent with those in the Atmospheric Chemistry and Physics Discussions (ACPD) paper.

The authors presented a laboratory work on the hygroscopic growth and phase transitions of oxalic acid (OA), ammonium sulfate (AS), and their mixed particles. The growth factor and the phase transition of deliquescence and efflorescence were determined using the spectra collected by confocal Raman spectroscopy at room temperature. It is showing that the particles with different mixing ratios showed different hygroscopicity during the hydration and dehydration cycles. At higher OA/AS ratio, the dehydration process produced less hygroscopic organic salt, such as NH4HC2O2, from in particle phase reaction within the aqueous droplet as it loses water. In addition, the manuscript shows the possible effects on the growth factor by the different drying rates. The manuscript also provides explanation for the discrepancy on the ERH of OA compared to the previous studies. This study provides a set of valuable data for the hygroscopicity of model particles generated in the lab. This work demonstrates the effects of aqueous phase reaction on particle hygroscopicity during dehydration which was overlooked in the past. There is a quite important implication to atmospheric chemistry. It is recommended for publication after a minor revision. Please see the following comments which the authors may want to consider in the revision.

Minor comments:

1. P1, L17, L18, "aerosol" refers to the mixture of particle and gases. It is suggested to change the "aerosol" to "particle".

Reply: *Thanks for your suggestion. P1, L17, L18, "aerosol"* ***is changed into*** *"particle" in the revised version.*

2. P1, L28, how do you define "the partial deliquescence relative humidity"?

Reply: *The partial deliquescence relative humidity is used to indicate the RH at which AS deliquesces while other coexisting components in the mixed particles remain solid during the hydration process.*

Related changes in the revised manuscript:

P1, L28, *to avoid the misunderstanding, "the partial deliquescence relative humidity (DRH) for mixed OA/AS particles"* **is revised to** *"the deliquescence relative humidity (DRH) of AS in mixed OA/AS particles".*

3. P3, L23, this statement is not clear, in the previous sentences the authors showed that there are several studies on the OA/AS system. Please provide additional information or references to support this statement.

Reply: *P3, L23, this statement means that the effects of OA on* ***deliquescence*** *behaviors of AS have been extensively investigated (Brooks et al., 2002; Prenni et al., 2003; Wise et al., 2003; Miñambres et al., 2013; Jing et al., 2016), while there is still lack of study on influence of OA on* ***efflorescence*** *behaviors of AS. In the original version, we have used the term "****deliquescence process****" or "****efflorescence process****" to distinguish the studies on hygroscopicity of the OA/AS mixed system.*

4. P4, L19, it is not clear how the authors would be able to prepare the 30-40 µm aqueous particles with a syringe.

Reply: *The sample solution was discharged from a syringe. Then, residual solution in the syringe was pushed rapidly to generate aerosol droplets spraying onto a PTFE substrate fixed to the bottom of the sample cell. At ~ 95% RH, the droplets with a diameter of 30~40 microns detected by an optical microscope (50× objective, 0.75 numerical aperture) were selected to acquire the Raman spectra.*

Related changes in the revised manuscript:

P4, L19: *The sentence "Using a syringe, droplets from the solutions were injected onto the polytetrafluorethylene (PTFE) film fixed to the bottom of the sample cell. The diameters of these droplets ranged from 30 to 40 µm at ~ 95% RH. Then, the sample cell was sealed by a transparent polyethylene film and the RH in the sample cell was regulated by nitrogen streams* *consisting of a mixture of water-saturated N_2 and dry N_2 at controlled flow rates."* ***is revised to*** *"The sample solution was discharged from a syringe. Then, residual solution in the syringe was pushed rapidly to generate aerosol droplets spraying onto a polytetrafluorethylene (PTFE) substrate fixed to the bottom of the sample cell. Then, the sample cell was promptly sealed by a transparent polyethylene film. The RH in the sample cell was regulated by nitrogen streams consisting of a mixture of water-saturated N_2 and dry N_2 at controlled flow rates. At ~ 95% RH, the droplets with a diameter of 30~40 microns detected by an optical microscope (50× objective, 0.75 numerical aperture) were selected to acquire the Raman spectra. The dry size of these particles after efflorescence ranged from 10 to 20 μm."*.

5. P4, L25, If the temperature accuracy is 0.7 K, the uncertainty of RH at 297 K and 95% should be 4%. How the sample temperature is controlled during the experiments?

Reply: *We thank for the reviewer's comment. Below 90% RH, the uncertainty of RH at 297 K was less than ±2.5%. We agree that the temperature accuracy of 0.7 K could result in uncertainty of 4% at RH of 95%. The temperature of the sample was maintained at 297 ± 0.5 K by using an automatic thermostat. We would like to add some changes to make it clear.*

Related changes in the revised manuscript:

P4, L24: *The sentence "The RH and temperature of the outflow from the sample cell was measured by a humidity/temperature meter (Centertek Center 313) with an accuracy of ±2.5% and ±0.7 K placed near the exit of the sample cell."* ***is changed into*** *"The RH and temperature of the outflow from the sample cell was measured by a humidity/temperature meter (Centertek Center 313) with an accuracy of ±2.5% below 90% RH and ±0.7 K placed near the exit of the sample cell."*.

P4, L26: We add *"The temperature accuracy of 0.7 K could result in uncertainty of 4% at RH of 95%. The temperature of the sample was maintained at 297 ± 0.5 K by using an automatic thermostat."*.

6. P5, L25, I also suggested to move the Raman spectra to the main text.

Reply: *Thanks for your suggestion. The Raman spectra of AS droplets are moved to the main text.*

Related changes in the revised manuscript:

P5, L24, *the sentence "The Raman spectra of AS droplets during the dehydration and hydration process as a function of RH can be found in Fig. S1 (a) and (b) in the supplement, respectively."* ***is revised to*** *"The Raman spectra of AS droplets during the dehydration and hydration process can be found in Fig. 1a and 1b, respectively.".*

7. P6, L11-12, it is not clear to me that how oxalic acid dihydrate can be converted to anhydrous form at these experimental conditions? How long it will take for such process and is it atmospheric relevant?

Reply: *In our experiments, oxalic acid particles after efflorescence exist in the form of dihydrate until 6.6% RH, at which the Raman spectrum of dihydrate remains unchanged for 40 min. Once RH decreases to 5%, oxalic acid dihydrate is* ***promptly*** *converted to anhydrous oxalic acid, as seen in Fig. 2a. This conversion only takes a few seconds during our observations. Our results indicate extremely dry conditions may favor the conversion of oxalic acid dihydrate into anhydrous form in the atmospheric environment.*

Related changes in the revised manuscript:

To make it clear, ***P6, L9, we add*** *"Oxalic acid particles after efflorescence exist in the form of dihydrate until 6.6% RH, at which the Raman spectrum of dihydrate remains unchanged for 40 min.".* ***P6, L9,*** *the sentence "As RH further decreases to ~5.0%, the peaks shift to 482, 828, 845, 1477, 1710, 2587, 2760 and 2909 cm^{-1},"* ***is changed into*** *"Once RH decreases to ~5.0%, the peaks promptly shift to 1477, 1710, 2587, 2760 and 2909 cm^{-1},".*

8. P7, L10, it is the reaction, not an equation.

Reply: *P7, L10, we replace the equal sign with an arrow for the reaction.*

9. P9, L6-11, the explanation for the discrepancy on the ERH of OA compared to the previous studies should be carefully addressed.

Reply: *We thank the reviewer for the helpful suggestion. After revisiting our explanation carefully, we give a more specific one as follows. The discrepancy on the ERH of OA compared to that reported by Peng et al. (2001) is likely due to the effects of substrate and sample purity. The size of dry particles ranging from 10 to 20 μm in our experiment is consistent with observation using*

EDB by Peng et al. (2001), which eliminates the influence of particle size. The substrate supporting droplets may promote the heterogeneous nucleation of oxalic acid while the levitated droplets in EDB study can avoid induced nucleation by the substrate. Ghorai et al. (2014) also reported the potential effects of substrate on the efflorescence transition of NaCl/dicarboxylic acid mixed particles. In addition, The OA purity in our study is 99.0% lower than that of 99.5% in study by Peng et al. (2001). Thus, trace amounts of impurities in OA droplets acting as a heterogeneous nucleus could contribute to crystallization and result in a higher ERH of OA. Due to the effects of substrate and sample purity, the heterogeneous nucleation should be responsible for the discrepancy on the observed ERH of OA.

Corresponding changes in the revised manuscript:

Page 9, Line 10-17: The sentence *"The discrepancies between this study and that by Peng et al. (2001) is likely due to the effects of droplet size, substrate and experimental method. According to classical nucleation theory, the probability of the formation of the critical nucleus is proportional to the particle volume (Martin, 2000; Parsons et al., 2006). Considering that the droplet size in our study was approximately 1-2 times larger than that observed by Peng et al. (2001), the droplets deposited on the substrate in our experiment may promote the heterogeneous nucleation while the levitated droplets using EDB can dispel the heterogeneous nucleation. Thus, the ERH of OA obtained in our study is higher than the observation of Peng et al. (2001)."* **is revised to** *"The discrepancy on the ERH of OA compared to that reported by Peng et al. (2001) is likely due to the effects of substrate and sample purity. The size of dry particles ranging from 10 to 20 μm in our experiment is consistent with observation using EDB by Peng et al. (2001), which eliminates the influence of particle size. The substrate supporting droplets may promote the heterogeneous nucleation of oxalic acid while the levitated droplets in EDB study can avoid induced nucleation by the substrate. Ghorai et al. (2014) also reported the potential effects of substrate on the efflorescence transition of NaCl/dicarboxylic acid mixed particles. In addition, The OA purity in our study is 99.0% lower than that of 99.5% in study by Peng et al. (2001). Thus, trace amounts of impurities in OA droplets acting as a heterogeneous nucleus could contribute to crystallization and result in a higher ERH of OA. Due to the effects of substrate and sample purity, the heterogeneous nucleation should be responsible for the discrepancy on the observed ERH of OA."*.

10. P11, L10-12, as suggested by the previous reviewers, it may be more straightforward if the authors can provide optical images to show the phase transitions. For this possible evidence on the coating of less hygroscopic materials, it may be easy to just provide Raman spectral at different location of particles or compositional mapping with the imaging mode.

Reply: *We appreciate the reviewer's comments. The optical images showing the phase transitions have been added in the text. Figure R1 presents the spatial distribution of chemicals within mixed OA/AS (OIR = 3:1) particles at 74.4% RH. The characteristic peak of 980* cm^{-1}*, 1050* cm^{-1} *and 1471* cm^{-1} *is assigned to* SO_4^{2-}*,* HSO_4^- *and* $HC_2O_4^-$*, respectively. The sharp absorption at 874* cm^{-1} *and obvious peak at 1471* cm^{-1} *indicate the abundant content of* $NH_4HC_2O_4$*. The comparison of characteristic peaks between inner and outer phase reveals that the major component on the surface of a mixed OA/AS (OIR = 3:1) particle is* $NH_4HC_2O_4$*. In contrast to the surface, the obvious features of 980* cm^{-1} *and 1050* cm^{-1} *at the core of the particle suggest that* $(NH_4)_2SO_4$ *and* NH_4HSO_4 *mainly exist in the inner aqueous phase. During the dehydration process, crystalline* $NH_4HC_2O_4$ *in the outer phase acts as a heterogeneous nucleus, leading to the crystallization of oxalic acid dihydrate,* $(NH_4)_2SO_4$ *and* NH_4HSO_4 *in the inner phase.*

Related changes included in the revised manuscript:

Figure R1 is added into the text. ***Page 11, Line 4:*** *The sentence "The crystallization of* $NH_4HC_2O_4$ *may act as crystallization nuclei for* NH_4^+*,* HSO_4^- *and OA in the mixed droplets to form* NH_4HSO_4 *crystal and oxalic acid dihydrate."* ***is changed into*** *"Figure 12 presents the spatial distribution of chemicals within mixed OA/AS (OIR = 3:1) particles at 74.4% RH. The characteristic peak of 980* cm^{-1}*, 1050* cm^{-1} *and 1471* cm^{-1} *is assigned to* SO_4^{2-}*,* HSO_4^- *and* $HC_2O_4^-$*, respectively. The sharp absorption at 874* cm^{-1} *and obvious peak at 1471* cm^{-1} *indicate the abundant content of* $NH_4HC_2O_4$*. The comparison of characteristic peaks between inner and outer phase reveals that the major component on the surface of a mixed OA/AS (OIR = 3:1) particle is* $NH_4HC_2O_4$*. In contrast to the surface, the obvious features of 980* cm^{-1} *and 1050* cm^{-1} *at the core of the particle suggest that* $(NH_4)_2SO_4$ *and* NH_4HSO_4 *mainly exist in the inner aqueous phase. During the dehydration process, crystalline* $NH_4HC_2O_4$ *in the outer phase acts as the heterogeneous nucleus, leading to the crystallization of oxalic acid dihydrate,* $(NH_4)_2SO_4$ *and* NH_4HSO_4 *in the inner phase.".*

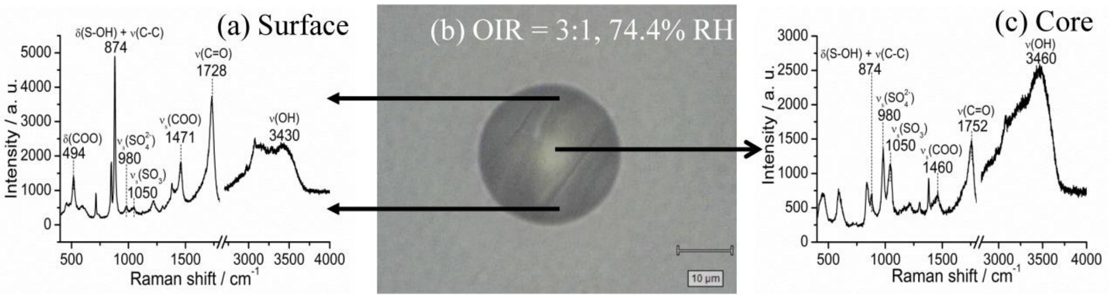

Figure R1. *The spatial distribution of chemicals within mixed oxalic acid/ammonium sulfate (OIR = 3:1) particles at 74.4% RH upon dehydration. (a) Raman spectrum acquired on the surface showing the shell mainly consisting of $NH_4HC_2O_4$. (b) Optical micrograph of a partially effloresced droplet composed of oxalic acid/ammonium sulfate (OIR = 3:1) mixtures at 74.4% RH upon dehydration. (c) Raman spectrum obtained at the core of the droplet showing the liquid phase dominated by oxalic acid and ammonium sulfate.*

11. P11, L28-29, it is not clear how the RH is controlled during the 10-12h experimental period, stepwise or continuously? What is the variation of sample temperature during this period?

Reply: *The RH was decreased stepwise from ~95% to ~0% over 10-12 h during the dehydration process. The decrease rate was typically 5-6 RH/40 min, and the rate remained 2-3 RH/40 min near the phase transition. The temperature of the sample was maintained at 297 ± 0.5 K by using an automatic thermostat. In the Experimental section, we have stated that RH was decreased stepwise during the slow drying process.*

Related changes included in the revised manuscript:

P5, L10, *the sentence "Subsequently, the RH was decreased stepwise for dehydration process, and increased from RH＜ 3% to high RH for hydration process."* ***is revised into*** *"Subsequently, the RH was decreased stepwise for a slow dehydration process, and then increased stepwise from RH＜ 3% to high RH for a hydration process. The decrease rate was typically 5-6 RH/40 min, and the rate remained 2-3 RH/40 min near the phase transition. The RH was decreased continuously in a few minutes for a rapid dehydration process.".*

12. Figure 4 and 5, It is suggested to compare the experimental results with model

estimation, such as E-AIM, ZSR, or AIOMFAC. For example, the E-AIM model (http://www.aim.env.uea.ac.uk/aim/aim.php) includes the dissociation equilibrium for some organic/inorganic systems. The oxalic acid is included in current E-AIM. What would E-AIM predict and how does that compare with your experimental data? This can not only serve as validation of the determined Raman growth factor but may also provide additional insides to the effects of reactions on particle's hygroscopicity.

Reply: *We thank the reviewer for the good suggestion. In fact, the Raman growth factors of pure ammonium sulfate and oxalic acid have been given in Fig. 5 (i.e., Fig. 9 in new version) for comparisons. It is clear that the two species show comparable hygroscopic growth at high RH (dehydration curve, Fig. 5(a)). According to the ZSR rule, the hygroscopic growth of mixtures of ammonium sulfate and oxalic acid should be close to that of pure ammonium sulfate or oxalic acid. Due to lack of Raman cross section data, our Raman growth factors could not be converted into ZSR-predictions. Thus, we used Raman growth factors of pure ammonium sulfate and oxalic acid to compare with that of mixtures in the original manuscript.*

As for the E-AIM, our previous study by Jing et al. (2016) has shown that E-AIM could well describe the hygroscopic growth of equal mass mixture of ammonium sulfate and oxalic acid, which underwent rapid dehydration in the HTDMA system. As stated in the Discussion section, the HTDMA studies observed no formation of ammonium hydrogen oxalate or influence of interactions between ammonium sulfate and oxalic acid on water uptake of mixtures. Also, the E-AIM does not consider the formation of solid ammonium hydrogen oxalate. As a result, it can be expected that the E-AIM could not well describe water uptake of mixed ammonium sulfate/oxalic acid particles undergoing the slow drying process. This situation also applies to AIOMFAC model.

References

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