Response to Reviewers:

Thanks for the reviewer's comments on our manuscript entitled "A comprehensive study on hygroscopic behaviour and nitrate depletion of $NaNO_3$ and dicarboxylic acid mixtures: Implication for the influence factors of nitrate depletion". The reviewers' comments are helpful for improving the quality of our work. The responses to the comments and the revisions in manuscript are given point-to-point below.

Reviewer #2:

Major comments

1. My main concern is with the presentation and interpretation of several of the results with regard to the loss of nitrate from the particles/droplets via evaporation of HNO_3. As the title indicates, nitrate depletion is a key interest of this work, yet most of the data provided does not appear to show direct evidence for nitrate depletion via HNO_3 loss to the gas phase – contrary to what is stated in the abstract (line 15) and the Results and Discussion section. The measurements provided characterize the composition and spectral features of nitrate and DCA species in the condensed phase(s) of deposited particles. However, unless I missed it, $HNO_3(g)$ is not measured, nor is the mass of nitrate in the particle phase tracked. If there is substantial loss of nitrate, the particles should change in nitrate content and overall mass. Moreover, the loss of nitrate would likely be accompanied by a loss of water. As pointed out in the specific comments that follow, there are several instances where statements like "... confirms nitrate depletion and HNO_3 release" are made (e.g. line 133), while the information provided does not directly support this conclusion. For example, the authors seem to equate the formation of liquid or solid $NaHC_2O_4$ as evidence for nitrate depletion. However, it is not discussed why that should be a unique signature of such a process. This reviewer argues that (at least some) dissolved or crystalline $NaHC_2O_4$ could also form in the absence of any nitrate depletion, simply as a result of aqueous solution chemistry and resulting equilibria. I strongly suggest that the authors rectify this issue and provide direct evidence for HNO_3 loss to the gas phase or otherwise clarify that their interpretation depends on certain assumptions about the relevant processes taking place.

To be clear, I also consider nitrate depletion via HNO_3 to be a plausible hypothesis and a likely explanation for the findings from this work. However, what is missing is quantitative evidence and/or clarity in the discussion in support of this hypothesis.

Author reply: First of all, the HCl/HNO_3 release from mixed nitrate/chloride and organic acid particles has been widely detected in field and laboratory measurements (Laskin et al., 2012;Wang and Laskin, 2014;Ma et al., 2019a;Ghorai et al., 2014;Shao et al., 2018). Laskin's group has employed the computer controlled scanning electron microscopy with energy dispersed analysis of X-rays (CCSEM/EDX) to measure the Cl/Na ratios in mixed organic acid/NaCl particles (Laskin et al., 2012;Ghorai et al., 2014) and N/Na ratios in mixed organic acid/$NaNO_3$ particles (Wang and Laskin, 2014). The measurement results clearly demonstrated the significant chloride/nitrate depletion by organic acids. Ma et al. (2013) measured the water adsorption isotherms of mixed NaCl/OA particles using vapor sorption analyzer. The decreased particle mass, i.e., water content therein, indicated the formation of less hygroscopic $Na_2C_2O_4$ in internally mixed particles. The corresponding Raman spectra results also confirmed the chloride depletion. Li et al. (2017) measured the Raman features of mixed NaCl/MA particles using in situ Raman microspectrometry and found the production of monosodium malonate in mixtures during the RH cycle, which demonstrated the chloride depletion and gaseous HCl release. Furthermore, the specific reactions of strong acids displaced by weak acids in aerosols have been summarized and discussed in our preivous review (Chen et al., 2021). Second, our group has persistently utilized the FTIR spectra to characterize the chemical composition evolutions of aerosol reaction systems (Wang et al., 2019;Shao et al., 2018;He et al., 2017;Du et al., 2020). For instance, Wang et al. (2019) observed the ammonium depletion and gaseous NH_3 release from mixed dicarboxylic acid salts and $(NH_4)_2SO_4$ aerosols during the RH cycle using the ATR-FTIR technique. Similar to this work, they measured the IR feature changes of dicarboxylic acid salts and corresponding DCAs, as well as the efflorescence transition behaviors of mixed particles. The results clearly demonstrated the compositional evolution and ammonium depletion in mixed dicarboxylic acid salts and $(NH_4)_2SO_4$ aerosols. Shao et al. (2018) determined the chemical composition evolution of MA/$NaNO_3$, MA/$Mg(NO_3)_2$ and MA/$Ca(NO_3)_2$ particles by vacuum FTIR method. The intensity changes of feature bands of COO^-, COOH and NO_3^- groups indicated the formation of malonate salts and HNO_3 release. Finally, the almost unchanged water content after nitrate depletion for DCA/$NaNO_3$ mixtures in this work, e.g., MA/$NaNO_3$ mixtures in Fig. 5a in the revised manuscript, might be due to the comparable hygroscopic properties of malonate salts and MA (Jing et al., 2018;Wu et al., 2011), or limited amounts of formed dicarboxylic acid salts.

Specific comments

2. Title: phrasing of "Implication for the influence factors of nitrate depletion" needs language improvement and perhaps a more direct link to aerosols. Consider replacing by "implications for nitrate depletion in tropospheric aerosols".

   Author reply: Thanks for the reviewer's suggestion. We have adopted reviewer's advice and revised our manuscript accordingly.

3. Line 15: make statement consistent with the data provided (see my major comment).

   Author reply: Thanks for the reviewer's suggestion. We have illuminated the agreements on the observations of nitrate/chlorine depletion and HNO_3/HCl release from mixed nitrate/chlorine and DCA particles via various measurement techniques (including FTIR spectra) from previous literatures. For clarity, we have revised "HNO_3 release" into "nitrate depletion" in Line 15.

4. Line 19: "... potentially indicating the transformation of amorphous solids to semisolid $NaNO_3$; ..."; consider: or the dissolution of $NaNO_3$ into a liquid DCA + Water rich phase?

   Author reply: As shown in Fig. S6, no obvious changes of the 1356 cm^{-1} band assigned to $v_3(NO_3^-)$ of amorphous $NaNO_3$ solids were observed at constant ~ 15% RH. Meanwhile, the liquid water content remained almost unchanged as RH increased from ~ 14.8% to ~ 61.0% (seen Fig. 3b). Therefore, we can conclude the transformation of amorphous solids to semisolid $NaNO_3$, rather than the dissolution of $NaNO_3$ solids as RH increased to ~ 15%.

5. Line 39: define abbreviations like DCA, ATR-FTIR and OA at first use in the main text (aside from the abstract).

   Author reply: Thanks for the reviewer's suggestion. We have adopted reviewer's advice and revised our manuscript accordingly.

6. Line 42: there are several directly relevant studies on hygroscopicity and surface tension effects that could be cited here; e.g. Peng et al. (2001, 10.1021/es0107531), Ovadnevaite et al. (2017, doi:10.1038/nature22806), Hodas et al. (2015, doi:10.5194/acp-15-5027-2015).

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

7. Line 43: "It is well known that the displacement of strong acids, i.e., HCl or HNO_3, by weak organic acids, e.g., DCAs, is not thermodynamically favoured in bulk solution". This statement requires citation of a relevant reference. Note that even if the thermodynamic equilibrium is favouring the left hand side of reaction (R1), there will be some amounts of HCl or HNO_3 dissolved and if gas phase exchange is possible, there will be a continuous loss of the right hand side, consuming the reactants of R1 over possibly long time (depending on bulk vs. small aerosols). Therefore, given that in an aqueous phase, $NaNO_3$ will be present mostly in the form of Na^+ and $NO_3^−$, some NaA(aq) (or solid) and/or Na^+ and $A^−$ may be present even in the absence of any evaporation of HNO_3.

Author reply: Thanks for the reviewer's suggestion. The HNO_3 and HCl are the stronger acids compared to DCAs, and the displacement of weak DCAs by strong HNO_3 or HCl is thermodynamically favoured in bulk solutions. Contrary to this, the displacement of strong acids by weak organic acids is not thermodynamically favoured in bulk solutions. While in aerosol phases, the equilibrium of reaction R1 would shift to the right due to the efficient evaporation of HCl from the particle phase to the gas phase, in view of the much higher surface-to-volume ratios of aerosols compared to bulk solutions. Indeed, in an aqueous phase, $NaNO_3$ would be present mostly in the form of Na^+ and $NO_3^−$, and HA can be dissociated into H^+ and A^-. Whereas, not considering the displacement reaction equilibrium, the amounts of dissociated H^+ and A^- are limited according to the acid dissociation constants of organic acids. Based on this, the formed NaA (aqueous or solid) and dissolved HCl or HNO_3 are very limited and cannot be detected by our IR spectra (seen Fig. 5d and 6d). Furthermore, HCl and HNO_3 have the very high volatility, i.e., low Henry's law constants (HCl: $< 2\times10^{-1}$; HNO_3: $> 2\times10^{5}$), and thus they tend to partition from the particle phase to the gas phase, causing the shift of the reaction R1 to the right and much more NaA formation.

8. Line 52: State for what concentration/conditions. Are you comparing at the same RH or the same water content or the same molar concentration of dissolved solutes?

   Author reply: Thanks for the reviewer's suggestion. We have stated that in mixed NaCl/citric acid droplets with molar ratio of 1:1, dissociated HCl concentration is ~ 10^{10} times higher than dissociated citric acid according to the different acid dissociation constants (K_{a1}) (HCl: > 1×10^{7}, citric acid: 8.4×10^{-4}) (Laskin et al., 2012).

9. Line 58: define the base of the logarithm and perhaps at first use, define the meaning of pKa1 formally using molal activities or standard chemical potentials, as appropriate given the values stated.

   Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

10. Line 66: what "substrate" is here referred to? do you mean material onto which particles were deposited in laboratory experiments?

    Author reply: The substrate materials referred to the substrates on which particles were deposited in the previous studies. For instance, in Ghorai's study, the submicrometer NaCl/MA(GA) particles were deposited on Si_3N_4 windows and TEM grids (Ghorai et al., 2014). In another study, the micron-sized $NaNO_3$/MA(GA) particles were deposited on carbon-filmed grids or Si_3N_4 windows (Wang and Laskin, 2014). While Ma et al. (2013) placed mixed NaCl/MA(GA) particles in aluminum sample holder or on Ge substrate.

11. Line 70: "... the substrate supporting OA droplets would crystallize to form"; do you mean the droplet / OA or really the substrate? Clarify phrasing.

    Author reply: Thanks for the reviewer's suggestion. We have revised "substrate supporting OA droplets" into "OA droplets deposited on polytetrafluoroethylene (PTFE) substrate".

12. Line 70: "OA dihydrate at 71% RH" Is it under conditions of dehumidification? Describe what kind of laboratory experiment you refer to.

    Author reply: Thanks for the reviewer's suggestion. We have revised "at ~ 71% RH" into "at ~ 71% relative humidity (RH) during dehydration".

13. Line 72: "Pure NaNO3 droplets might not be effloresced..." By "be effloresced" do you rather mean "crystallize" here? Note that effloresced is not necessarily the same as crystalline in the

context of amorphous solids as a possibility. Also, clarify under what conditions; here presumably dehydration in an isothermal (and isobaric) experiment.

Author reply: Thanks for the reviewer's suggestion. "Pure $NaNO_3$ droplets might not be effloresced but convert into amorphous state at low RH" indicated that $NaNO_3$ droplets could neither be crystallized, nor be effloresced to amorphous solids, but instead formed viscous supersaturated liquids at low RH (Liu et al., 2008). For clarity, we have revised "amorphous state at low RH" into "highly concentrated droplets at low RH upon drying" in the text.

14. Line 73: "certain RH values" Which ones? Please provide values/ranges.

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

15. Line 74: Given the stated list of options, how is "highly viscous" different from glassy or semisolid? One could say "highly viscous (i.e. semisolid or glassy), liquid, or mixed-phase (e.g. solid–liquid) mixing states.

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

16. Line 75: Koop et al. (2011, doi:10.1039/C1CP22617G) would be another key reference to cite here.

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

17. Line 82: phrasing: "would" or rather "does" it?

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

18. Line 85: delete "mixture"; it is redundant with solution.

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

19. Line 92: "... a brief was introduced here"; phrasing.

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

20. Line 103: "chamber, which could be used to calibrate the ambient RH"; in the context of this

description, it is mentioned that water vapor and CO_2 were removed by the vacuum pump. So, how was the RH established in the sample chamber? Is it due to remaining water vapor under low pressure conditions? If so, does that mean that the sample droplets are (potentially) evaporating water alongside with HNO_3 and DCA? The droplets may also outgas dissolved CO_2 during the experiment given the vacuum applied, which might have some effect on the acidity.

Author reply: Before the measurements, the water vapor and CO_2 were removed by the vacuum pump and the pressure in the sample chamber could arrive to ~ 0.01 kPa. After that, water vapor from the water reservoir was fed into the sample chamber to establish the ambient RH in the sample chamber. When the outlet of water vapour was closed, the water vapour pressure in the sample chamber would keep equilibrium with that of water reservoir, and the maximum RH at the certain temperatures could be reached. In addition, the liquid water in the sample droplets did evaporate alongside with very small amounts of HNO_3 and DCAs in the vacuuming process. The HNO_3 release and DCA salts formation during vacuuming have been indicated in the text. Besides, the dissolved CO_2 in micron-sized droplets was very limited, and it was conceivable that the influence of outgassing of dissolved CO_2 on droplet acidity, and thus the nitrate depletion in mixed $NaNO_3$/DCA particles, was negligible.

21. Line 127: “and anhydrous OA” I suggest to mention that you refer to crystalline anhydrous OA here.

Author reply: Thanks for the reviewer’s suggestion. We have adopted the reviewer’s advice and revised our manuscript accordingly.

22. Line 131: “... indicative of the $NaHC_2O_4$...”; Is this referring to an actual solid $NaHC_2O_4$ component forming or rather the presence of partially dissociated OA anions ($HC_2O_4^-$) in aqueous solution alongside Na^+? In the latter case, this should not be referred to as $NaHC_2O_4$ since it is not forming a compound of that structure nor stoichiometry. Also, in that case, this does not confirm directly the release of HNO_3, it only indicated the presence of partially dissociated OA. Please discuss.

Author reply: Thanks for the reviewer’s suggestion. We have revised “$NaHC_2O_4$” into “dissociated $HC_2O_4^-$” in the revised manuscript. As indicated above, the amounts of dissociated $HC_2O_4^-$ from OA were very limited and could not be detected by our IR spectra assuming that no displacement reactions occurred. Furthermore, the release of HNO_3, which has been demonstrated in the earlier studies and discussed above, would shift the reaction R1 to the right. Therefore, more OA was dissociated into $HC_2O_4^-$ in the presence of Na^+ along with continuous HNO_3 release, as indicated in reaction R2.

23. Line 132: “Likewise, Wang et al. (2017) observed the formation of $NH_4HC_2O_4$ in mixed $(NH_4)_2SO_4$/OA droplets upon drying. These scenarios confirm the nitrate depletion and HNO_3 release from $NaNO_3$/OA mixtures in the vacuuming process.” The provided data and discussion does not uniquely support this conclusion. While HNO_3 evaporation is possible, where is the evidence for it? Oxalate salts could form also without any loss of HNO_3 to the gas phase. For example, HNO_3(aq) could form or, more likely, H^+(aq) and NO_3^- (aq) alongside solid or dissolved OA salts. Please provide evidence or a more nuanced discussion.

Author reply: As discussed in the author reply for the major comment, the HNO_3 release from mixed nitrate and organic acid particles has been widely detected in field and laboratory measurements. Also, the HNO_3 in the aqueous phase tends to partition into the gas phase due to the high volatility, i.e., low Henry’s law constants ($> 2\times10^5$), of HNO_3 and the high surface-to-volume ratios of aqueous droplets. Therefore, the formation of OA salts would be accompanied by HNO_3 release, in other words, the oxalate salts formation did confirm the nitrate depletion and HNO_3 release from $NaNO_3$/OA mixtures.

24. Line 145: “Likewise, Ma et al. (2013) found that the DRH of NaCl component decreased in both external and internal NaCl/MA mixtures.” How could this be the case in an external mixture (assuming external means (pure) NaCl particles separate from MA particles)?

Also, worth mentioning in the context of DRH lowering: a lowering of the DRH in particles containing aqueous DCAs is expected from thermodynamic equilibrium theory and has been shown in many other measurements and by means of thermodynamic model predictions, such as those shown for MA or OA and ammonium sulfate by Bouzidi et al. (2020, doi:10.1016/j.atmosenv.2020.117481) and those shown by Hodas et al. (2015, doi:10.5194/acp-15-5027-2015) for mixtures of ammonium sulfate with DCAs and citric acid

Author reply: Thanks for the reviewer’s suggestion. In Ma’s study, they found that externally and internally mixed NaCl/MA particles exhibited DRH in the range of 65-70% RH and 60-65% RH, respectively, which were lower than the DRH of pure NaCl particles (75% RH). Indeed, it might be implausible that the dissolution of external NaCl particles were influenced by separated MA particles. One possible reason for this might be that the contact of solution films of separated NaCl and MA particles, caused by water absorption of solid particles at RH below the DRH (Bruzewicz et al., 2011;Wise et al., 2008), led to the decrease in surface tensions of solutions and enhancement of water absorption, which further reduced the DRH of pure components. Whereas for clarity, we have deleted this sentence and added the citations of relevant studies by Bouzidi et al. and Hodas et al.

25. Line 146: “Note that the OA dihydrate and crystalline $Na_2C_2O_4$ cannot be deliquesced due to their very high DRHs ...”. A note: the process of deliquescence, as more clearly observed in binary (water + 1 solute) systems, should not be confused with partial (gradual) dissolution in multicomponent, multiphase systems. Therefore, please clarify the sentence. At present it is misleading. While crystalline substances like OA and $Na_2C_2O_4$ may not fully dissolve, it should be noted that in the presence of an aqueous phase a solid–liquid equilibrium will be established (given enough time) and some amount of OA and $Na_2C_2O_4$ will be in the dissolved state, forming a saturated aqueous solution with respect to the pertaining crystalline phase or phases; see, e.g. the discussion by Hodas et al. (2016, doi:10.5194/acp-16-12767-2016).

Author reply: Thanks for the reviewer’s suggestion. We have adopted the reviewer’s advice and revised our manuscript accordingly.

26. Line 155: “Upon hydration, the water content at high RH is far below that upon dehydration, ...” This statement needs further clarification. It seems only to make sense when the dehydration refers to dehydration from an initial state of completely dissolved particles at very high RH. Of course, one could start dehydration at any RH and then the water content could be higher or lower than when arrived at that state from an initial state of low RH.

Author reply: Thanks for the reviewer’s suggestion. We have adopted the reviewer’s advice and revised our manuscript accordingly.

27. Line 159: I find Fig. S6 insightful and suggest that this figure and the related discussion be

moved to the main manuscript.

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

28. Line 160: "Besides, as shown in Fig. 1c, the absorbance of 1620 cm^{-1} band assigned to oxalate shows a slight increase at RH as low as 21.2%, implying the nitrate depletion proceeds at relatively low RH."

    In my opinion, what is missing are observations of the loss of nitrate/HNO_3 from the particles. Do the authors have comparison examples for cases where the gas phase exchange is limited (small gas volume) such that only a small loss could occur and, as a result, the signature in oxalate formation substantially different? Without such observations, or other quantitative measures of loss to the gas phase, the interpretation of the experiments hinges on assuming a nitrate depletion takes place without having the data to confirm it. Please discuss.

    Author reply: As already indicated, Li et al. (2017) observed the Raman features of monosodium malonate in NaCl/MA mixed aerosols during the RH cycle, indicating the chloride depletion and gaseous HCl release. Wang et al. (2019) confirmed the ammonium depletion and gaseous NH_3 release from mixed dicarboxylic acid salts and $(NH_4)_2SO_4$ aerosols during the RH cycle according to the IR feature changes of dicarboxylic acid salts and corresponding DCAs via the ATR-FTIR technique. Ma et al. (2013) also determined the oxalate formation and gaseous HCl release from NaCl/OA mixtures based on the Raman and ATR-FTIR characterization results. Therefore, the increase in absorbance of IR feature bands of oxalate is proved to be powerful evidence for nitrate depletion and gaseous HNO_3 release.

29. Line 173: "As RH increases to ~ 15%, the ΔA of ν_{as}(COO-) band exhibits a considerable increase, indicative of the occurrence of nitrate depletion."

    While indicative as an option, it remains speculative. It is indicative of the partial dissociation of OA in solution. Which is expected to increase with increasing particle water content and, hence, increasing RH.

    Author reply: As already indicated, there were no IR feature bands of COO^-, e.g., 1465 cm^{-1} band, in IR spectra of pure OA droplets, as shown in Fig. S3. Thus, the increase in ΔA of $\nu_{as}(COO^-)$ band did indicate the occurrence of nitrate depletion.

30. Line 177: “2013). Then, the 1620 cm^{-1} band appears and becomes stronger with time, suggesting $Na_2C_2O_4$ can be continuously produced at constant ~ 15% RH.”

    I think this is better evidence for $Na_2C_2O_4$ formation and associated nitrate depletion, because the system is observed at constant RH, which means it should maintain constant water activity (in sufficiently large particles where the Kelvin effect would not change with evaporation). It may be good to expand the discussion of this piece of evidence.

    Author reply: Thanks for the reviewer’s suggestion. We have adopted the reviewer’s advice and revised our manuscript accordingly.

31. Line 179: “... we can infer the conversion of amorphous $NaNO_3$ solids to highly viscous semisolids due to the uptake of trace amounts of moisture.”

    Please clarify: semisolids of what? if $NaNO_3$ dissolves partially and forms a viscous aqueous solution, this should not be called a $NaNO_3$ semisolid because the formed phase contains other species too.

    Author reply: Thanks for the reviewer’s suggestion. We inferred that amorphous $NaNO_3$ solids did not dissolve partially, based on the IR feature changes of NO_3^- as discussed above, but transformed into highly viscous $NaNO_3$ semisolids. We have adopted the reviewer’s advice and revised our manuscript accordingly.

32. Line 216: Define the R^2 metric.

    Author reply: Thanks for the reviewer’s suggestion. We have adopted the reviewer’s advice and revised our manuscript accordingly.

33. Line 231: “As RH increases to around 15%, amorphous solids are converted into viscous semisolids, ...”. Is there any evidence from the spectra for such a conversion and the approximate viscosity of the phase to classify it as semisolid?

    Author reply: Thanks for the reviewer’s suggestion. There were no spectra and viscosity data for the conversion of amorphous solids to semisolids. First of all, $NaNO_3$ has been proved to exist in unusual metastable states, e.g., amorphous solids or highly concentrated droplets, after drying (Ma et al., 2021;Liu et al., 2008;Hoffman et al., 2004). Then, the chemical reactivity to liquid OA did alter as RH increased to ~ 15% herein. Coupled with the particle morphology changes shown in Fig. 2, we can speculate that amorphous $NaNO_3$ solids were converted into viscous $NaNO_3$ semisolids as RH increased to ~ 15%.

34. Line 261: "... formation of monosodium malonate ...". Is this for a solid malonate phase or dissolved?

    Author reply: Li et al. (2017) measured the Raman spectra of pure monosodium malonate (MSM) aerosols at RH = 10% and 2:1 NaCl/MA mixed aerosols at very low RH of 9.1% upon dehydration, which did not resemble that of MSM powders, suggesting that the pure MSM aerosols and mixed NaCl/MA aerosols tended to form amorphous states after drying. Furthermore, in this work, the IR feature band of MSM, i.e., 1595 cm^{-1} band, showed no obvious changes during humidification, as shown in Fig. 5c, indicating no deliquescence transition of MSM occurrence. Based on these, we can infer that the MSM component in mixed $NaNO_3$/MA aerosols was in amorphous liquids, rather than solid phases.

35. Line 266: Clarify: "that the first acid dissociation constant (pKa1) of MA was about 2.83, which was ~ 3 orders of magnitude larger than the second one ...". 3 orders of magnitude in what? clearly not in pKa. Also, 2.83 is the pKa1 not Ka1 (which the current phrasing implies).

    Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

36. Line 270: band assigned to $\nu_{as}(COO^-)$ of monosodium malonate. Please clarify: why of monosodium malonate and not of the malonate anion? The COO^- functionality does not contain any sodium and in aqueous solution the malonate ion is likely dissociated from Na^+. Is the assigned band specific to the COO^- group in crystalline monosodium malonate only?

    Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

37. Line 277: "aqueous $NaNO_3$" should be "aqueous NO_3.

    Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

38. Line 279: "As compared to vacuum FTIR results, we can infer that the heterogeneous efficacy of Ge substrate is much higher than CaF_2 windows,...". It seems unclear whether this is really a substrate effect or rather an effect of the vacuum cell procedures applied

    Author reply: In our previous review, the efflorescence kinetics and nucleation mechanisms were discussed detailed. The substrate effects have been proved to be a key factor to induce heterogeneous nucleation of aerosol particles. Furthermore, the heterogeneous nucleation efficiency of CaF_2, Ge and ZnSe substrates for deposited particles have been demonstrated in our earlier studies (Ma et al., 2019b;Ji et al., 2017;Zhang et al., 2014;Ren et al., 2016).

39. Line 290, Fig. 5: What explains the difference in the normalized water contents comparing panels (a) and (b)? Did you compare the obtained water contents to model predictions of the water content or independent mass growth factor measurements to assess which technique provides more accurate hygroscopic cycles?

Author reply: The difference in the normalized water content in panels (a) and (b) was attributed to the different sequences of water cycles. In other words, the deposited droplets in vacuum FTIR were first dried in vacuum, and then underwent a humidification-dehumidification cycle. According to the weak absorbance intensity of 1548 cm^{-1} band shown in Fig. 6c in the revised manuscript, we can infer that the nitrate depletion was limited and might not alter the hygroscopic ability of mixed aerosols. While for ATR-FTIR measurement, the mixed droplets first underwent the dehumidification process and then a humidification process. Upon hydration, the GA component mainly existed in solid state and could not be dissolved completely even until 84% RH, and thus the water content could not match with that in the dehumidification process. Note that the complete deliquescence of mixed $NaNO_3$/GA particles in vacuum FTIR measurement might be due to the partial crystallization of GA in the vacuuming process.

Firstly, the formation and precipitation of organic acid salts have not been considered by the current version of E-AIM, thus, the model cannot provide accurate hygroscopic growth factors for $NaNO_3$/DCA mixtures. Second, the mixed aerosols (e.g., $NaNO_3$/OA mixtures) might exist in solid-liquid mixing state, not the aqueous solution state at high RH in the vacuum FTIR measurement. Therefore, we could not determine the mass growth factors of mixed particles through the absorbance of liquid water band and E-AIM predictions (even though the data was not accurate), according to the calculation method proposed by our earlier studies (Ma et al., 2019b;Ji et al., 2017). Note that the mass growth factors and E-AIM predictions of pure $NaNO_3$ and DCA aerosols have been determined and shown in the

Supplement.

40. Line 301: “appears upon hydration, indicating the formation of glutarate sodium salts.” Could you clarify whether this means that a solid crystalline salt phase is forming upon hydration in equilibrium with an aqueous solution?

Author reply: Thanks for the reviewer’s suggestion. According to the hygroscopic behaviours of mixed $NaNO_3$/GA particles and IR feature changes of $\nu_{as}(COO^-)$, which was similar to that of mixed $NaNO_3$/MA particles, we can infer that the formed glutarate sodium salts were present in aqueous solution state. Furthermore, we have revised our manuscript accordingly.

41. Line 314: “lower temperature of droplets” Is it just the temperature effect or also the drying to much lower effective RH than during the ATR-FTIR measurement cycles?

Author reply: The lowest RH in the two measurements was comparable, i.e., 3.4% RH in vacuum FTIR vs. 5.6% RH in ATR-FTIR. The temperature effect caused by rapid water evaporation has been introduced in our previous study, which can facilitate the nucleation of aqueous droplets (Ma et al., 2019b).

42. Line 335: Could you discuss in this context whether the size dependence effect is due to the Kelvin effect, leading to a lower water activity and higher pH in smaller particles compared to larger ones exposed to the same RH in the gas phase, or some other effect?

Author reply: Thanks for the reviewer’s suggestion. As indicated in our previous review, the depletion extent, ξ, was related to depleted mass (Δm) and initial mass (m_0) of a volatile species within a droplet with the radius r, which could be expressed as $\xi = \Delta m/m_0$ (Chen et al., 2021). The Δm could be calculated by $\Delta m = 4\pi rMDp_r/(RT\Delta t)$ via the Maxwell steady-state diffusive mass transfer equation, where M, D, and p_r denoted the volatile species molecular weight, diffusion coefficient in the air, and equilibrium partial pressure at the droplet surface, respectively; R, T, and Δt were the ideal gas constant, temperature, and reaction time, respectively. The m_0 of the volatile species could be expressed as $m_0 = 4\pi r^3c/3$, since the concentration of the volatile species (c) within the droplet kept constant at a fixed RH. Based on these, the ξ could be expressed as

$$\xi = \frac{k}{r^2}\Delta t, \quad \text{with } k = \frac{3MDp_r}{4\pi cRT} \qquad (1)$$

As seen, the depletion extent, ξ, was inversely proportional to r^2. Therefore, the size dependence effect of depletion extent was mainly due to the volatility difference, rather than the Kelvin effect.

43. Line 346, Eq. (5): check equation; it looks like the p of p_r is missing.

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

44. Line 358: Eq. (6), for consistency with Eq. (7), consider replacing P by $p*$.

Author reply: Thanks for the reviewer's suggestion. Firstly, we indicated the expression of the diffusion coefficient of HNO_3 in the gas phase according to Chapman-Enskog method. In other words, the D denoted to the diffusion coefficient of HNO_3 in the ATR-FTIR measurement. Then, the HNO_3 diffusion coefficient in vacuum FTIR measurement, which was defined as $D*$, was related to the ambient pressure in vacuum FTIR, $P*$. Thus, the P in the eq. (6) did not only denote to $P*$ in the eq. (7).

45. Line 373: "Therefore, the ambient pressure, dominating the diffusion coefficient of HNO_3 in the gas phase, tends to play an important role in nitrate depletion during the transport and aging of atmospheric aerosols."

This statement is not supported by any quantitative data. How big of a difference is expected in the troposphere? Obviously, one should not directly compare the vaccuum FTIR pressure to realistic tropospheric conditions without accounting for the differences in the ranges of total pressures. If nitrate-containing particles are given hours to days to undergo displacement reactions, the impact of pressure on HNO_3 diffusion may be unimportant. Do you have predictions to the contrary?

Author reply: Thanks for the reviewer's constructive suggestion. We have deleted the improper statement, i.e., "Therefore, the ambient pressure, dominating the diffusion coefficient of HNO_3 in the gas phase, tends to play an important role in nitrate depletion during the transport and aging of atmospheric aerosols." in the revised manuscript.

46. Line 409: "NaNO3 can be treated as a surrogate for a broad class of amorphous or semisolid species existing in atmospheric aerosols,..."

Please state in what RH range this semisolid state applies. NaNO3 is certainly dissolved and liquid-like in dilute aqueous aerosols at elevated RH (for aqueous NaNO3 viscosity data see e.g. Baldelli et al., 2016, doi:10.1080/02786826.2016.1177163; Lilek and Zuend, 2022, doi:10.5194/acp-22-3203-2022).

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

47. Line 427: "metastable or liquid-like state..." Please rephrase; metastable and liquid-like characterize two different properties. One related to the supersaturation of aqueous solutions with respect to a certain crystalline phase, while the other refers to a phase state (viscosity related).

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

Supplement: minor comments

48. SI, lines 20–36: How was that ERH determined? Was it based on just some features of the spectra? Fig. S1a does not seem to indicate any clear signature of efflorescence. Specifically, note that in the absence of severe kinetic limitations, one would expect a sharp change in mass growth factor at the ERH (point of crystallization) of a single-solute particle. Certainly so for a system at equilibrium with the gas phase. Why is that not the case for the systems shown in Fig. S1? Figure S2 shows also no indication of NaNO3 crystallization. Do the authors use the term "efflorescence" for a phase transition other than crystallization? If so, that would be untypical given the common use and meaning of this term and might need clarification in the text.

Author reply: The ERH of $NaNO_3$ was determined via the IR feature changes of NO_3^-, i.e., the broad ~ 1350 cm^{-1} band was transformed into a sharper peak, as shown in Fig. S1b and S2b. The absence of sharp decrease in mass growth factor at the ERH was attributed to the specific structure of nitrates after drying, i.e., amorphous solids. Likewise, Li et al. (2021) observed the hygroscopic behaviours of pure $(NH_4)_2SO_4$ and NH_4NO_3 particles during the RH cycles. They found that mass growth factor of $(NH_4)_2SO_4$ particles would decrease sharply at the ERH, while mass growth factor of NH_4NO_3 particles decreased routinely without the turning point at the ERH. Meanwhile, the 1435 cm^{-1} band assigned to NH_4^+ in the solution phase red-shifted to 1415 cm^{-1}, suggesting the occurrence of efflorescence of NH_4NO_3 particles at 25% RH. Furthermore, Tang and Fung (1997) found that Raman spectra characteristic of dried $Ca(NO_3)_2$ particles was obviously different from that of anhydrous crystals, indicating the amorphous solids formation. Meanwhile, no sharp decrease in the water content of $Ca(NO_3)_2$ particles was observed during the dehumidification, and the amorphous solids would deliquesce at RH well below the DRH of anhydrous crystals, which showed good agreement with the observations for $NaNO_3$ particles in this work. In addition, the term "efflorescence" did indicate the formation of amorphous solids rather than the crystallization here. For clarity, we have revised our manuscript accordingly.

49. SI, line 40: what about that of a $NaNO_3$ hydrate crystal? Would equilibrium thermodynamics not require that amorphous solids take up some water upon hydration (while single-solute crystalline particles may not)?

Author reply: As indicated in the Supplement, the $\nu_3(NO_3^-)$ feature bands after drying in the two measurements are inconsistent with the IR feature of $NaNO_3$ crystals, i.e., two shoulder peaks centred at 1383 and 1485 cm^{-1} arising from splitting of the degenerate ν_3 mode (Liu et al., 2008). Liu et al. (2008) also found small amounts of water present within particles after dehydration and the particles absorb water continuously upon hydration, indicating the formation of highly concentrated droplets after drying, rather than amorphous $NaNO_3$ solids. The amorphous nitrate solids (e.g., $Sr(NO_3)_2$ and $Ca(NO_3)_2$) would not obviously absorb water until their DRHs (Tang and Fung, 1997).

50. SI, lines 155–158, 166: these sentences are inconsistent. One is about HCl release, the other about HNO_3 but referring to the same study. Please clarify.

Author reply: Thanks for the reviewer's suggestion. We have revised the error in the revised manuscript.

51. SI, line 178: molecular weight (or rather molar mass) of water should be stated in kg mol^{-1} to stay consistent with the other units given. Other there will be an incorrect Kelvin effect value.

Author reply: Thanks for the reviewer's suggestion. We have revised the error in the revised manuscript.

52. SI, line 188: It should be stated that the true equilibria in aqueous solution involve use of the

activities of the species, not the molar concentrations. Also, on line 210, state that self-dissociation of H_2O is not considered.

Author reply: Thanks for the reviewer's suggestion. The calculated pH here can be defined as free-H^+ approximation of pH on a molality basis, as indicated by Pye et al. (2020). Furthermore, we have considered the self-dissociation of H_2O in eq. (11) in the revised Supplement.

53. SI, line 216: given definition of pH; note that this refers only to an approximate, molarity-based pH, as discussed by Pye et al. (2020, doi:10.5194/acp-20-4809-2020). The proper definition of pH involves the molality-based activity of H^+.

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised our manuscript accordingly.

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