Author's Response

Response to Referee #2:

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.

I have many of the same comments as Reviewer #1. In particular revising the discussion section to include atmospheric relevance is crucial before final publication. After revision, I believe the manuscript represents a contribution to scientific progress within the scope of ACP. The scientific approach and methods are valid. I recommend publication in ACP after the authors address the concerns of the reviewers.

Reply: *We thank the reviewer for the comments. We have supplemented atmospheric relevance as follows.*

Related changes in the revised manuscript:

Page 12 line 20: "4 Conclusions" is changed into "4 Conclusions and atmospheric implications".

Page 13 line 9-20: This paragragh is replaced by "*The prior hygroscopic studies suggest that crystallization of internally mixed ammonium sulfate/dicarboxylic acid particles may lead to the formation of trace organic salt. Lightstone et al. (2000) estimated that approximately 2% of the initial succinic acid may form ammoniated succinate within mixed ammonium nitrate/succinic acid particles during the efflorescence process. Ling and Chan (2008) inferred that crystallization of ammonium sulfate/succinic acid droplets likely generated metastable organic salt based on change in the Raman peak form of succinic acid. Braban and Abbatt (2004) reported that* NH_4HSO_4 *and ammoniated malonate were likely generated upon crystallization of mixed ammonium sulfate/malonic acid particles. However, due to the trace amount of organic salt below Raman or infrared detection limit, they found no apparent influence of organic salt formed upon dehydration on the water uptake or phase change of mixed particles. In contrast, our results indicate that the chemical processing upon drying of droplets containing OA and AS influences efflorescence transition and water uptake of mixed aerosols during the humidity cycle* *by modifying particulate component.*

Our results highlight the atmospheric importance of dicarboxylic acid−ammonium sulfate interactions in aerosol aqueous chemistry. Such chemical processing upon drying of aerosols comprised of organic acid/$(NH_4)_2SO_4$ *mixtures may enhance the acidity of aqueous phase in the intermediate RH due to the transformation of* $(NH_4)_2SO_4$ *into* NH_4HSO_4. *These experiments also imply that the chemical reaction between aqueous* $(NH_4)_2SO_4$ *and oxalic acid upon slow dehydration is a possible formation pathway for the low-volatility oxalate in ambient particles, which could enhance partitioning of dicarboxylic acids to aqueous particles with the presence of ammonium sulfate (Yli-Juuti et al., 2013; Hakkinen et al., 2014). It has been reported that the aerosol aqueous processing within organic acid/AS mixtures partly contributes to enhanced loadings of secondary organic aerosol (SOA) from biogenic precursors (Hoyle et al., 2011). Compared to aqueous processing such as condensed phase acid-catalyzed reactions relevant to formation of organosulfates, the contribution of other aerosol processing containing organic salt formation to SOA burden likely becomes important under less acidic condition. Formation of low-solubility organic salts from aqueous processing within aerosols alters particle-phase component and thus modifies aerosol's hygroscopicity, optical properties and chemical reactivity. Our findings provide fundamental insight into effects of drying conditions (drying rate or time) on formation of organic salt from reactions of organic acids with inorganic salts in particle phase under ambient RH conditions. Overall, a better understanding of the chemical interactions between species in a multicomponent system during the humidity cycle is critical for the accurate modeling efforts of aerosol phase behavior in thermodynamic models."***.**

1) I was wondering if the authors considered referencing and discussing Amundson et al. (2007) which provides a sulfate/ammonium/oxalic acid phase diagram.

Reply: *Thanks for the reviewer's suggestion. Amundson et al. (2007) presented a phase partitioning model (UHAERO) for mixtures of inorganic electrolytes and dicarboxylic acids. They assumed that solid oxalic acid was the only organic solid that could occur in the sulfate/ammonium/oxalic acid system. The limitations on the simple assumption for this system were a result of the lack of available thermodynamic data. Amundson et al. (2007) considered the incorporation of organic salts was crucial in the modeling of hygroscopic properties as well as* *multistage growth of organic/inorganic mixtures.*

Related changes in the revised manuscript:

P4, L2: We add *"Due to the lack of available thermodynamic data, the aerosol thermodynamic models typically assume that upon dehydration dicarboxylic acid could only form organic solid without the organic salt in the inorganic electrolyte/dicarboxylic acid system (Clegg and Seinfeld, 2006; Amundson et al., 2007). Thus, the incorporation of organic salts formed from interactions between inorganic salts and organic acids is crucial in the modeling of hygroscopic properties of mixed organic/inorganic particles.".*

2) Page 4, line 19: How did the authors create 30-40 micron particles with a syringe? This procedure needs to be explained better. Also, how was the environment of the particles maintained at 95% RH after injection? Aren't the particles subjected to the environment in the room which is surely less than 95% RH? Are 30-40 micron particles relevant in the atmosphere?

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. 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 droplet size of 30-40 micron in our study falls into the size range of cloud droplets (less than 50* μm*).*

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*.".*

3) Page 5, line 11: The authors state that the particles were equilibrated with water vapor for 40 minutes at a given RH value and they state that the slow dehydration process occurred in the time scale of hours. Why was the time scale of 40 minutes chosen? Why not 30 minutes or 60 minutes? Is 40 minutes the amount of time for the Raman spectrum to remain constant?

Reply: *We used intensity ratios of the water peak (3430* cm^{-1}*) to the sulfate peak (980* cm^{-1}*) to test the equilibration time of droplets at the given RH. Our results indicate that the intensity ratios remain almost unchanged after 20 min for a 30* μm *droplet. To achieve the full equilibration for particles with size range studied, the droplets were equilibrated with water vapor at an ambient relative humidity for about 40 min. After 40 min, the Raman spectra in our experiment remain constant. Yeung et al. (2009) determined the equilibration time of at least 15 min for a 20-30* μm *ammonium sulfate droplet based on the intensity ratio of the water peak (3430* cm^{-1}*) to the sulfate peak (980* cm^{-1}*) obtained by micro-Raman spectroscopy. They also found the equilibration time was longer for the same-sized particles containing organics.*

Related changes in the revised manuscript:

Page 5, Line 11: The sentence *"The particles were equilibrated with water vapor at a given RH for about 40 min."* **is revised to** *"The particles were equilibrated with water vapor at a given RH for about 40 min, during which the intensity ratios of the water peak (3430* cm^{-1}*) to the sulfate peak (980* cm^{-1}*) remained constant.".*

4) Page 5, equation 1: I understand the equation for the growth factor but when the authors create the hygroscopic growth curve is the growth factor an average of many particles or only 1 particle?

Reply: *Multiple particles (three or four) were selected to acquire the Raman spectra through each humidity cycle. Thus, the hygroscopic growth curve is derived from average growth factors of multiple particles. Each measurement for one particle was also repeated at least three times.*

Related changes in the revised manuscript:

Page 5, Line 13: We add the sentence *"Multiple particles (three or four) were selected to acquire the Raman spectra through each humidity cycle."*

Page 5, Line 20: *The sentence "Hygroscopic growth curves are acquired by plotting the Raman growth factor as a function of RH."* **is changed into** *"Hygroscopic growth curves are acquired by plotting the average Raman growth factor of duplicate particles as a function of RH.".*

5) Figure 1a: This is actually a problem I have with all the figures showing Raman spectra. There are just too many peak assignments and it clutters the figures up. Can the authors remove any peak assignments that don't illustrate the point of the figure? For example, in the OA dehydration process the peak at 1689 cm^{-1} is obviously important because that's the peak associated with the dihydrate. That peak should clearly be highlighted. Also can the authors remove any of the Raman spectra that don't highlight something interesting happening? All that's happening is the water peaks are getting smaller. Also, the oxalic acid dihydrate spectrum at the bottom of Figure 1a looks like it is part of the dehydration process. It took me a little bit of time to figure out that the spectrum wasn't part of the dehydration process in the figure. I understand the importance of this spectrum but can it be boxed in or something so the reader doesn't think it is part of the dehydration process?

Reply: *Thanks for the reviewer's suggestion. We remove some minor peak assignments in the figures. To avoid misunderstanding, the oxalic acid dihydrate spectrum at the bottom of Figure 2a is indicated by a black dash line in the modified version.*

Related changes in the revised manuscript:

Figure R1 is the Figure 2 in the modified version. The other figures are also modified according to the reviewer's suggestion.

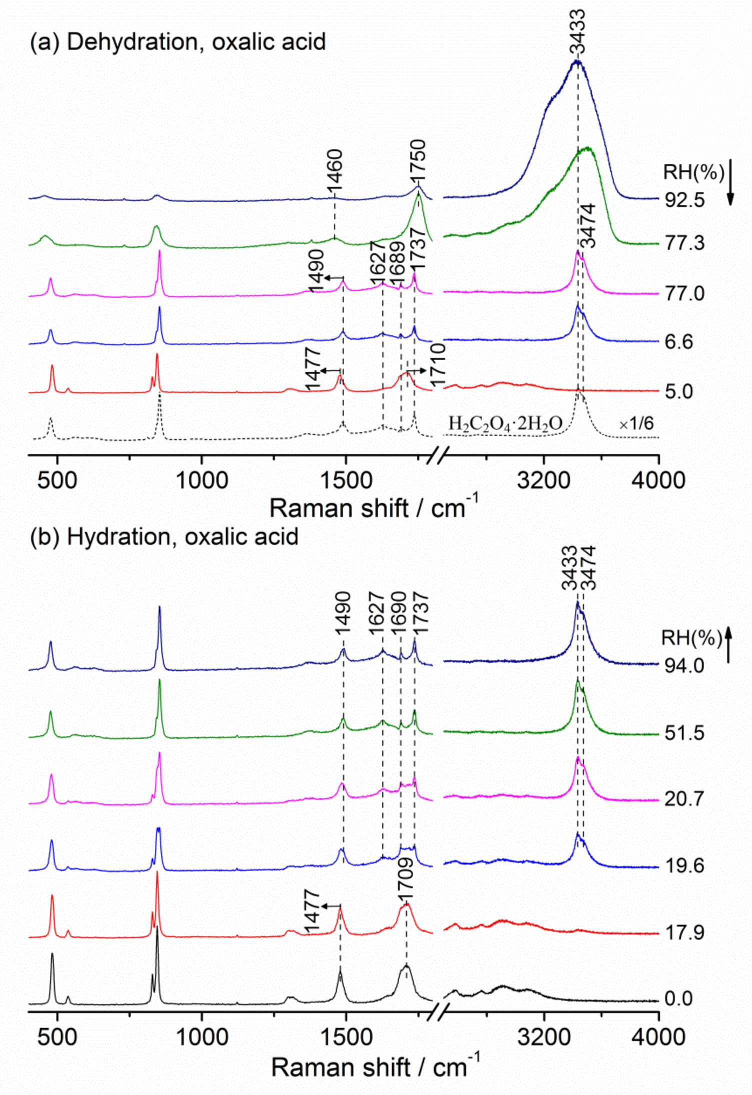

Figure R1. *Raman spectra of oxalic acid droplets during the (a) dehydration process and (b) hydration process. In panel (a), the black dashed line indicates the spectrum of pure $H_2C_2O_4$ $2H_2O$ particles with the peak height of ν(OH) located at 3433 cm^{-1} scaled by a factor of 1/6.*

6) Page 6, line 5: This comment is associated with the comment above. Again, there are too many peak assignments in the text. It clutters the paragraph up. Focus on the most important peaks.

Reply: *According to reviewer's suggestion, we remove some minor peak assignments in the text.*

Related changes in the revised manuscript:

Page 6, line 5: *"As seen in Fig. 1a, the feature bands for OA droplets are observed at 457, 845, 1460, 1636, 1750 and 3433 cm^{-1} at 92.5% RH. At lower RH around 77% (Fig. 1a, magenta line), these bands shift to 477, 855, 1490, 1627, 1737, 3433 and 3474 cm^{-1}, and a new band at 1689* *cm^{-1} occurs, which is entirely consistent with the spectrum of oxalic acid dihydrate (Fig. 1a, black line).”* **is changed into** *“As seen in Fig. 2a, the feature bands for OA droplets are observed at 1460, 1750 and 3433 cm^{-1} at 92.5% RH. At lower RH around 77% (Fig. 2a, magenta line), these bands shift to 1490, 1737, 3433 and 3474 cm^{-1}, and a new band at 1689 cm^{-1} occurs, which is entirely consistent with the spectrum of oxalic acid dihydrate (Fig. 2a, black dashed line).”.* *Similar modifications in other places are also made.*

7) General comment: I think it would be interesting to see pictures of the particles during the hydration and the dehydration process. Do the authors have pictures of the particles they could associate with the Raman spectra? The reason I bring this up is Wise et al. (2012) found that when aqueous sodium chloride particles effloresced at low temperatures the dihydrate formed. The morphology of those particles was different than the morphology of the dehydrated form. I am also wondering if the authors could physically see evidence of NH_4HSO_4 or $NH_4HC_2O_4$ they claim to see spectral evidence of on page 7, line 4. Additionally can the authors see any coatings they argue are present on page 11, line 11?

Reply: *We thank for the reviewer's suggestion. Although we have pictures of the particles associated with the Raman spectra, we could not distinguish the morphology of dry particles between dihydrate form and anhydrous one except for oxalic acid particles (Figure R2). Also, on page 7, line 4, NH_4HSO_4 or $NH_4HC_2O_4$ could not be identified from the solid phase by visual inspection, seen in Figure R3 (b). On page 11, line 11, $NH_4HC_2O_4$ coatings on 3:1 OA/AS particles were formed during the dehydration process, seen in Figure R4.*

Related changes in the revised manuscript:

Some important pictures of the particles during the humidity cycle are supplemented into the modified version.

The picture of 3:1 OA/AS particles with $NH_4HC_2O_4$ coatings formed during the dehydration process is added in the main text.

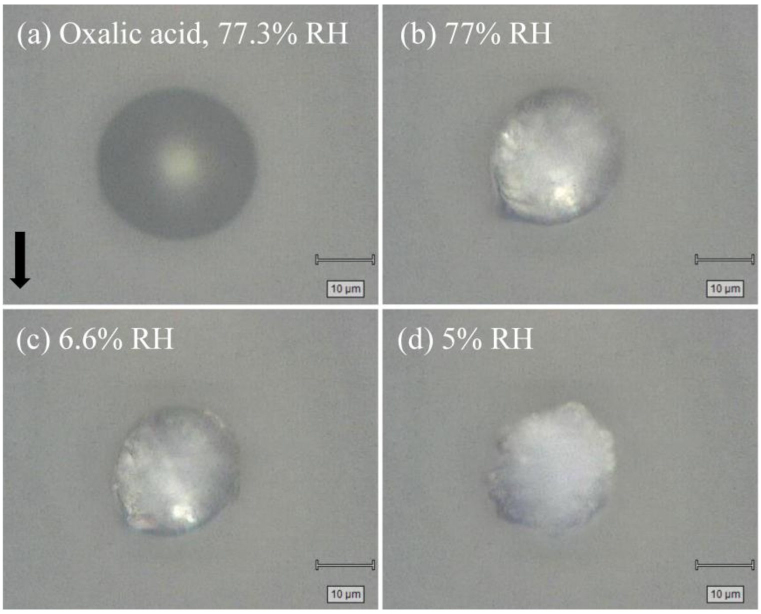

Figure R2. *Optical micrographs of the oxalic acid particle at (a) 77.3% RH, (b) 77% RH, (c) 6.6% RH and (d) 5% RH during the dehydration process, respectively.*

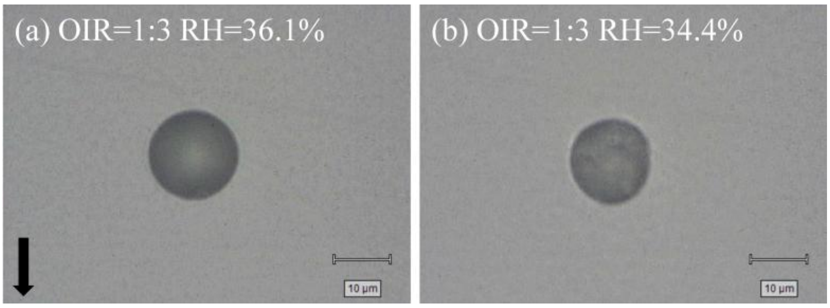

Figure R3. *Optical micrographs of the mixed oxalic acid/ammonium sulfate particle (OIR=1:3) upon dehydration: (a) 36.1% RH and (b) 34.4% RH.*

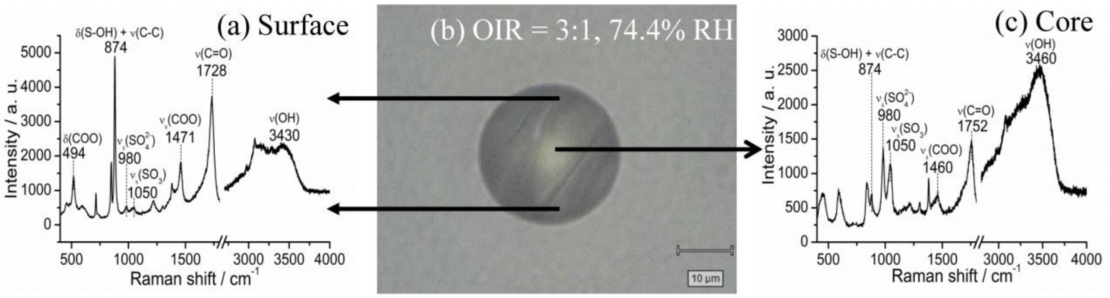

Figure R4. *The spatial distribution of chemicals within mixed oxalic acid/ammonium sulfate (OIR = 3:1) particles at 74.4% RH upon dehydration. (a) Raman spectrum acquired on the surface showing the shell mainly consisting of $NH_4HC_2O_4$. (b) Optical micrograph of a partially effloresced droplet composed 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.*

8) Page 7, line 10: There needs to be an arrow in the equation not an equal sign.

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

9) Page 10, line 5: Again, I think pictures of the particles might help strengthen the case for water uptake prior to deliquescence. The authors should be able to see the particles gain water prior to full deliquescence. I am now wondering if the authors could create hygroscopic growth curves utilizing the physical size of the particles and if that correlates with the Raman growth factors.

Reply: *Page 10, line 5, the picture of mixed OA/AS particles with an OIR of 1:3 prior to full deliquescence is given in Figure R5 (c). It can be seen that the size of 1:3 mixed OA/AS particle at 79.4% RH prior to deliquescence appears to be larger than that after complete efflorescence (Figure R5 (b)), suggesting slight water uptake, as also confirmed by the Raman spectrum. Due to the limitation of instrument, the picture resolution is not high enough to help identify distinct liquid water. In addition, the slight water content may exist in the veins and cavities of the particle.*

Since size-based hygroscopicity is sensitive to particle geometry, physical size of the particles may not reflect the additions of water mass due to morphology effects (Piens et al., 2016). Due to the lack of contact angle data, we cannot create hygroscopic growth curves based on the physical size of the particles. In fact, the spectra method is advantageous for probing the hygroscopic behavior and water content of atmospheric particles with regular or irregular morphologies.

Related changes in the revised manuscript:

Figure R5 and corresponding descriptions have been supplemented in the text.

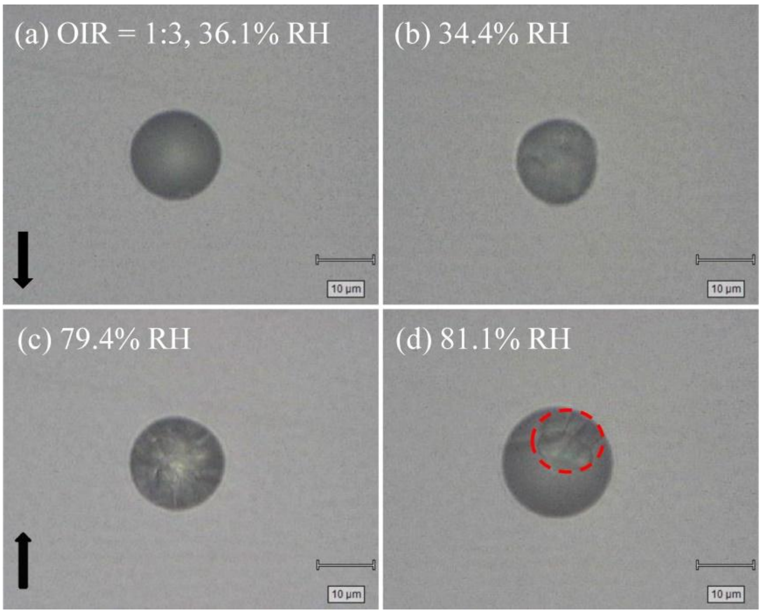

Figure R5. *Optical micrographs of the mixed oxalic acid/ammonium sulfate particle (OIR = 1:3) at phase change points. Dehydration: (a) 36.1% RH and (b) 34.4% RH. Hydration: (c) 79.4% RH and (d) 81.1% RH. In the image (d), the visual solid in aqueous phase is marked with a red dashed circle.*

10) General comment: Can the authors comment on the applicability of the data at temperatures lower than room temperature. Obviously, in the atmosphere the particles are going to experience temperatures much lower than room temperature.

Reply: *Zobrist et al. (2006) investigated the heterogeneous freezing points of the aqueous oxalic acid/ammonium sulfate solutions. They found that oxalic acid precipitated as* $NH_4H_3(C_2O_4)_2\cdot 2H_2O$ *in the mixed solution to act as a heterogeneous ice nucleus. The crystallization of oxalic acid/ammonium sulfate mixed systems at low temperature may show distinct behaviors relative to room temperature. Thus, we cannot give effective suggestions on applicability of our data at low temperatures.*

11) Page 5, line 25: Why did the authors decide to put the mixed hydration Raman spectra in the supplemental section? Surely, this data is important to the findings described in the paper.

Reply: *According to the reviewer's suggestion, we move the mixed hydration Raman spectra in the supplemental section to the text.*

Related changes in the revised manuscript:

P6, L24: *The sentence: "The Raman spectra of mixed OA/AS droplets with OIRs of 1:3, 1:1 and 3:1 at various RHs during the dehydration process are depicted in Fig. 2. The corresponding spectra for hydration process are given in Fig. S2 in the Supplement."* ***is revised to*** *"The Raman spectra of mixed OA/AS droplets with OIRs of 1:3, 1:1 and 3:1 at various RHs during the dehydration and hydration process are depicted in Fig. 3 and 4, respectively."*.

References

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