

1 Hygroscopic behavior and chemical composition evolution of 2 internally mixed aerosols composed of oxalic acid and ammonium 3 sulfate

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16 **Abstract**

17 Although water uptake of aerosol particles plays an important role in the atmospheric environment,
18 the effects of interactions between components on chemical composition and hygroscopicity of
19 particles are still not well constrained. The hygroscopic properties and phase transformation of
20 oxalic acid (OA) and mixed particles composed of ammonium sulfate (AS) and OA with different
21 organic to inorganic molar ratios (OIRs) have been investigated by using confocal Raman
22 spectroscopy. It is found that OA droplets first crystallize to form oxalic acid dihydrate at 71%
23 relative humidity (RH), and further lose crystalline water to convert into anhydrous oxalic acid
24 around 5% RH during the dehydration process. The deliquescence and efflorescence point for AS is
25 determined to be $80.1 \pm 1.5\%$ RH and $44.3 \pm 2.5\%$ RH, respectively. The observed efflorescence
26 relative humidity (ERH) for mixed OA/AS droplets with OIRs of 1:3, 1:1 and 3:1 is $34.4 \pm 2.0\%$
27 RH, $44.3 \pm 2.5\%$ RH and $64.4 \pm 3.0\%$ RH, respectively, indicating the elevated OA content appears
28 to favor the crystallization of mixed systems at higher RH. However, the deliquescence relative
29 humidity (DRH) of AS in mixed OA/AS particles with an OIR of 1:3 and 1:1 is observed to occur at
30 $81.1 \pm 1.5\%$ RH and $77 \pm 1.0\%$ RH, respectively. The Raman spectra of mixed OA/AS droplets
31 indicate the formation of ammonium hydrogen oxalate ($\text{NH}_4\text{HC}_2\text{O}_4$) and ammonium hydrogen

1 sulfate (NH_4HSO_4) from interactions between OA and AS in aerosols during the dehydration
2 process in the time scale of hours, which considerably influence the subsequent deliquescence
3 behavior of internally mixed particles with different OIRs. The mixed OA/AS particles with an OIR
4 of 3:1 exhibit no deliquescence transition over the RH range studied due to the considerable
5 transformation of $(\text{NH}_4)_2\text{SO}_4$ into $\text{NH}_4\text{HC}_2\text{O}_4$ with a high DRH. Although the hygroscopic growth
6 of mixed OA/AS droplets is comparable to that of AS or OA at high RH during the dehydration
7 process, Raman growth factors of mixed particles after deliquescence are substantially lower than
8 those of mixed OA/AS droplets during the efflorescence process and further decrease with elevated
9 OA content. The discrepancies for Raman growth factors of mixed OA/AS particles between the
10 dehydration and hydration process at high RH can be attributed to the significant formation of
11 $\text{NH}_4\text{HC}_2\text{O}_4$ and residual OA, which remain solid at high RH and thus result in less water uptake of
12 mixed particles. These findings improve the understanding of the role of reactions between
13 dicarboxylic acid and inorganic salt in the chemical and physical properties of aerosol particles, and
14 might have important implications for atmospheric chemistry.

15 **1 Introduction**

16 Atmospheric aerosols have vital impacts on the Earth's climate directly by scattering, reflecting and
17 absorbing solar radiation, and indirectly by influencing formation of clouds and precipitation (Tang
18 and Munkelwitz, 1994b; Jacobson et al., 2000; Penner et al., 2001; Pöschl, 2005; Martin, 2000; Von
19 Schneidemesser et al., 2015). Direct and indirect effects depend on the chemical and physical
20 properties of atmospheric aerosols, including size, structure, hygroscopicity and chemical
21 composition. Field observations indicate that aerosol particles are generally internal mixtures of
22 inorganic and organic compounds in the atmosphere (Saxena et al., 1995; Murphy et al., 1998;
23 Murphy et al., 2006; Pratt and Prather, 2010). Ammonium sulfate (AS) is one of the most abundant
24 inorganic constituents in the atmosphere, hygroscopicity of which has been widely investigated (Liu
25 et al., 2008; Cziczo et al., 1997; Laskina et al., 2015).

26 Oxalic acid (OA) is ubiquitous and has been identified as the dominant dicarboxylic acid in urban
27 and remote atmospheric aerosols (Chebbi and Carlier, 1996; Kanakidou et al., 2004; Yang and Yu,
28 2008; Wang et al., 2012; Kawamura and Bikkina, 2016). Previous studies have focused on
29 deliquescence behavior of pure OA (Peng et al., 2001; Braban et al., 2003; Miñambres et al., 2013;
30 Ma et al., 2013a; Jing et al., 2016). It was found that due to its high deliquescence point OA

1 exhibited no deliquescence transition or hygroscopic growth within relative humidity (RH) range
2 studied by an electrodynamic balance (EDB) (Peng et al., 2001), vapor sorption analyzer (Ma et al.,
3 2013a) or hygroscopicity tandem differential mobility analyzer (HTDMA) (Jing et al., 2016).
4 Braban et al. (2003) reported that OA could deliquesce at 98% RH using aerosol flow tube Fourier
5 transform infrared spectroscopy (AFT-FTIR). However, the study on the efflorescence behavior of
6 OA during the dehydration process remains limited (Peng et al., 2001; Mikhailov et al., 2009). Peng
7 et al. (2001) observed the efflorescence transition of OA using EDB while Mikhailov et al. (2009)
8 reported continuous hygroscopic growth of OA during both hydration and dehydration process
9 using the HTDMA.

10 The dicarboxylic acids can affect properties of internally mixed aerosol particles such as
11 hygroscopicity, phase transition, solubility and chemical reactivity (Lightstone et al., 2000; Brooks
12 et al., 2002; Sjogren et al., 2007; Pradeep Kumar et al., 2003; Treuel et al., 2011; Laskin et al., 2012;
13 Drozd et al., 2014; Peng et al., 2016; Jing et al., 2016; Li et al., 2017; Jing et al., 2017). Field
14 measurements have observed the formation of low-volatility organic salts in atmospheric particles
15 due to the reactions of organic acids with mineral salts, chloride salts, nitrate salts, ammonium and
16 amines (Sullivan and Prather, 2007; Laskin et al., 2012; Wang and Laskin, 2014; Smith et al., 2010).
17 The organic salts formed typically have varying hygroscopicity compared to the corresponding
18 organic acids. Thus, these drastic changes in aerosol composition have potential impacts on the
19 water uptake and related physicochemical properties of particles. The effects of OA on
20 deliquescence behaviors of AS have been extensively investigated (Brooks et al., 2002; Prenni et al.,
21 2003; Wise et al., 2003; Miñambres et al., 2013; Jing et al., 2016). The majority of studies found
22 that the presence of OA had no obvious impacts on the deliquescence process of OA/AS mixtures
23 with minor OA content (Brooks et al., 2002; Prenni et al., 2003; Wise et al., 2003). To our
24 knowledge, there is still a lack of studies on the efflorescence process of OA/AS mixed systems. In
25 fact, the efflorescence behavior is a critical hygroscopic characteristic of atmospheric aerosols,
26 which may favor specific chemical interactions between components within the supersaturated
27 droplets. For example, previous studies have found that the chloride depletion could occur in the
28 NaCl/dicarboxylic acids mixed aerosols during the dehydration or efflorescence process, which led
29 to the formation of organic salts and in turn affected subsequent deliquescence behaviors of aerosols
30 (Laskin et al., 2012; Ghorai et al., 2014). Oxalic acid has been found to react with both mono- and

1 di-valent cations to form low volatility and solubility compounds (Drozd et al., 2014). Miñambres
2 et al. (2013) proposed that OA might react with AS to form ammonium hydrogen oxalate and
3 ammonium hydrogen sulfate within OA/AS solution. Due to the lack of available thermodynamic
4 data, the aerosol thermodynamic models typically assume that upon dehydration dicarboxylic acid
5 could only form organic solid without the organic salt in the inorganic electrolyte/dicarboxylic acid
6 system (Clegg and Seinfeld, 2006; Amundson et al., 2007). Thus, the incorporation of organic salts
7 formed from interactions between inorganic salts and organic acids is crucial in the modeling of
8 hygroscopic properties of mixed organic/inorganic particles. It merits further investigation on the
9 interactions between OA and AS and related influence on the water uptake behaviors of aerosols
10 during the dehydration and hydration processes.

11 Raman spectroscopy is a powerful technique to characterize aerosol compositions, water contents,
12 molecular interactions, and particle phases especially for the efflorescence process (Ma and He,
13 2012; Laskina et al., 2013; Zhou et al., 2014; Wang et al., 2015). In this study, the phase
14 transformations and hygroscopic properties of OA and mixed OA/AS droplets with varying OA
15 content were studied by confocal Raman spectroscopy in conjunction with optical microscopy.
16 Furthermore, we explored the effects of reactions between OA and AS on the chemical
17 compositions and hygroscopic properties of mixed OA/AS droplets.

18 **2 Experimental section**

19 **2.1 Sample preparation**

20 Ammonium sulfate (AS) and oxalic acid dihydrate were purchased from Sinopharm Chemical
21 Reagent Co. Ltd. (99.0% purity) and used without further purification. The 0.5 mol L⁻¹ pure
22 component AS and OA solutions were prepared by dissolving AS and oxalic acid dihydrate in
23 ultrapure water (18.2 MΩ·cm, Barnstead Easypure II), respectively. The mixed OA/AS solutions
24 with different organic to inorganic molar ratios (OIRs) of 1:3, 1:1 and 3:1 were obtained by
25 dissolving a designated amount of OA into AS solutions. The sample solution was discharged from
26 a syringe. Then, residual solution in the syringe was pushed rapidly to generate aerosol droplets
27 spraying onto a polytetrafluorethylene (PTFE) substrate fixed to the bottom of the sample cell. Then,
28 the sample cell was promptly sealed by a transparent polyethylene film. The RH in the sample cell
29 was regulated by nitrogen streams consisting of a mixture of water-saturated N₂ and dry N₂ at
30 controlled flow rates. At ~ 95% RH, the droplets with a diameter of 30 ~ 40 microns detected by an

1 optical microscope (50× objective, 0.75 numerical aperture) were selected to acquire the Raman
2 spectra. The dry size of these particles after efflorescence ranged from 10 to 20 μm. The RH and
3 temperature of the outflow from the sample cell was measured by a humidity/temperature meter
4 (Centertek Center 313) with an accuracy of ±2.5% below 90% RH and ±0.7 K placed near the exit
5 of the sample cell. The temperature accuracy of 0.7 K could result in uncertainty of 4% at RH of
6 95%. The temperature of the sample was maintained at 297 ± 0.5 K by using an automatic
7 thermostat.

8 **2.2 Apparatus and conditions for the measurements**

9 The experimental setup used in this study was described in detail in previous work (Wang et al.,
10 2008; Dong et al., 2009; Zhou et al., 2014). Briefly, the Renishaw InVia confocal Raman
11 spectrometer equipped with a Leica DMLM microscope was used to acquire the Raman spectra. An
12 argon-ion laser (wavelength 514.5 nm, model Stellar-REN, Modu-Laser) was used as an excitation
13 source with an output power of 20 mW, and a 514.5 nm notch filter was adopted to remove the
14 strong Rayleigh scattering. An 1800 g mm^{-1} grating was used to obtain the spectra in the range of
15 $200\text{-}4000 \text{ cm}^{-1}$ with a resolution of about 1 cm^{-1} . Spectral calibration was made using the 520 ± 0.05
16 cm^{-1} Stokes shift of silicon band before performing measurements. Then, spectroscopic
17 measurements were made on droplets observed by using the Leica DMLM microscope with a 50×
18 objective lens (0.75 numerical aperture). The spectra were obtained with three spectral scans, and
19 each time with an accumulation time of 10 s. The sample droplets were injected onto the substrate
20 at high RH (~ 95% RH). Subsequently, the RH was decreased stepwise for a slow dehydration
21 process, and then increased stepwise from $\text{RH} < 3\%$ to high RH for a hydration process. The
22 decrease rate was typically 5-6 RH/40 min, and the rate remained 2-3 RH/40 min near the phase
23 transition. The RH was decreased continuously in a few minutes for a rapid dehydration process.
24 The particles were equilibrated with water vapor at a given RH for about 40 min, during which the
25 intensity ratios of the water peak (3430 cm^{-1}) to the sulfate peak (980 cm^{-1}) remained constant. The
26 spectra of AS, OA and mixed OA/AS droplets were monitored and measured through a full
27 humidity cycle. Multiple particles (three or four) were selected to acquire the Raman spectra
28 through each humidity cycle. Each humidity cycle experiment was repeated at least three times. All
29 the measurements were taken at ambient temperature of about 297 K.

30 Raman growth factor ($g(\text{RH})$) is defined as the ratio of integrated area of OH stretching mode of

1 water (3350–3700 cm^{-1}) at each RH (A_{RH}) normalized to that of a dry particle (A_{RH0}) according to
2 Eq. (1) (Laskina et al., 2015).

$$3 \quad g(\text{RH}) = A_{\text{RH}}/A_{\text{RH0}} \quad (1)$$

4 where A_{RH} is integrated area of OH stretching mode from water (3350-3700 cm^{-1}) at a specific RH
5 and A_{RH0} is that of a dry particle. Hygroscopic growth curves are acquired by plotting the average
6 Raman growth factor of duplicate particles as a function of RH.

7 **3 Results and discussion**

8 **3.1 Raman spectra of pure AS and OA droplets**

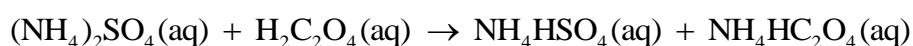
9 The Raman spectra of AS droplets during the dehydration and hydration process can be found in Fig.
10 1a and 1b, respectively. AS droplets effloresce at $44.3 \pm 2.5\%$ RH, as indicated by the disappearance
11 of the water peak centered at 3437 cm^{-1} and a red-shift in $\nu_s(\text{SO}_4^{2-})$ peak position from 979 to 974
12 cm^{-1} during the dehydration process. For the hydration process, the deliquescence of AS particles is
13 observed to occur at $80.1 \pm 1.5\%$ RH, resulting in an abrupt increase in the absorbance of the water
14 peak centered at 3437 cm^{-1} and a blue-shift in $\nu_s(\text{SO}_4^{2-})$ peak position from 974 to 979 cm^{-1} .

15 The Raman spectra of OA droplets with varying RH during the dehydration and hydration
16 process are shown in Fig. 2, and the assignments of the peaks for OA are presented in Table 1
17 according to previous studies (Hibben, 1935; Ebisuzaki and Angel, 1981; Mohaček-Grošev et al.,
18 2009). As seen in Fig. 2a, the feature bands for OA droplets are observed at 1460, 1750 and 3433
19 cm^{-1} at 92.5% RH. At lower RH around 71% (Fig. 2a, magenta line), these bands shift to 1490,
20 1737, 3433 and 3474 cm^{-1} , and a new band at 1689 cm^{-1} occurs, which is entirely consistent with
21 the spectrum of oxalic acid dihydrate (Fig. 2a, black dashed line). It indicates OA droplets
22 crystallize to form oxalic acid dihydrate. Oxalic acid particles after efflorescence exist in the form
23 of dihydrate until 6.6% RH, at which the Raman spectrum of dihydrate remains unchanged for 40
24 min. Once RH decreases to $\sim 5.0\%$, the peaks promptly shift to 1477, 1710, 2587, 2760 and 2909
25 cm^{-1} , and peaks at 3433 and 3474 cm^{-1} assigned to $\nu(\text{OH})$ vanish, which is the spectral feature of
26 anhydrous oxalic acid. This result implies that oxalic acid dihydrate is converted to anhydrous
27 oxalic acid in the RH around 5.0%. The Raman spectra of anhydrous oxalic acid particles during the
28 hydration process as a function of RH are shown in Fig. 2b. It can be found that the Raman spectra
29 feature for anhydrous oxalic acid particles occurs at $\text{RH} < 19.6\%$. At 19.6% RH, the peaks observed
30 at 1490, 1737, 3433 and 3474 cm^{-1} are identical to that of oxalic acid dihydrate (Fig. 2a, black

1 dashed line), indicating the formation of oxalic acid dihydrate. The observation of no spectral
2 change until 94% RH suggests that oxalic acid dihydrate shows no deliquescence transition in the
3 0-94 % RH range studied, consistent with previous studies (Peng et al., 2001; Braban et al., 2003;
4 Ma et al., 2013a; Jing et al., 2016). The transition point of anhydrous oxalic acid to oxalic acid
5 dihydrate upon hydration is 17.9-19.6% (Fig. 2b), in agreement with the results reported by Braban
6 et al. (2003) and Ma et al. (2013a).

7 **3.2 Raman spectra of OA/AS mixtures**

8 The Raman spectra of mixed OA/AS droplets with OIRs of 1:3, 1:1 and 3:1 at various RHs during
9 the dehydration and hydration process are depicted in Fig. 3 and 4, respectively. Since spectral
10 features upon hydration are identical to the dehydration process, here we only analysed spectral
11 evolution of efflorescence process in detail. The detailed assignments are summarized in Table 2.
12 For the mixed OA/AS droplets (OIR = 1:3) at 96.2% RH (seen in Fig. 3a), the bands at 979 cm⁻¹
13 and 1049 cm⁻¹ are characteristic peaks of aqueous SO₄²⁻ and HSO₄⁻ (ν_s(SO₃)), respectively. In
14 addition, the peak at 1741 cm⁻¹ and 1446 cm⁻¹ can be assigned to vibrating mode of aqueous OA
15 and HC₂O₄⁻, respectively. With decreasing RH, only small changes are observed in the spectra until
16 the RH reaches 34.4% RH. At 34.4% RH, the shift of ν_s(SO₄²⁻) peak from 979 cm⁻¹ to 974 cm⁻¹
17 indicates the crystallization of AS, as also seen in Fig. 10b. A new band centered at 874 cm⁻¹
18 corresponds to combination bands of the vibrational mode (δ(S-OH)) of HSO₄⁻ ion from NH₄HSO₄
19 (Dawson et al., 1986) and HC₂O₄⁻ ion vibrating (Villegin and Novak, 1971), suggesting the
20 formation of crystalline NH₄HC₂O₄. Moreover, the several new peaks at 1416, 1469 and 1660 cm⁻¹
21 can be attributed to the HC₂O₄⁻ ion vibrating of crystalline NH₄HC₂O₄ (Villegin and Novak, 1971).
22 Therefore, the evolution of Raman spectra of the mixed OA/AS droplets (OIR = 1:3) during the
23 dehydration process confirms that OA could react with AS to form NH₄HSO₄ and NH₄HC₂O₄,
24 which supports previous speculation for the reaction between OA and AS (Miñambres et al., 2013).
25 The reaction of OA with AS occurs via the following pathway:



27 For the mixed OA/AS droplets (OIR = 1:1, Fig. 3b), the evolution of spectra shows resemblance
28 to that of mixed droplets (OIR = 1:3). At 96.1% RH, the peaks at 979 cm⁻¹, 1751 cm⁻¹, 1051 cm⁻¹
29 and 1448 cm⁻¹ can be assigned to vibrating mode of SO₄²⁻, OA, HSO₄⁻ (ν_s(SO₃)) and HC₂O₄⁻,
30 respectively. At 75.0% RH, a new peak at 874 cm⁻¹ corresponding to the vibrational mode (δ(S-OH))

1 of HSO_4^- and the HC_2O_4^- ion vibrating as well as the new peaks at 494, 1469 and 1677 cm^{-1} due to
2 the HC_2O_4^- vibrating mode, indicates that crystalline $\text{NH}_4\text{HC}_2\text{O}_4$ is generated from the reaction of
3 OA with AS. As the RH further decreases to 44.3%, the $\nu_s(\text{SO}_4^{2-})$ band shifts from 979 cm^{-1} to 974
4 cm^{-1} , indicating the formation of crystallized AS particles.

5 For the mixed OA/AS droplets (OIR = 3:1, Fig. 3c) at 95.9% RH, the bands at 980 cm^{-1} , 1752
6 cm^{-1} and 1050 cm^{-1} are characteristic peak of the SO_4^{2-} ion, OA and HSO_4^- ion ($\nu_s(\text{SO}_3)$),
7 respectively. And the peak at 1460 cm^{-1} can be attributed to vibrating mode of HC_2O_4^- ion. When
8 the RH decreases to 74.4%, a new band at 874 cm^{-1} is contributed by the vibrational mode of both
9 HSO_4^- ($\delta(\text{S-OH})$) and HC_2O_4^- . Meanwhile, the bands at 494, 1471 and 1654 cm^{-1} can be attributed
10 to HC_2O_4^- vibrating mode, suggesting OA reacts with AS to yield crystalline $\text{NH}_4\text{HC}_2\text{O}_4$ during the
11 dehydration process. At 64.4% RH, the peaks at 494, 874, 1471, 1654, 1718 cm^{-1} , and the peak at
12 3426 cm^{-1} from oxalic acid dihydrate become sharp and narrow, indicating that the OA/AS droplets
13 (OIR = 3:1) completely crystallize to form $\text{NH}_4\text{HC}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. No obvious change in
14 spectral feature of the major bands is observed with RH decreasing from 64.4% to 1.1%.

15 **3.3 Hygroscopicity of pure AS, OA and OA/AS mixtures**

16 **3.3.1 Phase transitions and chemical transformation of AS in mixed systems**

17 Considering that the peak position is sensitive to the chemical environment in the aerosols, the
18 position of the $\nu_s(\text{SO}_4^{2-})$ mode can be used to determine the phase transitions of AS. The previous
19 studies have also applied the abrupt shift in characteristic peak position to indicate phase transition
20 of ammonium sulfate during the hygroscopic process (Braban and Abbatt, 2004; Ling and Chan,
21 2008; Yeung et al., 2009). Figure 5 presents the peak position of the $\nu_s(\text{SO}_4^{2-})$ for AS droplets and
22 mixed OA/AS droplets during the dehydration and hydration process, respectively. During the
23 dehydration process, a red shift from 979 to 974 cm^{-1} can be observed for AS and OA/AS mixed
24 particles with OIRs of 1:3 and 1:1, indicating crystallization of AS from droplets. During the
25 hydration process, the observations of blue shift from 974 cm^{-1} to 979 cm^{-1} for AS and OA/AS mixed
26 particles with OIRs of 1:3 and 1:1 suggest the deliquescence transition of AS from crystal phase to
27 aqueous solution. For OA/AS mixed particles with an OIR of 3:1, the peak shift between ~ 966 and
28 $\sim 979\text{ cm}^{-1}$ is determined during the whole RH cycle. The shift of $\nu_s(\text{SO}_4^{2-})$ mode to 966 cm^{-1}
29 suggests the formation of letovicite $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2(\text{s})$ (Damak et al., 1985). The DRH and ERH for
30 pure and mixed systems have been shown in Fig. 5 and detailed discussion is given in the following

1 section.

2 The peaks at ~ 1049 and ~ 979 cm^{-1} for mixed OA/AS droplets (OIRs = 1:3, 1:1 and 3:1) can be
3 attributed to the HSO_4^- and SO_4^{2-} stretching mode, respectively. The area ratio of Raman peaks
4 assigned to the HSO_4^- and SO_4^{2-} is used to indicate the degree of conversion of SO_4^{2-} into HSO_4^-
5 ($\alpha_{\text{HSO}_4^-}$) in mixtures, which can be expressed as following:

$$6 \quad \alpha_{\text{HSO}_4^-} = A_{1049} / (A_{1049} + A_{979}) \quad (2)$$

7 where A_{1049} and A_{979} is the peak area of the HSO_4^- and SO_4^{2-} , respectively. The ~ 1049 cm^{-1} for
8 HSO_4^- at solid mixture is not obvious compared to that for solutions. Thus, the calculations are
9 based on the bands at RH approaching the full efflorescence point. The estimated $\alpha_{\text{HSO}_4^-}$ value for
10 OIR = 1:3 (36.1% RH), OIR = 1:1 (46.2% RH) and OIR = 3:1 (66.2% RH) is 0.048, 0.368 and
11 0.644, respectively, indicating the enhanced conversion of SO_4^{2-} into HSO_4^- with increasing OA
12 content in the mixed systems. Due to the effects of Raman cross section, $\alpha_{\text{HSO}_4^-}$ could not represent
13 the actual degree of conversion. In fact, here $\alpha_{\text{HSO}_4^-}$ is only used for comparisons of degree of
14 conversion of SO_4^{2-} into HSO_4^- between mixed particles with varying OIRs.

15 **3.3.2 Hygroscopic growth of pure and mixed components**

16 Hygroscopicity curves of AS and OA particles are shown in Fig. 6. The optical images of the AS
17 particle at the phase change points can be seen in Fig. 7. The ERH of AS is determined to be $44.3 \pm$
18 2.5% RH, which generally falls into the range from 33 to 52% RH reported in the literature (Tang
19 and Munkelwitz, 1994a; Cziczo et al., 1997; Dougle et al., 1998; Laskina et al., 2015). The DRH of
20 AS particles is observed to occur at $80.1 \pm 1.5\%$ RH, which agrees well with reported values of
21 80% RH by EDB (Tang and Munkelwitz, 1994a) and $82.3 \pm 2.5\%$ RH by micro-Raman
22 spectroscopy (Laskina et al., 2015). As shown in Fig. 6b and Fig. 8, the measured ERH of OA is 71
23 $\pm 2.5\%$ RH, which deviates much from the reported value of 51.8-56.7% RH by Peng et al. (2001)
24 using the EDB technology. It is worthwhile to point out that the conversion of OA droplets to oxalic
25 acid dihydrate at 71% RH is inconsistent with the observation of Peng et al. (2001). They observed
26 that OA droplets crystallized to form anhydrous oxalic acid rather than oxalic acid dihydrate at
27 51.8-56.7% RH. The discrepancy on the ERH of OA compared to that reported by Peng et al. (2001)
28 is likely due to the effects of substrate and sample purity. The size of dry particles ranging from 10
29 to 20 μm in our experiment is consistent with observation using EDB by Peng et al. (2001), which
30 eliminates the influence of particle size. The substrate supporting droplets may promote the

1 heterogeneous nucleation of oxalic acid while the levitated droplets in EDB study can avoid
2 induced nucleation by the substrate. Ghorai et al. (2014) also reported the potential effects of
3 substrate on the efflorescence transition of NaCl/dicarboxylic acid mixed particles. In addition, The
4 OA purity in our study is 99.0% lower than that of 99.5% in study by Peng et al. (2001). Thus, trace
5 amounts of impurities in OA droplets acting as a heterogeneous nucleus could contribute to
6 crystallization and result in a higher ERH of OA. Due to the effects of substrate and sample purity,
7 the heterogeneous nucleation should be responsible for the discrepancy on the observed ERH of OA.
8 The water content of the supersaturated droplet at the onset of crystallization determines the form of
9 oxalic acid crystal generated, i. e., anhydrous OA or OA dihydrate. Due to a higher ERH, oxalic
10 acid droplets with more water content favor the formation of a dihydrate after crystallization. It
11 should be noted that our experiment appears to be favored in the atmospheric environment,
12 considering that insoluble material such as mineral dust mixed with OA may play the role of
13 substrate thus facilitating the heterogeneous nucleation of OA aerosols. The Raman growth factor of
14 OA shows no obvious change between ~71% and 6.6% RH upon dehydration. At RH lower than
15 5%, the Raman growth factors drop abruptly due to the transformation of crystalline $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
16 into anhydrous oxalic acid, as also indicated by Raman spectrum. It seems that the structure of
17 anhydrous OA particle is not as compact as that of dihydrate, seen in Fig. 8. Thus, the loss of crystal
18 water results in no obvious change in particle size. During the hydration process, the Raman growth
19 factor of OA shows a slightly increase at 19.6% RH, which can be attributed to the conversion of
20 anhydrous oxalic acid to dihydrate. The transition point of anhydrous oxalic acid to oxalic acid
21 dihydrate agrees with previous studies (Braban et al., 2003; Ma et al., 2013b; Miñambres et al.,
22 2013). No deliquescence behavior is observed for oxalic acid dihydrate even at 94% RH, consistent
23 with early observations (Ma et al., 2013b; Miñambres et al., 2013; Jing et al., 2016).

24 Figure 9 presents hygroscopic growth of OA/AS mixtures with OIRs of 1:3, 1:1 and 3:1. As can
25 be seen in Fig. 9a and 10b, mixed OA/AS droplets (OIR = 1:3) exhibit efflorescence transition at
26 lower $34.4 \pm 2.0\%$ RH relative to ERH ($44.3 \pm 2.5\%$) of pure AS. During the hydration process,
27 mixed particles start to absorb slight water before deliquescence at $81.1 \pm 1.5\%$ RH (seen in Fig. 9
28 and 10). It can be seen in Fig. 10 that the size of 1:3 mixed OA/AS particle at 79.4% RH prior to
29 deliquescence appears to be larger than that after complete efflorescence. The decrease in ERH and
30 slight water uptake before deliquescence for 1:3 mixed particles is likely due to the effects of

1 NH_4HSO_4 formed upon dehydration. NH_4HSO_4 has a low ERH (22-0.05%) and DRH (40%) (Tang
2 and Munkelwitz, 1994a), which may affect the nucleation and crystallization of AS upon
3 dehydration and lead to slight water uptake prior to the deliquescence of AS. The hygroscopic
4 growth of mixed particles upon dehydration is in fair agreement with that of pure AS or OA.
5 However, the Raman growth factors of mixed particles upon hydration show a considerable
6 decrease in comparison to that upon dehydration. The discrepancies for Raman growth factor at
7 high RH between the two processes can be attributed to the formation of $\text{NH}_4\text{HC}_2\text{O}_4$ and residual
8 solid OA, both of which have a high deliquescence point larger than 95% RH (Schroeder and Beyer,
9 2016). During the hydration process, $\text{NH}_4\text{HC}_2\text{O}_4$ and OA in the mixed aerosols remains solid even
10 at high RH (also seen in Fig. 10d), resulting in less water uptake of mixed particles. The similar
11 phenomenon is also observed for NaCl/OA mixed particles upon hydration due to the formation of
12 less hygroscopic sodium oxalate (Peng et al., 2016).

13 The mixed OA/AS droplets with an OIR = 1:1 first partially effloresce at $75.0\% \pm 1.6\%$ due to
14 the crystallization of $\text{NH}_4\text{HC}_2\text{O}_4$, as indicated by Raman spectra. Then, the full efflorescence occurs
15 at $44.3 \pm 2.5\%$ RH with the crystallization of AS. The full ERH of 1:1 OA/AS mixed droplets is
16 highly consistent with that of pure AS. During the hydration process, the Raman growth factor of
17 1:1 mixed particles increases slightly at 35.5% RH, and then remains almost invariable until 77%
18 RH, which is likely due to the formation of hydrate. The deliquescence transition occurs at $77 \pm$
19 1.0% RH slightly lower than DRH of AS, which agrees with literature results for AS particles
20 containing OA (Brooks et al., 2002; Jing et al., 2016). The water contents of mixed droplets after
21 deliquescence are significantly lower than those upon dehydration. The Raman features at 494 cm^{-1}
22 and 874 cm^{-1} have confirmed the presence of solid $\text{NH}_4\text{HC}_2\text{O}_4$ upon hydration across all RHs
23 studied (seen in Fig. 4), which should be responsible for the decreasing water uptake of the mixed
24 particles at high RH.

25 For mixed OA/AS droplets with an OIR = 3:1, the partial and full efflorescence transition could
26 be observed at $74.4 \pm 1.0\%$ RH and $64.4 \pm 3.0\%$ RH, respectively (seen in Fig. 9 and 11). As seen
27 in Fig. 3c, the bands at 494, 1471 and 1654 cm^{-1} suggest the formation of crystalline $\text{NH}_4\text{HC}_2\text{O}_4$ at
28 $74.4 \pm 1.0\%$ RH. Figure 12 presents the spatial distribution of chemicals within mixed OA/AS (OIR
29 = 3:1) particles at 74.4% RH. The characteristic peak of 980 cm^{-1} , 1050 cm^{-1} and 1471 cm^{-1} is
30 assigned to SO_4^{2-} , HSO_4^- and HC_2O_4^- , respectively. The sharp absorption at 874 cm^{-1} and obvious

1 peak at 1471 cm^{-1} indicate the abundant content of $\text{NH}_4\text{HC}_2\text{O}_4$. The comparison of characteristic
2 peaks between inner and outer phase reveals that the major component on the surface of a mixed
3 OA/AS (OIR = 3:1) particle is $\text{NH}_4\text{HC}_2\text{O}_4$. In contrast to the surface, the obvious features of 980
4 cm^{-1} and 1050 cm^{-1} at the core of the particle suggest that $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 mainly exist in
5 the inner aqueous phase. During the dehydration process, crystalline $\text{NH}_4\text{HC}_2\text{O}_4$ in the outer phase
6 acts as the heterogeneous nucleus, leading to the crystallization of oxalic acid dihydrate and other
7 components in the inner phase. Thus, the full ERH of 3:1 OA/AS mixed droplets is higher than that
8 of pure AS ($44.3 \pm 2.5\%$ RH) and NH_4HSO_4 ($22\text{-}0.05\%$ RH). During the hydration process, Raman
9 growth factors of mixed particles slightly increase at 34.5% RH. No deliquescence transition or
10 significant water uptake is observed over the RH range studied. This phenomenon can be explained
11 by the fact that the most of AS in the mixtures has been converted into $\text{NH}_4\text{HC}_2\text{O}_4$ and NH_4HSO_4 or
12 letovicite. Although NH_4HSO_4 with a low DRH may contribute to water uptake of mixed particles,
13 the minor NH_4HSO_4 or letovicite formed in the mixtures is likely to be coated by $\text{NH}_4\text{HC}_2\text{O}_4$ and
14 OA with a high DRH. Thus, the mixed OA/AS particles with an OIR = 3:1 show no obvious
15 hygroscopic growth upon hydration due to the change in aerosol composition and morphology
16 effects. The effects of morphology on the hygroscopic growth of aerosols have been reported for AS
17 particles containing adipic acid (Sjogren et al., 2007). The water uptake of AS particles containing
18 relatively high content of adipic acid could be suppressed due to AS enclosed by the crust of solid
19 adipic acid with a high DRH.

20 The observed efflorescence relative humidity (ERH) for mixed droplets was dependent on the
21 molar ratio of oxalic acid to ammonium sulfate. The mixed OA/AS droplets with an OIR of 1:3 are
22 observed to effloresce completely at $34.4 \pm 2.0\%$ RH relative to ERH of pure AS ($44.3 \pm 2.5\%$) or
23 OA ($71 \pm 2.5\%$). It can be seen that AS as a major fraction of the particle does not promote the
24 heterogeneous nucleation of OA. Meanwhile, the crystallization of AS is also influenced due to the
25 presence of OA. The similar phenomenon was also observed for malonic acid/ammonium sulfate
26 mixtures with minor organic content (Braban and Abbatt, 2004; Parsons et al., 2004). Braban and
27 Abbatt (2004) found that the ERH of malonic acid/ammonium sulfate mixed particles was
28 considerably decreased compared to that of pure ammonium sulfate for mass fractions of malonic
29 acid less than 0.3. They concluded that the presence of ammonium sulfate in the supersaturated
30 droplet could exert the extra barrier to nucleation of malonic acid crystals rather than play the role

1 of a heterogeneous nucleation site. As for 1:3 OA/AS mixed droplets, ammonium sulfate may also
2 inhibit the nucleation of oxalic acid at relatively high RH. With decreasing RH, aqueous oxalic acid
3 could enhance the viscosity of the droplet due to hydrogen bond interactions (Mikhailov et al.,
4 2009), thus limiting the nucleation of ammonium sulfate and resulting in a lower ERH with respect
5 to the value of pure AS (Parsons et al., 2004). In the case of mixed OA/AS droplets with an OIR of
6 1:1 and 3:1, the $\text{NH}_4\text{HC}_2\text{O}_4$ formed at ~75% RH upon dehydration likely acts as a heterogeneous
7 nucleus for crystallization of other components, which increases full efflorescence point of mixed
8 particles. One study indicated that Aldrich humic acid sodium salt (NaHA) could also promote the
9 ERH of ammonium sulfate (Badger et al., 2006). Similar to oxalic acid, succinic acid and adipic
10 acid have a high deliquescence point and low solubility. However, it has been found that the
11 efflorescence point of ammonium sulfate in mixed particles is not elevated even when the content
12 of succinic acid or adipic acid is more than 50% by mass or mole fractions (Ling and Chan, 2008;
13 Yeung et al., 2009; Laskina et al., 2015). The chemical nature of solid determines its ability to act as
14 a heterogeneous nucleus (Braban and Abbatt, 2004). In contrast to ammonium sulfate particles
15 containing succinic acid or adipic acid, our results suggest that the addition of oxalic acid into
16 ammonium sulfate droplets may trigger partial and full crystallisation of aerosols at relatively
17 higher RH upon dehydration due to $\text{NH}_4\text{HC}_2\text{O}_4$ product acting as an effective nucleus.

18 During the deliquescence process, the OA/AS mixed particles with an OIR of 1:3 and 1:1 exhibit
19 a slightly lower deliquescence point than that of pure ammonium sulfate, consistent with previous
20 observations of effects of crystalline oxalic acid on deliquescence transition of ammonium sulfate
21 (Brooks et al., 2002; Wise et al., 2003; Jing et al., 2016). It should be noted that prior literature
22 result also showed that continuous or smooth water uptake from low RH was observed for particles
23 composed of AS and OA with a mass ratio of 1.5:1 due to the fact that after drying processing
24 oxalic acid existing in an amorphous or liquid-like state prevented nucleation of ammonium sulfate
25 even under dry conditions (Prenni et al., 2003). In the present study, water uptake by the OA/AS
26 mixed particles at high RH upon hydration is dramatically lower than that upon dehydration and
27 significantly decreased with elevated OA content. This phenomenon distinguishes from hygroscopic
28 characteristics of typical water-soluble mixtures in literatures. It has been found that hydration
29 growth curve and dehydration growth curve are typically merged above deliquescence point for
30 mixed systems containing inorganic salts and water-soluble organic compounds (Choi and Chan,

1 2002; Chan and Chan, 2003; Gysel et al., 2004; Clegg and Seinfeld, 2006; Sjogren et al., 2007;
2 Pope et al., 2010; Ghorai et al., 2014; Estillore et al., 2016). In this study, Raman spectra and the
3 micrograph suggest the presence of solid $\text{NH}_4\text{HC}_2\text{O}_4$ and residual solid OA at high RH should be
4 responsible for the decreased water uptake during the hydration process. In contrast, Prenni et al.
5 (2003) reported that the hygroscopic growth of OA/AS mixed particles remained unchanged at 90%
6 RH with OA mass fraction ranging from 0.01 to 0.4. In addition, they also found that water uptake
7 after deliquescence was well described by the model method assuming complete dissolution of OA
8 in aqueous phase as well as no interactions between OA and AS, which was also observed by Jing et
9 al. (2016) using the HTDMA. The previous HTDMA studies for OA/AS mixed particles indicate no
10 composition change and no specific interactions existing between OA and AS (Prenni et al., 2003;
11 Jing et al., 2016). However, it should be noted that the HTDMA studies did not perform
12 measurements for the dehydration process such that aerosols underwent rapid drying on the time
13 scale of seconds, i.e., the total residence time for transformation of droplets into dry particles in the
14 drying section of HTDMA is typically tens of seconds (Prenni et al., 2003; Jing et al., 2016), much
15 shorter than that (10 ~ 12 h) in our study. In the HTDMA experiments, the combination of faster
16 drying and smaller particles with submicron size implies that the aqueous phase obtained higher
17 supersaturations than in our present study (Rosenoern et al., 2008), leading to less dissociation of
18 oxalic acid and thus less HC_2O_4^- formed in the droplets as well as the inhibited formation of
19 $\text{NH}_4\text{HC}_2\text{O}_4$. The fast evaporation of water from the surface of an aqueous droplet upon rapid drying
20 could result in a higher surface concentration of solutes than the slow drying process (Treuel et al.,
21 2011). The higher surface concentration of oxalic acid corresponds to less formation and hence
22 decreased supersaturation of HC_2O_4^- . Due to the dependence of nucleation rate on the extent of
23 supersaturation, it can be expected that the nucleation of $\text{NH}_4\text{HC}_2\text{O}_4$ is suppressed within OA/AS
24 mixed droplets undergoing rapid drying.

25 Considering the potential effects of drying time on the reactions between OA and AS, we
26 explored the hygroscopicity of OA/AS particles with an OIR of 1:1 after rapid drying process. The
27 mixed OA/AS droplets undergo dehydration to form dry particles in 3 ~ 5 min. We observed
28 one-step efflorescence of rapidly-dried particles (1:1, molar ratio) occurred at $47\% \pm 2.5\%$ RH,
29 compared to the two-step efflorescence of slowly-dried particles occurring at 75% and 44.3% RH,
30 respectively. The Raman spectra and hygroscopic curve upon hydration for OA/AS particles with an

1 OIR of 1:1 are presented in Fig. 13. The obvious discrepancies can be observed for spectra at ~2%
2 RH between the two drying processes. After rapid drying process, the spectra at ~2% RH show the
3 feature of crystalline AS (974 cm^{-1} , $\nu_s(\text{SO}_4^{2-})$) and anhydrous OA (1710 cm^{-1} , $\nu(\text{C=O})$; 1479 cm^{-1} ,
4 $\nu_s(\text{COO})$). Meanwhile, no characteristic peaks for $\text{NH}_4\text{HC}_2\text{O}_4$ (494 cm^{-1} , $\delta(\text{COO})$; 874 cm^{-1} , $\nu(\text{C-C})$;
5 1729 cm^{-1} , $\nu(\text{C=O})$; 1469 cm^{-1} , $\nu_s(\text{COO})$) and NH_4HSO_4 (874 cm^{-1} , $\delta(\text{S-OH})$) can be identified in
6 the spectra. It is clear that the drying time for transformation of droplets into dry particles has
7 impacts on the reactions of OA with AS in the aerosols due to particle-phase processes under kinetic
8 control. Previous studies found the longer drying time could lead to greater nitrate depletion
9 between nitrates and organic acids, which results from slow reaction and diffusion in the viscous
10 aerosols (Wang and Laskin, 2014). The Raman growth factors of mixed particles with an OIR of 1:1
11 also increase slightly at 36.5% RH due to the formation of OA dihydrate, as indicated by the Raman
12 feature. The deliquescence transition of mixed particles occurs at 79.3% RH. After deliquescence,
13 Raman growth factors of mixed particles after rapid drying process are lower than that after slow
14 drying process, which may be caused by the fact that at high RH the hygroscopic growth of AS is
15 slightly lower than that of NH_4HSO_4 formed in the particles after slow drying process (Tang and
16 Munkelwitz, 1977). In addition, it is found that after deliquescence OA dihydrate remains solid in
17 the mixed particles undergoing rapid drying.

18 **4 Conclusions and atmospheric implications**

19 In this work, confocal Raman spectroscopy is used to investigate the hygroscopic properties and
20 phase transformations of OA and internally mixed OA/AS droplets (OIRs = 1:3, 1:1 and 3:1). OA
21 droplets effloresce to form oxalic acid dihydrate at $71 \pm 2.5\%$ RH, and then oxalic acid dihydrate
22 further loses crystalline water to form anhydrous oxalic acid at ~5.0% RH during the dehydration
23 process. The Raman spectra of mixed OA/AS droplets reveal the formation of $\text{NH}_4\text{HC}_2\text{O}_4$ and
24 NH_4HSO_4 from the reaction of OA with AS in aerosols during the dehydration process. The
25 deliquescence and efflorescence point for AS is observed to occur at $80.1 \pm 1.5\%$ and $44.3 \pm 2.5\%$
26 RH, respectively. The ERH of the mixed OA/AS droplets with 1:3, 1:1 and 3:1 ratio is determined
27 to be $34.4 \pm 2.0\%$, $44.3 \pm 2.5\%$ and $64.4 \pm 3.0\%$ RH, respectively, indicating significant effects of
28 OA content on the efflorescence transition of AS. The mixed OA/AS particles with 1:3 and 1:1 ratio
29 show deliquescence transition at $81.1 \pm 1.5\%$ and $77 \pm 1.0\%$ RH, respectively, which is close to the
30 DRH of AS. The mixed OA/AS particles with 3:1 ratio exhibit no deliquescence transition over the

1 RH range studied due to the transformation of $(\text{NH}_4)_2\text{SO}_4$ into high-DRH $\text{NH}_4\text{HC}_2\text{O}_4$. The
2 hygroscopic growth of mixed particles at high RH upon hydration is substantially lower than that of
3 corresponding dehydration process and further decreases with increasing OA content. The
4 discrepancies for water content of mixed particles between the two processes at high RH can be
5 explained by the significant formation of low hygroscopic $\text{NH}_4\text{HC}_2\text{O}_4$ and residual OA, which still
6 remain solid and thus result in less water uptake of mixed particles.

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

20 Our results highlight the atmospheric importance of dicarboxylic acid–ammonium sulfate
21 interactions in aerosol aqueous chemistry. Such chemical processing upon drying of aerosols
22 comprised of organic acid/ $(\text{NH}_4)_2\text{SO}_4$ mixtures may enhance the acidity of aqueous phase in the
23 intermediate RH due to the transformation of $(\text{NH}_4)_2\text{SO}_4$ into NH_4HSO_4 . These experiments also
24 imply that the chemical reaction between aqueous $(\text{NH}_4)_2\text{SO}_4$ and oxalic acid upon slow
25 dehydration is a possible formation pathway for the low-volatility oxalate in ambient particles,
26 which could enhance partitioning of dicarboxylic acids to aqueous particles with the presence of
27 ammonium sulfate (Yli-Juuti et al., 2013; Hakkinen et al., 2014). It has been reported that the
28 aerosol aqueous processing within organic acid/AS mixtures partly contributes to enhanced
29 loadings of secondary organic aerosol (SOA) from biogenic precursors (Hoyle et al., 2011).
30 Compared to aqueous processing such as condensed phase acid-catalyzed reactions relevant to

1 formation of organosulfates, the contribution of other aerosol processing containing organic salt
2 formation to SOA burden likely becomes important under less acidic condition. Formation of
3 low-solubility organic salts from aqueous processing within aerosols alters particle-phase
4 component and thus modifies aerosol's hygroscopicity, optical properties and chemical reactivity.
5 Our findings provide fundamental insight into effects of drying conditions (drying rate or time) on
6 formation of organic salt from reactions of organic acids with inorganic salts in particle phase under
7 ambient RH conditions. Overall, a better understanding of the chemical interactions between
8 species in a multicomponent system during the humidity cycle is critical for the accurate modeling
9 efforts of aerosol phase behavior in thermodynamic models.

10 **Data availability.** All data are available upon request from the corresponding authors.

11 **Competing interests.** The authors declare that they have no conflict of interest.

12 **Author contribution.** *YZ, MG and BJ designed the experiments and XW carried them out. XW and
13 BJ performed the data analysis and prepared the manuscript with contributions from all
14 co-authors.*

15 **Acknowledgments.** This project was supported by the National Natural Science Foundation of
16 China (Contract No. 91544223, 21473009, and 21373026) and the National Key Research and
17 Development Program of China (2016YFC0202202).

18 **References**

19 Amundson, N. R., Caboussat, A., He, J. W., Martynenko, A. V., and Seinfeld, J. H.: A phase
20 equilibrium model for atmospheric aerosols containing inorganic electrolytes and organic
21 compounds (UHAERO), with application to dicarboxylic acids, *J. Geophys. Res.: Atmos.*, 112,
22 D24S13, doi: 10.1029/2007jd008424, 2007.

23 Badger, C. L., George, I., Griffiths, P. T., Braban, C. F., Cox, R. A., and Abbatt, J. P. D.: Phase
24 transitions and hygroscopic growth of aerosol particles containing humic acid and mixtures of
25 humic acid and ammonium sulphate, *Atmos. Chem. Phys.*, 6, 755-768, doi:
26 10.5194/acp-6-755-2006, 2006.

27 Braban, C. F., Carroll, M. F., Styler, S. A., and Abbatt, J. P. D.: Phase transitions of malonic and
28 oxalic acid aerosols, *J. Phys. Chem. A*, 107, 6594-6602, doi: 10.1021/jp034483f, 2003.

29 Braban, C. F., and Abbatt, J. P. D.: A study of the phase transition behavior of internally mixed
30 ammonium sulfate-malonic acid aerosols, *Atmos. Chem. Phys.*, 4, 1451-1459, doi:

1 10.5194/acp-4-1451-2004, 2004.

2 Brooks, S. D., Wise, M. E., Cushing, M., and Tolbert, M. A.: Deliquescence behavior of
3 organic/ammonium sulfate aerosol, *Geophys. Res. Lett.*, 29, 1917, doi: 10.1029/2002gl014733,
4 2002.

5 Chan, M. N., and Chan, C. K.: Hygroscopic properties of two model humic-like substances and
6 their mixtures with inorganics of atmospheric importance, *Environ. Sci. Technol.*, 37, 5109-5115,
7 doi: 10.1021/es034272o, 2003.

8 Chang, H., and Huang, P. J.: Thermal decomposition of $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$ studied by thermo-Raman
9 spectroscopy with TGA/DTA, *Anal. Chem.*, 69, 1485-1491, doi: 10.1021/ac960881l, 1997.

10 Chebbi, A., and Carlier, P.: Carboxylic acids in the troposphere, occurrence, sources, and sinks: A
11 review, *Atmos. Environ.*, 30, 4233-4249, doi: 10.1016/1352-2310(96)00102-1, 1996.

12 Choi, M. Y., and Chan, C. K.: The effects of organic species on the hygroscopic behaviors of
13 inorganic aerosols, *Environ. Sci. Technol.*, 36, 2422-2428, doi: 10.1021/es0113293, 2002.

14 Clegg, S. L., and Seinfeld, J. H.: Thermodynamic models of aqueous solutions containing inorganic
15 electrolytes and dicarboxylic acids at 298.15 K. 1. The acids as nondissociating components, *J.*
16 *Phys. Chem. A*, 110, 5692-5717, doi: 10.1021/jp056149k, 2006.

17 Cziczo, D. J., Nowak, J. B., Hu, J. H., and Abbatt, J. P. D.: Infrared spectroscopy of model
18 tropospheric aerosols as a function of relative humidity: Observation of deliquescence and
19 crystallization, *J. Geophys. Res.*, 102, 18843-18850, doi: 10.1029/97jd01361, 1997.

20 Damak, M., Kamoun, M., Daoud, A., Romain, F., Lautie, A., and Novak, A.: Vibrational study of
21 hydrogen bonding and structural disorder in $\text{Na}_3\text{H}(\text{SO}_4)_2$, $\text{K}_3\text{H}(\text{SO}_4)_2$ and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$
22 crystals. *J. Mol. Struct.*, 130, 245-254, doi: 10.1016/0022-2860(85)87006-X, 1985.

23 Dawson, B. S. W., Irish, D. E., and Toogood, G. E.: Vibrational spectral studies of solutions at
24 elevated temperatures and pressures. 8. A Raman spectral study of ammonium hydrogen sulfate
25 solutions and the HSO_4^- - SO_4^{2-} equilibrium, *J. Phys. Chem.*, 90, 334-341, doi:
26 10.1021/j100274a027, 1986.

27 Dong, J. L., Xiao, H. S., Zhao, L. J., and Zhang, Y. H.: Spatially resolved Raman investigation on
28 phase separations of mixed $\text{Na}_2\text{SO}_4/\text{MgSO}_4$ droplets, *J. Raman Spectrosc.*, 40, 338-343, doi:
29 10.1002/jrs.2132, 2009.

30 Dougle, P. G., Veefkind, J. P., and ten Brink, H. M.: Crystallisation of mixtures of ammonium

1 nitrate, ammonium sulphate and soot, *J. Aerosol Sci.*, 29, 375-386, doi:
2 10.1016/S0021-8502(97)10003-9, 1998.

3 Drozd, G., Woo, J., Häkkinen, S. A. K., Nenes, A., and McNeill, V. F.: Inorganic salts interact with
4 oxalic acid in submicron particles to form material with low hygroscopicity and volatility, *Atmos.*
5 *Chem. Phys.*, 14, 5205-5215, doi: 10.5194/acp-14-5205-2014, 2014.

6 Ebisuzaki, Y., and Angel, S. M.: Raman study of hydrogen bonding in α and β -oxalic acid
7 dihydrate, *J. Raman Spectrosc.*, 11, 306-311, doi: 10.1002/jrs.1250110416, 1981.

8 Estillore, A. D., Hettiyadura, A. P. S., Qin, Z., Leckrone, E., Wombacher, B., Humphry, T., Stone, E.
9 A., and Grassian, V. H.: Water uptake and hygroscopic growth of organosulfate aerosol, *Environ.*
10 *Sci. Technol.*, 50, 4259-4268, doi: 10.1021/acs.est.5b05014, 2016.

11 Ghorai, S., Wang, B., Tivanski, A., and Laskin, A.: Hygroscopic properties of internally mixed
12 particles composed of NaCl and water-soluble organic acids, *Environ. Sci. Technol.*, 48,
13 2234-2241, doi: 10.1021/es404727u, 2014.

14 Gysel, M., Weingartner, E., Nyeki, S., Paulsen, D., Baltensperger, U., Galambos, I., and Kiss, G.:
15 Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine
16 aerosol, *Atmos. Chem. Phys.*, 4, 35-50, doi: 10.5194/acp-4-35-2004, 2004.

17 Hakkinen, S. A. K., McNeill, V. F., and Riipinen, I.: Effect of inorganic salts on the volatility of
18 organic acids, *Environ. Sci. Technol.*, 48, 13718-13726, doi: 10.1021/es5033103, 2014.

19 Hibben, J. H.: The Raman spectra of oxalic acid, *J. Chem. Phys.*, 3, 675-679, doi:
20 10.1063/1.1749575, 1935.

21 Hoyle, C. R., Boy, M., Donahue, N. M., Fry, J. L., Glasius, M., Guenther, A., Hallar, A. G., Huff
22 Hartz, K., Petters, M. D., Petaja, T., Rosenoern, T., and Sullivan, A. P.: A review of the
23 anthropogenic influence on biogenic secondary organic aerosol, *Atmos. Chem. Phys.*, 11,
24 321-343, doi: 10.5194/acp-11-321-2011, 2011.

25 Jacobson, M. C., Hansson, H. C., Noone, K. J., and Charlson, R. J.: Organic atmospheric aerosols:
26 Review and state of the science, *Rev. Geophys.*, 38, 267-294, doi: 10.1029/1998RG000045,
27 2000.

28 Jing, B., Tong, S. R., Liu, Q. F., Li, K., Wang, W. G., Zhang, Y. H., and Ge, M. F.: Hygroscopic
29 behavior of multicomponent organic aerosols and their internal mixtures with ammonium sulfate,
30 *Atmos. Chem. Phys.*, 16, 4101-4118, doi: 10.5194/acp-16-4101-2016, 2016.

1 Jing, B., Peng, C., Wang, Y. D., Liu, Q. F., Tong, S. R., Zhang, Y. H., and Ge, M. F.: Hygroscopic
2 properties of potassium chloride and its internal mixtures with organic compounds relevant to
3 biomass burning aerosol particles, *Sci. Rep.*, 7, 43572, doi: 10.1038/srep43572, 2017.

4 Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van
5 Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y.,
6 Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E.,
7 Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos.*
8 *Chem. Phys.*, 5, 1053-1123, doi: 10.5194/acp-5-1053-2005, 2004.

9 Kawamura, K., and Bikkina, S.: A review of dicarboxylic acids and related compounds in
10 atmospheric aerosols: Molecular distributions, sources and transformation, *Atmos. Res.*, 170,
11 140-160, doi: 10.1016/j.atmosres.2015.11.018, 2016.

12 Laskin, A., Moffet, R. C., Gilles, M. K., Fast, J. D., Zaveri, R. A., Wang, B., Nigge, P., and
13 Shutthanandan, J.: Tropospheric chemistry of internally mixed sea salt and organic particles:
14 Surprising reactivity of NaCl with weak organic acids, *J. Geophys. Res.*, 117, D15302, doi:
15 10.1029/2012jd017743, 2012.

16 Laskina, O., Young, M. A., Kleiber, P. D., and Grassian, V. H.: Infrared extinction spectroscopy and
17 micro-Raman spectroscopy of select components of mineral dust mixed with organic compounds,
18 *J. Geophys. Res.*, 118, 6593-6606, doi: 10.1002/jgrd.50494, 2013.

19 Laskina, O., Morris, H. S., Grandquist, J. R., Qin, Z., Stone, E. A., Tivanski, A. V., and Grassian, V.
20 H.: Size matters in the water uptake and hygroscopic growth of atmospherically relevant
21 multicomponent aerosol particles, *J. Phys. Chem. A*, 119, 4489-4497, doi: 10.1021/jp510268p,
22 2015.

23 Li, X., Gupta, D., Lee, J., Park, G., and Ro, C. U.: Real-time investigation of chemical compositions
24 and hygroscopic properties of aerosols generated from NaCl and malonic acid mixture solutions
25 using in situ Raman microspectrometry, *Environ. Sci. Technol.*, 51, 263-270, doi:
26 10.1021/acs.est.6b04356, 2017.

27 Lightstone, J. M., Onasch, T. B., Imre, D., and Oatis, S.: Deliquescence, efflorescence, and water
28 activity in ammonium nitrate and mixed ammonium nitrate/succinic acid microparticles, *J. Phys.*
29 *Chem. A*, 104, 9337-9346, doi: 10.1021/jp002137h, 2000.

30 Ling, T. Y., and Chan, C. K.: Partial crystallization and deliquescence of particles containing

- 1 ammonium sulfate and dicarboxylic acids, *J. Geophys. Res: Atmos.*, 113, D14205, doi:
2 10.1029/2008JD009779, 2008.
- 3 Liu, Y., Yang, Z. W., Desyaterik, Y., Gassman, P. L., Wang, H., and Laskin, A.: Hygroscopic
4 behavior of substrate-deposited particles studied by micro-FT-IR spectroscopy and
5 complementary methods of particle analysis, *Anal. Chem.*, 80, 633–642, doi: 10.1021/ac701638r,
6 2008.
- 7 Ma, Q., and He, H.: Synergistic effect in the humidifying process of atmospheric relevant calcium
8 nitrate, calcite and oxalic acid mixtures, *Atmos. Environ.*, 50, 97-102, doi:
9 10.1016/j.atmosenv.2011.12.057, 2012.
- 10 Ma, Q., He, H., and Liu, C.: Hygroscopic properties of oxalic acid and atmospherically relevant
11 oxalates, *Atmos. Environ.*, 69, 281-288, doi: 10.1016/j.atmosenv.2012.12.011, 2013a.
- 12 Ma, Q., Ma, J., Liu, C., Lai, C., and He, H.: Laboratory study on the hygroscopic behavior of
13 external and internal C₂-C₄ dicarboxylic acid-NaCl mixtures, *Environ. Sci. Technol.*, 47,
14 10381-10388, doi: 10.1021/es4023267, 2013b.
- 15 Miñambres, L., Méndez, E., Sánchez, M. N., Castaño, F., and Basterretxea, F. J.: Water uptake of
16 internally mixed ammonium sulfate and dicarboxylic acid particles probed by infrared
17 spectroscopy, *Atmos. Environ.*, 70, 108-116, doi: 10.1016/j.atmosenv.2013.01.007, 2013.
- 18 Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline
19 aerosol particles interacting with water vapor: conceptual framework and experimental evidence
20 for restructuring, phase transitions and kinetic limitations, *Atmos. Chem. Phys.*, 9 9491–9522, doi:
21 10.5194/acp-9-9491-2009, 2009.
- 22 Mohaček-Grošev, V., Grdadolnik, J., Stare, J., and Hadži, D.: Identification of hydrogen bond
23 modes in polarized Raman spectra of single crystals of α -oxalic acid dihydrate, *J. Raman*
24 *Spectrosc.*, 40, 1605-1614, doi: 10.1002/jrs.2308, 2009.
- 25 Murphy, D. M., Thomson, D. S., and Mahoney, M. J.: In situ measurements of organics, meteoritic
26 material, mercury, and other elements in aerosols at 5 to 19 kilometers, *Science*, 282, 1664-1669,
27 doi: 10.1126/science.282.5394.1664, 1998.
- 28 Murphy, D. M., Cziczo, D. J., Froyd, K. D., Hudson, P. K., Matthew, B. M., Middlebrook, A. M.,
29 Peltier, R. E., Sullivan, A., Thomson, D. S., and Weber, R. J.: Single-particle mass spectrometry
30 of tropospheric aerosol particles, *J. Geophys. Res.*, 111, D23S32, doi: 10.1029/2006JD007340,

1 2006.

2 Pöschl, U.: Atmospheric aerosols: composition, transformation, climate and health effects, *Angew.*
3 *Chem. Int. Ed.*, 44, 7520-7540, doi: 10.1002/anie.200501122, 2005.

4 Parsons, M. T., Knopf, D. A., and Bertram, A. K.: Deliquescence and crystallization of ammonium
5 sulfate particles internally mixed with water-soluble organic compounds, *J. Phys. Chem. A*, 108,
6 11600-11608, doi: 10.1021/jp0462862, 2004.

7 Peng, C., Jing, B., Guo, Y. C., Zhang, Y. H., and Ge, M. F.: Hygroscopic behavior of
8 multicomponent aerosols involving NaCl and dicarboxylic acids, *J. Phys. Chem. A*, 120,
9 1029-1038, doi: 10.1021/acs.jpca.5b09373, 2016.

10 Peng, C. G., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and
11 multifunctional acids: Measurements and UNIFAC predictions, *Environ. Sci. Technol.*, 35,
12 4495-4501, doi: 10.1021/es0107531, 2001.

13 Penner, J. E., Andreae, M. O., Annegarn, H., Barrie, L., Feichter, J., Hegg, D., Jayaraman, A.,
14 Leaitch, R., Murphy, D., Nganga, J., and Pitari, G.: Aerosols, their direct and indirect effects, in:
15 *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third*
16 *Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University
17 Press, 289-348, 2001.

18 Pope, F. D., Dennis-Smith, B. J., Griffiths, P. T., Clegg, S. L., and Cox, R. A.: Studies of single
19 aerosol particles containing malonic acid, glutaric acid, and their mixtures with sodium chloride.
20 I. Hygroscopic growth, *J. Phys. Chem. A*, 114, 5335-5341, doi: 10.1021/jp100059k, 2010.

21 Pradeep Kumar, P., Broekhuizen, K., and Abbatt, J. P. D.: Organic acids as cloud condensation
22 nuclei: Laboratory studies of highly soluble and insoluble species, *Atmos. Chem. Phys.*, 3,
23 509–520, doi: 10.5194/acp-3-509-2003, 2003.

24 Pratt, K. A., and Prather, K. A.: Aircraft measurements of vertical profiles of aerosol mixing states,
25 *J. Geophys. Res.*, 115, D11305, doi: 10.1029/2009JD013150, 2010.

26 Prenni, A. J., DeMott, P. J., and Kreidenweis, S. M.: Water uptake of internally mixed particles
27 containing ammonium sulfate and dicarboxylic acids, *Atmos. Environ.*, 37, 4243–4251, doi:
28 10.1016/S1352-2310(03)00559-4, 2003.

29 Rosenoern, T., Schlenker, J. C., and Martin, S. T.: Hygroscopic growth of multicomponent aerosol
30 particles influenced by several cycles of relative humidity, *J. Phys. Chem. A*, 112, 2378-2385,

1 doi: 10.1021/jp0771825, 2008.

2 Saxena, P., Hildemann, L. M., McMurry, P. H., and Seinfeld, J. H.: Organics alter hygroscopic
3 behavior of atmospheric particles, *J. Geophys. Res.*, 100, 18755-18770, doi: 10.1029/95JD01835,
4 1995.

5 Schroeder, J. R., and Beyer, K. D.: Deliquescence relative humidities of organic and inorganic salts
6 important in the atmosphere, *J. Phys. Chem. A*, 120, 9948–9957, doi: 10.1021/acs.jpca.6b08725,
7 2016.

8 Shippey, T. A.: Very strong hydrogen bonding: single crystal raman studies of potassium hydrogen
9 oxalate and sodium hydrogen oxalate monohydrate, *J. Mol. Struct.*, 57, 1-11, doi:
10 10.1016/0022-2860(79)80227-6, 1979.

11 Sjogren, S., Gysel, M., Weingartner, E., Baltensperger, U., Cubison, M. J., Coe, H., Zardini, A. A.,
12 Marcolli, C., Krieger, U. K., and Peter, T.: Hygroscopic growth and water uptake kinetics of
13 two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures, *J.*
14 *Aerosol Sci.*, 38, 157-171, doi: 10.1016/j.jaerosci.2006.11.005, 2007.

15 Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H.,
16 Williams, B. J., and McMurry, P. H.: Observations of ammonium salts in atmospheric nanoparticles
17 and possible climatic implications, *Proc. Nat. Acad. Sci. U. S. A.*, 107, 6634-6639, doi:
18 10.1073/pnas.0912127107, 2010.

19 Spinner, E.: Raman-spectral depolarisation ratios of ions in concentrated aqueous solution. The
20 next-to-negligible effect of highly asymmetric ion surroundings on the symmetry properties of
21 polarisability changes during vibrations of symmetric ions. Ammonium sulphate and
22 tetramethylammonium bromide, *Spectrochim. Acta, Part A*, 59, 1441-1456, doi:
23 10.1016/s1386-1425(02)00293-7, 2003.

24 Sullivan, R. C., and Prather, K. A.: Investigations of the diurnal cycle and mixing state of oxalic
25 acid in individual particles in Asian aerosol outflow, *Environ. Sci. Technol.*, 41, 8062-8069, doi:
26 10.1021/es071134g, 2007.

27 Tang, I. N., and Munkelwitz, H. R.: Aerosol growth studies—III ammonium bisulfate aerosols in a
28 moist atmosphere, *J. Aerosol Sci.*, 8, 321-330, doi: 10.1016/0021-8502(77)90019-2, 1977.

29 Tang, I. N., and Munkelwitz, H. R.: Water activities, densities, and refractive indices of aqueous
30 sulfates and sodium nitrate droplets of atmospheric importance, *J. Geophys. Res.*, 99,

1 18801-18808, doi: 10.1029/94JD01345, 1994a.

2 Tang, I. N., and Munkelwitz, H. R.: Aerosol phase-transformation and growth in the atmosphere, *J.*
3 *Appl. Meteorol.*, 33, 791-796, doi: 10.1175/1520-0450(1994)033<0791:Aptagi>2.0.Co;2, 1994b.

4 Treuel, L., Sandmann, A., and Zellner, R.: Spatial separation of individual substances in effloresced
5 crystals of ternary ammonium sulphate/dicarboxylic acid/water aerosols, *ChemPhysChem*, 12,
6 1109-1117, doi: 10.1002/cphc.201000738, 2011.

7 Villepin, J. D., and Novak, A.: Vibrational spectra of and isotope effect in hydrogen bonded
8 potassium hydrogen oxalate, *Spectrosc. Lett.*, 4, 1-8, doi: 10.1080/00387017108078634, 1971.

9 Von Schneidmesser, E., Monks, P. S., Allan, J. D., Bruhwiler, L., Forster, P., Fowler, D., Lauer, A.,
10 Morgan, W. T., Paasonen, P., Righi, M., Sindelarova, K., and Sutton, M. A.: Chemistry and the
11 linkages between air quality and climate change, *Chem. Rev.*, 115, 3856-3897, doi:
12 10.1021/acs.chemrev.5b00089, 2015.

13 Wang, B., and Laskin, A.: Reactions between water-soluble organic acids and nitrates in
14 atmospheric aerosols: Recycling of nitric acid and formation of organic salts, *J. Geophys. Res.*,
15 119, 3335-3351, doi: 10.1002/2013jd021169, 2014.

16 Wang, F., Zhang, Y. H., Zhao, L. J., Zhang, H., Cheng, H., and Shou, J. J.: Micro-Raman study on
17 the conformation behavior of succinate in supersaturated sodium succinate aerosols, *Phys. Chem.*
18 *Chem. Phys.*, 10, 4154-4158, doi: 10.1039/b719457a, 2008.

19 Wang, G. H., Kawamura, K., Cheng, C. L., Li, J. J., Cao, J. J., Zhang, R. J., Zhang, T., Liu, S. X.,
20 and Zhao, Z. Z.: Molecular distribution and stable carbon isotopic composition of dicarboxylic
21 acids, ketocarboxylic acids, and α -dicarbonyls in size-resolved atmospheric particles from Xi'an
22 City, China, *Environ. Sci. Technol.*, 46, 4783-4791, doi: 10.1021/es204322c, 2012.

23 Wang, Y., Ma, J. B., Zhou, Q., Pang, S. F., and Zhang, Y. H.: Hygroscopicity of mixed
24 glycerol/Mg(NO₃)₂/water droplets affected by the interaction between magnesium ions and
25 glycerol molecules, *J. Phys. Chem. B*, 119, 5558-5566, doi: 10.1021/acs.jpcc.5b00458, 2015.

26 Wise, M. E., Surratt, J. D., Curtis, D. B., Shilling, J. E., and Tolbert, M. A.: Hygroscopic growth of
27 ammonium sulfate/dicarboxylic acids, *J. Geophys. Res.*, 108, 4638, doi: 10.1029/2003jd003775,
28 2003.

29 Yang, L., and Yu, L. E.: Measurements of oxalic acid, oxalates, malonic acid, and malonates in
30 atmospheric particulates, *Environ. Sci. Technol.*, 42, 9268-9275, doi: 10.1021/es801820z, 2008.

- 1 Yeung, M. C., Lee, A. K. Y., and Chan, C. K.: Phase transition and hygroscopic properties of
2 internally mixed ammonium sulfate and adipic acid (AS-AA) particles by optical microscopic
3 imaging and Raman spectroscopy, *Aerosol Sci. Technol.*, 43, 387–399, doi:
4 10.1080/02786820802672904, 2009.
- 5 Yli-Juuti, T., Zardini, A. A., Eriksson, A. C., Hansen, A. M. K., Pagels, J. H., Swietlicki, E.,
6 Svenningsson, B., Glasius, M., Worsnop, D. R., Riipinen, I., and Bilde, M.: Volatility of organic
7 aerosol: evaporation of ammonium sulfate/succinic acid aqueous solution droplets, *Environ. Sci.*
8 *Technol.*, 47, 12123-12130, doi: 10.1021/es401233c, 2013.
- 9 Zhou, Q., Pang, S. F., Wang, Y., Ma, J. B., and Zhang, Y. H.: Confocal Raman studies of the
10 evolution of the physical state of mixed phthalic acid/ammonium sulfate aerosol droplets and the
11 effect of substrates, *J. Phys. Chem. B*, 118, 6198-6205, doi: 10.1021/jp5004598, 2014.
- 12

1 **Table 1.** Molecular vibration assignments of pure oxalic acid and ammonium sulfate droplets.

Solid H ₂ C ₂ O ₄		H ₂ C ₂ O ₄	(NH ₄) ₂ SO ₄	Refs	Assignments
Anhydrous	Dihydrate	Droplets (92.5% RH)	Droplets (94.8% RH)		
			450	(Spinner, 2003)	$\delta_s(\text{SO}_4^{2-})$
482	477	457		(Hibben, 1935)	$\delta(\text{OCO})$
828				(Ebisuzaki and Angel, 1981)	$r(\text{OCO})$
845	855	845		(Ebisuzaki and Angel, 1981)	$\nu(\text{C-C})$
			979	(Spinner, 2003)	$\nu_s(\text{SO}_4^{2-})$
1477	1490	1460		(Ebisuzaki and Angel, 1981)	$\nu_s(\text{COO})$
	1627	1636		(Ebisuzaki and Angel, 1981)	$\delta(\text{HOH})$
	1689			(Ebisuzaki and Angel, 1981)	$\nu(\text{C=O})$
1710	1737	1750		(Hibben, 1935)	$\nu(\text{C=O})$
2587, 2760				(Mohaček-Grošev et al., 2009)	Combinations
2909			3080	(Spinner, 2003)	Combinations
			3240	(Spinner, 2003)	$\nu(\text{OH})$
	3433, 3474	3433	3437	(Spinner, 2003; Ebisuzaki and Angel, 1981)	$\nu(\text{OH})$

ν : stretching; δ : bending; r: rocking; s: symmetric mode.

Table 2. Molecular vibration assignments of mixed oxalic acid/ammonium sulfate systems

$\text{H}_2\text{C}_2\text{O}_4\text{-(NH}_4)_2\text{SO}_4$ (1:3), RH = 96.2%	$\text{H}_2\text{C}_2\text{O}_4\text{-(NH}_4)_2\text{SO}_4$ (1:1), RH = 96.1%	$\text{H}_2\text{C}_2\text{O}_4\text{-(NH}_4)_2\text{SO}_4$ (3:1), RH = 95.9%	Refs	Assignments
450	450	461	(Spinner, 2003)	$\delta_s(\text{SO}_4^{2-})$
	852	850	(Ebisuzaki and Angel, 1981)	$\nu(\text{C-C})$
979	979	980	(Spinner, 2003)	$\nu_s(\text{SO}_4^{2-})$
1049	1051	1050	(Dawson et al., 1986)	$\nu_s(\text{SO}_3)$
	1382	1382	(Chang and Huang, 1997)	$\omega(\text{OCO})$
1446	1448	1460	(Ebisuzaki and Angel, 1981)	$\nu_s(\text{COO})$
1694			(Ebisuzaki and Angel, 1981)	$\nu(\text{C=O})$
1741	1751	1752	(Ebisuzaki and Angel, 1981)	$\nu(\text{C=O})$
3430	3427	3426	(Spinner, 2003)	$\nu(\text{OH})$

ν : stretching; δ : bending; ω : wagging; s: symmetric mode.

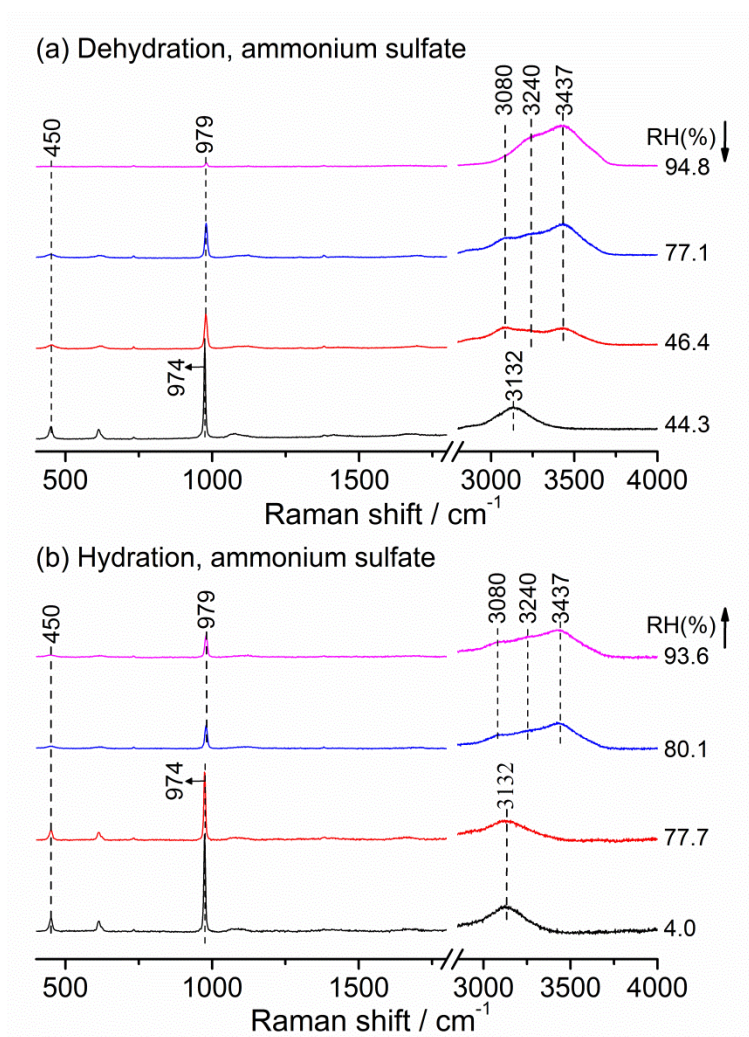
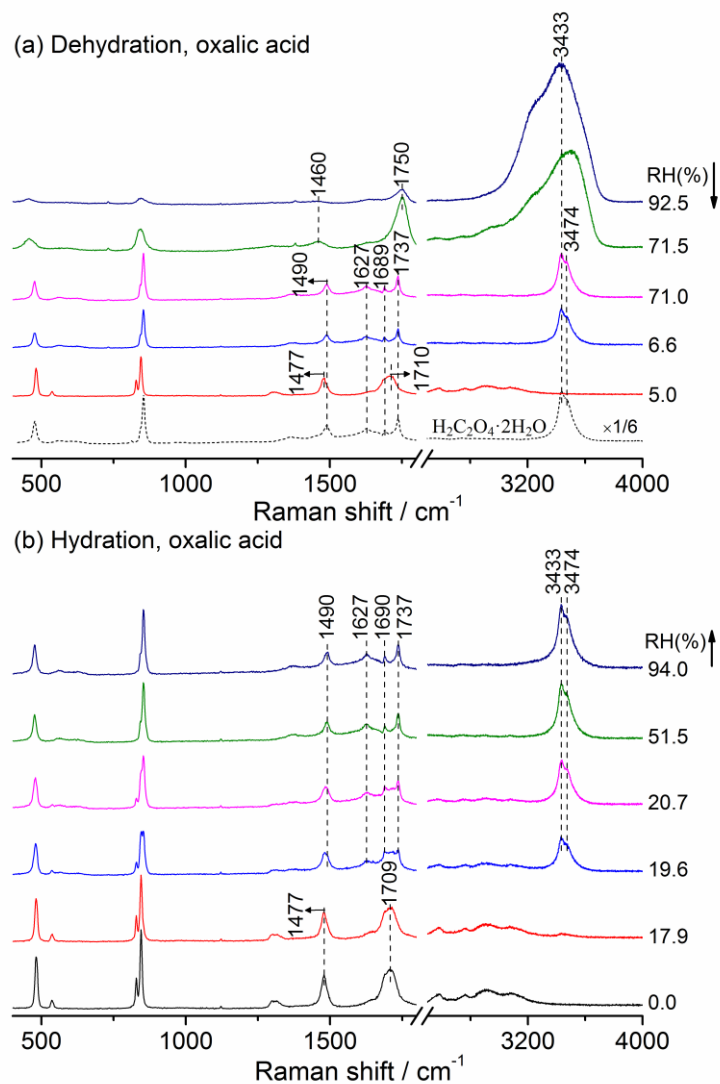


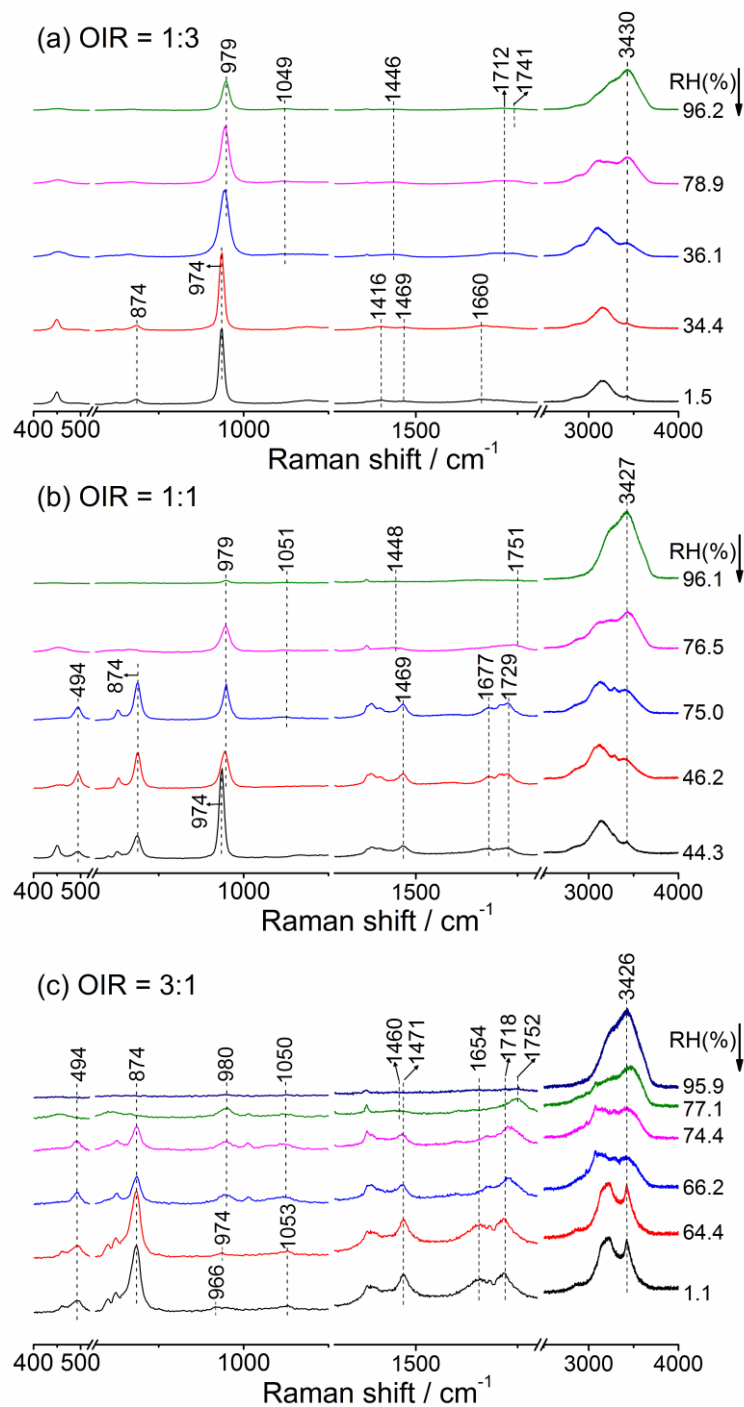
Figure 1. Raman spectra of ammonium sulfate droplets at various RH values during the (a) dehydration process and (b) hydration process.



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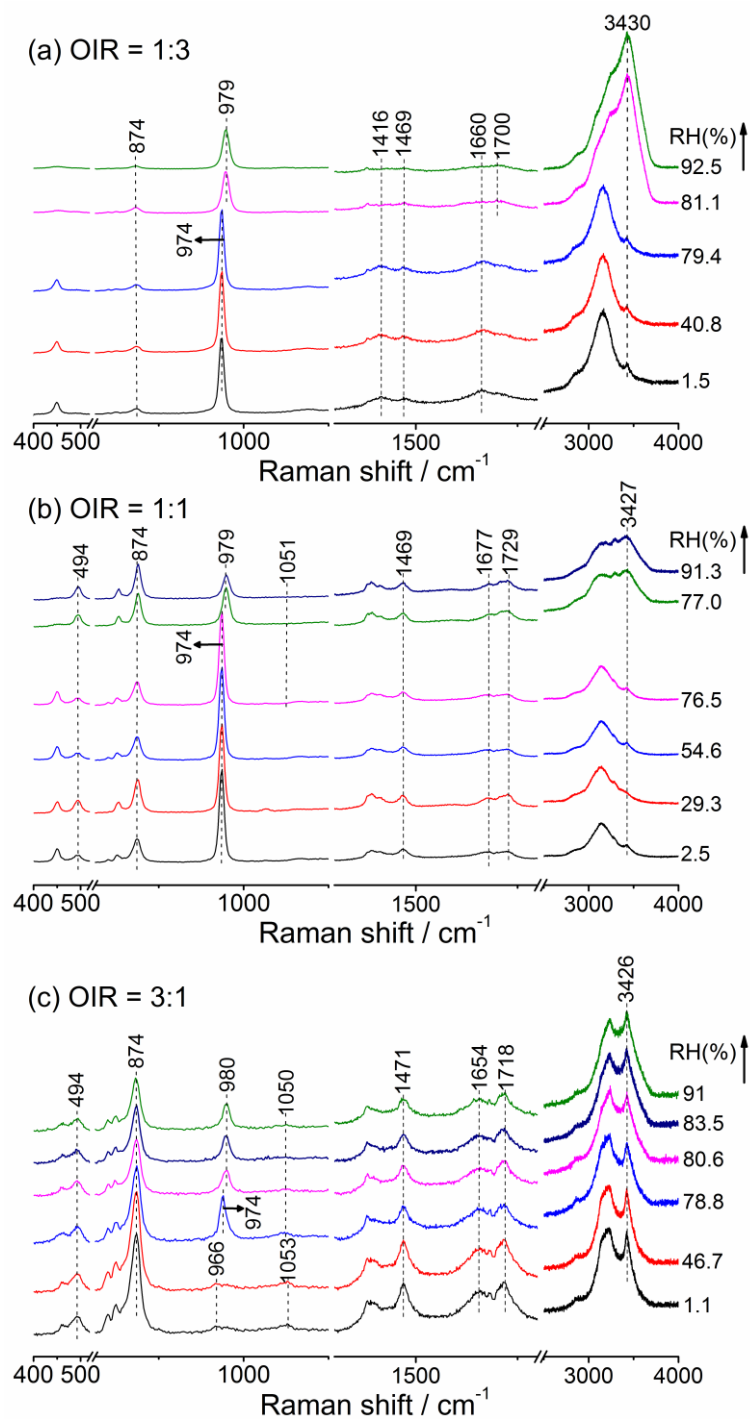
2 **Figure 2.** Raman spectra of oxalic acid droplets during the (a) dehydration process and (b)
 3 hydration process. In panel (a), the black dashed line indicates the spectrum of pure $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
 4 particles with the peak height of $\nu(\text{OH})$ located at 3433 cm^{-1} scaled by a factor of $1/6$.

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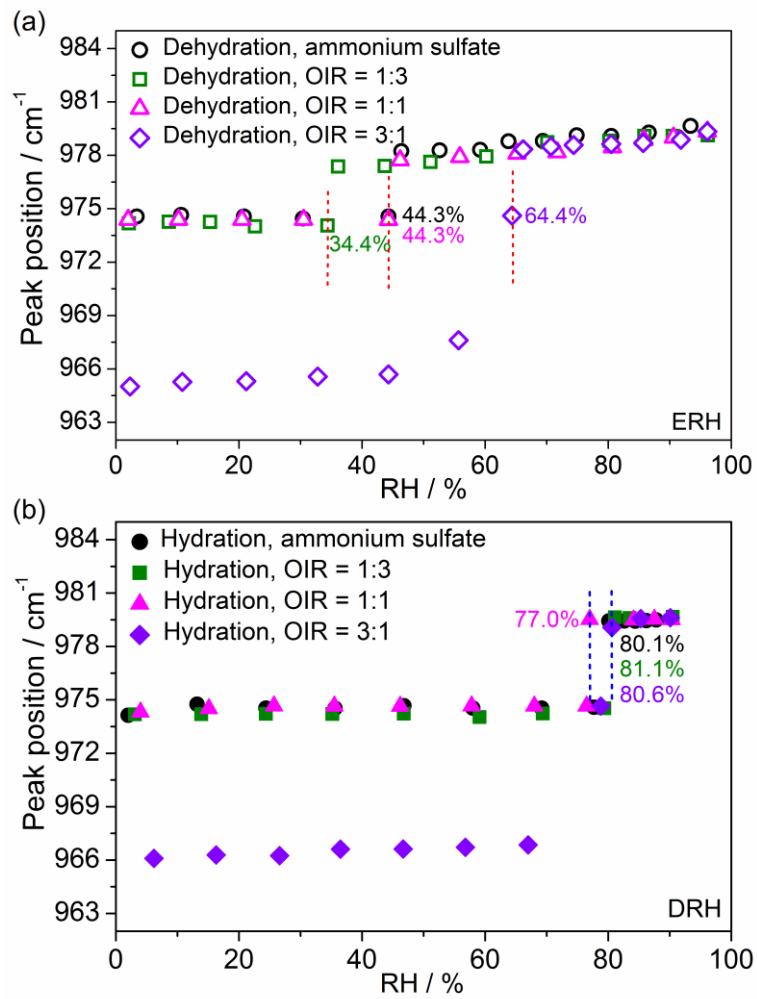
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Figure 3. Raman spectra of mixed oxalic acid/ammonium sulfate droplets with OIRs of (a) 1:3, (b) 1:1 and (c) 3:1 at various RH values during the dehydration process.



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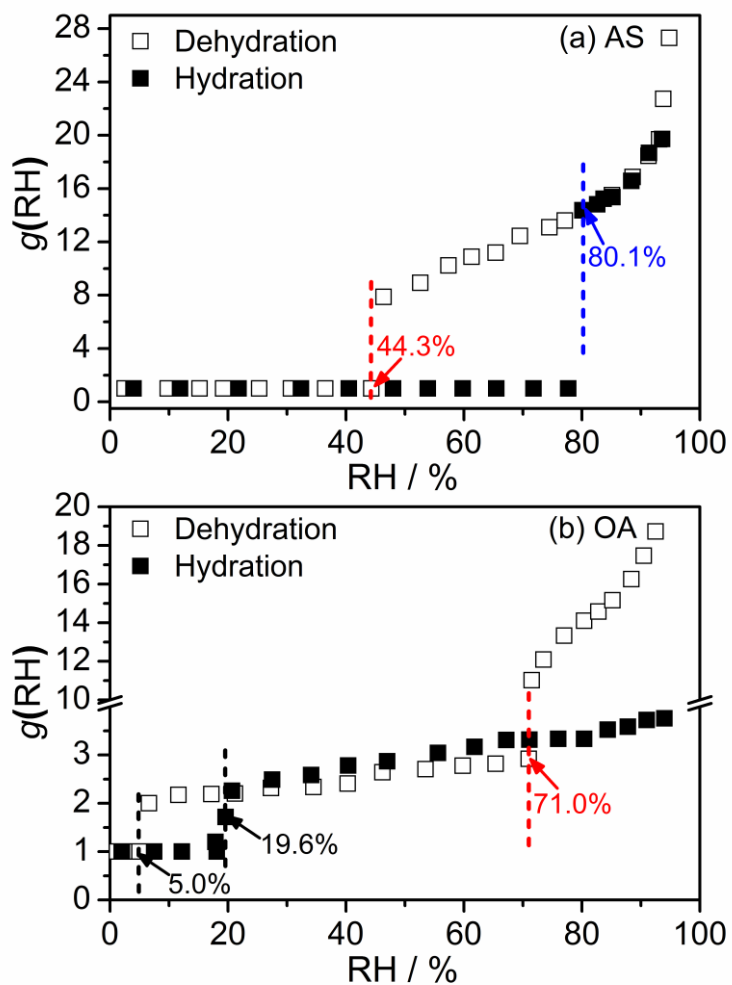
2 **Figure 4.** Raman spectra of mixed oxalic acid/ammonium sulfate droplets with OIRs of (a) 1:3, (b)
 3 1:1 and (c) 3:1 at various RH values during the hydration process.



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2 **Figure 5.** The peak position of the $\nu_1\text{-SO}_4^{2-}$ peak of mixed OA/AS particles and pure AS particles at
 3 various RHs during the (a) dehydration and (b) hydration process. The red and blue dashed lines
 4 indicate the ERH and DRH, respectively.

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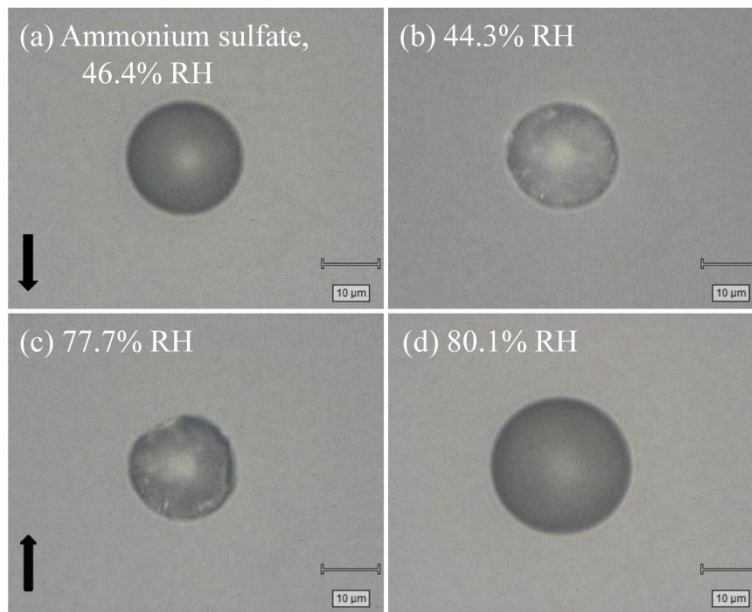


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2 **Figure 6.** Hygroscopicity of (a) AS and (b) OA as a function of RH. The red and blue dashed lines
 3 indicate the ERH and DRH, respectively. The black lines show phase transition point for the
 4 transformation between oxalic acid dihydrate and anhydrous oxalic acid.

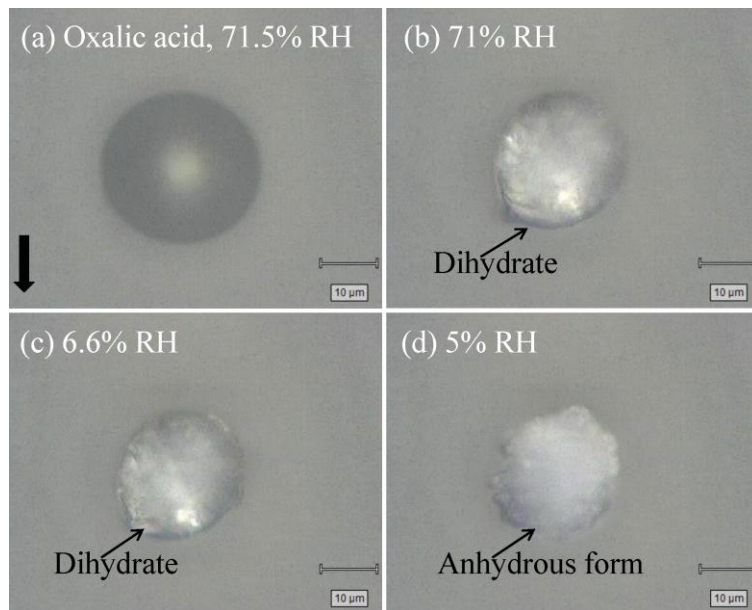
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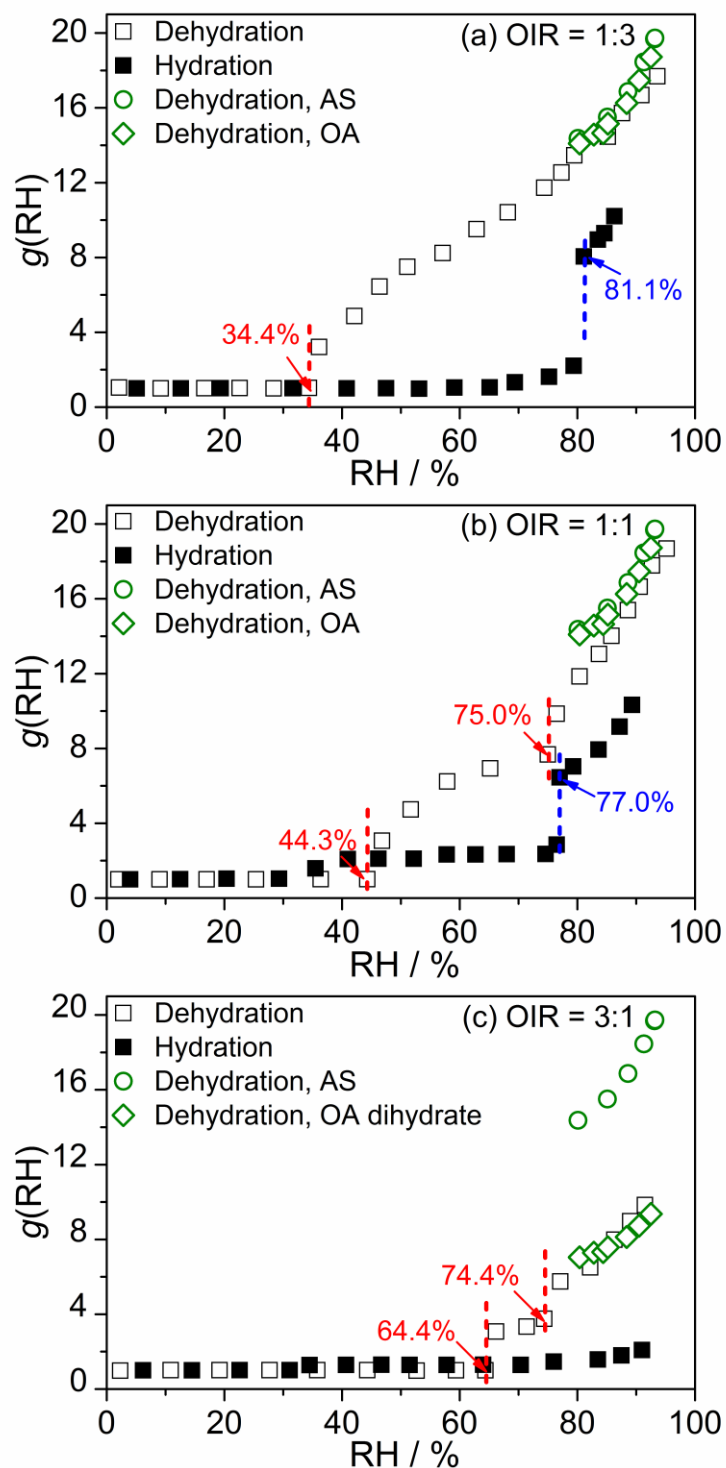
Figure 7. Optical micrographs of the ammonium sulfate particle at the phase change points. Dehydration process: (a) 46.4% RH and (b) 44.3% RH. Hydration process: (c) 77.7% RH and (d) 80.1% RH.



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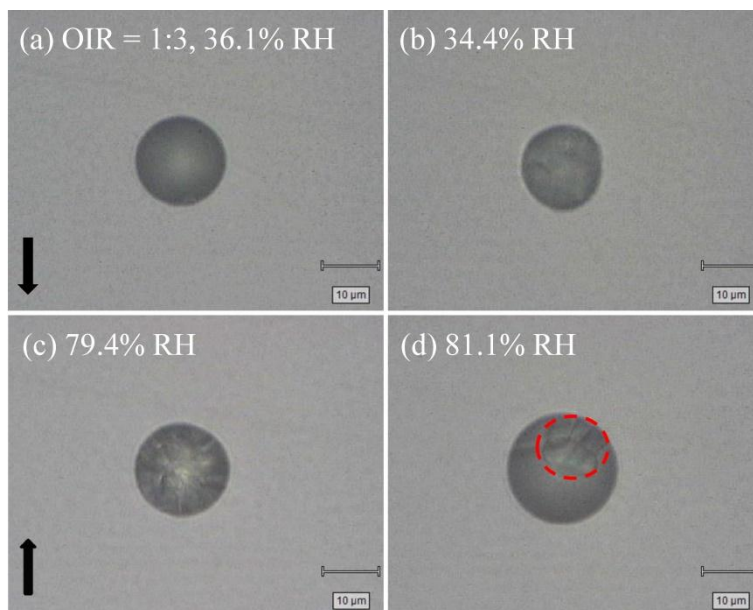
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3 **Figure 8.** Optical micrographs of the oxalic acid particle at (a) 71.5% RH, (b) 71% RH, (c) 6.6%
4 RH and (d) 5% RH during the dehydration process, respectively.



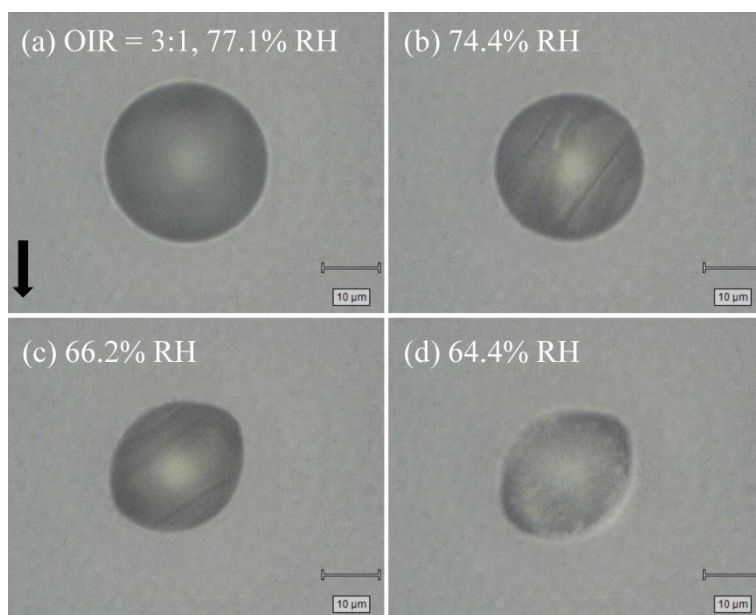
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2 **Figure 9.** Hygroscopicity of OA/AS mixtures with OIRs of (a) 1:3, (b) 1:1 and (c) 3:1 as a function
 3 of RH. The red and blue dashed lines indicate the ERH and DRH, respectively. In panels (a) and (b),
 4 Raman growth factors of pure AS and OA above 80% RH in the dehydration process are also
 5 included for comparisons. In the panel (c), Raman growth factors of pure AS and OA dihydrate
 6 above 80% RH during the dehydration process are also given for comparisons.



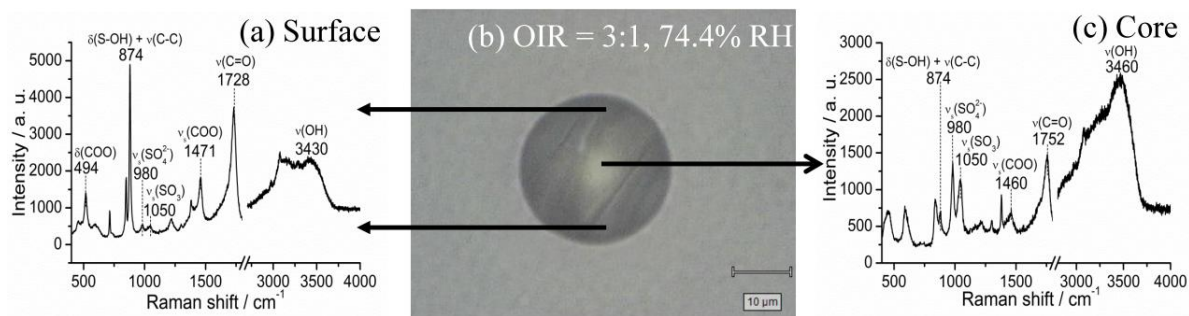
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Figure 10. Optical micrographs of the mixed oxalic acid/ammonium sulfate particle (OIR = 1:3) at phase change points. Dehydration: (a) 36.1% RH and (b) 34.4% RH. Hydration: (c) 79.4% RH and (d) 81.1% RH. In the image (d), the visual solid in aqueous phase is marked with a red dashed circle.



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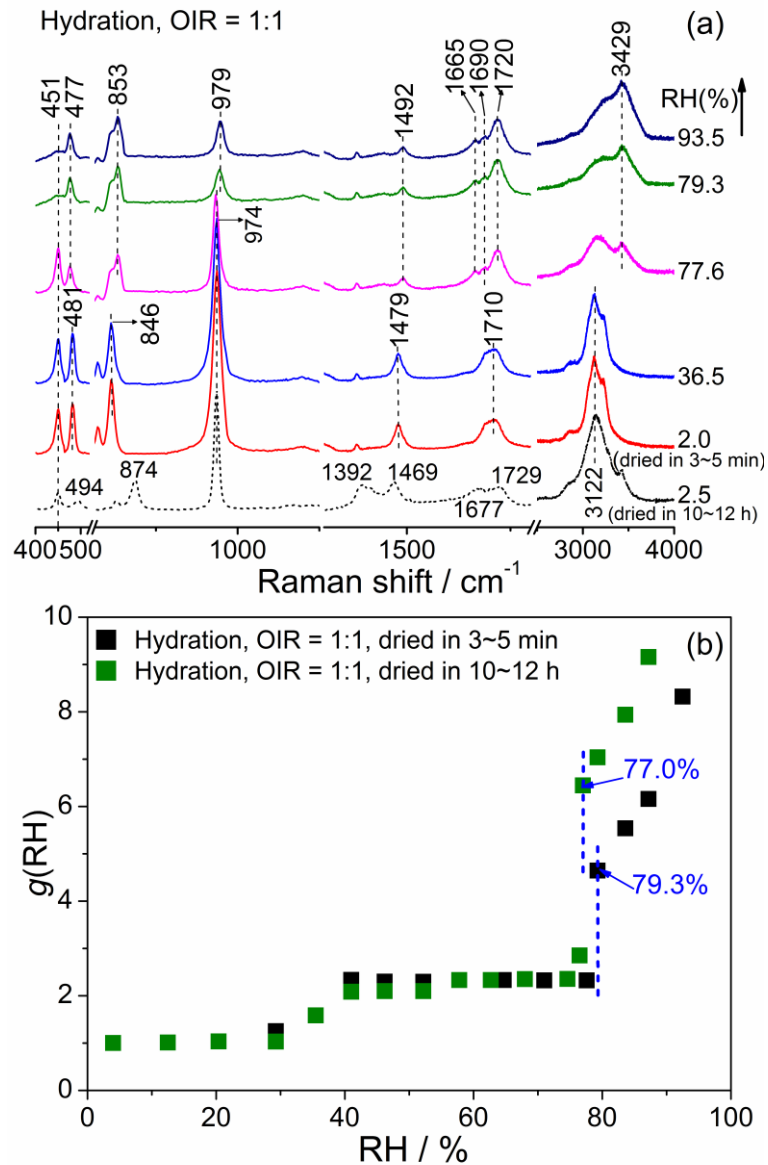
Figure 11. Optical micrographs of the mixed oxalic acid/ammonium sulfate particle (OIR = 3:1) at (a) 77.1% RH, (b) 74.4% RH, (c) 66.2% RH and (d) 64.4% RH during the dehydration process, respectively.



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Figure 12. 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 $\text{NH}_4\text{HC}_2\text{O}_4$. (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.

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3 **Figure 13.** (a) Raman spectra of equal molar mixed OA/AS particles after rapid drying process at
 4 various RH values upon hydration. The Raman spectrum (black short dash) at 2.5% RH obtained
 5 from the slow drying process is also given for comparisons. (b) Deliquescence curve of OA/AS
 6 mixtures with an OIR of 1:1. The hygroscopic curve (olive line) of particles after slow drying
 7 process is also included for comparisons. The blue dashed lines indicate the DRH.

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