Author's Response

Response to Referee #1:

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.

While this paper uses sound techniques, cites relevant literature, and is well written, it ultimately fails to address relevant scientific questions within the scope of ACP. The reviewer admits this work presents two new pieces of novel data. First, the ERH of the studied mixtures was dependent on the molar ratio of oxalic acid to ammonium sulfate. Second, aqueous reactions in drying droplets of OA and AS can produce nonhygroscopic products. This novel data, however, is not discussed within the framework of our current knowledge in the literature. Thus, it is not clear to the reviewer how atmospherically relevant or important this work is.

This reviewer suggests two pathways to increase the efficacy of this work. In one pathway, the authors would expand this work especially the discussion section. Currently, the discussion section contains no effort to frame the results of this study into the existing literature. In the second pathway, the authors could to submit to a technical journal that does not emphasize "studies with general implications for atmospheric science." In addition to this very general comment, several general comments and specific comments are outlined below. Technical comments, however, are omitted in this initial review.

Reply: *According to the reviewer's suggestion, we expand relevant discussion on our results within the framework of the existing literature to highlight atmospheric relevance.*

The observed efflorescence relative humidity (ERH) for mixed droplets was dependent on the molar ratio of oxalic acid to ammonium sulfate. The mixed OA/AS droplets with an OIR of 1:3 are observed to effloresce completely at 34.4 ± 2.0% RH relative to ERH of pure AS (44.3 ± 2.5%) or OA (77 ± 2.5%). It can be seen that AS as a major fraction of the particle does not promote the heterogeneous nucleation of OA. Meanwhile, the crystallization of AS is also influenced due to the presence of OA. The similar phenomenon was also observed for malonic acid/ammonium *sulfate mixtures with minor organic content (Braban and Abbatt, 2004; Parsons et al., 2004). Braban and Abbatt (2004) found that the ERH of malonic acid/ammonium sulfate mixed particles was considerably decreased compared to that of pure ammonium sulfate for mass fractions of malonic acid less than 0.3. They concluded that the presence of ammonium sulfate in the supersaturated droplet could exert the extra barrier to nucleation of malonic acid crystals rather than play the role of a heterogeneous nucleation site. As for 1:3 OA/AS mixed droplets, ammonium sulfate may also inhibit the nucleation of oxalic acid at relatively high RH. With decreasing RH, aqueous oxalic acid could enhance the viscosity of the droplet due to hydrogen bond interactions (Mikhailov et al., 2009), thus limiting the nucleation of ammonium sulfate and resulting in a lower ERH with respect to the value of pure AS (Parsons et al., 2004). In the case of mixed OA/AS droplets with an OIR of 1:1 and 3:1, the* $NH_4HC_2O_4$ *formed at ~75% RH upon dehydration likely acts as a heterogeneous nucleus for crystallization of other components, which increases full efflorescence point of mixed particles. One study indicated that Aldrich humic acid sodium salt (NaHA) could also promote the ERH of ammonium sulfate (Badger et al., 2006). Similar to oxalic acid, succinic acid and adipic acid have a high deliquescence point and low solubility. However, it has been found that the efflorescence point of ammonium sulfate in mixed particles is not elevated even when the content of succinic acid or adipic acid is not less than 50% by mass or mole fractions (Ling and Chan, 2008; Yeung et al., 2009; Laskina et al., 2015). In contrast to ammonium sulfate particles containing succinic acid or adipic acid, our results suggest that the addition of oxalic acid into ammonium sulfate droplets may trigger partial and full crystallisation of aerosols at relatively higher RH upon dehydration due to* $NH_4HC_2O_4$ *product acting as an effective nucleus.*

During the deliquescence process, the OA/AS mixed particles with an OIR of 1:3 and 1:1 exhibit a slightly lower deliquescence point than that of pure ammonium sulfate, consistent with previous observations of effects of crystalline oxalic acid on deliquescence transition of ammonium sulfate (Brooks et al., 2002; Wise et al., 2003; Jing et al., 2016). It should be noted that prior literature result also showed that continuous or smooth water uptake from low RH was observed for particles composed of AS and OA with a mass ratio of 1.5:1 due to the fact that after drying processing oxalic acid existing in an amorphous or liquid-like state prevented nucleation of ammonium sulfate even under dry conditions (Prenni et al., 2003). In the present study, water *uptake by the OA/AS mixed particles at high RH upon hydration is dramatically lower than that upon dehydration and significantly decreased with elevated OA content. This phenomenon distinguishes from hygroscopic characteristic of typical water-soluble mixtures in literatures. It has been found that hydration growth curve and dehydration growth curve are typically merged above deliquescence point for mixed systems containing inorganic salts and water-soluble organic compounds (Choi and Chan, 2002; Chan and Chan, 2003; Gysel et al., 2004; Clegg and Seinfeld, 2006; Sjogren et al., 2007; Pope et al., 2010; Ghorai et al., 2014; Estillore et al., 2016). In this study, Raman spectra and micrograph (Figure R2 (d)) suggest the presence of solid* $NH_4HC_2O_4$ *and residual solid OA at high RH should be responsible for the decreased water uptake during the hydration process. In contrast, Prenni et al. (2003) reported that the hygroscopic growth of OA/AS mixed particles remained unchanged at 90% RH with OA mass fraction ranging from 0.01 to 0.4. In addition, they also found that water uptake after deliquescence was well described by the model method assuming complete dissolution of OA in aqueous phase as well as no interactions between OA and AS, which was also observed by Jing et al. (2016) using the HTDMA. The previous HTDMA studies for OA/AS mixed particles indicate no composition change and no specific interactions existing between OA and AS (Prenni et al., 2003; Jing et al., 2016). However, it should be noted that the HTDMA studies did not perform measurements for the dehydration process such that aerosols underwent rapid drying on the time scale of seconds, i.e., the total residence time for transformation of droplets into dry particles in the drying section of HTDMA is typically tens of seconds (Prenni et al., 2003; Jing et al., 2016), much shorter than that (10 ~ 12 h) in our study. In the HTDMA experiments, the combination of faster drying and smaller particles with submicron size implies that the aqueous phase obtained higher supersaturations than in our present study (Rosenoern et al., 2008), leading to less dissociation of oxalic acid and thus less* $HC_2O_4^-$ *formed in the droplets as well as the inhibited formation of* $NH_4HC_2O_4$*. The fast evaporation of water from the surface of an aqueous droplet upon rapid drying could result in a higher surface concentration of solutes than the slow drying process (Treuel et al., 2011). The higher surface concentration of oxalic acid corresponds to less formation and hence decreased supersaturation of* $HC_2O_4^-$*. Due to the dependence of nucleation rate on the extent of supersaturation, it can be expected that the nucleation of* $NH_4HC_2O_4$ *is suppressed within OA/AS mixed droplets undergoing rapid drying.*

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.*

Related changes in the revised manuscript:

Page 11 line 18-29: The sentences from line 18 to 29 are replaced by *"The observed efflorescence relative humidity (ERH) for mixed droplets was dependent on the molar ratio of oxalic acid to ammonium sulfate. The mixed OA/AS droplets with an OIR of 1:3 are observed to effloresce completely at 34.4 ± 2.0% RH relative to ERH of pure AS (44.3 ± 2.5%) or OA (77 ± 2.5%). It can be seen that AS as a major fraction of the particle does not promote the heterogeneous nucleation of OA. Meanwhile, the crystallization of AS is also influenced due to the presence of OA. The similar phenomenon was also observed for malonic acid/ammonium sulfate mixtures with minor organic content (Braban and Abbatt, 2004; Parsons et al., 2004). Braban and Abbatt (2004) found that the ERH of malonic acid/ammonium sulfate mixed particles was considerably decreased compared to that of pure ammonium sulfate for mass fractions of malonic acid less than 0.3. They concluded that the presence of ammonium sulfate in the supersaturated droplet could exert the extra barrier to nucleation of malonic acid crystals rather than play the role of a heterogeneous nucleation site. As for 1:3 OA/AS mixed droplets, ammonium sulfate may also inhibit the nucleation of oxalic acid at relatively high RH. With decreasing RH, aqueous oxalic acid could enhance the viscosity of the droplet due to hydrogen bond interactions (Mikhailov et al., 2009), thus limiting the nucleation of ammonium sulfate and resulting in a lower ERH with respect to the value of pure AS (Parsons et al., 2004). In the case of mixed OA/AS droplets with an OIR of 1:1 and 3:1, the* $NH_4HC_2O_4$ *formed at ~75% RH upon dehydration likely acts as a heterogeneous nucleus for crystallization of other components, which increases full efflorescence point of mixed particles. One study indicated that Aldrich humic acid sodium salt (NaHA) could also promote the ERH of ammonium sulfate (Badger et al., 2006). Similar to oxalic acid, succinic acid and adipic acid have a high deliquescence point and low solubility. However, it has been found that the efflorescence point of ammonium sulfate in mixed particles is not elevated even when the content of succinic acid or adipic acid is not less than 50% by mass or mole fractions (Ling and Chan, 2008; Yeung et al., 2009; Laskina et al., 2015). In contrast to ammonium sulfate particles containing succinic acid or adipic acid, our results* *suggest that the addition of oxalic acid into ammonium sulfate droplets may trigger partial and full crystallisation of aerosols at relatively higher RH upon dehydration due to* $NH_4HC_2O_4$ *product acting as an effective nucleus.*

During the deliquescence process, the OA/AS mixed particles with an OIR of 1:3 and 1:1 exhibit a slightly lower deliquescence point than that of pure ammonium sulfate, consistent with previous observations of effects of crystalline oxalic acid on deliquescence transition of ammonium sulfate (Brooks et al., 2002; Wise et al., 2003; Jing et al., 2016). It should be noted that prior literature result also showed that continuous or smooth water uptake from low RH was observed for particles composed of AS and OA with a mass ratio of 1.5:1 due to the fact that after drying processing oxalic acid existing in an amorphous or liquid-like state prevented nucleation of ammonium sulfate even under dry conditions (Prenni et al., 2003). In the present study, water uptake by the OA/AS mixed particles at high RH upon hydration is dramatically lower than that upon dehydration and significantly decreased with elevated OA content. This phenomenon distinguishes from hygroscopic characteristic of typical water-soluble mixtures in literatures. It has been found that hydration growth curve and dehydration growth curve are typically merged above deliquescence point for mixed systems containing inorganic salts and water-soluble organic compounds (Choi and Chan, 2002; Chan and Chan, 2003; Gysel et al., 2004; Clegg and Seinfeld, 2006; Sjogren et al., 2007; Pope et al., 2010; Ghorai et al., 2014; Estillore et al., 2016). In this study, Raman spectra and micrograph suggest the presence of solid $NH_4HC_2O_4$ *and residual solid OA at high RH should be responsible for the decreased water uptake during the hydration process. In contrast, Prenni et al. (2003) reported that the hygroscopic growth of OA/AS mixed particles remained unchanged at 90% RH with OA mass fraction ranging from 0.01 to 0.4. In addition, they also found that water uptake after deliquescence was well described by the model method assuming complete dissolution of OA in aqueous phase as well as no interactions between OA and AS, which was also observed by Jing et al. (2016) using the HTDMA. The previous HTDMA studies for OA/AS mixed particles indicate no composition change and no specific interactions existing between OA and AS (Prenni et al., 2003; Jing et al., 2016). However, it should be noted that the HTDMA studies did not perform measurements for the dehydration process such that aerosols underwent rapid drying on the time scale of seconds, i.e., the total residence time for transformation of droplets into dry particles in the drying section* *of HTDMA is typically tens of seconds (Prenni et al., 2003; Jing et al., 2016), much shorter than that (10 ~ 12 h) in our study. In the HTDMA experiments, the combination of faster drying and smaller particles with submicron size implies that the aqueous phase obtained higher supersaturations than in our present study (Rosenoern et al., 2008), leading to less dissociation of oxalic acid and thus less* $HC_2O_4^-$ *formed in the droplets as well as the inhibited formation of* $NH_4HC_2O_4$*. The fast evaporation of water from the surface of an aqueous droplet upon rapid drying could result in a higher surface concentration of solutes than the slow drying process (Treuel et al., 2011). The higher surface concentration of oxalic acid corresponds to less formation and hence decreased supersaturation of* $HC_2O_4^-$*. Due to the dependence of nucleation rate on the extent of supersaturation, it can be expected that the nucleation of* $NH_4HC_2O_4$ *is suppressed within OA/AS mixed droplets undergoing rapid drying.".*

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.".*

General Comments:

Page 5, line 15: In general, the reviewer feels that the authors did not take advantage of the microscope in their experiment. Do the authors know the contact angle of water on their Raman substrate? If so, the physical growth factor of a spherically equivalent drop could be determined; this measurement would greatly increase confidence in the spectroscopic growth factor measurement. A physical growth factor measurement could also help explain the low-RH results in Figure 4b, where it is unclear if OA shrinks when it transitions from its dihydrate form to it anhydrous form.

Reply: *We thank the reviewer for the suggestion. We have no contact angle data for droplets on our substrate. In fact, the spectra methods have been proved to be sensitive and reliable for study of aerosol hygroscopicity including phase transition and water uptake (Cziczo et al., 1997; Cziczo and Abbatt, 2000; Braban et al., 2003; Brooks et al., 2003; Braban and Abbatt, 2004;*

Garland et al., 2005; Badger et al., 2006; Liu et al., 2008a; Liu et al., 2008b; Yeung et al., 2009; Minambres et al., 2010; Yeung and Chan, 2010; Ghorai et al., 2014; Laskina et al., 2015; Zawadowicz et al., 2015).

As shown in Figure R1, the size of an effloresced oxalic acid particle remains almost unchanged when oxalic acid dihydrate is transformed into anhydrous form. However, the corresponding Raman spectra indicate the changes in crystal water of OA particles. The other studies using infrared spectrometer and vapor sorption analyzer also observed the transition between anhydrous oxalic acid and dihydrate based on water mass changes in solid OA particles (Braban et al., 2003; Ma et al., 2013). Since size-based hygroscopicity is sensitive to particle geometry, the size growth factor of particles without a compact structure may not reflect the actual changes in water mass due to morphology effects (Piens et al., 2016). It seems that the structure of anhydrous OA particle is not as compact as that of dihydrate, seen in Figure R1. Thus, the loss of crystal water results in no obvious change in particle size. Overall, the spectra method is advantageous for probing the hygroscopic behavior of atmospheric particles with irregular morphologies.

Related changes included in the revised manuscript:

Figure R1 is supplemented in the main text. ***Page 9, Line 5:*** *"As shown in Fig. 4b, the measured ERH of OA is 77 ± 2.5% RH"* ***is revised to*** *"As shown in Fig. 6b and 8, the measured ERH of OA is 77 ± 2.5% RH".* ***Page 9, Line 26: We add*** *"It seems that the structure of anhydrous OA particle is not as compact as that of dihydrate, seen in Fig. 8. Thus, the loss of crystal water results in no obvious change in particle size.".*

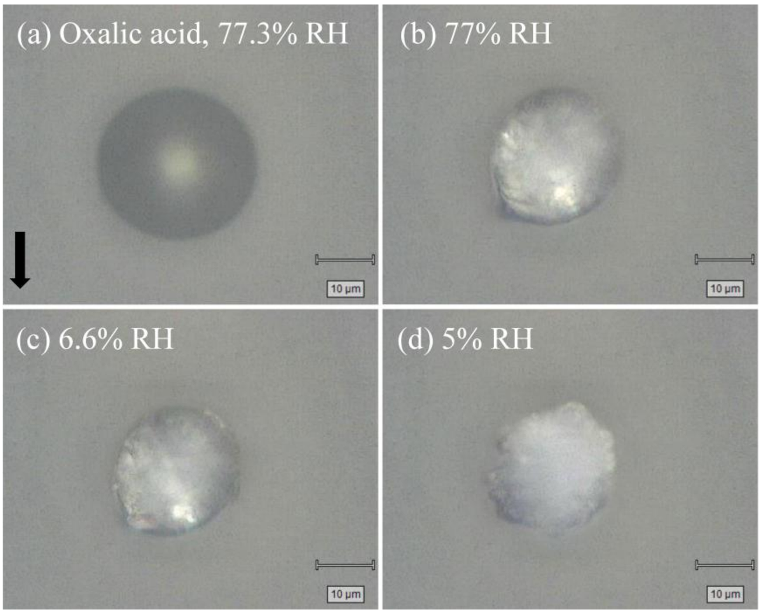

Figure R1. *Optical micrographs of the oxalic acid particle at (a) 77.3% RH, (b) 77% RH, (c) 6.6% RH and (d) 5% RH during the dehydration process, respectively.*

Page 7, Line 1: Do the authors have an image of the effloresced particle to affirm that the $\nu(SO_4^{2-})$ peak shift corresponds with a hygroscopic phase change?

Reply: *As seen in Figure R2, the crystallization of OA/AS particles (OIR = 1:3) occurs at 34.4% RH, corresponding with the Raman peak shift of $\nu_s(SO_4^{2-})$ from 979 cm^{-1} to 974 cm^{-1} at the same RH. The previous studies have also applied the abrupt shift in characteristic peak position to indicate phase transition of ammonium sulfate during the hygroscopic process (Braban and Abbatt, 2004; Ling and Chan, 2008; Yeung et al., 2009; Yeung and Chan, 2010).*

Related changes in the revised manuscript:

Figure R2 is supplemented in the main text. ***Page 7, Line 1:*** *The sentence "At 34.4% RH, the shift of $\nu_s(SO_4^{2-})$ peak from 979 cm^{-1} to 974 cm^{-1} indicates the crystallization of AS."* ***is revised to*** *"At 34.4% RH, the shift of $\nu_s(SO_4^{2-})$ peak from 979 cm^{-1} to 974 cm^{-1} indicates the crystallization of AS, as also seen in Fig. 10b.".* ***Page 8, Line 6: We add*** *"The previous studies have also applied the abrupt shift in characteristic peak position to indicate phase transition of ammonium sulfate during the hygroscopic process (Braban and Abbatt, 2004; Ling and Chan, 2008; Yeung et al., 2009).".*

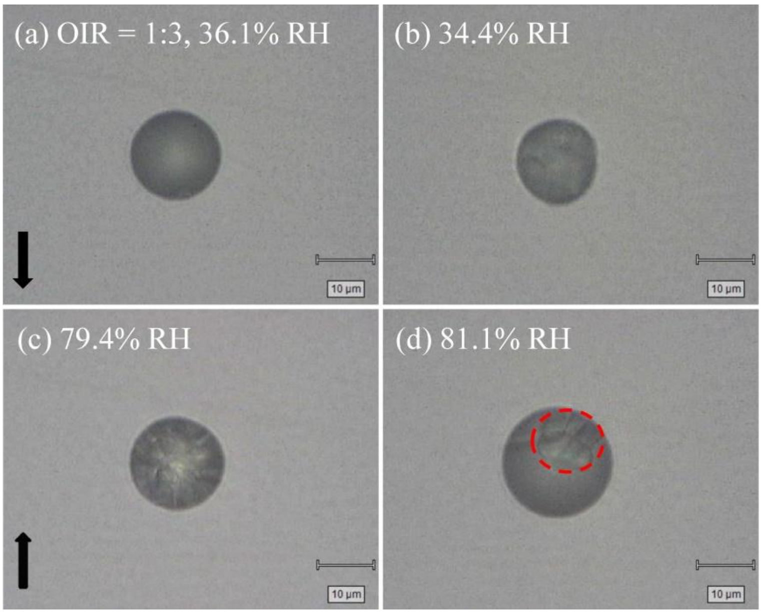

Figure R2. *Optical micrographs of mixed oxalic acid/ammonium sulfate particles (OIR = 1:3) at phase change points. Dehydration: (a) 36.1% RH and (b) 34.4% RH. Hydration: (c) 79.4% RH and (d) 81.1% RH. In the image (d), the visual solid in aqueous phase is marked with a red dashed circle.*

Page 8, Line 2: Since multiple components are crystallizing, can the authors take advantage of the high spatial resolution of Raman microscopy to tell if there is a spatial distribution of chemicals? These results would explain if components are efflorescing in specific order and, consequently, if effloresced components are heterogeneously nucleating other components.

Reply: *We appreciate the reviewer's suggestion. Figure R3 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 heterogeneous nucleus, leading to the crystallization of oxalic acid dihydrate,* $(NH_4)_2SO_4$ *and* NH_4HSO_4 *in the inner phase.*

Related changes in the revised manuscript:

Figure R3 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.".*

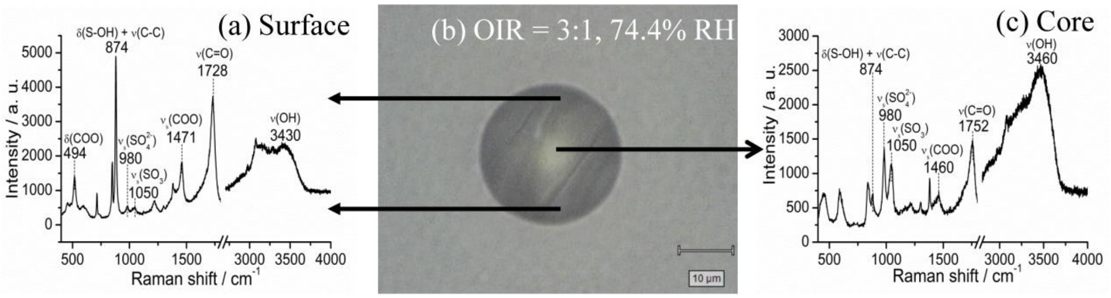

Figure R3. *The spatial distribution of chemicals within the mixed oxalic acid/ammonium sulfate (OIR = 3:1) particle at 74.4% RH upon dehydration. (a) Raman spectrum acquired on the surface showing the shell mainly consisting of* $NH_4HC_2O_4$. *(b) Optical micrograph of a partially effloresced droplet 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.*

Specific Comments:

Page 3, Line 16: Is there a reference for the reactions of organic acids with mineral salts, chloride salts, nitrate salts, and ammonium and amines?

Reply: *We add several references for the reactions of organic acids with mineral salts, chloride* *salts, nitrate salts, and ammonium and amines.*

Related changes in the revised manuscript:

Page 3, Line 13: *The sentence "Field measurements have observed the formation of low-volatility organic salts in atmospheric particles due to the reactions of organic acids with mineral salts, chloride salts, nitrate salts, ammonium and amines."* **is revised to** *"Field measurements have observed the formation of low-volatility organic salts in atmospheric particles due to the reactions of organic acids with mineral salts, chloride salts, nitrate salts, ammonium and amines (Sullivan and Prather, 2007; Laskin et al., 2012; Wang and Laskin, 2014; Smith et al., 2010)."*

Page 4, Line 21: What was the dry diameter of these particles?

Reply: *The dry diameter of these particles after efflorescence ranged from 10 to 20 μm.*

Related changes in the revised manuscript:

Page 4, Line 21: We add the sentence *"The dry size of these particles after efflorescence ranged from 10 to 20 μm.".*

Page 5, Line 8: What is the numerical aperture of the 50x objective?

Reply: *The numerical aperture of the 50× objective is 0.75.*

Related changes in the revised manuscript:

Page 5, Line 8: *The sentence "Then, spectroscopic measurements were made on droplets observed by using the Leica DMLM microscope with a 50× objective lens."* **is revised to** *"Then, spectroscopic measurements were made on droplets observed by using the Leica DMLM microscope with a 50× objective (0.75 numerical aperture)."*

Page 5, Line 12: Why was 40 minutes chosen for the equilibration time? Do the authors have spectral evidence of this equilibration (perhaps from the area under the OH water peak?)

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.".*

Page 7, Line 3: It is unclear from the text if 874 cm^{-1} corresponds to only HSO_4^- or both HSO_4^- and $HC_2O_4^-$. The reviewer suggests this be clarified.

Reply: *The band centred at 874 cm^{-1} is contributed by both HSO_4^- and $HC_2O_4^-$. Dawson et al. (1986) reported the absorption of vibrational mode (δ(S-OH)) of HSO_4^- ion from NH_4HSO_4 occurred at 869 cm^{-1}. The absorption of ν(C-C) of $HC_2O_4^-$ in crystal was observed at 879 cm^{-1} by Shippey (1979). Thus, the peak centred at 874 cm^{-1} corresponds to both HSO_4^- and $HC_2O_4^-$.*

Related changes in the revised manuscript:

Page 7, Line 3: *The sentence "A new band centered at 874 cm^{-1} corresponds to the vibrational mode (δ(S-OH)) of HSO_4^- ion from NH_4HSO_4 and the $HC_2O_4^-$ ion vibrating (Irish and Chen, 1970; Dawson et al., 1986; Villepin and Novak, 1971; Shippey, 1979),"* **is revised to** *"A new band centered at 874 cm^{-1} corresponds to combination bands of the vibrational mode (δ(S-OH)) of HSO_4^- ion from NH_4HSO_4 (Dawson et al., 1986) and $HC_2O_4^-$ ion vibrating (Shippey, 1979)".*

Page 9, Line 11: The statement "likely due to drop size, substrate, and experimental methods" is vague. Can the authors be more specific about the cause of OA's high ERH in this study?

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.".*

Page 9, Line 16: Do the authors believe that 77% is the true ERH of OA, or that heterogeneous nucleation is occurring? If the latter, the reviewer suggests that the authors refrain from using the phrase "ERH of OA" hereafter.

Reply: *Yes, we determine that 77% is the true ERH of pure OA from the Raman spectra. As stated in the initial manuscript, the Raman spectra indicated OA droplet was converted into oxalic acid dihydrate at 77% RH during the dehydration process. In addition, the images of OA particles upon dehydration also show the full efflorescence of OA occurs at 77% RH, seen in Figure R1.*

Related changes in the revised manuscript:

Figure R1 is supplemented in the main text. ***Page 9, Line 5:*** *"As shown in Fig. 4b, the measured ERH of OA is 77 ±2.5% RH"* ***is revised to*** *"As shown in Fig. 6b and 8, the measured ERH of OA is 77 ±2.5% RH".*

Page 12, Line 8: Do the "rapidly-dried" particles look physically different than the "regularly-dried" particles? Furthermore, do the rapidly-dried particles have a different ERH? This could help discern the underlying mechanism of efflorescence.

Reply: *As shown in Figure R4, the morphology of rapidly-dried OA/AS particles with equal molar ratio could not be obviously distinguished from that of regularly-dried particles. However, the spectra evidence has shown significant compositional difference between the two kinds of particles. We observed one-step efflorescence of rapidly-dried particles (1:1, molar ratio) occurred at 47% ± 2.5% RH, compared to the two-step efflorescence of slowly-dried particles occurring at 75% and 44.3% RH, respectively.*

Related changes in the revised manuscript:

Page 12, line 2: We add "*We observed one-step efflorescence of rapidly-dried particles (1:1, molar ratio) occurred at 47% ±2.5% RH, compared to the two-step efflorescence of slowly-dried particles occurring at 75% and 44.3% RH, respectively.* ***".***

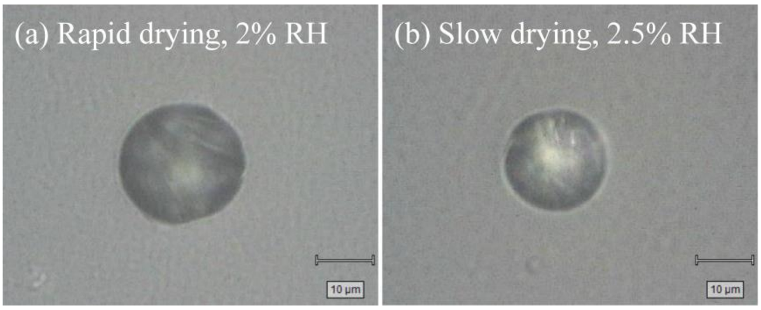

Figure R4. *Optical micrographs of equal molar mixed oxalic acid/ammonium sulfate particles after (a) rapid drying at 2% RH and (b) slow drying at 2.5% RH, respectively.*

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