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A laboratory study on the hygroscopic behavior of $H_2C_2O_4$-containing mixed particles

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GRAPHICAL ABSTRACT

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ABSTRACT

The climatic effect of atmospheric particles is greatly dependent on their hygroscopicity and chemical composition. Although the hygroscopic behavior of individual components of aerosol has been widely studied, the effect of coexisting species on the hygroscopic behavior of mixed constituents is still not clear. In this study, we used Raman spectroscopy to investigate how particles with different hygroscopic behaviors affect each other when they are combined together in mixtures. The effect of coexisting hygroscopic components, e.g. NaCl, NH_4NO_3, and $(NH_4)_2SO_4$, on the hygroscopic behavior of externally mixed $H_2C_2O_4/CaCO_3$ was studied. We found that coexisting NH_4NO_3 can promote the conversion of $H_2C_2O_4/CaCO_3$ to $CaC_2O_4{\cdot}H_2O$ in the humidifying process by providing a deliquesced solution to dissolve H^+ in the oxalic acid matrix. Moreover, competition and blocking effects existed in the case of coexisting $(NH_4)_2SO_4$. Reactions between $(NH_4)_2SO_4$ and $CaCO_3$ led to the formation of $CaSO_4{\cdot}2H_2O$ and $(NH_4)_2C_2O_4$ instead of CaC_2O_4. NaCl reacted with $H_2C_2O_4$ in solution to form $Na_2C_2O_4$. These results suggested that synergistic effects between coexisting components in mixed particles during the humidifying-dehumidifying process may change their chemical composition, mixing state, and hygroscopicity. In addition, chemical reactions should be considered in future studies on the hygroscopic behavior of mixed particles.

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1. Introduction

Atmospheric aerosols affect climate directly through scattering and absorption of solar radiation, and indirectly through changing the optical properties and lifetime of clouds by acting as cloud condensation nuclei (CCNs)(Ramanathan et al., 2001) and ice nucleating particles (Tang et al., 2018). Although the sum of the direct and indirect cooling effects of aerosols has been established to be almost equivalent to the warming effect of carbon dioxide, the negative forcing of atmospheric aerosols remains the largest source of uncertainty in predictions of the future global climate(Solomon, 2007). Therefore, a number of studies have focused on the physicochemical properties of aerosols, especially the hygroscopic behavior. In general, solid salt particles that are hygroscopic in nature take up water in the atmosphere and form aqueous droplets. This hygroscopic growth influences the light scattering, cloud formation and precipitation, atmospheric lifetime and chemical reactivity of atmospheric particles (Charlson et al., 1992). The hygroscopic properties of an aerosol also determine which fraction of aerosol particles can act as CCN and thus contribute to the indirect aerosol effect (Pilinis et al., 1995). Due to their great importance, the hygroscopic behavior of aerosol particles as well as the atmospheric processes related to the hygroscopic behavior of aerosol have received much attention.

Atmospheric aerosol is usually found to be a mixture of various inorganic and organic components in field measurements (Andreae et al., 1986; Li and Shao, 2009a, b; Poschl, 2005; Sullivan et al., 2007; Sullivan and Prather, 2007). The hygroscopic behaviors of individual inorganic salts or organic components commonly found in atmospheric aerosols are well characterized nowadays. However, the effect of mixing state on the hygroscopic behavior of coexisting components in mixed aerosol particles remains unrevealed (Hallquist et al., 2009; Wu et al., 2011). The Zdanovskii-Stokes-Robinson (ZSR) model has been applied to predict the hygroscopicity of mixed particles using the volume or mass fraction of each component. For example, the water activity of mixtures of NaCl with $MgSO_4$, Na_2SO_4 or $MgCl_2$ was studied (Chan et al., 2000). Good agreement was found between the predictions of the ZSR model and the experimental data over the entire range of water activity for all mixtures studied before crystallization occurred. The hygroscopic growth factors (GFs) of internally mixed NaCl-glutaric acid and NaCl-pinonic acid mixtures measured with a hygroscopicity tandem differential mobility analyzer (H-TDMA) system showed that the GFs of mixtures agreed with the predictions of the ZSR approach (Cruz and Pandis, 2000). Pope et al. also found that the properties of aqueous mixtures of malonic acid and glutaric acid with NaCl could be estimated well based on those of the pure solutions (Pope et al., 2010). However, a recent study found that the ZSR model is not suitable for predicting the hygroscopic behavior of externally mixed components, especially when chemical reactions occur (Ma et al., 2013c). Therefore, the hygroscopic behavior of mixed particles needs further study.

Previous laboratory studies on the hygroscopic behavior of inorganic-organic mixtures mainly focused on the water-soluble constituents. For instance, the effects of dicarboxylic acids (DCAs) on hygroscopic inorganic compounds like $(NH_4)_2SO_4$, NaCl, $NaNO_3$, $MgCl_2$, $CaCl_2$, $CaCO_3$, etc. in mixtures have been widely studied (Braban and Abbatt, 2004; Brooks et al., 2002; Choi and Chan, 2002; Cruz and Pandis, 2000; Drozd et al., 2014; Laskina et al., 2015; Ma and He, 2012; Ma et al., 2013c; Prenni et al., 2003; Shao et al., 2018; Wang et al., 2017; Wise et al., 2003). Oxalic acid ($H_2C_2O_4$) is the most abundant contributor to DCAs, which represent a significant portion of the organic fraction of aerosols in the atmosphere (Chebbi and Carlier, 1996; Sullivan and Prather, 2007; Wang et al., 2012). It was found that the presence of oxalic acid has no measurable effect on the deliquescence relative humidity of ammonium sulfate due to its lower solubility (Brooks et al., 2002; Wise et al., 2003), but that it apparently inhibits the nucleation of ammonium sulfate (Prenni et al., 2003). However, a recent study by Wang et al. showed that ammonium hydrogen oxalate ($NH_4HC_2O_4$) and ammonium hydrogen sulfate (NH_4HSO_4) are formed from interactions between $H_2C_2O_4$ and $(NH_4)_2SO_4$ in aerosols during the dehydration process (Wang et al., 2017). The reaction between oxalic acid and NaCl or $NaNO_3$ also occurs in the dehydration process of oxalic acid-containing mixtures, which leads to the formation of $Na_2C_2O_4$ and volatile inorganic acids like HNO_3 and HCl (Laskin et al., 2012; Ma et al., 2013c; Wang and Laskin, 2014).

On the other hand, the interaction between soluble components and insoluble mineral dust is still not clear. Field measurement results analyzing Asian dust by single particle mass spectrometry (ATOFMS) showed that oxalic acid was predominantly mixed with mineral dust during transport in the atmosphere (Sullivan and Prather, 2007; Yang et al., 2009). It has been proposed that the origin of DCA/mineral dust mixtures is heterogeneous and aqueous oxidation of DCAs' precursors on alkaline Asian dust surfaces (Sullivan and Prather, 2007). Wang et al. suggested that oxalic acid in coarse mode originated from evaporation from fine mode particles and subsequent condensation/adsorption onto pre-existing coarse particles (Wang et al., 2012). By using X-ray absorption fine structure spectroscopy (XAFS), Furukawa and Takahashi(Furukawa and Takahashi, 2011) found that most of the oxalic acid in mineral mixtures is present in the form of metal oxalate complexes in aerosols, especially Ca and Zn oxalate complexes. Although the affinity between oxalic acid and calcite has been widely proposed, the formation mechanism of metal-complexed oxalate species in mixed mineral dust particles is still not well recognized (Furukawa and Takahashi, 2011). Calcite ($CaCO_3$) is considered to be a reactive component of mineral dust aerosols. Due to its alkalinity, calcite has a significant neutralization effect on atmospheric acidic constituents, such as H_2SO_4, SO_2, HNO_3, NO_2, and carboxylic acids (Al-Abadleh et al., 2003; Al-Hosney and Grassian, 2005; Crowley et al., 2010; Dentener et al., 1996; Laskin et al., 2005; Ma et al., 2012; Tang et al., 2016; Usher et al., 2003). The interaction between oxalic acid and calcite in mixtures during the humidifying process has also been considered in recent laboratory studies. Gierlus et al. (2012) determined that cloud processes under supersaturation conditions can trigger reaction between mixtures of $H_2C_2O_4$ and $CaCO_3$, resulting in the formation of CaC_2O_4. Meanwhile, in a previous study (Ma and He, 2012), we found that there exists a synergistic effect in the humidifying process of atmospherically relevant calcium nitrate, calcite, and oxalic acid mixtures. Substitution of strong acid (HNO_3) by weaker acid ($H_2C_2O_4$) occurred when water vapor was absorbed in $Ca(NO_3)_2/H_2C_2O_4$ mixtures. Moreover, coexisting hygroscopic nitrate shows a promotive effect on the reaction between $H_2C_2O_4$ and $CaCO_3$ under ambient conditions by providing an aqueous solution after deliquescence. Since mineral dust represents one of the biggest contributors to atmospheric aerosol, it is necessary to further study the hygroscopic behavior of inorganic-organic mixtures containing mineral dust.

In previous studies, Gierlus et al. (2012) and Laskina et al. (2013) found that Ca oxalate was formed in the internally mixed particles generated by atomizing a suspension of insoluble powder in an aqueous solution. However, the aqueous reaction process was not observed directly. In this study, we prepared externally mixed particles to investigate the aqueous reaction process in the humidifying-dehumidifying process using Raman spectroscopy. Typical atmospheric hygroscopic component, e.g., NaCl, NH_4NO_3, or $(NH_4)_2SO_4$, were chosen to study whether they were involved in this reaction. The results suggested that, besides cloud process, the chemical reaction between $H_2C_2O_4$ and $CaCO_3$ under unsaturated humidity condition could be also an important pathway for the formation of coated or internally mixed oxalate with mineral dust when hygroscopic components coexist.

2. Experimental section

In situ Raman spectroscopy: Raman spectroscopy has been widely used to study the hygroscopic behavior of aerosols (Liu et al., 2008; Tang and Fung, 1997). A UV/Vis resonance Raman spectrometer (UVR

DLPC-DL-03) was used to record the in situ Raman spectra, which has been described elsewhere (Liu et al., 2010). The exciting laser was a continuous diode-pumped solid state (DPSS) laser (532 nm) with source power of 40 mW. The spectra resolution was 2.0 cm^{-1}. In a typical experiment, particles were placed in an in situ cell and the temperature was 293 K. The relative humidity in the stream was measured by a moisture meter (CENTER 314, China, ± 2% RH, ± 0.1 K). Each RH point was equilibrated for more than 40 min if not otherwise stated. A humidifying-dehumidifying (H-D) cycle consisted of increasing the RH around the samples from 0 to 95% and then decreasing it to zero.

Chemicals: The externally mixed samples were prepared by grinding different components together. The molar ratio of oxalic acid and calcite was unity according to the stoichiometry. $CaCO_3$ (AR, Beijing Yili Fine Chemical Co. Ltd.), $H_2C_2O_4{\cdot}2H_2O$ (AR, Beijing Yili Fine Chemical Co. Ltd.), NaCl (AR, > 99.5%, Sinopharm Chemical Reagent Co. Ltd.), NH_4NO_3 (AR, > 99.5%, Sinopharm Chemical Reagent Co. Ltd.), and $(NH_4)_2SO_4$ (AR, > 99% Beijing Chemical Reagent) were used as purchased. Distilled H_2O was degassed by heating prior to use.

3. Results and discussions

3.1. Hygroscopic behavior of mixed $CaCO_3/H_2C_2O_4$ particles

Fig. 1 shows the Raman spectra of mixed $H_2C_2O_4/CaCO_3$ particles before (line a) and after (line b) a humidifying-dehumidifying process. Several peaks at 120, 182, 286, 485, 545, 715, 850, 1088, 1320, 1488, and 1707 cm^{-1} are seen. Compared to the spectrum of anhydrous $H_2C_2O_4$ particles (line c), peaks at 286, 715, and 1088 cm^{-1} are assigned to calcite while others are attributed to anhydrous oxalic acid particles (Ma and He, 2012). The assignments of characteristic peaks in various spectra were summarized in Table 1. The spectrum of mixed particles before the humidifying process (line a) is very similar to the spectrum of mixed particles after the humidifying process (line b) without any shifting of peaks or the presence of new peaks. The spectrum of $CaC_2O_4{\cdot}H_2O$ in the form of whewellite is also shown in Fig. 1 (line d) for comparison (Frost and Weier, 2003). Peaks belonging to $CaC_2O_4{\cdot}H_2O$ did not appear in the spectrum of $H_2C_2O_4/CaCO_3$ (line b), indicating that no reaction took place between oxalic acid and calcite in the humidifying-dehumidifying cycle. Since calcite and oxalic acid are not deliquescent in the range of 0–95% RH, reaction between the two different kinds of solid particles hardly takes place, especially in external mixtures.

It is important to note that the reaction between $H_2C_2O_4$ and $CaCO_3$ has been observed by Gierlus et al. (2012) and Laskina et al. (2013) previously. Such a discrepancy is likely to be associated with the differences in experimental conditions and aerosol preparation, as explained by Laskina et al. (2013). In the work of Gierlus et al. (2012) and Laskina et al. (2013), internally mixed particles were generated by a constant output atomizer from an aqueous suspension of calcite and oxalic acid solution, in which H^+ is available for decomposition of calcite. In contrast, in externally mixed calcite and oxalic acid particles, the H^+ is fixed in the oxalic acid matrix and does not decompose calcite.

Table 1
The assignments of characteristic peaks in the spectra of particles.

Raman shift (cm^{-1})	assignment	reference
286, 715, 1088	$CaCO_3$	Ma and He (2012)
485, 850, 1320, 1488	$H_2C_2O_4$	Ma et al. (2013a)
1464, 1491	$CaC_2O_4{\cdot}H_2O$ (whewellite)	Frost and Weier (2003)
1046	NH_4NO_3	Ma et al. (2013b)
974, 981	$(NH_4)_2SO_4$	Ma et al. (2013b)
1007, 1137	$CaSO_4{\cdot}2H_2O$	Ma et al. (2013b)
1416, 1451	$Na_2C_2O_4{\cdot}2H_2O$	Ma et al. (2013c)
1490	$CaC_2O_4{\cdot}H_2O$ (weddelite)	Frost and Weier (2003)

3.2. The effect of NH_4NO_3 on the hygroscopic behavior of mixed $CaCO_3/H_2C_2O_4$ particles

The presence of 20 *wt*% NH_4NO_3 can promote the reaction between oxalic acid and calcite during the humidifying process, as seen in Fig. 2. For dry mixed particles, peaks at 1485 and 850 cm^{-1} were attributed to $H_2C_2O_4$, while peaks at 1088 and 286 cm^{-1} were attributed to $CaCO_3$ (Ma and He, 2012). The peak at 1046 cm^{-1} was assigned to NH_4NO_3. When RH increased to 30%, the peaks at 1485 and 850 cm^{-1} shifted to 1496 and 860 cm^{-1}, respectively. These shifts were due to the conversion of anhydrous oxalic acid to the dihydrate (Ma and He, 2012). As RH further increased to 50%, the peak at 1046 cm^{-1} (the symmetric stretching mode of NO_3^-) shifted to 1050 cm^{-1} due to the deliquescence of NH_4NO_3. This measured deliquescence RH (DRH) of NH_4NO_3 in this mixed particles is lower than the DRH of NH_4NO_3 individually at room temperature, namely ~62% RH (Ma et al., 2010), indicating that the coexistence of $H_2C_2O_4$ or calcite can affect the hygroscopic behavior of NH_4NO_3. When the vapor exposure time was increased, peaks due to both $H_2C_2O_4$ and calcite decreased and finally disappeared. Meanwhile, peaks at 1632, 1491, 1464, 896, 197, and 140 cm^{-1} were observed and these peaks were assigned to $CaC_2O_4{\cdot}H_2O$ according to line d in Fig. 1 (Frost, 2004; Ma and He, 2012). These results suggested that the

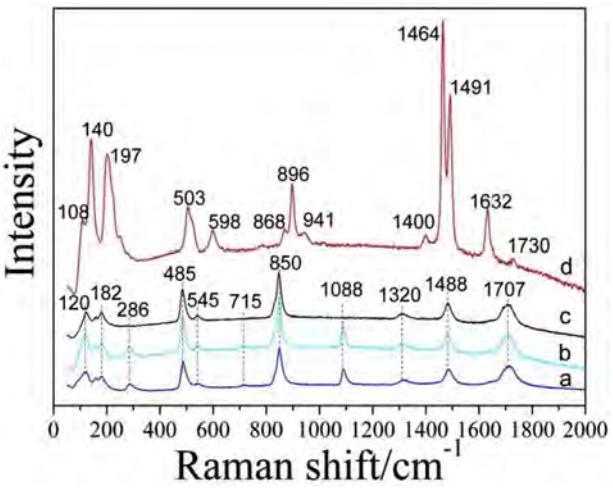

Fig. 1. Comparison of Raman spectra of mixed $H_2C_2O_4/CaCO_3$ particles (a) before and (b) after a humidifying-dehumidifying process, (c) anhydrous $H_2C_2O_4$, and (d) $CaC_2O_4{\cdot}H_2O$.

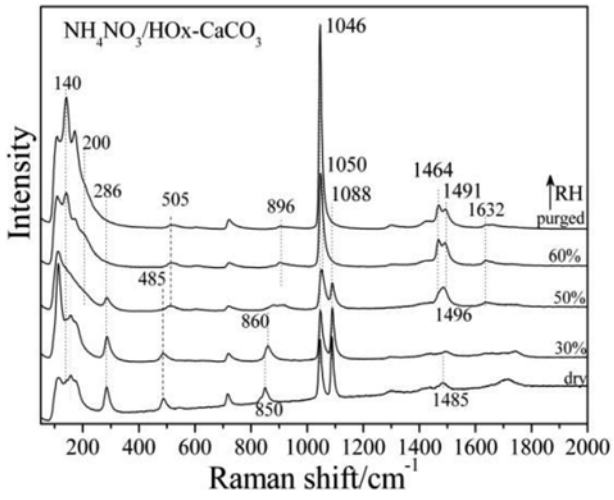

Fig. 2. Raman spectra of mixed 20 *wt*%NH_4NO_3—$H_2C_2O_4/CaCO_3$ particles exposed to vapor with different RH and then purged with dry N_2.

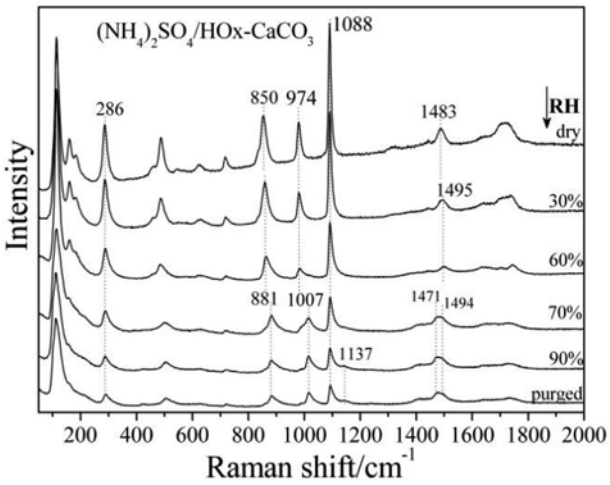

Fig. 3. Raman spectra of mixed 20 *wt*% $(NH_4)_2SO_4$—$H_2C_2O_4/CaCO_3$ particles exposed to vapor with different RH and then purged with dry N_2.

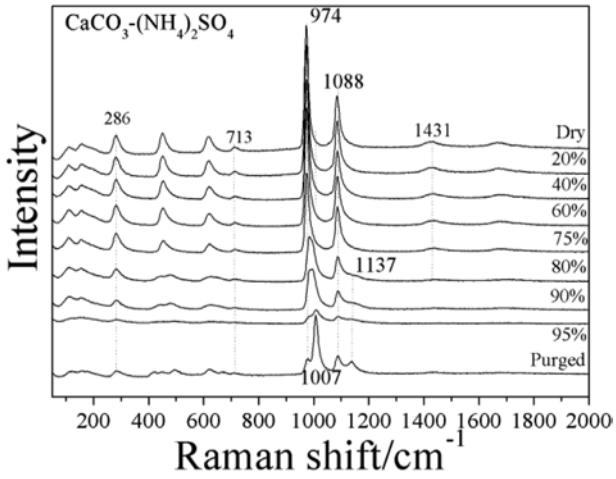

Fig. 4. Raman spectra of mixed $(NH_4)_2SO_4/CaCO_3$ particles exposed to different RH and then purged with dry N_2.

consumption of $H_2C_2O_4$ and calcite took place during the vapor absorption process, resulting in the formation of $CaC_2O_4{\cdot}H_2O$. When the mixture was purged with dry nitrogen, the intensities of peaks at 1046 cm^{-1} attributed to NH_4NO_3 finally increased. This is due to the deposition of NH_4NO_3 on the surface of $CaC_2O_4{\cdot}H_2O$, since Raman spectroscopy is surface sensitive.

As discussed above, the H^+ in externally mixed $H_2C_2O_4$ and $CaCO_3$ particles is not available for decomposing calcite in the humidifying process. When hygroscopic components coexist, NH_4NO_3 in this case, the deliquescence of NH_4NO_3 can dissolve $H_2C_2O_4$ and release H^+, which makes the reaction between $H_2C_2O_4$ and $CaCO_3$ possible. Therefore, in the presence of NH_4NO_3, conversion of $CaCO_3$ and $H_2C_2O_4$ to $CaC_2O_4{\cdot}H_2O$ occurred in the humidifying process.

3.3. The effect of $(NH_4)_2SO_4$ on the hygroscopic behavior of mixed $CaCO_3$/$H_2C_2O_4$ particles

In the case of the 20 *wt*% $(NH_4)_2SO_4$—$H_2C_2O_4/CaCO_3$ mixture, the hygroscopic behavior was different from the case when NH_4NO_3 was part of the mixture. As seen from Fig. 3, the peak at 974 cm^{-1} is attributed to $(NH_4)_2SO_4$ (Ma et al., 2013b). When RH increased to 30%, the conversion of anhydrous $H_2C_2O_4$ to dihydrate particles was observed as exposure time increased (Ma and He, 2012; Ma et al., 2013a). However, as RH was further increased to 70%, the intensity of the peak at 1088 cm^{-1} attributed to calcite decreased, indicating consumption of calcite during the humidifying process. Unlike previous results (Ma and He, 2012), peaks belonging to calcium oxalate at 140, 200, and 900 cm^{-1} were not detected, although two peaks at 1471 and 1494 cm^{-1} were observed. Meanwhile, several new peaks at 1007 and 1137 cm^{-1} appeared. These peaks at 1007 and 1137 cm^{-1} were assigned to the symmetric and asymmetric stretching modes of SO_4^{2-} in gypsum (Ma et al., 2013b; Tomic et al., 2010). These results implied that reaction between $(NH_4)_2SO_4$ and $CaCO_3$ took place and resulted in the formation of gypsum. On the other hand, the peak at 860 cm^{-1} attributed to oxalic acid shifted to 881 cm^{-1}, indicating that $(NH_4)_2C_2O_4$ formed during the reaction (Frost, 2004). This also implied that $H_2C_2O_4$ was involved in this reaction.

Although $H_2C_2O_4$ and $CaCO_3$ were prepared with the mole ratio of 1:1, $CaCO_3$ in this case was not completely decomposed, unlike in the case with NH_4NO_3 present (Fig. 2). There are two possible reasons. Firstly, the reaction between $(NH_4)_2SO_4$ and $CaCO_3$ results in the consumption of hygroscopic $(NH_4)_2SO_4$, and consequently decreases the water content of particles. Thus, the complete dissolution of $H_2C_2O_4$ as well as decomposition of $CaCO_3$ ceased. Secondly, the formation of gypsum on the surface of $CaCO_3$ blocks the further reaction of $CaCO_3$ with $H_2C_2O_4$, since gypsum is weakly hygroscopic (Gu et al., 2017; Ma et al., 2013b).

To confirm the reaction between $(NH_4)_2SO_4$ and $CaCO_3$ during the humidifying process, we further studied the humidifying process of an equi-molar $(NH_4)_2SO_4/CaCO_3$ mixture. As seen in Fig. 4, the characteristic peaks at 974 and 1088 cm^{-1} were assigned to SO_4^{2-} and CO_3^{2-}, respectively. When RH increased to 80%, a peak shift from 974 cm^{-1} to 981 cm^{-1} was observed due to the deliquescence of $(NH_4)_2SO_4$. The intensity of the peak at 1088 cm^{-1} decreased when RH further increased to 95% and then decreased to dry conditions, indicating the decomposition of $CaCO_3$ during the deliquescence of coexisting $(NH_4)_2SO_4$. Meanwhile, two new peaks at 1007 and 1137 cm^{-1} assigned to SO_4^{2-} in gypsum were observed. These results confirmed that the chemical reaction between $CaCO_3$ and $(NH_4)_2SO_4$ during the humidifying process of mixed particles leads to the formation of gypsum.

3.4. The effect of NaCl on the hygroscopic behavior of mixed $CaCO_3$/$H_2C_2O_4$ particles

When 20 *wt*% NaCl was added into mixed $H_2C_2O_4$/calcite particles, a promotion effect on the reaction between $H_2C_2O_4$ and calcite during the humidifying process could also be observed. Fig. 5 shows the

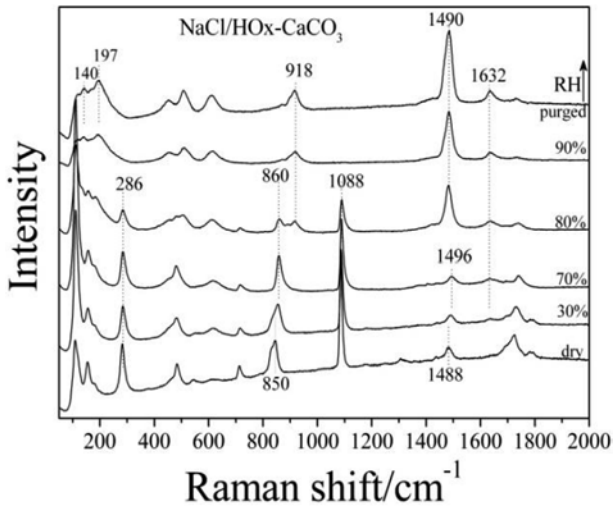

Fig. 5. Raman spectra of mixed 20 *wt*%NaCl—$H_2C_2O_4/CaCO_3$ particles exposed to vapor with different RH and then purged with dry N_2.

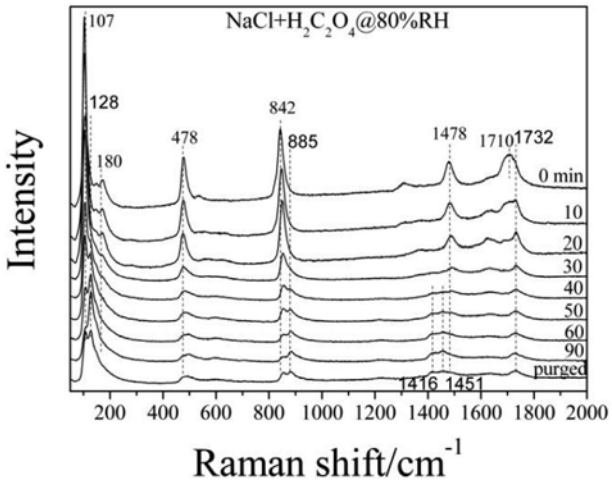

Fig. 6. Raman spectra of mixed NaCl—$H_2C_2O_4$ particles exposed to vapor at 80% RH as a function of time and then purged with dry N_2.

Raman spectra of mixed 20 *wt*% NaCl—$H_2C_2O_4$/$CaCO_3$ particles exposed to vapor as a function of RH. As RH increased to above 30%, peak positions due to the conversion of anhydrous oxalic acid particles to oxalic acid dihydrate particles was also observed (Ma and He, 2012). As RH further increased to 80%, which is above the deliquescence point of NaCl, *i.e.* 75% RH, the bands attributed to $CaCO_3$ at 286 and 1088 cm^{-1} decreased. These bands finally disappeared after RH increased to 90%. Decrease in the peak intensities of oxalic acid was also detected. Meanwhile, several new peaks at 140, 197, 1490, and 1632 cm^{-1} were observed after the dehumidifying process. These peaks can be assigned to $CaC_2O_4{\cdot}2H_2O$ in the form of weddellite according to Frost and Weier (2003). These results suggest that the presence of coexisting NaCl promoted the reaction between oxalic acid and calcite during the humidifying process.

To investigate whether NaCl was involved in the reaction between $CaCO_3$ and $H_2C_2O_4$ during the humidifying process, we further studied the humidifying process of a NaCl/$H_2C_2O_4$ mixture with mole ratio of 2:1. As shown in Fig. 6, anhydrous $H_2C_2O_4$ was first converted to dihydrate particles as exposure time increased. Then, a decrease in the peak intensity of $H_2C_2O_4$ was observed, which was due to the solvation effect of the deliquescent NaCl solution. As the exposure time further increased, several new peaks at 128, 885, 1416, 1451, and 1732 cm^{-1} were observed. These peaks can be assigned to sodium oxalate particles (Frost, 2004; Ma et al., 2013c). In a previous study, it was demonstrated that replacement of chloride by oxalate occurred in the humidifying process of NaCl and $H_2C_2O_4$ mixtures, because of the weak hygroscopicity of sodium oxalate particles (Ma et al., 2013c). The peak at 918 cm^{-1} in Fig. 5 could be assigned neither calcium oxalate nor sodium oxalate, which is possible due to the formation of Na—Ca double oxalate in this system. These results suggested that NaCl was involved in the reaction, rather than simply triggering the reaction by supplying a deliquescent solution. Calcite was completely decomposed in the humidifying process of the NaCl—$H_2C_2O_4$/$CaCO_3$ mixture, as seen in Fig. 5, which is different from the case when $(NH_4)_2SO_4$ was present (Fig. 3). This is because the consumption of $H_2C_2O_4$ by reaction with NaCl eventually produced HCl. The HCl formed in the solution can decompose calcite quickly, and residual $CaCl_2$ may be present in the mixture after dehumidification.

4. Conclusions and atmospheric implications

In this study, the effect of coexisting hygroscopic components on the hygroscopic behavior of mixed $H_2C_2O_4$/$CaCO_3$ particles was studied by Raman spectroscopy. It was determined that the existence of hygroscopic components promoted the reaction between $H_2C_2O_4$ and $CaCO_3$ during the humidifying process by providing an aqueous environment. These reactions resulted in the formation of insoluble $CaC_2O_4{\cdot}H_2O$ in the presence of NaCl or NH_4NO_3. NH_4NO_3 exhibited a promotion effect but was not involved in the reaction. In contrast, coexisting $(NH_4)_2SO_4$ had a competition effect on the reaction between $H_2C_2O_4$ and $CaCO_3$, and resulted in the formation of $CaSO_4{\cdot}2H_2O$ and $(NH_4)_2C_2O_4$. NaCl can react with $H_2C_2O_4$ to form sodium oxalate, which was mixed with calcium oxalate in the final mixed particles.

In general, hygroscopicity is the ability of a substance to attract and hold water molecules from the surrounding environment. It is now well known that the hygroscopic behavior of particles is greatly dependent on their composition. For insoluble particles like calcite, the water adsorption isotherm exhibits a curve typical of multilayer adsorption, and the water content of fresh calcite at 90% RH was determined to be less than 1% (Al-Hosney and Grassian, 2005; Gustafsson et al., 2005; Ma et al., 2012), indicating its hygroscopicity is quite weak. The hygroscopic behavior of calcite particles could be depicted as a water adsorption-desorption process. For oxalic acid, the reported deliquescence point is above 98% RH (Braban et al., 2003), indicating that the deliquescence of oxalic acid rarely happens in the atmosphere since the typical ambient RH is in the range of 20–90%. Unlike calcite, however, the humidifying-dehumidifying process of oxalic acid and other oxalates was determined to be a hydration-dehydration process under typical ambient RH (Braban et al., 2003; Ma and He, 2012; Ma et al., 2013a; Peng et al., 2001; Wu et al., 2011). In the case of hygroscopic compounds, e.g. NaCl, NH_4NO_3, and $(NH_4)_2SO_4$, water absorption at DRH makes these particles mainly occur in a metastable state in the atmosphere (Ma et al., 2010; Martin, 2000; Rood et al., 1989; Schuttlefield et al., 2007; Swietlicki et al., 2008). This results in the dissolution of particles, with cations and anions that re-combine together after efflorescence. Thus, the hygroscopic behavior of hygroscopic particles is always a dissolution-recrystallization process, namely deliquescence and efflorescence. The traditional view always considers the hygroscopic behavior of aerosol mixtures particles as a physically vapor adsorption/absorption-desorption process, in which chemical reaction is neglected. However, as shown in this study, chemical reactions may occur in the humidifying process of mixed particles. In the case of $CaCO_3$, coexisting hygroscopic components can greatly increase its water content after the deliquescence of these hygroscopic components. The aqueous circumstance can promote the chemical reaction between $CaCO_3$ and acidic species (e.g., $H_2C_2O_4$) in the atmosphere. Moreover, the formation of insoluble or less hygroscopic components in the aqueous chemical reaction in the humidification-dehumidification process will change the hygroscopic behavior as well as climate effect of particles.

Declaration of interest statement

The authors have no competing interests to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2018.11.056.

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