



Controlling Phase Evolution of Inorganic Salt Systems with Polyhydroxy Substances in Atmospheric Aerosols

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Abstract. Polyhydroxy compounds, as key aerosol constituents, exhibit unique hygroscopicity and modulate inorganic salt hygroscopicity due to variable hydrogen bonding. However, when intermolecular H-bonds and ionic bonds coexist, their relative contributions to hygroscopicity and phase transitions remain unclear. This work studied the hygroscopicity of aerosols from tartaric acid (a proxy for polyhydroxy diacids), its acid and neutral salts, and their mixtures with inorganics. Cyclic humidity-induced morphological transformations show that at low RH, particles are glassy, crystalline, and gel phases from tartaric acid to sodium bitartrate to sodium tartrate, owing to progressively enhanced electrostatic forces. Unexpected phase behaviors emerge when these polyhydroxy compounds are mixed with sodium sulfate at a 1:1 molar ratio. For tartaric acid/ Na_2SO_4 system, Na_2SO_4 performs “effloresce upon hydration” at 36.3% RH. For sodium bitartrate/ Na_2SO_4 particles upon dehydration, solid Na_2SO_4 precipitates first, followed by SBT efflorescence. Upon following hydration, the crystallization is enhanced at 52% RH. In the sodium tartrate/ Na_2SO_4 mixture, solid Na_2SO_4 and tartrate- Na-SO_4^{2-} complexes simultaneously form at 57.4% RH during humidification. Shifts in the formation–dissociation equilibrium of these complexes induce “efflorescence–deliquescence–efflorescence–deliquescence on hydration”. Further experiments on sodium bitartrate–inorganic salt mixed aerosols show that ammonium salts lose ammonia, triggering intercomponent reactions and compositional changes that yield solid tartaric acid and sodium salts at low humidity. These findings indicate that organic–inorganic intermolecular interactions regulate particle hygroscopicity and phase state, affecting aerosol chemical reactions and cloud condensation nuclei activity.

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1 Introduction

25 The phase state of particulate matter significantly influences the atmospheric environment, affecting atmospheric climate, cloud condensation nucleus (CCN) activity, and atmospheric visibility. Numerous studies have demonstrated that the phase state of aerosol particles, e.g., liquid, solid, highly viscous, phase separated, etc., exhibits a strong dependence on relative humidity (RH), temperature, and chemical composition. (Huang et al., 2024; Lei et al., 2022; Wang et al., 2021). For example, at low ambient relative humidity (RH), inorganic salts such as $(\text{NH}_4)_2\text{SO}_4$ and NaCl exist as regular crystals, whereas at high

30 humidity, they can form droplets (Dougle et al., 1998; Orr et al., 1958; Wang et al., 2017). Black carbon (BC) produced by combustion is a non-hygroscopic solid particle that tends to remain solid and has a strong ability to scatter and absorb solar radiation (Li et al., 2021b; Liu et al., 2021; Pandey et al., 2020). When organic compounds are introduced into the atmosphere, the phase transitions become more complicated for organic/inorganic aerosol particles. (Mikhailov et al., 2009; Riemer et al., 2019; You et al., 2014). For instance, when black carbon mixes with organic coatings or sulfates, it can form a "core-shell

35 structure" consisting of a solid core wrapped by a liquid shell (Lee et al., 2017; Schmedding et al., 2020; Shiraiwa et al., 2017). After adsorbing liquid substances, mineral dust can form an organic film or water film on the surface, resulting in a "solid-liquid coexistence" structure (Freedman, 2017; Tang et al., 2016). Inorganic ions and organic molecules may form ion-molecule composite gel networks, thereby affecting the phase behavior of aerosols (Li and Gong, 2024; Liu et al., 2023; Richards et al., 2020; Sheldon et al., 2023). Pöhlker et al. measured the hygroscopic response of aerosol particles collected from the Amazon

40 rainforest to changes in atmospheric relative humidity. The collected aerosols were rich in sulfates, black carbon, and secondary organic matter. The study found that as humidity increased, sulfate crystals appeared in the particles, a phenomenon known as efflorescence on hydration. With a further increase in temperature, the particles deliquesced and formed a solution. Composition analysis indicated that the black carbon originally embedded within the organic matter and sulfates was redistributed to the particle surface, resulting in internal component reorganization (Pöhlker et al., 2014).

45 Polyhydroxy compounds are ubiquitous organic components in atmospheric aerosols, primarily originating from biogenic emissions, biomass burning, and secondary atmospheric chemical reactions (Vincenti, et al. 2022). Characterized by multiple hydroxyl functional groups in their molecular structures, these compounds possess strong hydrophilicity, high viscosity, and



50 excellent water-binding capacity, which endow them with unique physical and chemical properties distinct from conventional inorganic aerosol components (Hallquist et al. 2009). Our research found that when gluconic acid and tartaric acid are mixed with inorganic salts such as ammonium sulfate and sodium chloride, the inorganic salts exhibit the rare “efflorescence on hydration”, while the organic acids do not undergo obvious phase transitions (Dong et al., 2024; Yang et al., 2024; Zhu et al., 2022). From a chemical structure perspective, gluconic acid contains five hydroxyl groups and one carboxyl group, while tartaric acid contains two hydroxyl groups and two carboxyl groups. These polyhydroxy organic acids can possess extensive hydrogen bonds, which can form gels. They can form gel structures through intermolecular hydrogen bonds, thereby inducing the hygroscopic efflorescence of inorganic salts (Alonso et al., 2021; Hadži and Orel, 1973; Li et al., 2021a; Sato et al., 2021). However, more research regarding the influence of intermolecular interactions on the phase behavior of complex atmospheric particulates is still very lacking.

Tartaric acid is a typical dicarboxylic compound. Its concentration in aerosols is second only to succinic acid and malic acid, and it mainly originates from the photo-oxidative decomposition of toluene (Alonso et al., 2021; Gowda and Kawamura, 2018; Sato et al., 2021). A recent study showed that in a ternary aerosol system composed of acid, base, and water, the presence of tartaric acid can trigger proton transfer from acid to base molecules, forming new covalent bonds or strengthening existing ones, thereby promoting the aerosol nucleation process (Wang et al., 2023). In the atmosphere, tartaric acid can gradually lose protons to form bitartrate (acid salt) and tartrate (normal salt) (Barron, 1978; Bhattacharjee et al., 1989; Kuo et al., 2011; Treuel et al., 2008). What kind of phase behavior story will unfold when they encounter inorganic salt particles? This paper uses morphological observations combined with Raman spectroscopy to thoroughly investigate the differences in intermolecular interactions of tartaric acid, its acid salt, and its normal salt particles under different humidity conditions. Furthermore, we observe the differences in phase behavior when they are mixed with sodium sulfate, as well as the hygroscopicity and phase states of the constituent materials when different inorganic salts are mixed with the acid salt.

2 Materials and methods

70 2.1. Sample preparation



The chemical reagents including sodium bitartrate monohydrate (SBT, $\text{C}_4\text{H}_5\text{NaO}_6 \cdot \text{H}_2\text{O}$, 98 %), DL-tartaric acid (TA, $\text{C}_4\text{H}_6\text{O}_6$, AR), sodium sulfate (Na_2SO_4 , $\geq 99\%$), and sodium chloride (NaCl, analytical grade, $\geq 99.99\%$) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. While ammonium chloride (NH_4Cl , $\geq 99\%$), ammonium nitrate (NH_4NO_3 , $\geq 99\%$), and sodium tartrate dihydrate (ST, $\text{C}_4\text{H}_4\text{Na}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, AR) were purchased from Beijing Chemical Works. In experiment, ST, SBT, and TA were individually dissolved in triple-distilled water to prepare $0.2 \text{ mol} \cdot \text{L}^{-1}$ solutions as required and fresh solutions were then sprayed using a syringe to generate micrometer-sized droplets for optical microscopy imaging and Raman spectroscopy analysis. For mixed droplets, solutions of two different compounds were mixed to obtain a mixture with a molar ratio of 1:1 and then form microdroplets.

2.2. Microscopic observations of particles

An optical microscope equipped with a camera (Nikon Ti-S, 1.0 numerical aperture, 60 $\times$ objective lens, Japan) was coupled with a humidity control system to observe and record the morphological changes of aerosols. The experimental setup, illustrated in Fig. 1(a), primarily consists of three components: a humidity control system, an image observation and acquisition system, and a data recording and processing system. The image observation and acquisition system serves as the core of the apparatus, comprising a sample cell and the microscope. The sample cell, positioned above the inverted objective lens, is a circular metal ring with a transparent quartz glass plate embedded at the bottom. The polytetrafluoroethylene (PTFE) substrate with the area of 1 cm^2 is placed on this lower glass plate. At the start of the experiment, syringe-sprayed monodispersed droplets with radii ranging from 5 to 100 μm deposit on substrates. Subsequently, another quartz glass plate is placed on top to seal the sample cell. Light passes through the droplets from the bottom, and the camera captures images from below, yielding clear visualizations.

The humidity control system was utilized to regulate the relative humidity (RH) inside the sample cell. Pure nitrogen (N_2) supplied directly from a gas cylinder was split into two streams: a dry stream and a wet stream. The dry stream was connected directly to a mass flow controller (MC-1SLPM, Alicat Scientific), while the wet stream was bubbled through a water bottle after passing through its respective flow meter. The two streams were then mixed and introduced into the sample cell. The humidity of the outlet gas was measured using a hygrometer (CENTRE 313, $\pm 2.5\%$ RH, $\pm 0.7^\circ\text{C}$) after exiting the cell. During



the experiment, the flow rates of the dry and wet N₂ were adjusted to produce a stepwise change of ~5% RH in humidity, as illustrated in Fig. 1(b). Each humidity step was maintained for approximately 5 minutes, with an interval of roughly 5% RH between adjacent steps. Images of the particles observed and captured by the microscope were transmitted to a computer for subsequent quantitative analysis.

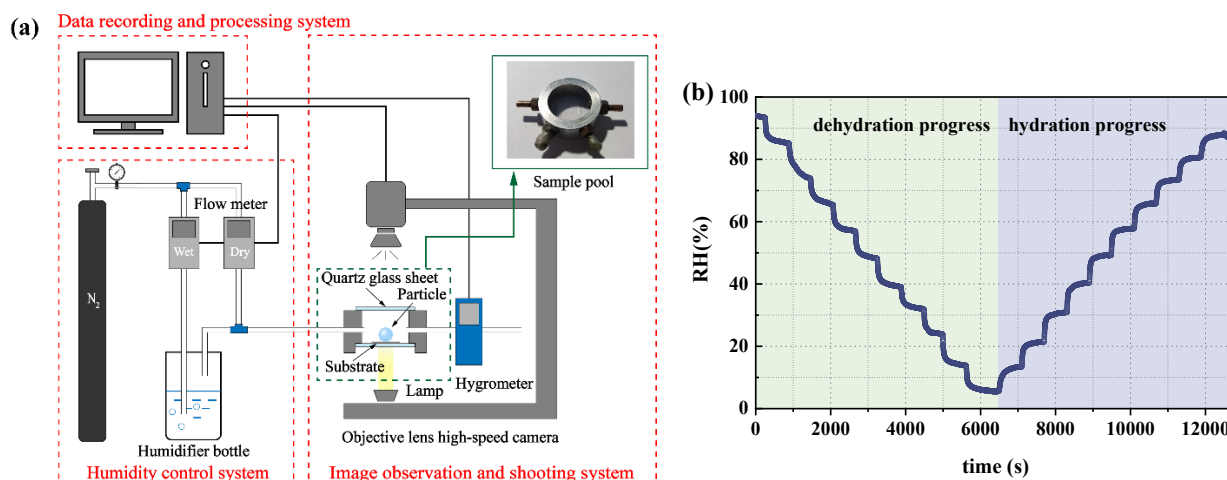


Figure 1: (a) Microscopic morphology observation device and (b) the humidity steps during a humidity down-up cycle.

2.3. Raman measurements of mixed particles

The Raman measurements were performed using a Renishaw InVia confocal Raman spectrometer with a Leica DMLM microscope (50 × objective, 0.75 numerical aperture), which has been described in detail in previous studies (Wang et al., 2005; Zhou et al., 2014). In experiment, Raman spectra were collected using a 514 nm laser excitation wavelength and a 1800 grooves/mm grating. The spectral range covered Raman shifts from 100 to 4000 cm⁻¹ with a resolution of 1 cm⁻¹. The experiment was performed at room temperature. The particles preparation and ambient RH adjustment is same to that in optical observation.

2.4. Hygroscopic growth measurements

Hygroscopicity was characterized by size growth factor, which was derived from the particle measured in the micrographs. The two-dimensional projected area (A) of all particles was measured using OLD-SG software at a fixed pixel-to-length ratio and



then was converted to an equivalent circle diameter (D). By using Eq. 1, the size growth factor (GF) was calculated (Wu et al., 2011).

$$GF = \frac{D_{RH}}{D_{dry}} \quad (1)$$

D_{RH} and D_{dry} represent the equivalent circle diameters of the aerosol particles at any given RH and at the lowest RH, respectively.

3 Results and Discussion

3.1 Hygroscopic Properties and Phase of Tartaric Acid and Its Sodium Salts

In the atmosphere, depending on the ambient acidity, tartaric acid can exist in different protonation states, as illustrated in Fig. 2. From a molecular structural perspective, the fully protonated tartaric acid molecule contains two carboxyl groups ($-\text{COOH}$), enabling intermolecular hydrogen bonds through interactions between alcoholic hydroxyl and carbonyl groups, alcoholic hydroxyl groups themselves, as well as carboxylic acid groups. In addition, intramolecular hydrogen bonds can be formed between the alcoholic hydroxyl and carbonyl groups within a single tartaric acid molecule. In contrast, sodium bitartrate molecules possess one carboxyl group ($-\text{COOH}$) and one carboxylate group ($-\text{COO}^-$), resulting in a unique 'molecule-ion hybrid' structure. So Intermolecular hydrogen bonds and electrostatic forces co-occur in sodium hydrogen tartrate systems. For sodium tartrate, which contains two carboxylate groups ($-\text{COO}^-$), the dominant intermolecular interaction is ionic bonding accompanying weak hydrogen bonds between alcoholic hydroxyls. Due to these distinct intermolecular forces, the physical state transitions of droplets formed by tartaric acid, sodium tartrate, and sodium bitartrate vary as the relative humidity decreases.

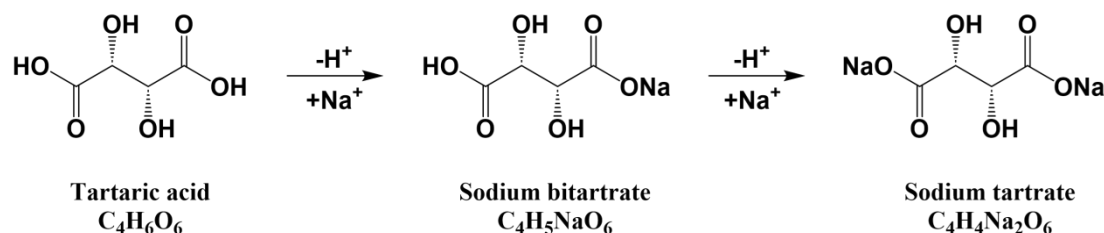


Figure 2: The deprotonation process from tartaric acid (TA) to sodium bitartrate (SBT) and then to sodium tartrate (ST).



Figure S1(a) presents the morphological evolution of a single tartaric acid particle during a dehydration-hydration cycle. During dehydration, the particle remains a smooth, homogeneous spherical droplet at RH spanning from 94.5% to 31.4%. At 24.9% RH, the particle suddenly becomes textured and rough, indicating the formation of a surface solid-like state. No further morphological changes are observed as RH decreases to 7.6%. During the following hydration, the textured morphology persists without a smooth liquid droplet observed even when RH is increased back to 93.1%. It is may attributed to the strong hydrogen-bonding network in the dehydrated tartaric acid matrix. The GF curve of the particles is presented in Fig. S1(b). As the RH decreases on dehydration, the GF decreases monotonically from ~ 1.4 to 1.0. During the subsequent hydration, however, the GF remained nearly constant at 1.0 across the entire RH range, even at RH approaching 100%, indicating that the dehydrated tartaric acid particles did not take up water.

While for SBT shown in Fig. S2, the particle remains a smooth, homogeneous spherical droplet in the RH range from 93.6% to 78.5%. At the critical RH of 71.6%, it undergoes a sudden morphological transition, forming a non-spherical, irregular solid morphology, and remains unchanged till 21.0%RH. Upon following RH increase from 21.0% to 96.5%, the particle retains its irregular solid shape throughout hydration, showing no reversion to a liquid droplet. When the particle was exposed onto 96.5% RH for 40 minutes, partially liquid-like can be found but still irregular morphology, suggesting limited water-transfer. The GF declines from 1.6 at 93.6% RH down to 1.0 at 21% RH and remains at ~ 1.0 on humidification. After prolonged exposure at 96.5% RH, it only slightly increases to ~ 1.4 after 40 min.

Distinct from the phase behavior of both TA and SBT, the ST particle (in Fig. S3) remains a fully transparent, smooth spherical droplet at all times on the dehydration-hydration process with size change, indicating the gel state. The GF decreases from ~ 1.55 at $\sim 95\%$ RH to 1 at 37% RH on dehydration and increases from 1 to 1.45 on hydration. A little hysteresis was observed, consistent with the fully reversible, liquid-only behavior observed in microscopy.

Raman spectroscopy is a highly sensitive probe to identify physical phases and unravel the correlation between intermolecular interactions and phase transition behaviors. Fig. 3(a) compares the Raman spectra of tartaric acid (TA) particles measured at 94.5% RH, 7.6% RH, and pure crystalline TA. The spectrum of crystalline TA displays a series of well-resolved, sharp characteristic peaks at 752, 888, 988, 1151, 1260, 1455, 1653, 1691, 2921, 2969, 3349 and 3405 cm^{-1} , consistent with the coexisting intramolecular and intermolecular hydrogen-bond networks within the TA crystal lattice (Sasikala et al., 2014;



Alonso et al., 2021). For TA particles equilibrated at 94.5% RH (dark yellow trace), a broad envelope centered at 3446 cm^{-1} verifies an aqueous state, which agrees well with to the smooth and homogeneous spherical particles seen in microscopic images. Correspondingly, the C=O stretching band shifts to 1728 cm^{-1} , while $\alpha\text{-C-H}$ stretching converges to a single band at 2950 cm^{-1} , originating from unconfined free molecular rotation in fully solvated environments. At 7.6% RH (red trace), the sharp crystal-derived peaks at 752, 888, 988 and 1151 cm^{-1} are markedly attenuated. Meanwhile, dual $\alpha\text{-C-H}$ stretching signals emerge at 2921 and 2950 cm^{-1} . These spectral evolutions collectively evidence the coexistence of intermolecular and intramolecular hydrogen bonds inside particles; nevertheless, the population of gauche conformers declines, and rigid intramolecular O-H $\cdots$ O=C chelate hydrogen bonds are substantially weakened. Furthermore, the band at 3233 cm^{-1} is assigned to O-H stretching of strongly hydrogen-bonded cyclic carboxylic dimers. The triplet peaks at 3400, 3442 and 3485 cm^{-1} separately arise from intermolecular hydroxyl–hydroxyl hydrogen bonds, intramolecular O-H $\cdots$ O=C chelating interactions, and weakly associated free hydroxyl groups (Bhattacharjee, et al., 1989; Kim, et al., 2020). The simultaneous presence of these four bands demonstrates that the intermolecular and intramolecular hydrogen-bond networks in particulate TA are less extensive and ordered relative to crystalline TA. The observed C=O band at 1705 cm^{-1} further indicates only weak, short-range intermolecular contacts are retained. In addition, the emergence of the 1298 cm^{-1} band, which matches the characteristic signal observed in fully aqueous samples, reflects some disorder in molecular packing. Taken together, these spectroscopic signatures support the formation of a glassy matrix sustained by complex inter- and intramolecular hydrogen-bond networks, as seen the particle with wrinkled surfaces in micrographs.

Figure 3(b) presents the Raman spectra of SBT particles measured at 93.6% RH, 21% RH, and pure $\text{C}_4\text{H}_5\text{NaO}_6\cdot\text{H}_2\text{O}$ solid. The solid-state spectrum (blue trace) verifies the formation of strong intermolecular hydrogen bonds within crystalline SBT, as characterized by the distinct Raman bands at 1718 cm and 3450 cm. The spectral profile featuring a dominant C–H stretching band at 2961 cm with a weak shoulder at 2951 cm is indicative of defective microcrystalline aggregates with dynamically unstable and weakened intramolecular O–H $\cdots$ O=C chelating hydrogen bonds. The long-range intermolecular hydrogen-bond networks, constructed by water-bridged interlayer interactions and charge-assisted carboxyl–carboxylate linkages, are fragmented and poorly ordered in such defective crystals. This structural disorder reduces the spatial differentiation between the two $\alpha\text{-C-H}$ bonds, thereby resulting in insignificant peak splitting (Chen et al., 2015). At 93.6% RH, the SBT particles

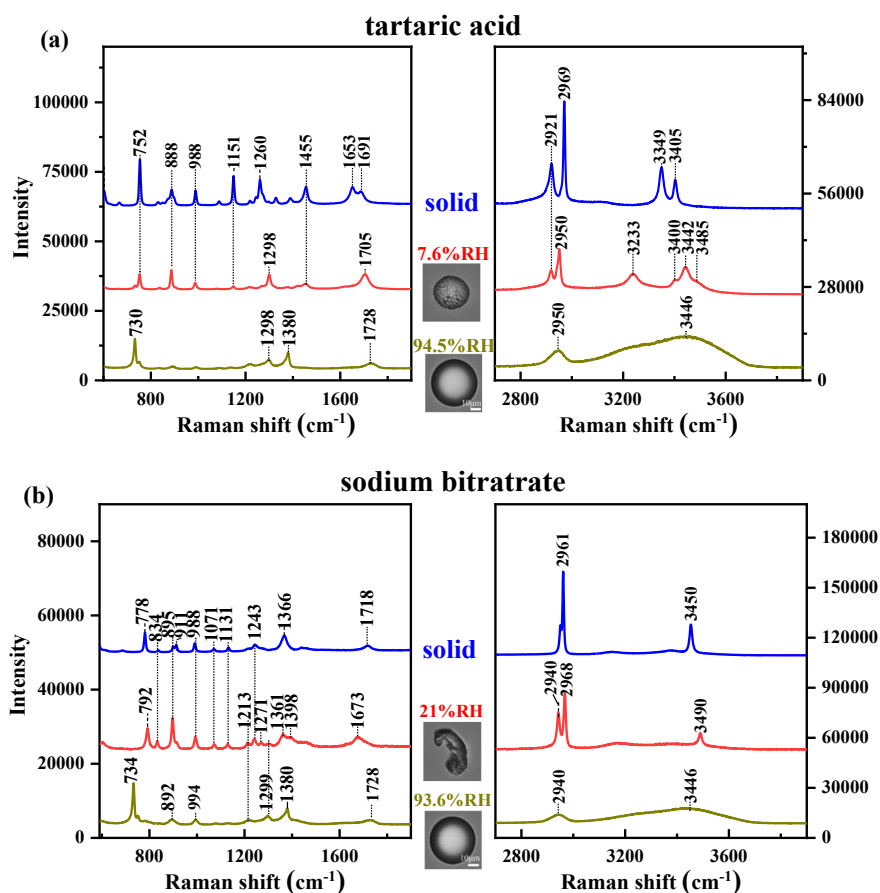


180 exhibit typical Raman signatures of an aqueous liquid state, including a broad O–H stretching envelope centered at 3446 cm⁻¹ and a single C–H stretching band at 2940 cm⁻¹. The characteristic band at 1728 cm⁻¹ further confirms the formation of C=O···HO intermolecular hydrogen bonds, which corresponds to the spherical morphology of aqueous SBT droplets observed in micrographs. In contrast, the spectrum of particles equilibrated at 21% RH, which corresponds well with the irregular solid morphology in micrographs, displays well-resolved sharp doublets at 2940 and 2968 cm⁻¹, confirming the formation of highly
 185 ordered SBT crystals. Single-crystal X-ray diffraction results demonstrate that the perfect orthorhombic lattice possesses continuous layered intermolecular hydrogen-bond networks and rigid intramolecular O–H···O=C chelate rings (Titaeva et al., 2015). These stable hydrogen-bonding frameworks firmly lock the gauche conformation of SBT molecules, maximize the spatial environmental difference between the two α -C–H bonds, and consequently produce distinctly separated C–H stretching peaks. The emerging band at 3490 cm⁻¹ reflects weak intermolecular hydrogen-bond interactions between adjacent molecular
 190 layers, while the characteristic 1673 cm⁻¹ band provides solid spectroscopic evidence for the coexistence of intermolecular and intramolecular hydrogen-bond networks within crystalline SBT. Collectively, these spectral variations unambiguously verify the formation of crystalline SBT at low relative humidity.

In the Raman spectrum of sodium tartrate shown in Fig. 3(c), the characteristic sharp peak at 1600 cm⁻¹ in crystalline sodium tartrate is assigned to the asymmetric stretching vibration of fully deprotonated carboxylate anion ($\nu_{as}\text{-COO}^-$), which
 195 is different from the monoprotic SBT with protonated -COOH (~1718 cm⁻¹ C=O stretch) (Polavarapu et al., 2022). The band at 2932 cm⁻¹ corresponds to symmetric α -C–H stretching vibration of the tartrate skeleton. Its slight red shift relative to the standard single-crystal value at 2947 cm⁻¹ arises from electron polarization induced by rigid Na⁺ coordination to carboxylate groups. The sharp band at 3162 cm⁻¹ is attributed to the stretching vibration of α -OH groups engaged in strong six-membered intramolecular O–H···O(COO⁻) chelate hydrogen bonds. While for aerosols at 92.2% RH, the disappearance of the diagnostic
 200 1600 cm⁻¹ crystalline band and peak broadening, consistent with previous tartrate salt hygroscopicity research on atmospheric organic aerosols (Han et al., 2022). The 2932 cm⁻¹ peak is drastically weakened and broadened, accompanied by the emergence of a broad absorption band centered near 3400 cm⁻¹. This implies that hydrogen bonds are formed between ST and H₂O molecules. At 16.0% RH, the low-frequency Raman bands are largely consistent with those of solid disodium tartrate (ST), such as the band at 1600 cm⁻¹, yet their peak profiles are markedly broadened. The high-frequency region resembles the



205 spectral features of the liquid state, while the C–H stretching band undergoes a blue shift to 2945 cm^{-1} . These observations demonstrate that the particles adopt a gel-like state dominated by electrostatic interactions between ST molecules, Consistent with micrograph evidence showing merely volume contraction and unchanged particle shape.



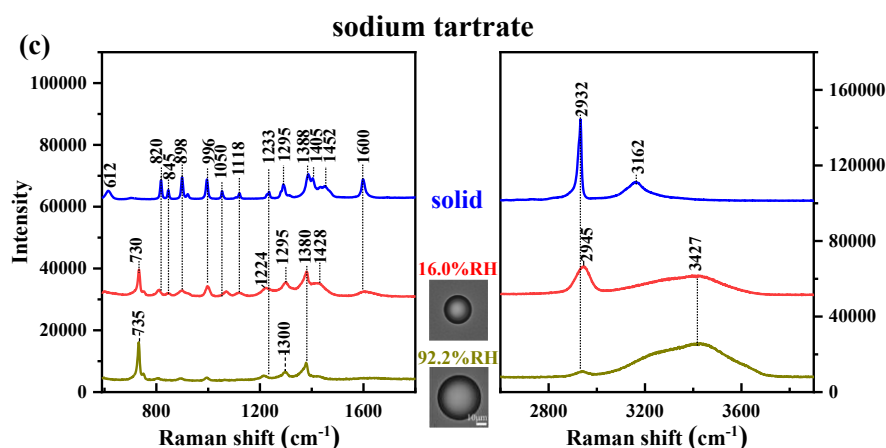


Figure 3: Raman spectra and corresponding microscopic images of tartaric acid, sodium bitartrate, and sodium tartrate in different phase states.

Above intermolecular interaction information obtained from Raman spectroscopic measurements enables the elucidation of morphological evolution and hygroscopicity profiles of TA, SBT and ST throughout RH cycling processes. At high humidity, intermolecular hydrogen bonding is established between tartaric acid moieties and water molecules in the droplet. With the decrease in RH, water inside the particles evaporates progressively, accompanied by alterations in intermolecular interactions among organic molecules. For TA aerosols, the intramolecular and intermolecular O-H $\cdots$ O=C hydrogen bond formation and -COO-H $\cdots$ O=C hydrogen bond enhanced. Upon reaching 24.9% RH, a rigid three-dimensional hydrogen bond network is constructed, which functions as a sturdy "molecular mesh" and renders glassy particles as wrinkled spherical morphologies. This highly stable structure resists disruption of its robust hydrogen bond network by water molecules during subsequent humidification, leading to the absence of hygroscopic behavior. When TA undergoes partial deprotonation to form SBT, the intermolecular hydrogen bonding between SBT and H₂O is displaced by intermolecular hydrogen bonding and ionic bonding within the sodium bitartrate matrix. During the dehydration process of SBT droplets, the ion-water dipole interactions and water-water hydrogen bonds gradually weaken and eventually disappear. In their place, the electrostatic interactions between ions (ion pairs/ionic lattices) are strengthened, while intermolecular among bitartrate anions and intramolecular H-bonds between the alcoholic hydroxyl groups and carboxylate groups within tartaric acid molecules progressively form. At a humidity of 7.6% RH, a distinctive "molecule-ion hybrid" crystalline is constructed via the synergistic interplay of hydrogen bonds and



ionic bonds. This structure possesses superior stability arising from the "locking" effect of its three-dimensional spatial network, and its hygroscopic behavior is analogous to that of tartaric acid (TA). Yet, under extended high-humidity conditions, the strong coordinative interaction between Na^+ cations and water molecules result in the disruption of this spatial architecture, thereby inducing water absorption by the particulate samples. In contrast to TA and SBT, ST is an ionic compound. In aqueous solution, carboxylate anions and Na^+ ions form hydrated ions via coordination with water molecules. With the reduction in humidity, the water content within the droplets decreases progressively, leading to a decline in the number of hydration molecules associated with the ions and the gradual transition of the particles into a viscous colloid. Upon an increase in humidity, additional water molecules can re-bind to the ions, which consequently imparts slow dehydration and water absorption properties to the particles.

3.2 Phase and Structure of Mixed Aerosols containing polyhydroxy compounds and Sodium Sulfate

In the atmosphere, collisions between organic and inorganic aerosols occur throughout atmospheric transport, leading to the formation of internally mixed particles with both organic and inorganic components. Sulfate is a key constituent of atmospheric particles, accounting for as high as 15%–20% of the total content. Therefore, we prepared internally mixed aerosol particles by mixing tartrate species different protonation states with Na_2SO_4 , respectively, to investigate the effects of organic species on the hygroscopicity and phase state of sodium sulfate.

Figure 4 shows the hygroscopic curves and typical droplet morphologies of internally mixed particles composed of Na_2SO_4 and TA, SBT, ST with a molar ratio of 1:1, respectively. For the TA/ Na_2SO_4 mixed droplets shown in Fig. 4(a), a uniform spherical shape is maintained with only a gradual reduction in volume during the humidity decreasing process, suggesting the absence of obvious phase transition. In the subsequent humidity increasing process, a solid phase emerges on the droplet surface when the RH rises to 36.3%. Thereafter, crystals grow slowly in a dendritic pattern, with the solid phase serving as the nucleation center. However, the solid phase does not spread across the entire droplet, and the majority of the particulate matter remains in a liquid state. Distinct dendritic solids are observed as the RH increases to 74.9%. With a further increase in humidity, the particles absorb water leading to solid phase dissolution. A significant reduction in the solid fraction is observed at 77.6% RH, and complete deliquescence is achieved at 91.4% RH. The growth factor (GF) exhibits a gradual



downward and upward trend throughout a RH decrease-rise cycle with a slight hydration hysteresis. GF exhibits no significant response to solid precipitation.

Figure 4(b) displays images of droplets formed along with the GF trend by equimolar mixing of SBT and Na_2SO_4 during a single dehumidification-humidification cycle. Upon dehumidification, nuclei form at 86% RH with unchanged morphology above 52.4% RH, yet particles undergo persistent size reduction quantifiable by the GF change from 1.5 to 1.0. When RH drops to 52.4%, the solid phase rapidly expands on pre-existing crystalline nuclei to form porous spherical particles at 12.6% RH, while the particle size remains unchanged with a constant GF of 1. In the following humidification process, the particle exhibits almost invariant morphology and size under $\text{RH} < 52\%$ size. Once RH reaches 52%, the grayscale of particle images rises, indicating second efflorescence without any particle size variation. With a further increase in humidity, the particle begins to absorb water, reflected by GF increase. As the RH rises to 85.0%, both solid and liquid phases coexist within the particles and GF reaches ~ 1.3 . During the RH cycle, the GF exhibits distinct turning points with a significant decrease and increase at 53% RH and 85% RH, respectively. However, these turning points do not correspond to phase transitions.

Figure 4(c) illustrates the phase evolution of droplets formed by equimolar mixing of ST and Na_2SO_4 during a hygroscopic cycle. During the dehumidification process, the droplets gradually lose water and shrink in volume without any change in particle morphology, indicating the absence of phase transition in this stage. The corresponding GF decreases from ~ 2.8 to 1.0. On following hydration, distinct solid phases can be found on the droplet surface at 57.4% RH. With further increase in RH to 65.2%, the solid particles become indistinct, suggesting partial dissolution of the solids upon water absorption. When the RH is elevated again to 69.3%, dense fine solid particles appear, indicating the formation of a large quantity of solids. This phenomenon may be attributed to the residual small crystals from the first efflorescence acting as seeds for the second crystallization, triggering contact efflorescence of the particles (Davis et al. 2015). As the RH rises to 73.8%, the fine solid particles become indistinct again, i.e., re-dissolution occurs. At 94.7% RH, the particles complete deliquesce to form homogeneous droplets. This phenomenon is referred to as "repeated efflorescence on hydration". During the dehumidification process, the particle size remains essentially unchanged at $\text{RH} < 44.3\%$. During the humidification process, GF shows no response to the two crystallization events; however, a slight increase in GF is observed at 65.2% RH, corresponding to the first solid dissolution. After one complete down-up RH cycle, the particle size decreases significantly. At 94.7% RH during

humidification, the GF is 1.31, which is nearly half of the maximum GF (2.21) during the initial dehumidification.

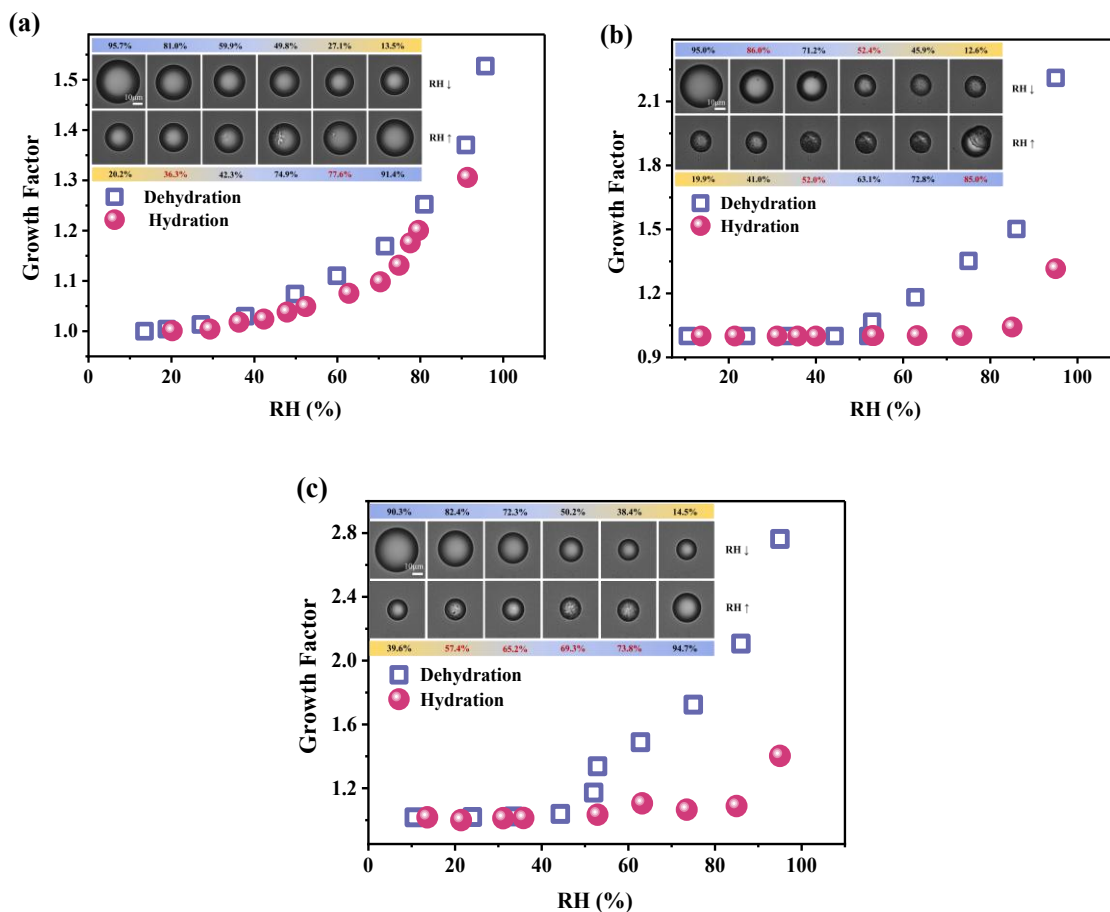


Figure 4: The morphological change and GF evolution of a single mixed particle containing Na_2SO_4 and (a) tartaric acid, (b) sodium bitartrate and (c) sodium tartrate during a down-up RH cycle.

Summarizing the hygroscopicity of mixed particles found water absorption process on hydration promotes efflorescence, which is similar to previous reported aerosols containing polyhydroxy compound (gluconic acid) and inorganics (NaCl and $(\text{NH}_4)_2\text{SO}_4$ (Zhu, et al. 2022, Dong, et al. 2024).

To clarify the exact composition of the solids formed in the particles, Raman spectroscopy measurements were further performed on the organic-inorganic mixed particles. Figure 5 presents the typical Raman spectra and the intensity of bands at 996 cm^{-1} and 980 cm^{-1} . The peak height minimum of the characteristic band at 980 cm^{-1} was used for normalization. Green



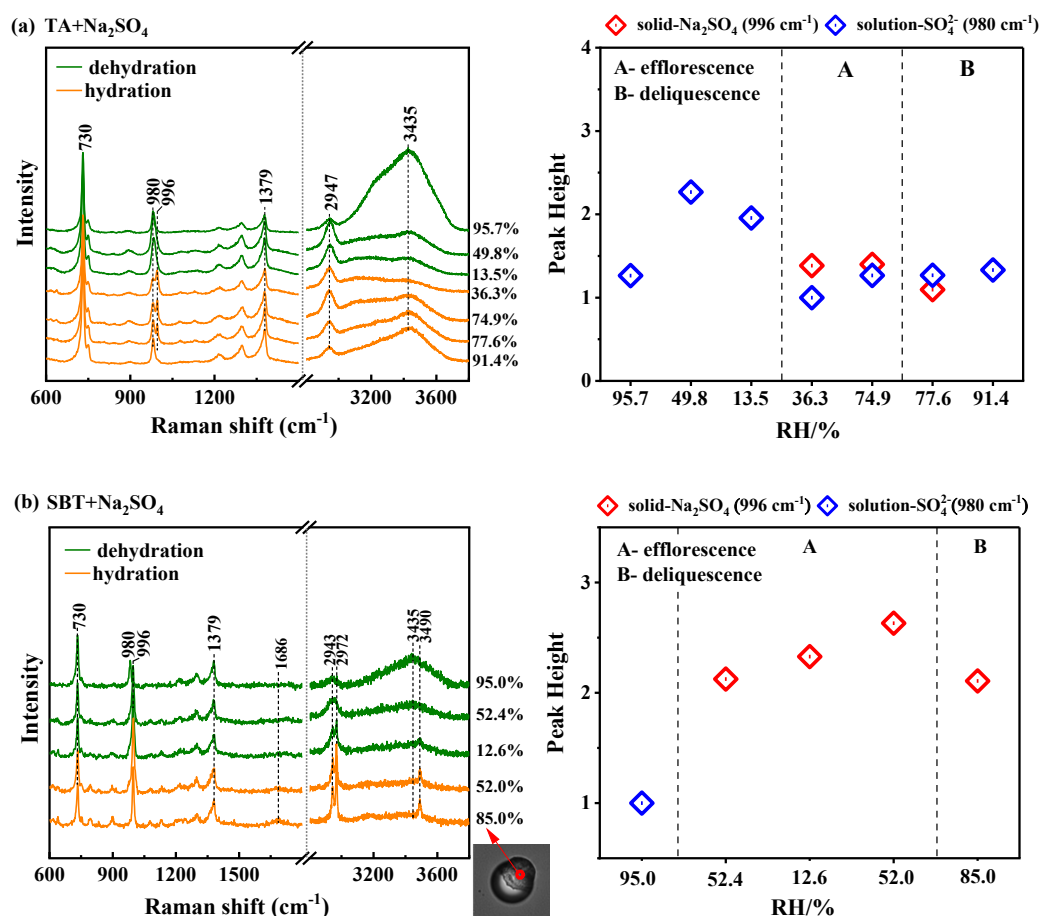
spectra correspond to the dehydration process, while orange spectra represent the humidification process. In Fig. 5(a), the characteristic peak at 3435 cm^{-1} corresponding to water content fades gradually on dehydration and persists weakly at 13.5%. The bands at 980 cm^{-1} and 2947 cm^{-1} meaning aqueous SO_4^{2-} (Zhou et al. 2014) and aqueous tartaric acid (Bhattacharjee et al. 1989), respectively, show no obvious changes throughout the process. Upon hydration, the volume and water content increase slightly under $\text{RH} < 36.3\%$. As RH reaches 36.3%, the 980 cm^{-1} peak declines and a sharp peak at 996 cm^{-1} meaning solid Na_2SO_4 appears (Zhang et al., 2002). Both the 980 cm^{-1} and 996 cm^{-1} bands coexist thereafter down to 76.3% RH. Upon reaching 91.4% RH, the 996 cm^{-1} peak disappears, leaving only the 980 cm^{-1} band. From the peak heights shown in the right region of Fig. 5(a), the band intensity of 996 cm^{-1} band is higher than that of 980 cm^{-1} band in part A, showing most solid Na_2SO_4 within the particles. In part B, the intensity of 980 cm^{-1} band is more stronger meaning Na_2SO_4 deliquescence. At the maximum humidity, sulfate salts in the system are mainly present as aqueous state.

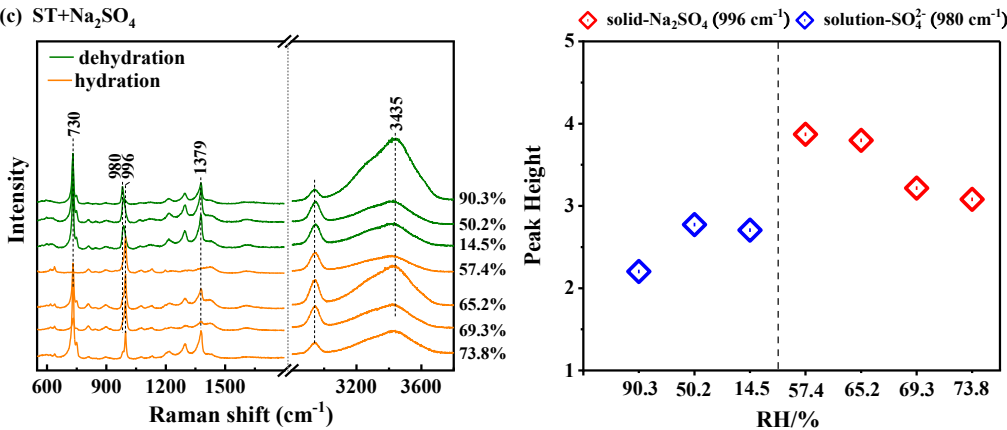
Figure 5(b) shows Raman spectra for SBT/ Na_2SO_4 particles. At 95.0% RH, the diagnostic peak at 980 cm^{-1} confirms the aqueous sulfate salts in particles. And the signature bands at 2943 and 3435 cm^{-1} are the hallmark of aqueous SBT state. When the RH decreases to 52.4%, the disappearance of the 980 cm^{-1} peak and the simultaneous emergence of a new peak at 996 cm^{-1} suggest the precipitation of solid Na_2SO_4 in the particle. At 12.6% RH, a distinct doublet at 2943 cm^{-1} and 2972 cm^{-1} , accompanying the weak band at 1686 cm^{-1} and a sharp peak at 3459 cm^{-1} , indicates the formation of solid SBT. Upon the followed humidification, the intensities of 1686 , 2943 cm^{-1} , 2972 cm^{-1} and 3490 cm^{-1} bands increase significantly from orange spectra, demonstrating the continuous efflorescence and crystallization of SBT. It should be noted that the Raman spectrum collected at 85% RH corresponds to the solid region, as highlighted by the red circle in the figure. From the quantitative description of band intensity, the 996 cm^{-1} band intensity increases in part A, showing more and more solid Na_2SO_4 . While in part B, the 996 cm^{-1} band intensity decreases, meaning some Na_2SO_4 dissolved.

For ST/ Na_2SO_4 mixed aerosols in Fig. 5(c), the SO_4^{2-} feature shifts from 980 cm^{-1} to 985 cm^{-1} with RH decrease from 90.3% to 14.5%, together with the weaker band at 3435 cm^{-1} . It reveals the transform from aqueous SO_4^{2-} ions to $\text{Na}^+\text{-H}_2\text{O-SO}_4^{2-}$ ion pairs (Zhang et al. 2002). Peak profiles of other bands are largely invariant during humidification, suggest aqueous SBT in the particle. On following hydration, the band at 980 cm^{-1} replaced by the band at 996 cm^{-1} at 57.4% RH, showing solid Na_2SO_4 formation. Concurrently, the characteristic Raman peak at 1379 cm^{-1} vanishes, accompanied by an



obvious drop in the intensity of the 3435 cm^{-1} band, which suggests that Na^+ acts as a bridge linking tartrate and sulfate anions simultaneously, forming multicomponent ion clusters and complex ion pairs with the decrease in water content (Wang et al. 2017). As the RH increases to 65.2%, a shoulder at 980 cm^{-1} appears, accompanying appearance of 1379 cm^{-1} and obvious enhancement of the 3435 cm^{-1} band. It shows the tartrate- Na^+ - SO_4^{2-} broken owing to water absorption. With a further increase in humidity to 69.3% RH, the absorption band of water and 1379 cm^{-1} both decline conversely, meaning the complexes via tartrate- Na^+ - SO_4^{2-} interactions formation again. As the RH increases to 73.8%, water content almost keeps constant while the 1379 cm^{-1} band intensifies. This indicates the tartrate- Na^+ - SO_4^{2-} complexes dissociation again. The quantitative intensity shows solid Na_2SO_4 content decreases from 57.4% RH on hydration, the content of solid Na_2SO_4 keeps decreasing continuously.





325 **Figure 5: Raman spectra corresponding to typical morphology and Na₂SO₄ phase evolution of a single mixed particle containing Na₂SO₄ and (a) tartaric acid, (b) sodium bitartrate and (c) sodium tartrate during a down-up RH cycle.**

330 The above analytical results are summarized in Table 1. For TA/Na₂SO₄ mixed aerosol particles, no efflorescence and crystallization occur during the dehydration process. In the subsequent hydration stage, solid Na₂SO₄ emerges at 36.3% RH; as RH further increases to 77.6% RH, the solid fraction diminishes and deliquescence begins. This phase transition behavior is analogous to that previously reported for gluconic acid/ammonium sulfate mixtures. Similar to gluconic acid, tartaric acid is a polyhydroxy organic carboxylic acid. Upon humidity reduction, polyhydroxy acid molecules construct a three-dimensional hydrogen-bonded gel network, in which inorganic Na⁺ and SO₄²⁻ ions are confined and cannot approach one another to precipitate solid Na₂SO₄. As humidity rises, particles absorb water molecules and disrupt the hydrogen-bonded network, enabling Na⁺ and SO₄²⁻ to associate and form crystalline Na₂SO₄, which then dissolves with further hydration. No phase transformation of TA is observed throughout the full RH dehydration–hydration cycle.

Table 1 the phase behavior summary of mixed aerosols containing Na ₂ SO ₄ and polyhydroxy compounds			
mixed aerosols	dehydration		hydration
TA/Na ₂ SO ₄	No phase transition		ERH 36.3% Na ₂ SO ₄ (s) DRH 77.6%
SBT/Na ₂ SO ₄	ERH ₁ 80.6% Na ₂ SO ₄ (s) ERH ₂ 52.4% SBT(s)	ERH 52% DRH 85%	Na ₂ SO ₄ (s)
ST/Na ₂ SO ₄	No phase transition		ERH(1) 57.4% Na ₂ SO ₄ (s) + complex



DRH(1) 65.2% complex dissociation
 ERH(2) 69.3% complex formation
 DRH(2) 73.8% complex dissociation

The SBT/Na₂SO₄ system exhibits distinct behavior compared with the TA/Na₂SO₄ mixture. Intermolecular interactions within SBT include both hydrogen bonds and ionic bonds, which weaken the self-assembly effect and yield a looser three-dimensional network structure. Consequently, solid particles form at 86% RH, and their amount remains stable within a certain humidity range. When relative humidity drops to 52.4%, partial collapse of the three-dimensional network occurs, accompanied by a prominent signal of solid Na₂SO₄; meanwhile, ionic interactions between SBT molecules are strengthened. Further reduction of RH to 12.6% triggers the precipitation of solid SBT. During hydration, water uptake completely destroys the three-dimensional network and generates more solid Na₂SO₄. Continuous hydration dissolves crystalline Na₂SO₄, whereas solid SBT became more until RH reaches 85%. When SBT undergoes further deprotonation to form ST, yielding ST/Na₂SO₄ mixed aerosols, ionic bonds dominate the interactions between components. At low RH, weak hydrogen bonds formed between hydroxyl groups, as well as between hydroxyl groups and the C=O moieties of carboxylate groups, raise the viscosity of particles and generate Na⁺–H₂O–SO₄²⁻ ion pairs. During the hydration process, hydrogen bonds break at 57.4% RH to produce solid Na₂SO₄; simultaneously, Na⁺ acts as bridging cations that coordinate with both tartrate and sulfate anions to form multicomponent complexes. Nevertheless, these complexes are thermodynamically unstable and dissociate when RH increases to 65.2%. Further elevation of relative humidity initiates the dissolution of Na₂SO₄, and full deliquescence of particles into liquid droplets is achieved at 94.8% RH.

3.3 Study on internally mixed particles of Sodium bitartrate with various inorganics

To further explore the effect of inorganic salts on the phase transition of mixed particles, SBT was mixed separately with representative nitrates and chlorides such as NH₄NO₃, NH₄Cl, and NaCl to prepare aerosol particles. The phase behavior, hygroscopicity, and composition changes of the mixed particles during the hygroscopic cycle were investigated.

From the detailed image evolution dependent upon RH in Fig. S5, the morphological evolution can be found. At 90.3% RH, the particle exists as a homogeneous spherical liquid droplet. Upon RH decreasing to 74.3%, faint nucleation embryos



(marked by the red oval) emerge inside the droplet. Further reduction of RH to 60.8% triggers complete efflorescence: the particle morphology abruptly transforms from spherical liquid droplet to irregular cuboid-like solid crystalline particle, accompanied by significantly increased image grayscale. With continuous dehydration down to 9.8% RH, the solid crystalline particle retains its blocky shape with deepened grayscale and visible crystal fractures. In the hydration branch, particles retain an irregular solid morphology at RH below 78.1%. From 78.1% RH, the particles undergo gradual deliquescence to 95.0%; no full deliquescence back to spherical droplets is observed even at the maximum measured RH of 95.0%, and the particles remain solid phase throughout the entire humidification process. Figure 6(a) presents the typical Raman spectra, corresponding microscopic images, and hygroscopic curves of SBT-NH₄NO₃ particles at typical humidity levels. To obtain phase state information more clearly, the spectra of pure ammonium nitrate (NH₄NO₃) and pure sodium nitrate (NaNO₃) solids are also provided. The antisymmetric stretching vibration peak of NO₃⁻ for NH₄NO₃ is located at 1041 cm⁻¹ and at 1068 cm⁻¹ for NaNO₃, respectively, which can be applied the diagnostic peaks. In addition, there are two peaks at 3122 and 3128 cm⁻¹ assigned to N-H vibration of solid NH₄NO₃. For SBT/NH₄NO₃ mixed particles at 90.3% RH, a characteristic peak is detected at 1048 cm⁻¹, corresponding to aqueous NO₃⁻ ions. When the RH=9.8%, the antisymmetric stretching vibration peak of NO₃⁻ shifts slightly to higher wavenumber from 1048 cm⁻¹, and a sharp characteristic peak emerges around 1068 cm⁻¹, which also strongly confirms the formation of solid NaNO₃. Simultaneously, four doublet peaks appear simultaneously at 1673/1706 cm⁻¹, 3081/3125 cm⁻¹, 2950/2962 cm⁻¹, and 3322/3369 cm⁻¹. Considering intermolecular interactions and combining the Raman diagnostic peaks of pure TA and solid NH₄NO₃ as shown in Fig. 3(a), the three doublets at 1673/1706 cm⁻¹, 2950/2962 cm⁻¹ and 3322/3369 cm⁻¹ were concluded as solid TA, while the doublet at 3081/3125 cm⁻¹ confirms the persistent presence of solid NH₄NO₃. So the solid phases corresponding microscopic morphology within the particles consist of NaNO₃, NH₄NO₃ and TA. When the humidity rises to 78.1% RH upon hydration, the four doublet peaks remain observable, whereas the band at 1068 cm⁻¹ vanishes and the intensity of the 1052 cm⁻¹ peak rises, indicating the dissolution of NaNO₃. Nevertheless, solid NH₄NO₃ and solid TA remain present in the particles. Therefore, the following reaction occurring in the particles can be inferred as eq. (1):



From the perspective of the hygroscopic curve, during the dehumidification process, the particles exhibit obvious



efflorescence when the humidity decreases to 60.8% RH, whereas only slight water absorption is observed in the particles during the humidification process. However, the tiny solid seed appears at 74.3% RH from optical images as seen in Fig. S4. It reveals no response of growth factor to partial solid precipitation. Previous studies have shown that the efflorescence point of pure NH_4NO_3 and NaNO_3 droplets is approximately 25%~32% RH and 34%RH (Chan et al. 1992; Zhang et al. 2014), and the deliquescence point is 61.4% RH and 74.5% RH (Zhang et al. 2021). Some studies have also indicated that pure NH_4NO_3 droplets do not transform into a solid state during dehumidification but instead exist in an amorphous state (Wang et al., 2024). Our research shows that the addition of SBT facilitates the efflorescence of NH_4NO_3 and advances its efflorescence and deliquescence points. Moreover, efflorescence on hydration takes place for NaNO_3 and TA formed by eq. (1).

The morphological change during the dehumidification-humidification process can be found in Fig. S5. At 91.5% RH, the particle exists as a smooth, fully homogeneous spherical aqueous droplet. As the RH decreased to 84.0%, a tiny solid nucleus emerges at the particle center (circled in red) while an outer liquid layer remains intact, forming a core-shell liquid-solid coexistence structure, and this central solid nucleus slightly expands at 49.7% RH with the layered liquid-solid morphology maintained. Once RH falls to and below the critical efflorescence point of 39.5%, part of the particle develops abundant folded, dendritic crystalline textures accompanied by mild spherical shrinkage, while a small fraction retained a smooth, liquid-like domain. And no further obvious morphological variation occurs as RH continuously drops to 14.2%, signifying a stable fully crystalline solid state under low humidity. On following hydration, the particle preserves a rigid solid structure covered with radiating folded crystalline patterns till 64.4% RH. upon reaching 70.9% RH, the particle begins to absorb ambient water, and surface folds fade away and particle edges turn rounded to launch the solid-to-liquid phase transformation, and persistent water uptake with further RH increase. When the RH arrives to 91.5%, part solid is still kept in the particle.

Figure 6(b) shows the Raman spectra of particles formed by mixing of NH_4Cl and SBT, together GF dependent upon RH. Comparison of Raman spectra collected from aerosol particles at 91.5% RH and 14.2% RH reveals three distinct doublet bands at $1673/1706\text{ cm}^{-1}$, $2950/2962\text{ cm}^{-1}$, and $3322/3369\text{ cm}^{-1}$ for the sample measured at 14.2% RH. These vibrational signatures closely match those previously observed in NH_4NO_3 /SBT mixed particles at 9.8% RH, demonstrating the formation of solid tartaric acid (TA) within the particles under this low-humidity condition. Furthermore, two diagnostic peaks characteristic of



crystalline ammonium salts are detected at 3047 cm⁻¹ and 3125 cm⁻¹, which are also similar to the spectral features of
 410 NH₄NO₃/SBT particles at 9.8% RH. This observation confirms that crystalline NH₄Cl coexists alongside solid TA in the
 particle matrix at 14.2% RH. Smooth liquid-like domains (labeled Region 2) and dendritic crystalline textures (labeled Region
 1) can be clearly distinguished in the micrograph acquired at 85% RH; hence, we conducted separate Raman spectroscopic
 measurements on these two distinct micro-regions. Spectral comparison between these two micro-regions reveals that the
 spectrum of Region 2 (denoted 85.5%-2) is identical to the spectrum recorded at 91.5% RH, confirming that all components
 415 within this domain exist in a fully liquid state. In contrast, the spectrum of Region 1 (denoted 85.5%-1) exhibits substantially
 stronger intensities for the three doublet bands at 1673/1706 cm⁻¹, 2950/2962 cm⁻¹, and 3322/3369 cm⁻¹ relative to the
 corresponding Raman bands observed at 14.2% RH, which demonstrates a greater extent of solid TA formation within the
 crystalline solid domain. Meanwhile, the prominent intensification of the characteristic band of ammonium chloride at 3125
 cm⁻¹ indicates an elevated content of crystalline NH₄Cl within the particle. Based on this information, it can be inferred the
 420 similar chemical process to NH₄NO₃/SBT aerosols as shown in eq. (2):



The hygroscopic curve indicates that the humidity decreases almost linearly to 40% RH, and GF reaches its minimum
 value. During the humidification process, the particle size remains unchanged when RH is lower than 70.9%; thereafter, the
 particle size increases, indicating obvious water absorption by the particles. When the maximum humidity is reached, the
 425 particles still exist in a solid-liquid separated state.

The morphological evolution of mixed particles containing NaCl and SBT at a molar ratio of 1:1 is displayed in Fig. S6.
 When the RH drops to 84.0%, a tiny crystalline nucleus emerges at the particle center. As the RH further decreases to the
 critical efflorescence point of 69.0%, the particle undergoes dramatic morphological deformation, losing its spherical shape
 and developing folded, curved crystalline textures with residual liquid pockets retained inside the particle. And then water
 430 evaporation and particles became smaller and form an irregular crescent-like solid with prominent wrinkled internal structures
 as RH continues to decrease to finally 9.8%. On hydration, persistent invariant solid texture from 10.3% RH to 70.7% RH.
 When RH reaches the critical deliquescence threshold of 74.3%, the particle starts to absorb water and irregular outline
 becomes rounded with a liquid film formation at the particle periphery. Upon reaching 94.1% RH, the particle recovers a

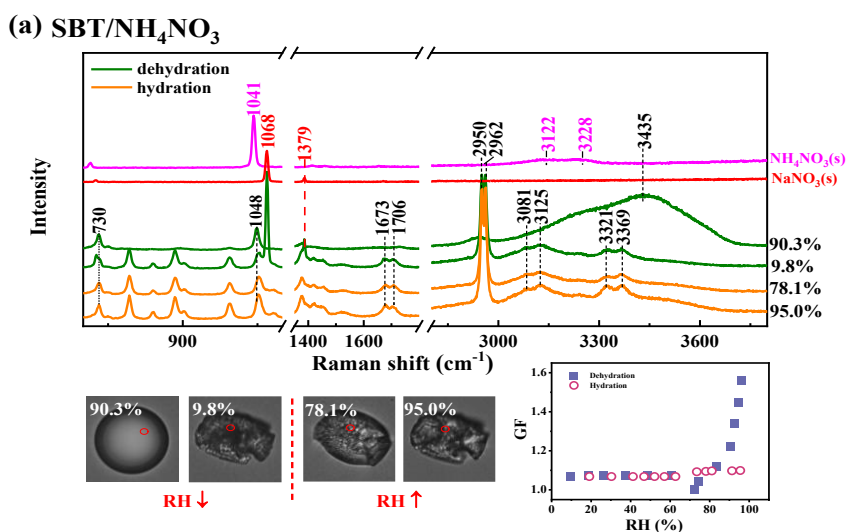


smooth, intact spherical liquid droplet, with only a minor fraction of solid residues retained at the surface. The Raman spectra
 435 corresponding representative morphologies of 1:1 SBT/NaCl aerosol particles are shown in Fig. 6(c). Red circles in the
 micrograph mark the probing spots of Raman measurements. As the relative humidity decreased from 91.3% to 9.8%, the
 particle morphology transformed from liquid droplets to quasi-solid phases, accompanied by distinct changes in Raman spectra.
 The most prominent spectral differences are summarized as follows: the broad water band at 3435 cm^{-1} nearly disappeared
 and was replaced by two weak, broad Raman bands at 3264 and 3401 cm^{-1} ; the single broad band centered at 2940 cm^{-1} split
 440 into two intense broad bands at 2940 and 2980 cm^{-1} . Meanwhile, the weak broad band at 1730 cm^{-1} vanished, and a broad
 band at 1670 cm^{-1} emerged with substantially enhanced intensity. This is because free water is largely lost, eliminating the
 water band at 3435 cm^{-1} and exposing intrinsic hydroxyl stretching bands of tartrate at 3264 and 3401 cm^{-1} derived from $\text{O}-$
 $\text{H}\cdots\text{Cl}^-$ and weak intramolecular $\text{OH}\cdots\text{OOC}^-$ hydrogen bonds (3401 cm^{-1}) within the quasi-solid matrix. The removal of
 hydration shells facilitates Na^+ -carboxylate contact ion pairing, lifting the degeneracy of C-H vibrations and splitting the
 445 original single peak into two strong bands at 2940 and 2980 cm^{-1} . In addition, dehydration alters the protonation equilibrium
 of tartrate, resulting in COO^- stretching mode shift from 1730 to 1670 cm^{-1} . As the RH increases to 75.9% following
 dehydration, particles begin uptake water and marked region in the image show increased brightness. A dominant broad water
 stretching envelope at 3435 cm^{-1} appears. The coexistence of partially solvated tartrate, contact Na^+ -carboxylate ion pairs and
 Cl^- -associated hydroxyl groups create three chemically distinct $-\text{CH}(\text{OH})-$ microenvironments, giving rise to the resolved C-
 450 H triplet at 2921 , 2940 and 2972 cm^{-1} . Moreover, increased water content modulates the extent of tartrate partial protonation
 and C=O bond character, leading to the enhanced intensity of the carbonyl band at 1670 cm^{-1} .

From the hygroscopic curve, during the dehumidification process, the mutation point of GF is at 65% RH, which is close
 to that of pure SBT and significantly higher than the efflorescence point of NaCl (45% RH). During the humidification process,
 the GF begins to increase at 75% RH, which is significantly lower than the deliquescence point of NaCl. Clearly, SBT promotes
 455 the efflorescence and deliquescence of NaCl.

A comparison of Raman spectra of dehydrated SBT/NaCl and SBT/ Na_2SO_4 mixed aerosol droplets reveals substantial
 discrepancies in Raman bands above 2800 cm^{-1} . Such distinct spectral features indicate divergent intermolecular interactions,
 which are primarily induced by the different inorganic salt anions. The triplet/doublet splitting of C-H stretches serve as a

diagnostic marker to distinguish Cl^- vs sulfate-driven hydrogen-bond rearrangement and ion pairing in low-humidity organic-salt mixed aerosols. Bare Cl^- anions segregate at tartrate grain boundaries upon dehydration and form strong $\text{O-H}\cdots\text{Cl}^-$ hydrogen bonds with tartrate hydroxyl groups. This interaction weakens adjacent C–H bonds and generates the red-shifted 2921 cm^{-1} band unique to NaCl systems (Heisler et al. 2010). In contrast, high charge density of SO_4^{2-} retains tightly bound hydration water at low RH, creating a steric barrier that prevents close-range hydroxyl–sulfate hydrogen bonding; no equivalent strongly H-bonded CH microenvironment exists, eliminating the $\sim 2920\text{ cm}^{-1}$ sub-band (Qiao, M. D. 2022). In addition, NaCl releases abundant free Na^+ to form tight contact ion pairs with tartrate COO^- ion, enhancing electron-withdrawing effects and producing a strongly blue-shifted peak at 2980 cm^{-1} . Divalent SO_4^{2-} electrostatically sequesters Na^+ ions, reducing the population of close Na^+-COO^- pairs and weakening C–H blue shift to 2972 cm^{-1} . The third cause is that spherical Cl^- clusters introduce steep chemical gradients across tartrate crystal domains, yielding three non-equivalent CH(OH)^- sites. Tetrahedral sulfate ions form smoother organic-inorganic interfaces with weaker environmental variation, leaving only two distinguishable CH vibrational environments and a two-band Raman signature.



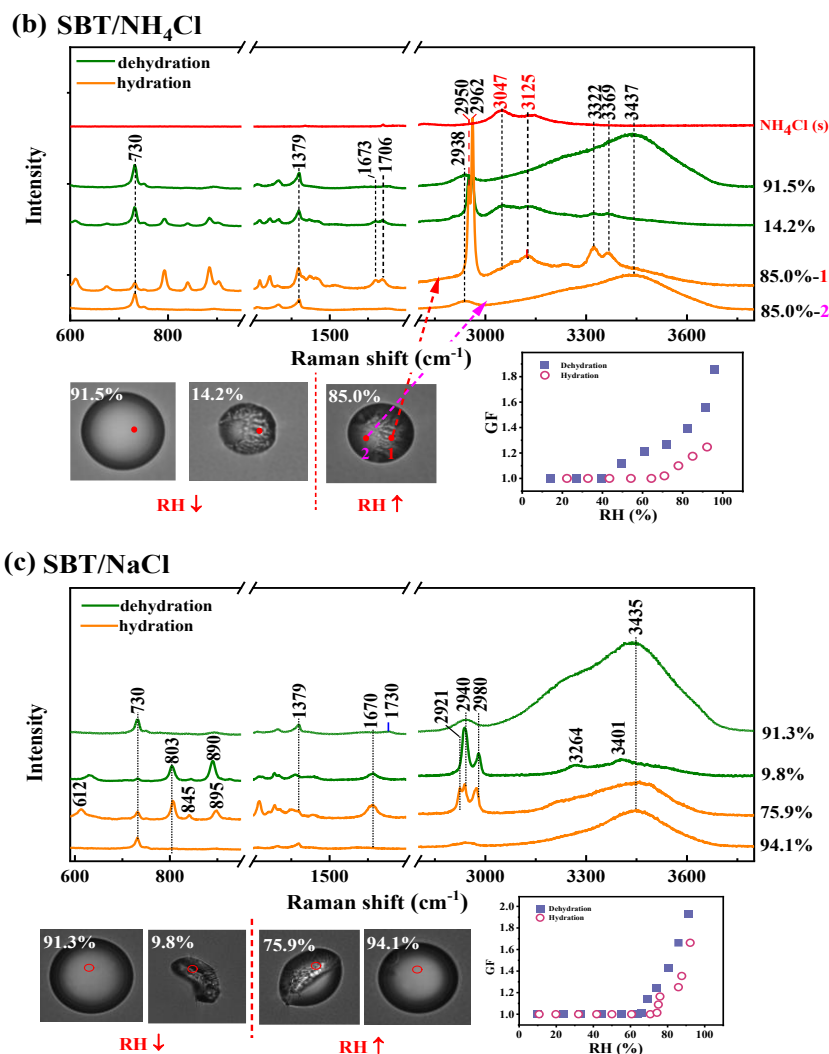


Figure 6: Raman spectra a single mixed particle of (a) SBT- NH_4NO_3 , (b) SBT- NH_4Cl and (c) SBT- NaCl , and the bottom images corresponding to Raman spectra and hygroscopic curve

4 Conclusions

This study investigates the RH-cycle-dependent hygroscopic and phase-transition behaviors of tartaric acid, sodium bitartrate and sodium tartrate aerosols. Polyhydroxy and carboxylate groups sustain intra- and intermolecular hydrogen bonds, retaining residual water under dry conditions. The transition from tartaric acid to mono- and disodium tartrate weakens hydrogen bonds and strengthens ionic bonds, producing amorphous solids for acid/acid salt and colloidal phases for fully deprotonated tartrate



at low RH. Mixed with Na₂SO₄, three tartrate compounds modify sulfate efflorescence pathways drastically. Tartaric acid drives Na₂SO₄ efflorescence during humidification without solidification of itself, sodium bitartrate delays rapid sulfate crystal growth down to 52% RH despite nucleation at 86% RH. Rehydration induces synchronous crystallization of both components, and further water uptake dissolves Na₂SO₄ to facilitate sodium bitartrate crystallization. Reversible efflorescence cycles in sodium tartrate–Na₂SO₄ mixtures are attributed to reversible formation and breakdown of tartrate–Na⁺–sulfate complexes, as validated by Raman spectroscopy. A weak-base displacement reaction occurs when ammonium salts are mixed with sodium bitartrate, altering particle chemical compositions. Substitution of Na₂SO₄ with NaCl gives efflorescence at 65% RH and deliquescence at 75% RH. The distinct hydrogen-bond affinity of SO₄²⁻ and Cl⁻ toward hydroxyl groups ultimately differentiates the hygroscopic evolution of SBT/Na₂SO₄ and SBT/NaCl aerosols. This work provides molecular-level insights into anion-controlled intermolecular interactions in organic-inorganic atmospheric aerosols.

Our observation of anion-specific effects between sulfate and chloride is consistent with prior Raman investigations of malonic acid–NaCl systems and earlier findings regarding surfactant-regulated aerosol surface tension, reinforcing that inorganic anions can substantially alter intermolecular interactions and phase evolution in organic-inorganic aerosol mixtures. It suggests systematic differences in the hygroscopic evolution of anthropogenic sulfate and marine sea-salt aerosols and helps improve the parameterization of mixed organic–inorganic aerosols in atmospheric models (Bain et al., 2025; Peng et al., 2016). While many previous laboratory studies focused on the effect of hydroxyl-free water-soluble dicarboxylic acids, including succinic acid and oxalic acid on inorganic salts (Wang et al., 2019; Wang et al., 2017), our results highlight that polyhydroxy organic acids and their neutralized salts strongly perturb the typical crystallization and efflorescence pathways of widespread atmospheric inorganic species including ammonium salts, ammonium sulfate, and sea-salt NaCl. Abundant intra- and intermolecular hydrogen bonding inherent to polyhydroxy acids and their neutralized salts facilitates the assembly of interconnected three-dimensional hydrogen-bond networks (Zou et al., 2025). Upon mixing with inorganic salts, these rigid organic frameworks hinder the typical crystallization and efflorescence pathways of inorganic species, triggering anomalous phase behaviors such as limited partial efflorescence and efflorescence upon humidification, altering the water uptake capacity of tropospheric aerosols over the full humidity cycle (Zhu et al., 2022; Dong et al., 2024). And such phase heterogeneity controls trace gas diffusion and heterogeneous reaction rates (Pöschl and Shiraiwa, 2015), modifying the production of



secondary organic aerosols and inorganic particulate pollutants.

Collectively, this study provides molecular-level spectroscopic evidence for understanding hygroscopic evolution, phase partitioning, and environmental impacts of internally mixed polyhydroxy organic–inorganic aerosols under realistic tropospheric conditions. Further quantitative work is required to constrain how polyhydroxy-compound-driven anomalous phase transitions affect heterogeneous reaction kinetics and secondary aerosol formation potential. The complex phase behaviours and compositional evolution originating from varied microenvironments in mixtures of polyhydroxy acids, acid salts, fully neutralized disalts, sulfates, and sea salts should be incorporated into climate and air-quality models, delivering molecular-scale foundations to refine parameterizations for organic–inorganic mixed aerosol modules.

Data availability

The data supporting this article have been included in the main text and as part of the Supplement: Figures S1–S6.

Supplement

The supporting information includes further experimental details and supplementary figures that are associated with the main text.

Author contributions

S.P. conceptualized, designed the study. Y.Z., S.P. supervised the study. F.D., M.S. conducted the experiments. F.D., S.P. analyzed and visualized the data, and wrote the original draft. S.P. reviewed and edited the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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