

## Response to referee 1's comments

In Yang and co-workers describe laboratory measurements of internally mixed organic-inorganic aerosol systems. Mainly based on FTIR, their experiments demonstrate how replacement reactions in aqueous aerosols can alter the composition, with subsequent implications for the aerosol phase state, an important property that determines the impacts of aerosol particles on air quality and climate.

Overall, I find the experiments interesting and the topic falls within the scope of Atmospheric Chemistry and Physics. However, I would like the authors to address the points below, before their work can be considered for publication.

**Author reply:** We are grateful for the careful review, the positive feedback, and the constructive suggestions from the referee. These suggestions are of great significance in enhancing the quality of our manuscript and facilitating readers' better understanding of our work. We have incorporated the referee's comments and suggestions into our manuscript. In the response to the referee, we list each comment, followed by our detailed responses, corresponding revisions with accompanying line numbers, and additional figures. We believe that the changes have resulted in a much stronger manuscript.

**1L16: Please rewrite and clarify the list of numbers: Do you mean 65.5% to 60.1%?**

**Reply:** Thanks for the careful review. We have carefully checked the manuscript and corrected this error.

**Revision: line 15-17:** "For SP/ammonium aerosols, the produced  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  crystallized from 35.7% to 12.7%, and from 65.7% to 60.1% RH, respectively, lower than pure inorganics ( $62.5 \pm 9$ –32% RH for  $\text{NaNO}_3$  and  $82 \pm 7$ – $68 \pm 5$ % RH for  $\text{Na}_2\text{SO}_4$ )."

**L17: Please add RH uncertainties to your quoted DRH values. Consider also adding the DRH values of pure inorganics in parenthesis at the end of this sentence, so that the increase in DRH becomes more quantitative.**

**Reply:** Thank you for this helpful suggestion. We have added the uncertainties and the DRH of pure  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$ .

**Revision: line 17-19:** "Upon hydration, the crystalline  $\text{Na}_2\text{SO}_4$  and  $\text{NaNO}_3$  deliquesced at 88.8%–95.2% and  $76.5 \pm 2$ –81.9%, higher than those of pure  $\text{Na}_2\text{SO}_4$  ( $74 \pm 4$ %–98% RH) and  $\text{NaNO}_3$  ( $65$ – $77.1 \pm 3$ % RH)."

**L29: Please check your reference formatting. This reference is from the year 2011, not 2001.**

**Reply:** Thank you for pointing this out. This has been corrected in the revised manuscript.

**Revision: line 32-33:** "...water (Koop et al., 2011),"

**L33: Please check your reference formatting. This reference should read "Kreidenweis".**

**Reply:** Thank you for pointing this out. We have corrected the reference format and checked the format for other for our manuscript.

**Revision: line 34:** “...(Svenningsson et al., 1997; Kreidenweis et al., 2005),”

**L37:** “... with carboxylic acids/salts and ammonium salts as one of the most abundant...” Please add appropriate references to this statement.

**Reply:** Two references have been added according to the referee's suggestion.

**Revision: line 39-40:** “...components, respectively (Huang et al., 2014; Trebs, et al., 2005).”

**line 501-505:** “Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E., Prévôt, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, *Nature*, 514, 218-222, <http://doi:10.1038/nature13774>, 2014.”

**line 617-620:** Trebs, I.; Metzger, S.; Meixner, F. X.; Helas, G. N.; Hoffer, A.; Rudich, Y.; Falkovich, A. H.; Moura, M. A. L.; da Silva, R. S.; Artaxo, P.; Slanina, J.; Andreae, M. O. The  $\text{NH}_4^+$ - $\text{NO}_3^-$ - $\text{Cl}^-$ - $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$  aerosol system and its gas phase precursors at a pasture site in the amazon basin: How relevant are mineral cations and soluble organic acids? *J. Geophys. Res.-Atmos.* 110 (D7), D07303, <http://doi.org/10.1029/2004JD005478>, 2005.

**L44:** “Organics can decrease...”. Please add appropriate references to this statement, as well as to the following sentence.

**Reply:** Thank you very much for your suggestion. Two references have been added.

**Revision: line 47-49:** “Organics can decrease the surface activity of particles due to hydrophobic carbon chains and hydrophilic head groups (Petters et al., 2007). Additionally, viscous states owing to intermolecular interactions at low humidity can be formed, leading to limited water absorption (Reid et al., 2018 ).”

**line 578-580:** “Petters. M. D., Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.* 7,1961-1971, <https://doi.org/10.5194/acp-7-1961-2007>, 2007.”

**line 591-593:** “Reid, J. P., Bertram, A. K., Topping, D. O., Laskin, A., Martin, S. T., Petters, M. D., Pope, F. D., Rovelli, G.: The viscosity of atmospherically relevant organic Particles, 9, 956, <https://doi.org/10.1038/s41467-018-03027-z>, 2018”

**L47:** Please add more relevant references, e.g.: 10.1021/jp0556759

**Reply:** Thank you. The reference has been added in revised paper.

**Revision: line 49-50:** “...organic acids and inorganic salts (Shi et al., 2012; Wang et

al., 2017; Marcolli et al., 2006)”

**line 554-556:** “Marcolli, C., Kreidenweis, U. K.: Phase Changes during Hygroscopic Cycles of Mixed Organic/Inorganic Model Systems of Tropospheric Aerosols, *J. Phys. Chem. A*, 110, 1881–1893, <https://doi.org/10.1021/jp0556759>, 2006.”

**L50-51:** Please either give a review article here as reference, or add further primary refs for each of the named processes, i.e. reactivity, heterogeneous uptake...

**Reply:** Thank you for your suggestion, we cited a review article as our reference.

**Revision: line 53:** “...trace gases (Herrmann et al., 2015).”

**Line 495-497:** “Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M.; Otto, T.: Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase, *Chem. Rev.* 115, 4259-4334, <https://doi.org/10.1021/cr500447k>, 2015.”

**L52:** This is the first time you mention “replacement reaction”. I would encourage the authors to give a brief, general definition and maybe a relevant example, so that a reader can follow more easily.

**Reply:** We thank the referee for the suggestion. The definition and an example of replacement reaction has been added in revised paper and highlighted.

**Revision: line 56-58:** “Here and throughout this paper, we refer the replacement reaction to the exchange of ions between two ionic compounds (e.g.,  $\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \rightarrow \text{NaBr} + \text{CH}_3\text{CH}_2\text{OH}$ ).”

**L54: Check reference:** “Ma et al. (Ma et al., 2019)”

**Reply:** Thanks, it has been corrected.

**Revision: line 58:** “Ma et al. (2019)...”

**L56:** “... the impact of ... on hygroscopic growth”: It would be good to more precisely specify the impact. Did oxalate formation lead to a decrease or increase in hygroscopic growth?

**Reply:** Thank you for the comment. This sentence has been revised to improve clarity.

**Revision: line 59-60:** “...validated that the metal oxalate complex formation led to a decrease in hygroscopic growth.”

**L57: Check reference:** “Ma et al. (Ma et al., 2022)”

**Reply:** I have checked the ref. and corrected the reference.

**Revision: line 61:** “Ma et al. (2022)...”

**L60: Consider changing “liberate” to “release” or “formation”**

**Reply:** Thank you. We have revised the sentence and removed this expression.

**L64: No need to write Chen et al. twice in the sentence. Rewrite as : “Chen et al. (2020) elucidated..., respectively.” Also, is it really appropriate to say “elucidated”, since in the next sentence you write how information on aerosol phase state was missing.**

**Reply:** Thanks, the reference has been corrected. In addition, we replace “elucidated” with “discussed” in this sentence for a more objective expression.

**Revision: line 66:** “...Chen et al. (2022) discussed ...”.

**L64: I am unclear what “lack of information” or “uncertainty in aerosol phase state” you refer to, please specify? Do you mean a lack of knowing the crystallization RH?**

**Reply:** Thank you for your comment. The sentence has been revised for clarification. In the cited article, due to the lack of crystallization RHs of the produced salts, the thermodynamics and kinetic analysis on depletion of chloride, nitrate, or ammonium in atmospheric aerosols were discussed without considering crystallization RHs of the produced salts. In the original sentence, we refer the “lack of information” to the lack of crystallization of RH of reaction products, and the “uncertainty” was referred to limited knowledge about possible gel or amorphous phase formation, which was also not discussed in the cited paper.

**Revision: line 68-69:** “However, due to the lack of crystallization RH of each replacement reaction products, and the limited knowledge about potential gel or amorphous phase formation, the kinetic processes based on the model cannot accurately take aerosol phase state into account.”

**L70-72: This sentence reads cumbersome, please reformulate. I think you are trying to say that phase states such as LLPS can promote the inhomogeneity of components? Your references seems appropriate for the first part (“The inhomogeneity of aerosol components can significantly impact the degree of reactivity”). I would move it there and then consider adding other references for the occurrence of LLPS, liquid-solid coexistence etc.**

**Reply:** Thank you for the suggestions. The sentence has been revised for clarity and a reference was also added.

**Revision: line 71-74:** “Reactions in atmospheric aerosols, such as replacement reaction, can alter aerosol phase state. Atmospheric aerosol phase states can be complex, including the coexistence of crystalline solid and liquid (Yang et al., 2019), liquid-liquid phase separation (Zhou et al., 2019), and solid in a viscous phase. (Zhu et al., 2022). These varying phase states promote the inhomogeneity of aerosol components, significantly impacting the degree of reactivity. (Zong et al., 2022).”

**Line 651-653:** “Zhou, S., Hwang, B. C. H., Lakey, P. S. J., Zuend, A., Abbatt, J. P. D., Shiraiwa, M.: Multiphase reactivity of polycyclic aromatic hydrocarbons is driven by phase separation and diffusion limitations, 24, 11658-11633, <https://doi.org/10.1073/pnas.1902517116>, 2019.”

**L76-79:** “Therefore, ...” I am a bit stuck with this statement. On L69-70 you write that “replacement reactions and phase state are intercorrelated parameters”, which I think is a fair way to put it. Now, on this line here you argue about the impact of replacement reactions *on* aerosol phase state. However, at the same time these replacement reactions in turn depend on the aerosol phase state. What is the correct line of reasoning, i.e. replacement reactions affecting phase state or phase state affecting replacement reactions...? Maybe it would be fairer to reformulate this here to something like: “Exploring the interplay of different organic and inorganic salts on reactivity, particularly the reactivity of replacement reactions, on the one hand side, and aerosol phase state on the other hand side, is important to understand atmospheric aerosols”. The title of the manuscript should be adjusted accordingly.

**Reply:** Thank you very much. The sentence has been rewritten as your recommendation. And the title of the manuscript has been adjusted.

**Revision: line 77-79:** “... exploring the interplay of different organic and inorganic salts on reactivity, particularly the reactivity of replacement reactions, and aerosol phase state on the other hand, is important to understand atmospheric aerosols.”

**Line 1-3:** “The Interplay between Aqueous Phase Replacement Reaction and the Phase State of Internally Mixed Organic/ammonium Aerosols”

**L77: Change “significance” to “important”**

**Reply:** Thank you. The word “significance” has been changed to “important” which can be seen in last reply.

**Line 77-79:** “is important to understand atmospheric aerosols”

**L87: See my comment above: It might be good to replace “correlation” here with “interplay”**

**Reply:** Thanks, we have replaced correlation with “interplay”.

**Revision: line 89:** “...a better understanding of the interplay between chemical composition...”

**L93: What is “three distilled water”?**

**Reply:** Thank you. The “three distilled water” means that the water was distilled three times. It has been corrected as “triple distilled water”

**Revision: line 95-96:** “...were prepared using triple distilled water.”

**L97: Please indicate compound purities when introducing the chemicals, along with supplier.**

**Reply:** Thanks for your suggestion. The purity and supplier has been added in revised paper.

**Revision: line 96-99:** “The organic acid salts include sodium pyruvate (SP, Aladdin

Reagent Co., Ltd.,  $\geq 99.0\%$ ), sodium citrate (SC, Beijing Chemical Reagents Company,  $\geq 99.0\%$ ), and sodium tartrate (ST, Beijing Chemical Reagents Company,  $\geq 99.0\%$ ). The ammonium salts include  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  (all from Beijing Chemical Reagents Company,  $\geq 99.0\%$ ).”

**L97: How was this diameter measured? Please specify. Also, were FTIR experiments done for differently sized particles? How was particle homogeneity verified, i.e. absence of e.g. liquid-liquid phase separation, that could affect results.**

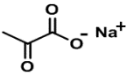
**Reply:** We thank the reviewer for the comment. The diameter was measured by optical microscopy. In our experiment, droplets were deposited onto the substrate and kept at the highest level ( $>87\%$  RH) for about 30 min before size measurement. The droplet size distribution follows a Gaussian distribution with a mean of 5 micrometers. The homogeneity of the droplets was also verified according to optical images. No LLPS was observed at relatively high RH prior to efflorescence.

**Table 1: Please add spaces between numeric values and units, e.g. 100 g instead of 100g.**

**Reply:** Thanks, we have checked the whole paper and add spaces between numeric values and units. The revised parts have been highlighted.

**Revision:**

**Table 1: The molecular structure of inorganic and organic compounds**

Compound	Molecular structure	Dissociation constant of conjugate acid	Solubility in 100g H <sub>2</sub> O (20°C)	Molecular weight (Da)
Ammonium nitrate	$\text{NH}_4\text{NO}_3$	NA	190 g	80.043
Ammonium chloride	$\text{NH}_4\text{Cl}$	NA	37.2 g	53.49
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	NA	75.4 g	132.14
Sodium pyruvate		$K_a = 3.2 \times 10^{-3}$	47 g	82.03

Sodium citrate		$K_{a,1} = 7.4 \times 10^{-4}$ $K_{a,2} = 1.7 \times 10^{-5}$ $K_{a,3} = 4.0 \times 10^{-7}$	154 g	258.07
Sodium tartrate		$K_{a,1} = 1.04 \times 10^{-3}$ $K_{a,2} = 4.55 \times 10^{-5}$	33.3 g	194.05

### L104: bump → pump

**Reply:** The “bump” has been replaced by “pump”.

**Revision: line 107:** “...mass flowmeter and vacuum pump...”

**Section 3 general:** It would be helpful to add a Table to the SI where the different peaks and the corresponding chemical groups and inferred phase state were summarized, as it is in parts very hard to follow the discussion throughout this Section.

**Reply:** We thank the reviewer for the helpful suggestion. Table S1 has been added, as well as the statement in paper.

**Revision: line 145-146:** “...and band assignments can be found in Table S1”

**Table S1** Assignments of IR Peaks Attributed to Ammonium and Carboxylates

		831			$\nu_2\text{-NO}_3^-$
		1055(s)			$\gamma(\text{CH}_2)$
		1069(l)			$\gamma(\text{CH}_2)$
1176(l)					$\nu(\text{C-C}) + \gamma(\text{COO}^-)$ (liquid)
			1180		
1186(s)					$\nu_3(\text{SO}_4^{2-})$
	1278	1276(s)			$\nu(\text{C-C}) + \gamma(\text{COO}^-)$
	1308				$\nu(\text{C-C})$
1353					$\omega(\text{CH}_2)$
	1386	1388(l)			$\delta_s(\text{CH}_3)$
1404(s)		1417(s)	402(s)	1412(s)	$\nu_s(\text{COO}^-)$
					$\nu_2(\text{NH}_4^+)$ (solid)
1424(l)	1436(s)	1448(l)	1440(l)	1443(l)	$\nu_s(\text{COO}^-)$

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1568		$v_2(\text{NH}_4^+)$ (liquid)
1608(l)		$v_{\text{as}}(\text{COO}^-)$
1627(s)		$\delta(\text{OH}) + \nu(\text{CO})$
1654(s)		$v_{\text{s}}(\text{COO}^-)$
1709		$v_{\text{s}}(\text{COO}^-)$
		$v_{\text{as}}(\text{COO}^-)$
	1754	$v_{\text{as}}(\text{C=O})$
	2804	
	3036	$\nu(\text{NH}_4^+)$
3360	3130	$\nu(\text{NH}_4^+)$
		$\nu(\text{NH}_4^+)$
		$v_{\text{as}}(\text{O-H})$

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s: solid state, l: liquid state

**L126: add “is” shifted to**

**Reply:** Thank for your careful reading, the “is” has been added.

**Revision: line 149:** “1176  $\text{cm}^{-1}$  is shifted to 1186  $\text{cm}^{-1}$ ”

**L140: I would encourage to specify here and elsewhere as “crystalline solid phase”, as the “viscous phase” can also be solid (== glassy) or semi-solid, which both denote amorphous solid phase states.**

**Reply:** The advice is very good. We have specified the “crystalline solid phase” in appropriate place to avoid the confusion with amorphous solid phase states, all of which have been highlighted.

**L142: Here and elsewhere, please give RH uncertainties.**

**Reply:** In revised paper, the RH uncertainties have been added in some places and highlighted.

**Revision: line 168:** “...at 55.7–59% RH for sodium tartrate aerosols, where an error margin is 1%.”

**L145-147: I am unclear about what you write here. If the sodium citrate aerosol is highly viscous, why is the water uptake than not gradual, but “abrupt”, as you write? To me the humidification curves on sodium citrate and sodium tartrate look like curves with a sharp deliquescence, which I would only expect for crystalline material. Please clarify why you nonetheless think that these phase states are “viscous”, which you seem to use to describe an amorphous solid state.**



**Reply:** The viscous state was concluded by little water retained at the lowest RH, which can be seen from the water content dependent upon the RH during dehydration as seen in Fig. 1. The more detailed description has been added. On hydration, the viscous state can transform into solution at a certain RH, which is gel-broken point.

**Revision: line 163-164:** "...and the retained normal water content of 0.25 and 0.15 for ST and SC, respectively, at the lowest RH..."

**Section 3: This Section has many different subsections and the connection of these is not always obvious. It would be good to add a brief description of what topic is treated where to guide the reader a bit at the start of the Results and Discussions.**

**Reply:** Based on referee's suggestion. A brief description that guides the reader to different topics was added at the start of the Results and Discussions.

**Revision: line 123-141:** "The phase behaviour of mixed aerosols is dependent upon the chemical composition, molar ratio and chemical process. Herein we selected three organic salts including SP, ST and SC, along with  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ , to study the interplay between phase state, composition evolution, and aqueous phase replacement reactions in aerosols during RH changing cycles. This section consists of seven parts. In *part 3.1*, we analysed the IR spectra of pure organic salts and inorganic salts to obtain the differences in characteristic peaks for aqueous and solid phases. Based on this, in *part 3.2*, SP was mixed with different ammonium salts with various stoichiometric ratio to form aerosols, and the infrared spectra of the mixed aerosols were tested to analyse the characteristic absorption peaks in the second section. The results showed that SP underwent a substitution reaction with the ammonium salts, and the mixed aerosols containing different ammonium salts exhibited distinct phase behaviours. Therefore, in *parts 3.3 and 3.4*, we discussed in detail the substitution reactions and the resulting changes in water content and phase transition regions of the compounds. The phase transition regions of the reaction products were compared with those of the pure components. The relative content of the mixed components may vary in different regions. In *part 3.5*, we took the SP/ $\text{NH}_4\text{Cl}$  system as an example to study the impact of different component contents on phase transition behaviour. After investigating the hygroscopic behaviour of mixed aerosols containing different ammonium salts with the same organic salt, in *part 3.6*, we examined the phase evolution of aerosols induced by mixing different organic salts, SC and ST, with ammonium sulphate. By combining infrared spectroscopy and optical images, we discovered that the mixture of tartaric acid and ammonium sulphate not only underwent substitution reactions but also exhibited unexpected hygroscopic weathering behaviour. Therefore, in *part 3.7*, we discussed the causes of this special phase behaviour."

**Section 3.1 general: It could make sense to move your Fig. S2 to the main text. That way, a reader could follow the described spectral changes with changes in RH better. Also, Fig. S2 misses a proper legend indicating what the black and red data points correspond to.**

**Reply:** Thanks for the advice. Fig. S2 have been moved to the main text as Fig. 1 and

a proper legend has been added.

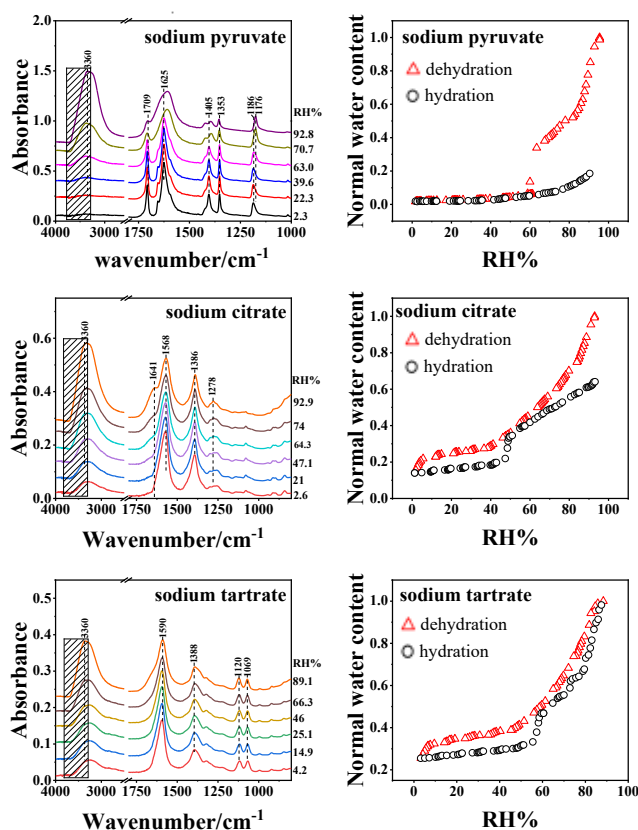
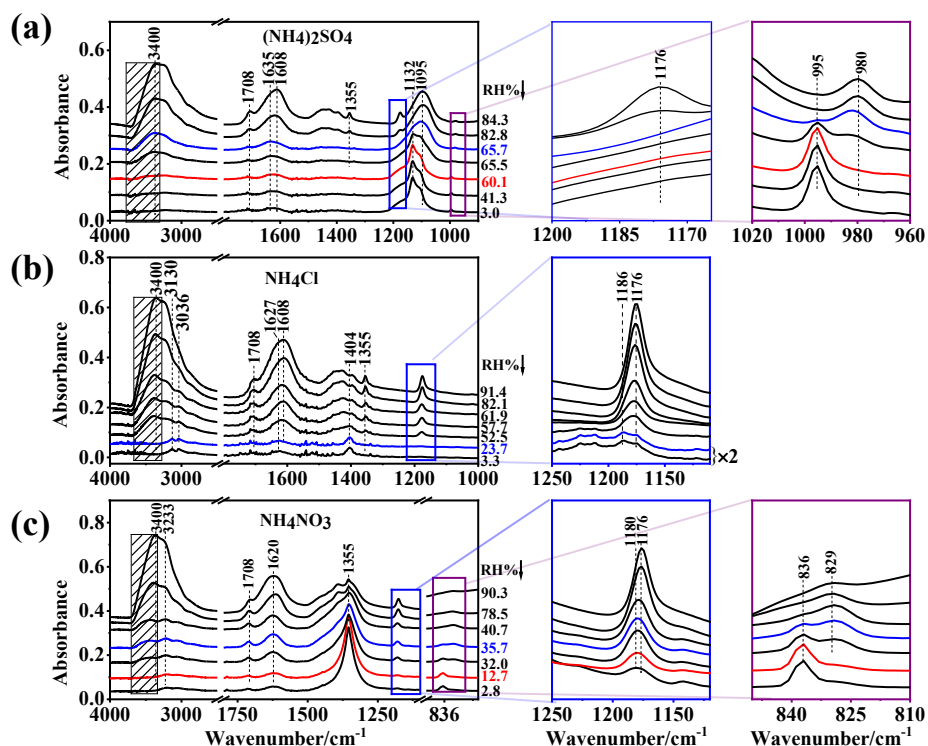


Fig. 1. The IR spectra of organic salts on dehydration and hygroscopic behavior during a down-up RH cycle. The shaded area shows the chosen integration region for liquid water. The spectra for sodium pyruvate was previously reported by Yang et al (2019).

**L153-155/Fig.1:** In the blue-framed enlarged image: Where is the blue and the red lines? Please color your lines as in the left most panel or the violet-framed enlarged image. Otherwise, it is impossible to connect the RH values to the individual lines. Note, this also concerns Fig. 1c.

**Reply:** Thanks for the advice. The lines in the left panel and right enlarged curves are correspondingly matched in the revised Fig. 1.

**Revision:**



**L159: Reference formatting: No need to have “Tan et al.” twice in this sentence, please change.**

**Reply:** Thank you. This has been corrected in revised paper.

**Revision: line 188:** “...RH. Tan et al (2014) investigated...”

**L185-195: Please add appropriate references the subpanels of Fig. S3, to make it clearer what you are describing here.**

**Reply:** Thank you. In revised version, a sentence to describe Fig. S2 (Fig. S3 in the original SI) has been added.

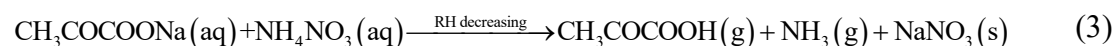
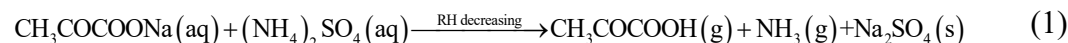
**Revision: line 211-212:** “Following the dehydration, the hydration of three SP/ammonium aerosols was performed. Fig. S2 presents the IR spectra on hydration.”

**Section 3.3 general: The structure of this section should be improved. In the beginning, the authors introduce relevant replacement reactions. The middle part (L202-210) then discusses some literature findings. The last part (L210-235) then discusses hygroscopicity data from the present manuscript, but the link to the topic of replacement reactions remains unclear. This requires improvement in a revised version.**

**Reply:** Thank you for your suggestion. We believe that the whole paragraph has been improved following your suggestion. We have revised Section 3.3 including the topic and the first paragraph.

**Revision: line 228-242: “ 3.3 The replacement reactions in SP/ammonium aerosols and the resulting hygroscopicity**

Above analysis on IR features showed the following reactions (1) - (3) in mixed SP/ammonium aerosols:

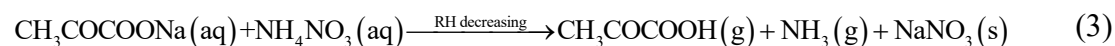
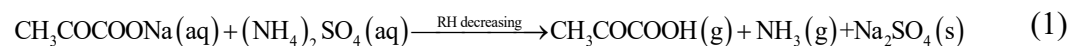


It can be seen that pyruvic acid and ammonia are formed and depleted from particles alongside the crystalline solid formation of various inorganic salts during dehydration, which proceeded the replacement reaction between SP and ammonium. Herein, aerosol particles act as micro-reactors, with their larger specific surface area than bulk solution facilitating similar processes. In fact, the replacement reactions in aerosols driven by gas released or compound formation with lower solubility have been reported in previous work. For example, Wang et al. (2017) observed the reaction in aerosols composed of oxalic acid and ammonium sulfate, which was driven by formation of lower hygroscopic ammonium hydrogen oxalate ( $\text{NH}_4\text{HC}_2\text{O}_4$ ) and ammonium hydrogen sulfate ( $\text{NH}_4\text{HSO}_4$ ) during the dehydration process. While Wang et al. (2019) reported the fact of the formation of crystalline solid  $\text{Na}_2\text{SO}_4$  from  $(\text{CH}_2)_n(\text{COONa})_2$  ( $n = 1, 2$ )/ $(\text{NH}_4)_2\text{SO}_4$  aerosols upon dehydration. Building upon their findings, crystalline solid  $\text{NaNO}_3$  and  $\text{NaCl}$  are also formed, as shown in equations (2) and (3).

**L198-200: Please indicate phase states of reactants too. Please also indicate whether these reactions take place for decreasing or increasing RH.**

**Reply:** Thank you for the suggestion. The phase states of reactants and reaction condition have been added in revised paper.

**Revision: line 230-232:**



**L206: “larger specific surface area” compared to what? Bulk solutions? Unclear.**

**Reply:** The aerosol particles are microdroplets, which has larger specific surface area than bulk solution under the condition of the same volume. In revised paper, the sentence has been corrected.

**Revision: line 235:** "...with their larger specific surface area than bulk solution facilitating..."

**L215:** "...water loss or uptake". Add <https://doi.org/10.1021/cr990034t> or other appropriate refs.

**Reply:** Thanks. the literature has been added in revised paper and highlighted.

**Revision: line 247:** "...water loss or uptake (Martin, 2000)"

**Line 557-558** "Martin, S. T.: Phase Transitions of Aqueous Atmospheric Particles, Chem. Rev., 100, 3403–3453, <https://doi.org/10.1021/cr990034t>, 2000."

**L221: "These processes...": Can you quantify "sudden" here? Also, please elaborate how spectral changes in this case do not reflect the water content. What does this mean to the spectral changes in your Fig. 1 (and others) discussed above?**

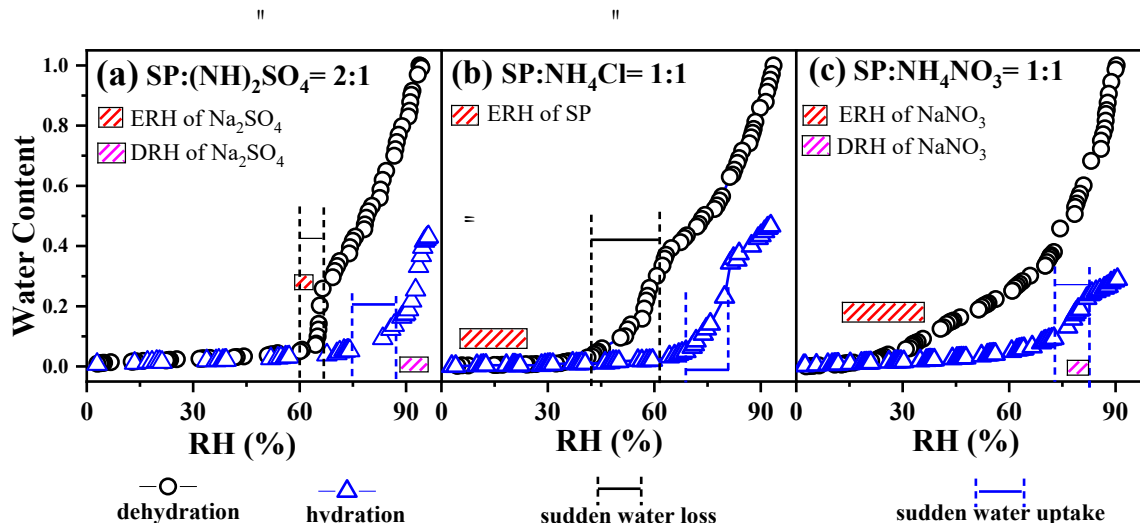
**Reply:** Thank you for pointing this out. The word sudden was misplaced in this sentence. Here, we meant that not like sudden water content changes for inorganic aerosols, which coincides with spectral change, atmospheric aerosols can exhibit phase transition with gradual water content change along with spectral changes. Therefore, both aerosol water content change and spectral change should be analyzed to accurately depict evolutions of atmospheric aerosols. We have rephrased the sentence for clarification.

**Revision: Line 256** "Therefore, changes in water content and IR spectra of aerosols need to be considered collaboratively to accurately understand the reactions and phase transitions of these aerosols."

**Fig. 2: Please add labels for the red and pink shaded area directly into the Fig. to make inter-pretation easier.**

**Reply:** According to your advice, the labels have been put into the Fig. 3 (origin Fig.2).

**Revision:**



**L224-241:** • Please add references to appropriate subpanels in Fig. 2 directly to the text, as you jump quickly between the individual panels.

**Reply:** Thank you. In the revised paper, the subpanels has been added when it was described and was also highlighted.

**Revision: line 256-257:** “Fig. 3 (Fig.2 in the original paper) shows the water content evolution during a RH cycle and their comparison with the phase transition point of compounds.”

• Please add information on the rate of RH changes during your experiments to the text. Was the rate slow enough to allow for equilibration of the particles and the surrounding RH?

**Reply:** Thank you. This information has been added.

**Revision: line 253-254:** “The RH changes stepwise and the rate is  $< 5\% \text{ min}^{-1}$ . And the stay time at each level is 30 minutes to allow for equilibration between particles and the surrounding RH.”

**L261:** Check title, should this read: “The effect of molar ratio on the replacement...”

**Reply:** Thank the careful check. The title has been revised.

**Revision: line 297:** “3.5 The effect of molar ratio on the replacement reaction and phase transition”

**L265:** Please provide reasoning for the chosen ratio in the context of typical organic-to-inorganic ratio found in atmospheric aerosols.

**Reply:** Thank you for the important suggestion. We added justification for the selected organic to inorganic ratio in Material and methods. In atmospheric aerosols, the groups

and ions were usually gained and it is difficult to measure detailed organic-to-inorganic ratio and chemical structure. However, it is well established that the emissions of various substances are dependent upon regions. Thus in this work, the ratios of 2:1, 1:1 and 1:2 represent different regions that may have excess organic matter, a balance between organic and inorganic matter, and excess inorganic matter.

**Revision: line 103-105:** “In the atmosphere, the organic to inorganic ratio varies regionally, but mostly remains at the same order of magnitude. Thus, the selected ratios herein can effectively represent different regions.”

**L267-270:** I suggest to repeat in parenthesis the meaning of the named peaks at e.g. 3130 cm<sup>-1</sup> etc., to make it easier for the reader to follow here.

**Reply:** The meaning of the 3130 cm<sup>-1</sup> band has been added.

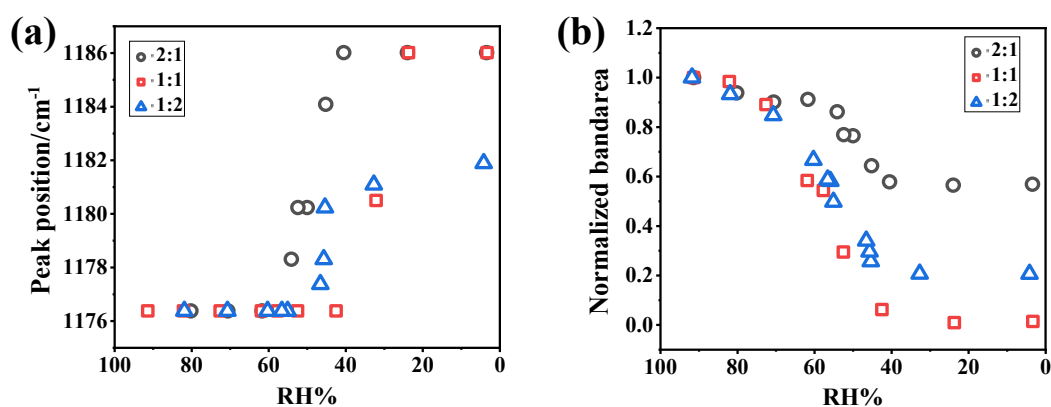
**Revision: line 303:** “...the 3130 cm<sup>-1</sup>,  $\nu$  (NH<sub>4</sub><sup>+</sup>) band of solid NH<sub>4</sub>Cl.”

**L278:** “From Fig. 4a...” Looking at the red squares in Fig. 4a, the shift from 1176/cm to 1186/cm appears to be pretty broad from about 40% RH to 20% RH. How can you get such a precise ERH value as 41% for the 1:1 mixture? Also, for the 2:1 mixture the peak shift seems to appear over an even broader RH range, so how do you get to the quoted 23.7% RH? Please clarify in the text.

**Reply:** Thank you for your questions. In our experiment, the RH changes as stepwise mode rather than linear mode, and the IR spectra were measured at every RH levels. So the ERH value gained at a specific RH value. Even though the ERH range is broad, but the onset of efflorescence is a specific RH value. In the articles, 23.7% RH and 41% both refer to the onset of ERH rather than precise ERH, as described in line 315.

**Fig. 4: What is the difference between grey symbols with a horizontal vs. vertical grey line across the symbol?**

**Reply:** There are no difference and only a different symbol. In revised paper, the symbols have been corrected as grey circle.



**L294:** Please delete “et al.”

**Reply:** Thanks. The “et al.” has been deleted.

**Line 330-331:** "...replacement reaction and dissociation"

**L295:** mixing → mixed, was → were

**Reply:** Thank you, the "mixing" and "was" have been replaced by "mixed" and "were"

**Line 332:** "...various organic salts, mixed with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were measured..."

**L303:** Replace "escalated" with more appropriate wording.

**Reply:** The word "escalated" has been replaced by "became stronger".

**Line 340:** "...for crystalline sulfate became stronger"

**Fig. 7: Why was there no crystallization observed in the left-hand side images at 12.1% RH? Please clarify in text.**

**Reply:** The left-hand side images in Fig. 8 shows the phase evolution for 1:1 ST/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosols on dehydration, where no crystal was formed, as reflected by the absence of 995 cm<sup>-1</sup> band in IR spectra (Fig. 6(b)). So no crystallization was observed at 12.1%.

**L332-341: More information should be added how these experiments were done? What was the rate of RH changes? Was the first RH cycle started at high or low RH? How long were the particles exposed to these (high) RH conditions? The latter would help to get a better idea how fast these replacement reactions are.**

**Reply:** Thank you for your suggestions. The information of RH change has been added in revised paper.

**Revision: line 369-371:** "...the IR spectra of SO<sub>4</sub><sup>2-</sup> and organic salts remained distinguishable as the RH changes from ~88.7% to ~2.0% RH stepwise with the rate lower than 5% RH min<sup>-1</sup>, indicating incomplete reaction likely due to mass transfer limitations in viscous aerosol particles for about 30 min at every RH level"

**L352: "substantial work" should be followed by appropriate refs.**

**Reply:** The refs have been added.

**Revision: line 390:** "previous substantial work on the phase state evolution of internally mixed organic/inorganic particles (Wang et al. 2019, Ma et al., 2022, Shao et al., 2018)."

**Line 601-603:** "Shao, X., Wu, F.-M., Yang, H., Pang, S.-F., Zhang, Y.-H.: Observing HNO<sub>3</sub> release dependent upon metal complexes in malonic acid/nitrate droplets, Spectrochim Acta A, 201, 399-404, <https://doi.org/10.1016/j.saa.2018.05.026>, 2018."

**L354: "retained in a viscous"**

**Reply:** Thanks, it has been corrected.



**Revision: line 393:** “SC particles retained in a viscous state at lower RH levels”

**L359: Please check if you really mean “dehydration” here or “hydration”?**

**Reply:** Yes, it is dehydration. In present work, SC and ST are both viscous state, but the phase behavior is different for their mixture with  $(\text{NH}_4)_2\text{SO}_4$ . For SC/ $(\text{NH}_4)_2\text{SO}_4$  aerosols, crystalline solid  $\text{Na}_2\text{SO}_4$  formed on dehydration, otherwise, it happened on hydration for ST/ $(\text{NH}_4)_2\text{SO}_4$  particles.

**L360: “Grayson...” verb is missing. Please avoid repetition of references; otherwise check for correct punctuation, i.e. “Grayson et al. have demonstrated...”**

**Reply:** Thanks. The sentence has been revised.

**Revision: line 399:** “Grayson et al. (2017) has confirmed viscosity increasing as the number of hydroxyl groups in the molecule.”

**L361: “As the RH decreased...” Please add ref to this statement and provide a brief explanation of “gel” for the reader here (you could move the explanation you give on L367 up).**

**Reply:** In accordance with the reviewers' suggestions, we have provided a brief description of the gel.

**Revision: line 400:** “As the RH decreased, the polyhydroxy chain with a carboxyl group is prone to form a gel owing to intermolecular hydrogen bonding. Gels are two-phase mixtures of liquids dispersed in (semi-)solid amorphous matrices, and the uptake of water into a gel can involve gradual swelling as well as stepwise volume increases related to thermodynamically well-defined phase transitions (Pang et al., 2002).”

**L371: which → where**

**Reply:** Thanks, “which” has changed to “where”

**Revision: line 410:** “in these gels where mechanical entanglements”

**L372: How does this trapping work? Just by physical uptake of water due to capillary condensation or is this due to chemisorption? This should be added to the text.**

**Reply:** It is generally believed that the gel captures water due to both the chemical adsorption of water molecules onto the gel fibers and physical uptake of water due to capillary condensation. In revised version, the statement has been added.

**Revision: line 411-412:** “trap water molecules owing to both the chemical adsorption of water molecules onto the gel fibers and physical uptake of water due to capillary condensation”

**L373: Break up sentence: “... bound around fibres. Hence, migration of  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  ions was inhibited, so that these ions cannot come in contact and nucleate a crystalline phase.”**

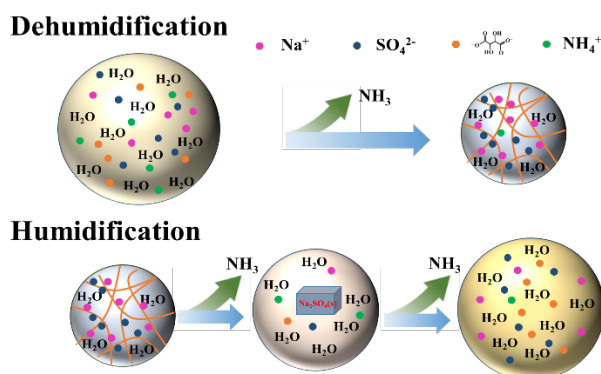
**Reply:** We thank the referee for the suggestion. The sentence has been corrected.

**Revision: line 412-414:** “Due to the strong interaction between OH groups and  $\text{SO}_4^{2-}$  ions, anions were bound around fibers. Hence, migration of  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  ions was inhibited, so that these ions cannot come in contact and nucleate a crystalline phase.”

**Fig. 8:** I like the idea of having a schematic, but I think this figure can be improved to clarify aspects described in the text. It is unclear what the different colors correspond to. A legend is missing to indicate the fibrous particles as “gel-like”. Is there a better way to make the “OH groups and  $\text{SO}_4^{2-}$  ions bound around the fibers” (L372) more obvious? Outgassing of  $\text{NH}_3$  is depicted but not mentioned in the text.

**Reply: Thank you for your suggestion.** Fig. 8 has been improved by color-coding solid spheres to represent different ions. We hope it makes “ions bound around fibers” more obvious. Moreover,  $\text{NH}_3$  release has been described in the article.

**Revision: Line 408:** “...gradually gelatinized water due to a decrease in water content, along with  $\text{NH}_3$  release.” And **line 417:** “...further form a solid nucleus, accompanying continuous  $\text{NH}_3$  release.”



**L387:** “of atmospheric SOA.” Please add more appropriate refs.

**Reply:** Two refs have been added.

**Revision: Line 428-429:** “...of atmospheric secondary aerosols (Yang, et al., 2008; Kawamura et al., 2016; Huang et al., 2022)” and the refs are follows:

**Line 513-515:** “Kawamura, K., Bikkina, S.: A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation. *Atmos. Res.*, 170, 140–160, 10.1016/j.atmosres.2015.11.018, 2016.”

**Line 637-638:** “Yang, L. M., Yu, L. E.: Measurements of oxalic acid, oxalates, malonic acid, and malonates in atmospheric particulates, *Environ. Sci. Technol.*, 42 (24), 9268–9275, <https://doi.org/10.1021/es801820z>, 2008.”

**L401-404:** Please see my previous comment: Replacement reactions can certainly

**impact the aerosol phase state as you document, but in turn these are also dependent on the phase state of the aerosol particle. This aspect should be better represented in your Conclusion section.**

**Reply:** Thank you. In revised paper, the impact of phase state in chemical process has been added.

**Revision: Line 445-448:** “Our findings highlight the intricate interplay between chemical components of organic/inorganic aerosol, such as organic molecular structure, molar ratio, replacement reaction and their collective impact on aerosol phase state, but in turn these are also dependent on the phase state of the aerosol particle. For example, the special chemical process in aerosols adopted gel state upon humidifying.”

**L397-398:** “Additionally, we observed...” **This is certainly a very interesting finding of this study. I would like to see some more discussion, which atmospheric processes could be influenced by such “crystallization upon hydration”. Also, can the authors speculate how important this process is and if they would expect it for other atmospherically relevant aerosol systems?**

**Reply:** Thank you for your comment. We very much appreciate your interest in “crystallization on hydration”. Usually, the reactive uptake of gas from atmosphere occurs in liquid phase, which further provoke chemical composition evolution, and in turn change the optical property and CCN activity. This statement has been added in revised paper. We also expect similar phenomenon to happen in other dicarboxylic acids and AS mixture aerosols as long as it can potentially form gel-like structure prior to typical efflorescence during dehydration.

**Revision: Line 440-442:** “...which can reduce the possibility of further composition evolution and reactive gas uptake due to the absence of ion mobility in solid at higher RH. Hence, light absorbance and CCN activity, which strongly depend on chemical composition, will change. Future studies are needed to further investigate this phenomenon, as it is also expected to occur in other organic/inorganic aerosols that can potentially form gel-like state prior to typical efflorescence.”

**L405-409: I am unclear what “targeted strategies to mitigate air pollution” the authors refer to. Please elaborate or remove this statement.**

**Reply:** According to suggestion, this statement has been deleted.

**Fig. 9: This figure is not mentioned and discussed in the text, please do that or delete the figure.**

**Reply:** Thanks, Figure 9 has been deleted.