

Interactive comment on “Heterogeneous uptake of ammonia and dimethylamine into sulfuric and oxalic acid particles” by Sauerwein and Chan

Meike Sauerwein¹ and Chak Keung Chan^{1,2,3}

- 5 ¹Division of Environment, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
²Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology, Clear Water
Bay, Kowloon, Hong Kong
³School of Energy and Environment, City University of Hong Kong, Kowloon, Hong Kong

Correspondence to: Chak Keung Chan (Chak.K.Chan@cityu.edu.hk)

10

The authors would like to thank Anonymous Referee #1 for the comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have done to the manuscript.

Anonymous Referee #1: The manuscript describes time-dependent measurements of the competitive partitioning of ammonia and dimethyl amine to droplets/particles containing sulfuric acid or oxalic acid deposited on a substrate. Although many previous measurements have studied the partitioning of one of these gas phase species, this paper provides insight into the relative abundances of the species in the gas and condensed phase at different gas phase concentrations and relative humidities when acting in competition. The manuscript is helpful in providing a qualitative exploration of the problem although I believe some of the quantitative aspects need to be interpreted with some caution due to experimental uncertainties, particles sizes, etc. The inherently qualitative interpretation of the measurements does limit the more general application of the work (and is sometimes quite hard to follow). However, the insights provided are sufficiently new that the manuscript merits publication - I do suggest the authors respond to the following suggestions before the paper can be accepted.

Page 5, line 40: The authors suggest that re-volatilization occurs at long times with the neutralization ratio decreasing from 1.7 to 1.5. Looking at the data in Figure 1, this seems to me to be over-interpreting the data. Firstly the “noise” in the calculated ratio seems to be larger than the error bars included with the points (e.g. see the fluctuations in the points around 17 hours for the DMA 0.15 ppm measurement at 50 % RH) – I suggest the authors consider again the uncertainties in their measurements. Secondly, how do the authors know that any such small change is not just due to a drift in environmental conditions (e.g. RH or temperature)? Infact, there is very little discussion of experimental errors in the analyses and the magnitude of uncertainties is quite key in verifying the veracity of trends identified in the data. I recommend a fuller discussion of experimental reproducibility and uncertainties.

Response: We thank the anonymous referee #1 for the valuable comment. Uncertainties as indicated by error bars in the figures originate from the analysis of particle composition with ion chromatography analysis, while additional uncertainties that could explain fluctuations in particle phase concentration can only be described qualitatively. Those include:

1. Particle number - Variation in total particle count deposited on the hydrophobic film of 2000 ± 100 droplets can cause a noticeable acceleration (if less particles were deposited) or delay (if more particles were deposited) in neutralization of the total sample including all particles.
2. Uncertainties resulting from variation in DMA/NH₃ gas ratios or gas concentration - Gas concentrations were estimated from regular gravimetric measurements of the permeation tubes to determine permeation rates. The small diffusion rates would lead to small changes between successive weight measurements and resulted in a few percent uncertainty. In addition, small variations in temperature (293.3 ± 0.2 K) can cause small fluctuations in permeation rates (see additions made to the supplemental information). Though the uncertainty in gas concentrations was estimated and listed in Table 1, the effect of those uncertainties on the final particle phase concentration could not be quantified. Gas testing procedures and uncertainty estimations were added to the supplementary information.

3. Variations in temperature (296.3 ± 1.0 K) and RH ($10\% \pm 2\%$ and $50\% \pm 3\%$) within the flow cells may have had small influences on uptake kinetics, and yet those uncertainties could not be further quantified.

In order to address the comments of Referee #1, in addition to the added information the supplement of the manuscript, we have added a qualitative description of the uncertainties into section 2.3, which reads as follows:

5 “Uncertainties as shown in the figures were calculated based on errors resulting from IC measurements. Additional uncertainties of particle phase DMAH and NH_4 resulting from independent parameters such as the variations in total particle count, and uncertainties in generation and determination of gas concentrations also led to some fluctuations beyond the quantified errors.”

The authors further agree with the referee’s argumentation, that the decrease in neutralization ratio towards equilibrium lies within the margin of error if unquantifiable uncertainties are also considered. The paragraphs starting from line 38 - 41 on page 5, the sentence on line 11-13 on page 11, and the sentence in line 25-26 on page 12 were deleted. The subsequent sentence on page 11 line 14 was changed to

“Under amine-free atmosphere, the neutralization ratio of these equilibrated particles decreased to $X_{\text{N}_2} = 1.2 \pm 0.2$ at 10% RH and $X_{\text{N}_2} = 1.7 \pm 0.2$ at 50% RH, as a result of DMA evaporation (Table 1).

15 On page 10, under consideration of uncertainties, we changed lines 23-25 to

“DMAH/ NH_4 ratios (Figure 8b) stayed roughly constant.”

On page 11 line 39-41 was changed to

20 “Under exposure to N_2 , DMAH- NH_4 mixed particles that were originally in liquid phase state and contained large amounts of DMAH (Fig. 9 h, k) exhibited a decrease in X , reflecting that the equilibrium compositions of these droplets were sensitive to changes in DMA and NH_3 gas concentrations.”

And the sentence on page 12 line 27 was moved to line 14 and altered as follows:

“When NH_4 is present in neutralized, DMAH-rich sulfate droplets, DMA from the surrounding gas phase can displace NH_4 from droplets, and prompt additional NH_3 to evaporate to form non-neutralized particles.”

25 Despite the adjustments to more accurately describe the uncertainties of the measurements, we believe that the main conclusions of this work on the roles of particle phase and extent of neutralization in the co-uptake are not affected.

Anonymous Referee #1: Pages 6-7: I find the discussion of the change in neutralization and DMAH/ NH_4 ratios along with the surface acidity quite confusing. Given the large size of the droplets and the long timescales for the measurements, I can’t see that different surface kinetic parameters (uptake coefficients) for the amine and ammonia can govern the change in these ratios. Indeed, I don’t think this is what the authors are saying – if they are, then they need to consider competing rates of gas diffusion limited uptake, diffusional mixing within these liquid droplets, sensitivity of such large droplets to surface kinetics etc. Whichever is correct, the discussions is very confusing. This need for clarity is even more true when the authors then state that Figure 4 confirms that the uptake of DMA and NH_3 proceed independently.

Response: We thank the anonymous referee #1 for pointing out those ambiguities. As mentioned at the end of section 3.2.1, the comparison of mixed gas with single gas uptake as shown in Figure 4 indicates that the initial NH_3 and DMA partitioning into acidic particles happens independently from each other. Thus, using uptake coefficients from earlier studies on single gas uptake to elucidate the mixed gas uptake process seems reasonable. Based on uptake coefficients reported in the literature which are larger for NH_3 than for DMA, one would expect the observed trend of the DMAH/ NH_4 ratio to decrease as uptake proceeds since NH_3 uptake is faster than DMA. Yet it is unclear why the initial DMAH/ NH_4 ratios (particle phase) are similar to DMA/ NH_3 ratios (gas phase). Our discussion of surface acidity pertains to the very initial periods of uptakes.

The uptake coefficient describes the overall uptake process. This includes inter-related processes such as gas phase diffusion, immediate reaction of gas molecules colliding with the aerosol surface or adsorption and dissolution, followed by further liquid phase diffusion and proton transfer in the bulk particle.

Judging based on calculated mean thermal velocities $\omega_{\text{NH}_3} = 607 \text{ m s}^{-1}$ and $\omega_{\text{DMA}} = 373 \text{ m s}^{-1}$ (296K) (based on diffusion coefficients of Massman, 1998 and Yaws 1995), NH_3 diffuses faster than DMA in gas phase. Yet, DMA possesses a higher gas phase and particle phase basicity than NH_3 (Brauman et al., 1971; Parrillo et al., 1993, Ge et al., 2011a) and a higher effective Henry's law constant than NH_3 for uptake into acidic solutions (Ge et al. 2011b) such as the sulfuric acid particles. Surface acidity was consequently considered to be one possible explanation why the stronger basicity of DMA may contribute to the equality of the DMAH/ NH_4 in fresh particles and DMA/ NH_3 ratios. This effect, however, diminishes as the particle gets gradually neutralized.

To add clarity to the discussion in section 3.2.1, we have added more description and rearranged paragraphs from lines 7-8 on page 7 as well as lines 34-40 from page 6 as follows:

10 “Starting from the second measured values, a clear decrease in DMAH/ NH_4 ratios can be observed. Figure 4 compares the uptake of DMA and NH_3 in single and mixed gas experiments. The initial uptake trends of single gas and co-uptake do not deviate noticeably, indicating that DMA and NH_3 uptake took place independent of each other. Consequently, earlier reported uptake coefficients from single gas uptake NH_3 and DMA into sulfuric acid may be used for co-uptake analysis.”

15 And

 “Wang et al. (2010) reported an uptake coefficient (γ_{DMA}) of about 0.03 for DMA uptake into concentrated H_2SO_4 of $\geq 62 \text{ wt}\%$ ($\leq 10\% \text{ RH}$) at 283 K. The coefficient is noticeably smaller than that of close to unity reported for NH_3 uptake into H_2SO_4 of similar acidity (Swartz et al., 1999). In the current study, NH_3 uptake into fresh H_2SO_4 droplets was not overwhelmingly dominant. However, as the uptake continued, the DMAH/ NH_4 ratios decreased by 30-40% for all experimental conditions within the first 1-2 hours (Fig. 3 a-d), which indicates a preferential uptake of NH_3 . Since the gas concentrations of both NH_3 and DMA were constant, it is likely that the decreasing particle acidity and increasing neutralization ratio caused this change.”

Anonymous Referee #1: Page 12, lines 30-36: The authors consider the relevance of the high gas phase concentrations studied here when compared to atmospheric concentrations. It seems equally important to consider the importance of the particle size range studied. How do the authors expect their results to impact on our understanding of the much smaller particles that must be considered in the atmosphere? There is a brief comment on this at the very end of the summary section.

When considering the application of the current results to submicron particles, two aspects might be of importance:

1. The overall gas uptake would likely be accelerated. For submicron particles gas phase diffusion limitations would also have to be taken into consideration. Yet, we believe that the major findings in our paper i.e. the initially independent uptake of both gases into acidic particles as well as the roles of phase state and neutralization in DMAH or NH_4 competition and displacement is not expected to change.
2. Impact of particle size on crystallization behavior or inhibition of crystallization. DMAH, even if its concentration was low compared to NH_4^+ (DMAH/ $\text{NH}_4 = 0.05$), was able to suppress NH_4HSO_4 precipitation. As it is generally easier to induce crystallization in larger particles, we assume that this effect should extend to particles of smaller sizes.

To stronger illustrate these aspects, the following sentence in the Summary and Conclusions section was modified to:

 “‘It should also be mentioned that particle size may affect the gas uptake kinetics, as well as the crystallization behavior of the particle. When applying the results of this study to submicron particles, one may expect a considerably faster uptake and thus changes in DMAH/ NH_4 ratios in acidic particles. Yet the overall trends of displacement reactions based on phase state and neutralization ratio as well as crystallization inhibition by DMAH are considered applicable to particles of smaller size. Nevertheless,[...]”

Minor changes/corrections:

Anonymous Referee #1: Page 3, line 20: The method for checking the gas phase ratios is not clearly described. The sentence describing this procedure needs to be expanded on: "To ensure accuracy of the gas ratio, measures were taken including conditioning the setup for a prolonged period, separating RH conditioning cells and reaction cells."

Response: NH₃ and DMA are both very "sticky" gases (Robacker and Bartelt 1996, Hansen et al. 2013, Dawson et al. 2014), and are prone to adsorb to instrumental surfaces. Yet, the stickiness varies among different amines and ammonia (Namieśnik et al. 2003, Dawson et al. 2014). Measurements of the reestablishment of gas concentrations after the system underwent a cleaning process showed that the time to reach stable gas concentrations at the inlet of the flow cell took up to 4 hours for NH₃ and up to 8 hours for DMA. A much shorter recovery time was observed if only the gas supply was temporarily interrupted (e.g. for weighing permeation tubes, and/or changing the N₂ cylinder). In that case the time for re-establishment of stable concentrations took <1 hour for both gases. Since a drop in the concentration of one or both gases (e.g. due to wall losses) would result in a change of DMA/NH₃ ratio, we allowed 2 h equilibration time when the gas supply was interrupted and about 12 hours for reconditioning after the setup was cleaned. Since flow cells were likewise conditioned with DMA and NH₃ gas, we equilibrated the sulfuric acid or oxalic acid particles to the respective RH of 10% or 50% in separate clean cells.

In order to address the reviewers comment we have clarified the sentence as follows:

15 "To ensure accuracy of the gas ratio, the system was conditioned for several hours to minimize wall losses either one or both gases prior to the uptake experiment (see supplemental information for detailed descriptions)."

We added more detail on the gas generation system, including the conditioning procedure, into the supplement of the paper.

Anonymous Referee #1: Page 6, line 6: Presumably the authors are referring to Sections 3.3 and 3.4 here?

20 We thank the referee for this remark, the section numbering has been updated throughout the manuscript.

Anonymous Referee #1: Page 9, line 21: The error bar on this line is 0.00 – this is presumably not correct.

We thank the referee for the comment. We increased the number of significant digits for this case in order to account for the uncertainties retrieved from IC. The sentence now reads as follows:

25 "DMAH/NH₄ ratios at the time of neutralization (t_{neutral}) reached 0.032 ± 0.001 for the 0.1_{10%} condition and 0.19 ± 0.01 for the 0.5_{10%} condition (Table 2), showing a slight enrichment of NH₄⁺ in the particle over the gas phase."

References

- 30 Brauman, J. I., Riveros, J. M., and Blair, L. K.: Gas-phase basicities of amines, *J. Am. Chem. Soc.*, 93, 3914–3916, 1971.
Dawson, M.L., Varner, M.E., Perraud, V., Ezell, M.J., Wilson J, Zelenyuk A, Gerber R.B., Finlayson-Pitts B.J.: Amine–Amine Exchange in Aminium–Methanesulfonate, *Aerosols. J. Phys. Chem. C*, 118 (50), 29431–29440, 2014.
Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part I. A review, *Atmos. Environ.*, 45, 524–546, 2011a.
Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part II. Thermodynamic properties and gas/particle partitioning, *Atmos. Environ.*, 45, 561–577, 2011b.
35 Hansen, M.J., Adamsen, A.P.S., Feilberg, A.: Recovery of odorants from an olfactometer measured by proton-transfer-reaction mass spectrometry. *Sensors*, 13(6), 7860–7871, 2013.
Massman, W.J.: A review of the molecular diffusivities of H₂O, CO₂, CH₄, CO, O₃, SO₂, NH₃, N₂O, NO, and NO₂ in air, O₂ and N₂ near STP, *Atmos. Environ.*, 32, 1111–1127, 1998 .
40 Namieśnik J., Jastrzębska, A., Zygmunt, B.: Determination of volatile aliphatic amines in air by solid-phase microextraction coupled with gas chromatography with flame ionization detection. *J. Phys. Chem. A*, 1016(1), 1–9, 2003.
Parrillo, D. J., Gorte, R. J., and Farneth, W. E.: A calorimetric study of simple bases in H-ZSM-5: A comparison with gas-phase and solution-phase acidities, *J. Am. Chem. Soc.*, 115, 12441–12445, 1993.

Robacker D.C., Bartelt R.J.: Solid-Phase Microextraction Analysis of Static-Air Emissions of Ammonia, Methylamine, and Putrescine from a Lure for the Mexican Fruit Fly (*Anastrephaludens*), *J. Agric. Food Chem.*, 44(11), 3554–3559, 1996.

Yaws C.L.: *Handbook of Vapor Pressure: Inorganic Compounds and Elements*, Volume 4, Gulf Professional Publishing, 1995.

5 **Interactive comment on “Heterogeneous uptake of ammonia and dimethylamine into sulfuric and oxalic acid particles”** **by Sauerwein and Chan**

Meike Sauerwein¹ and Chak Keung Chan^{1,2,3}

¹Division of Environment, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

10 ²Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

³School of Energy and Environment, City University of Hong Kong, Kowloon, Hong Kong

Correspondence to: Chak Keung Chan (Chak.K.Chan@cityu.edu.hk)

The authors would like to thank Anonymous Referee #2 for the comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have done to the manuscript.

15

Anonymous Referee #2: p2, line 10: The phrase “highest in marine particles as well as urban and rural aerosols” is confusing. It is not clear whether the authors are highlighting the importance of alkylammonium ions in marine aerosols, or the 140-560 nm size range.

Response: We thank the anonymous referee #2 for the comment. To improve clarity the sentence was changed to

20

“In fact, mass loadings of alkylammonium ions (R_3NH^+) are the highest in particles with a diameter of 140-560 nm, both in urban and rural, as well as in marine aerosols (Müller et al., 2009; VandenBoer et al., 2011; Youn et al., 2015).”

Anonymous Referee #2: p2, line 28: Do the particles actually absorb more water than ammonium sulfate particles across different compositions and sizes? Or are there some limits (e.g., only below the deliquescence point of ammonium sulfate)?

25

Response: Recent studies on the hygroscopicity of methyl- and ethyl-ammonium sulfate salts and their mixtures with sulfuric acid (Chu et al. 2015, Sauerwein et al. 2015, Rovelli et al. 2016) have shown that short-chain alkyl-ammonium sulfates are significantly more hygroscopic than ammonium sulfate up to 95% RH, hence beyond the deliquescence point of ammonium sulfate. In all three studies, hygroscopicity of alkyl-ammonium sulfates was shown to increase from primary to tertiary ammonium sulfate. The difference in hygroscopicity decreases as extent of neutralization decreases to bisulfate composition, where

30 ammonium and ammonium bisulfate possess similar hygroscopic properties (Sauerwein et al. 2015).

Anonymous Referee #2: p3, line 30: Are the first experimental parameters for the sulfuric acid particles? If so, may want to specify that.

Response: We agree with anonymous referee #2. To no leave any ambiguity, we added the following for clarification

35

“Combination of the DMA flow (0.15 or 0.9-1.0 ppm) and the NH_3 flow (1.8-1.9 ppm) resulted in DMA/ NH_3 ratios of 0.07 ± 0.01 and 0.46 ± 0.04 at 10% RH, as well as 0.07 ± 0.01 and 0.49 ± 0.02 at 50% RH for experiments with H_2SO_4 (Table 2), and 0.49 ± 0.02 at 10% and 0.52 ± 0.01 at 70% RH for experiments with $H_2C_2O_4$.”

Further changes were made as suggested by anonymous referee #2 as follows:

40

Anonymous Referee #2: p6, line 4: Add ‘-’ to SO_4 (as appears later in Section 3.2).

Response: Changes were made as follows:

“Figure 2 depicts the temporal profiles of DMAH/SO₄, NH₄/SO₄ and X at the different gas ratios and RH. At 10% RH particles solidified during the experiment (Fig. 2a and b, indicated by crosshatched areas) and needed 2 to > 18 hours (for 0.5_{10%} and 0.1_{10%}, respectively) to completely neutralize sulfate.”

5 **Anonymous Referee #2:** p6, section 3.2: Check section numbers here and throughout.

Response: We thank the referee for this comment, the section numbering has been updated throughout the manuscript.

Anonymous Referee #2: Section 3.2: NH₃ displaced DMAH...should this be NH₄? And then in paragraph below NH₄ displaced by DMA...should be DMAH? Recommended to check throughout.

10 **Response:** We agree with anonymous referee #2 that the displacement of one alkaline species by another alkaline gas is inseparable connected with the gas absorption and protonation, and hence technically the argumentation, that DMAH⁺ is displaced by NH₄⁺ is correct. Yet, the authors like to follow the terminology that is commonly used in literature focused on similar kind of displacement reactions such as Qiu et al. 2011.

15 **Anonymous Referee #2:** Also recommended to check notation such as NH₄ vs. NH₄⁺, which appears to be used inconsistently.

Response: Following the definition in section 2.3, we use DMAH to represent particle phase $n\text{NH}_2(\text{CH}_3)_2^+ + n\text{NH}(\text{CH}_3)_2$, NH₄ to represent $n\text{NH}_4^+ + n\text{NH}_3$, SO₄ to indicate total amount of sulfate species = $n\text{H}_2\text{SO}_4 + n\text{HSO}_4^- + n\text{SO}_4^{2-}$, and C₂O₄ to indicated total amount of oxalate species (*n* denotes the molar amounts of each compound). The manuscript was reviewed
20 and expressions such as NH₄⁺ and NH₄-species were consistently named as NH₄, the same was done for DMAH.

Anonymous Referee #2: p8, line 40: “During the”

Response: Following the suggestion the sentence was rewritten as:

25 “During NH₃-DMA co-uptake the absorbed DMAH seems to have suppressed the precipitation of NH₄HSO₄ in particles with a composition of $1.1 < \text{NH}_4/\text{SO}_4 < 1.5$, so that the phase change started only at a NH₄/SO₄ around 1.5 (Fig. 5a and b).”

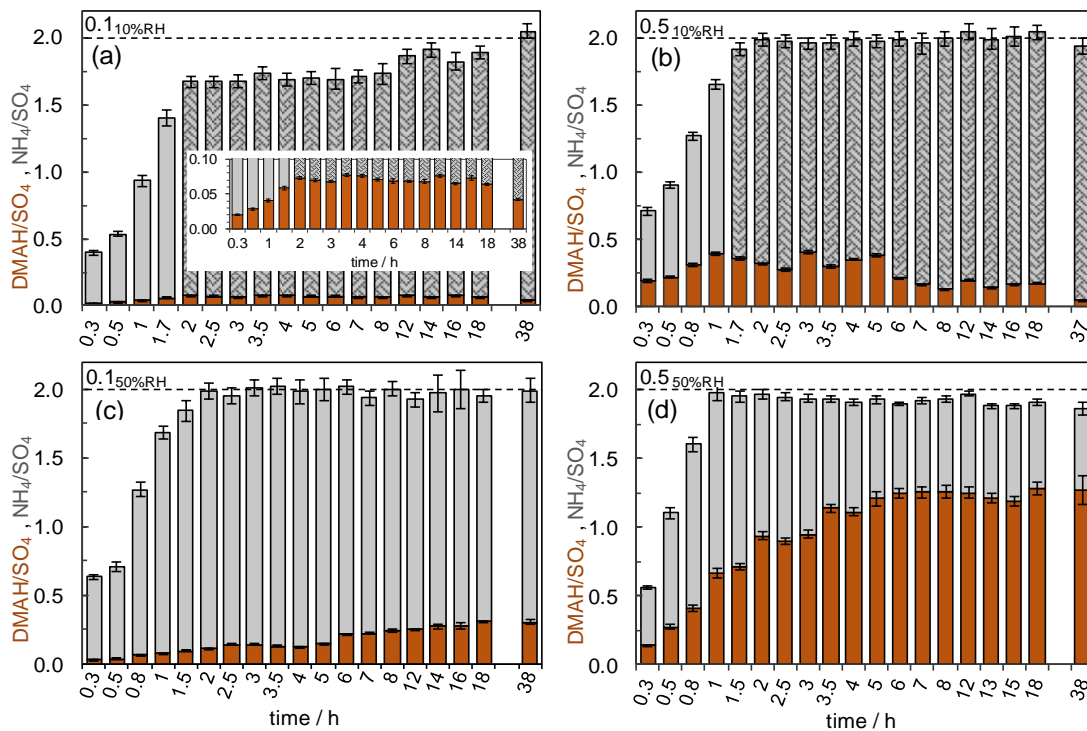
Anonymous Referee #2: Table 1: The subscript on the N looks like a superscript.

Response: the term X_{N2} in Table 1 and the table caption have been updated to X_{N₂}.

30

Anonymous Referee #2: Fig. 2: x-axis font in panel b appears larger than in other panels. Some other inconsistencies between panels-recommended to check closely

Response: The figure has been updated as shown below



5 References

- Chu, Y., Sauerwein, M., and Chan, C. K.: Hygroscopic and phase transition properties of alkyl aminium sulfates at low relative humidities, *Phys. Chem. Chem. Phys.*, 17, 19789–19796, 2015.
- Qiu, C., Wang, L., Lal, V., Khalizov, A. F., and Zhang, R.: Heterogeneous reactions of alkylamines with ammonium sulfate and ammonium bisulfate, *Environ. Sci. Technol.*, 45, 4748–4755, 2011.
- 10 Rovelli, G., Miles, R. E. H., Reid, J. P., and Clegg, S. L.: Hygroscopic Properties of Aminium Sulphate Aerosols, *Atmos. Chem. Phys. Discuss.*, in review, 2016.
- Sauerwein, M., Clegg, S. L., and Chan, C. K.: Water Activities and Osmotic Coefficients of Aqueous Solutions of Five Alkylaminium Sulfates and Their Mixtures with H₂SO₄ at 25°C, *Aerosol Sci. Tech.*, 49, 566–579, 2015.

Heterogeneous uptake of ammonia and dimethylamine into sulfuric and oxalic acid particles

Meike Sauerwein¹ and Chak Keung Chan^{1,2,3}

¹Division of Environment, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

5 ²Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

³School of Energy and Environment, City University of Hong Kong, Kowloon, Hong Kong

Correspondence to: Chak Keung Chan (Chak.K.Chan@cityu.edu.hk)

Abstract. Heterogeneous uptake is one of the major mechanisms governing the amounts of short-chain alkyl-amines and ammonia (NH₃) ~~gases resident~~ in atmospheric particles. Molar ratios of aminium to ammonium ions detected in ambient aerosols often exceed typical gas phase ratios. The present study investigated the simultaneous uptake of dimethylamine (DMA) and NH₃ into sulfuric and oxalic acid particles at gaseous DMA/NH₃ molar ratios of 0.1 and 0.5 at 10%, 50%, and 70% relative humidity (RH). Single gas uptake and co-uptake were conducted under identical conditions and compared. Results showed that the particulate dimethyl-aminium/ammonium molar ratios (DMAH/NH₄) changed substantially during the uptake process, which was ~~predominantly-severely~~ influenced by the extent of neutralization and the particle phase state. In general, DMA uptake and NH₃ uptake into concentrated H₂SO₄ droplets were initially similarly efficient, yielding DMAH/NH₄ that were similar to DMA/NH₃ ratios. As the co-uptake continued the DMAH/NH₄ gradually dropped due to a preferential uptake of NH₃ into ~~partially neutralized still~~ acidic droplets. At 50% RH, Once-once the sulfate droplets at 50% RH were neutralized, the stronger base DMA displaced some of the ammonium absorbed earlier, leading to DMAH/NH₄ ~~that~~ were ratios up to four times higher than the corresponding gas phase ratios. However, a At 10% RH, crystallization of partially neutralized sulfate particles prevented further DMA uptake, while NH₃ uptake continued, and displaced DMAH⁺ ~~after the solid particles were completely neutralized~~, forming almost pure ammonium sulfate. Displacement of DMAH⁺ by NH₃ has also been observed in neutralized, solid oxalate particles. The results ~~illustrate why can explain why~~ DMAH/NH₄ ratios in ambient liquid aerosols ~~the DMAH/NH₄ can be larger than DMA/NH₃, despite of an excess of NH₃ in the gas phase.~~ The uptake of DMA to aerosols consisting of crystalline ammonium salts, however, is unlikely, even ~~if the gas concentrations of~~ comparable DMA and NH₃ are of the same magnitude gas phase concentrations.

1. Introduction

NH₃ and short-chain alkyl-amines (R₃N) gases are frequently detected in the atmosphere. Total emissions of NH₃ largely dominate those of R₃N (Schade and Crutzen, 1995). The characteristic ambient mixing ratios of NH₃ and R₃N are in the order of several parts per billion by volume and parts per trillion, respectively (Ge et al., 2011; You et al., 2014; Zheng et al., 2015). Many of the emission sources of R₃N such as agricultural and industrial activities also release NH₃ (Behera et al., 2013). Hence, elevated R₃N gas concentrations are likely accompanied by enhanced concentrations of NH₃ (Schade and Crutzen, 1995; Zheng et al., 2015). Despite the ~~2-3~~ two to three orders of magnitude difference in gas phase concentration, particle phase aminium-to-ammonium (R₃NH/NH₄) molar ratios of up to 0.2 have been detected. For instance, average R₃NH/NH₄ molar ratios of 0.0045–0.17 were measured in PM_{1.8} in urban and rural continental air masses over urban and rural sites in Ontario, Canada (VandenBoer et al., 2011), 0.02 in PM_{1.0} in an urban area of Arizona, USA (Youn et al., 2015) and 0.23 in particles with a vacuum aerodynamic diameter of 50–800 nm in California, USA (Sorooshian et al., 2008).

Large R₃NH/NH₄ ratios in particles below 20 nm have been correlated to enhanced particle formation (VandenBoer et al., 2011; Youn et al., 2015). Laboratory studies (Almeida et al., 2013; Jen et al., 2014), field measurements (Mäkelä et al., 2001;

Kulmala et al., 2013), as well as computational methods (Kurtén et al., 2008; Olenius et al., 2013) have indicated that clusters of sulfuric acid (H_2SO_4) and DMA are more stable than clusters formed from NH_3 - H_2SO_4 nucleation, and thus R_3N may contribute more to new particle formation than NH_3 ~~does~~. Furthermore, R_3N are able to ~~form sulfuric acid amine clusters by replacing NH_3 replace NH_4^+ from~~ ammonium-sulfuric acid clusters (Bzdek et al., 2010a; Bzdek et al., 2010b) and ammonium nitrate nanoparticles (Lloyd et al., 2009), despite the presence of NH_3 in the gas phase (Lloyd et al., 2009). If not directly participating in the ~~formation of particles nucleation of particles~~, R_3N can also efficiently partition into clusters and small particles (Kürten et al., 2016) to promote particle growth.

However, R_3N are not only detected in the nucleation mode (Mäkelä et al., 2001; Smith et al., 2008), but also in aerosols exceeding 100 nm in diameter. In fact, mass loadings of alkylammonium ions (R_3NH^+) ~~are the highest in particles with a diameter of 140-560 nm, both in urban and rural, as well as in marine aerosols are the highest in marine particles as well as urban and rural aerosols with a diameter of 140-560 nm~~ (Müller et al., 2009; VandenBoer et al., 2011; Youn et al., 2015). These ammonium ions were observed to be internally mixed with sulfate, nitrate or organic acids (Sorooshian et al., 2008; Müller et al., 2009; Pratt et al., 2009; Smith et al., 2010; VandenBoer et al., 2011; Healy et al., 2015; Youn et al., 2015), suggesting that heterogeneous reactions forming ammonium salts are an important sink for atmospheric R_3N (Youn et al., 2014; Tao et al., 2016). On the other hand, enhanced NH_4^+ concentrations in particles of the accumulation mode typically dominate R_3NH^+ concentrations, leading to low observed $\text{R}_3\text{NH}/\text{NH}_4$ molar ratios. A second peak of $\text{R}_3\text{NH}/\text{NH}_4$ in the coarse mode has been reported (VandenBoer et al., 2011; Youn et al., 2015), although the causes of these higher ratios in larger particles are not resolved to date.

Chemical characteristics of R_3N and their salts can deviate significantly from those of NH_3 and its salts. For instance, due to the electron donor effect of the alkyl groups, the nitrogen atom of R_3N molecules is more nucleophilic towards hydronium ions, making them stronger bases than NH_3 (Breitmaier and Jung, 2005). Furthermore, short-chain methyl- and ethyl- ammonium nitrates, chlorides, and sulfates possess higher osmotic coefficients than their ammonium counterparts (Bonner, 1981; Macaskill and Bates, 1986; Chu et al., 2015; Sauerwein et al., 2015; Rovelli et al., 2016), which increases the aerosol hygroscopicity and liquid water content. Besides, secondary and tertiary ammonium sulfates remain in ~~the~~ liquid state even at RH below 3% (Chan and Chan, 2013) and they effectively lower the deliquescence RH of the particles when mixed with ammonium sulfate (Qiu and Zhang, 2012). Particles with a large $\text{R}_3\text{NH}/\text{NH}_4$ ratio are consequently less acidic and could absorb more water than ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) ~~can~~, even at low RH.

Particulate R_3NH^+ concentrations in ambient aerosols are positively correlated with particle acidity, liquid water content, and RH (Sorooshian et al., 2008; Rehbein et al., 2011; VandenBoer et al., 2011; Youn et al., 2015). Numerous laboratory uptake experiments of R_3N into H_2SO_4 (Wang et al., 2010), ammonium nitrate, sulfate and bisulfate ~~aerosols~~ have confirmed such correlations (Lloyd et al., 2009; Bzdek et al., 2010b; Qiu et al., 2011; Chan and Chan, 2012, 2013). However, the conditions in those experiments would also promote heterogeneous uptake of NH_3 (Swartz et al., 1999). Although there are many studies on the uptake of either NH_3 (Huntzicker et al., 1980; McMurry et al., 1983; Daumer et al., 1992; Swartz et al., 1999; Hanson and Kosciuch, 2003; Liggio et al., 2011) or R_3N (Bzdek et al., 2010a; Bzdek et al., 2010b; Wang et al., 2010; Bzdek et al., 2011; Qiu et al., 2011; Chan and Chan, 2012) into acidic particles, ~~to date~~ none has been ~~reported~~ on the simultaneous uptake of NH_3 and R_3N ~~to date~~.

Barsanti et al. (2009) were the first to model the relative importance of R_3N (using DMA as a model compound) and NH_3 in gas-particle partitioning. They showed that even when NH_3 gas phase concentrations exceeded those of R_3N by an order of magnitude, ammonium R_3NH^+ ~~ions~~ can still dominate NH_4^+ in ~~the~~ aqueous acetic acid particles, due to their stronger basicity.

Yet, owing to the lack of chemical and physical parameters available, the study relied strongly on estimations of group contributions.

The present study is the first to investigate the simultaneous uptake of R_3N and NH_3 by acidic particles with analysis of particle phase composition. We explored the temporal changes in R_3NH/NH_4 molar ratios during the uptake of DMA and NH_3 into H_2SO_4 and oxalic acid ($H_2C_2O_4$) particles at different DMA/ NH_3 gas ratios (0.1 and 0.5) and RH (10% and 50% RH). We used supermicron particles because they enabled a longer observation ~~window period and phase state identification~~, and sufficient mass concentrations for studying the temporal changes in particle composition during the uptake until equilibrium was reached. The results also reveal the influence of the extent of neutralization and the change in phase state on the uptake behavior of both gases. DMA was chosen as the model R_3N due to its atmospheric abundance (Müller et al., 2009; Rehbein et al., 2011; Hu et al., 2015; Youn et al., 2015) and unique characteristics, such as forming a non-crystallizing DMAS droplet even at low RH (Chan and Chan, 2013) and its higher hygroscopicity than that of $(NH_4)_2SO_4$.

2. Methods

Supermicron particles deposited on a hydrophobic substrate were placed in a temperature- and humidity-controlled flow-cell coupled to a Raman microscope setup (Yeung et al., 2009). DMA and NH_3 at low ppm levels were generated by directing a humidified N_2 carrier flow through permeation tubes holders containing tubes filled with pure liquefied NH_3 and DMA at controlled temperatures. The two gases were mixed and introduced to four cells in parallel. Post reaction samples were analyzed by ion chromatography (IC). R_3N and NH_3 gas molecules and aminium ions in solution tend to adsorb on surfaces (Dawson et al., 2014; Hansen et al., 2013; Robacker and Bartelt, 1996). ~~To ensure accuracy of the gas ratio, measures were taken including conditioning the setup for a prolonged period, separating RH conditioning cells and reaction cells.~~ To ensure accuracy of the gas ratio, the system was conditioned for several hours to minimize wall losses either one or both gases prior to the uptake experiment (see supplemental information for detailed descriptions). A schematic of the experimental setup is shown in the supplemental information Fig. S1.

2.1 Generation and detection of NH_3 and DMA gases

A humidified N_2 carrier flow was directed into two electronic mass flow controllers (MKS Instruments Inc., GE50A) at $1000 \pm 10 \text{ cm}^3 \text{ min}^{-1}$ and subsequently introduced into glass permeation tube holders (Fig. S1). The tube holders consisted of a water coated coil and a chamber containing the permeation tubes of either NH_3 or DMA (VICI Metronics, Dynacal), as well as a thermocouple to regulate the temperature to $293.3 \pm 0.2 \text{ K}$. Permeation rates were determined gravimetrically to calculate the mixing ratio of each gas.

Combination of the DMA flow (0.15 or 0.9-1.0 ppm) and the NH_3 flow (1.8-1.9 ppm) resulted in DMA/ NH_3 ratios of 0.07 ± 0.01 and 0.46 ± 0.04 at 10% RH, as well as 0.07 ± 0.01 and 0.49 ± 0.02 at 50% RH ~~for experiments with H_2SO_4~~ (Table 2), and 0.49 ± 0.02 at 10% and 0.52 ± 0.01 at 70% RH for experiments with $H_2C_2O_4$. We denote these experimental conditions for uptake into H_2SO_4 by $0.1_{10\%}$, $0.5_{10\%}$, $0.1_{50\%}$, and $0.5_{50\%}$, and for uptake into $H_2C_2O_4$ by $ox0.5_{10\%}$ and $ox0.5_{70\%}$. For co-uptake gas flows from both permeation devices were mixed and split equally into four custom-made PTFE flow cells. Single gas flows were generated by bypassing one of the permeation tubes. The cells were maintained at $296.3 \pm 1.0 \text{ K}$ and RH of $10\% \pm 2\%$ and $50\% \pm 3\%$. The system including the PTFE cells was equilibrated with the NH_3 and/or DMA gas for ~~about~~ $> 12 \text{ h}$ before the start of each experiment. The stability of the generated gas concentrations arriving at the PTFE cells was confirmed by ion-molecule reaction mass spectrometry (IMR-MS, AirSense, V&F Analyse-und Messtechnik GmbH).

2.2 Particle generation

The stock solutions of 30 wt% H₂SO₄ or ~~highly concentrated saturated~~ H₂C₂O₄ were prepared from ultrapure water (18.2 MΩ) and concentrated H₂SO₄ (97 wt%, Acros Organics, titrated against standardized NaOH) or H₂C₂O₄ powder (99%, Aldrich). For each experiment, a few mL of the solution were drawn into a piezoelectric particle generator (MicroFab Tech., Inc.).

5 Approximately 2000±100 droplets of 60 μm in diameter were deposited on a hydrophobic film (FEP membranes, YSI Inc.) The sample was then inserted into a clean flow cell connected to humidified high purity N₂ (~1000 cm³min⁻¹) to equilibrate to either 10 or 50% RH for 45 min. The sample films were subsequently transferred into the PTFE reaction cells. RH conditioning and transfer of films took place inside a glove bag (GLOVEBAG, Glas Col®) to avoid exposure of the samples to room air and humidity.

10

2.3 Particle analysis

For each condition, the experiment was repeated in different time intervals to complete one time series. The samples were removed from the cell and submerged in ~12 mL of ultrapure water for extraction and subsequent chemical analysis. Both cation and anion contents were measured by IC (Metrohm, 881 compact IC Pro) as described by Sauerwein et al. (2015).

15

IC yields total values for DMA and NH₃ species, and hence the distribution between molecules and ions in the samples could not be determined. In the following we use DMAH to represent $n\text{NH}_2(\text{CH}_3)_2^+ + n\text{NH}(\text{CH}_3)_2(\text{aq})$ and NH₄ to represent $n\text{NH}_4^+ + n\text{NH}_3(\text{aq})$ in the particles, where n denotes the molar amounts of each compound. The same is true for the distribution between acidic species. Hereafter the molar amount of the total sulfate is indicated by $\text{SO}_4 = n\text{H}_2\text{SO}_4 + n\text{HSO}_4^- + n\text{SO}_4^{2-}$,

20 and the total oxalate ~~is indicated as-by~~ C₂O₄. Molar ratios in the particle phase are accordingly denoted by DMAH/NH₄, DMAH/SO₄, and NH₄/SO₄, while gaseous molar ratios are denoted by DMA/NH₃.

DMAH concentrations of the first measurement points for particles in the 0.1_{10%} and 0.1_{50%} conditions lay at the lower end of the IC calibration range. A conservative estimation of up to 15% uncertainty for these values would decrease the DMAH/NH₄ ratio by 0.02, which has negligible impacts on the observed trends and values ~~(see Fig. 3).~~ [Uncertainties as shown in the figures were calculated based on errors resulting from IC measurements. Additional uncertainties of particle phase DMAH and NH₄ resulting from independent parameters such as the variations in total particle count, and uncertainties in generation and determination of gas concentrations also led to some fluctuations beyond the quantified errors.](#)

25

30

After 35-38 hours, samples showed no significant changes in particle composition and were thus considered to be in equilibrium. Equilibrated samples were divided into two groups, with one directly undergoing IC analysis and the other placed in clean cells under an N₂ atmosphere for > 5 hours prior to IC analysis to further investigate their compositional stability [in an amine- and ammonia- free environment](#).

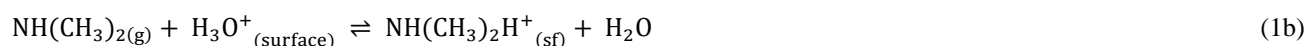
35

Furthermore, uptake experiments at 0.5_{10%} and of NH₃ at 10% RH were repeated with particles of 60-200 μm in size in flow cells equipped with a quartz window to track alterations in chemical composition and concurrent morphological changes with a Raman microscope (Renishaw RM series) as described by Yeung et al. (2009) and Chu et al. (2015). A 20 mW Argon ion laser (514.5 nm) was deployed for sample excitation and a 1800 g mm⁻¹ grating was selected to obtain spectra in the range of 200 to 4000 cm⁻¹ with a resolution of 1.4 cm⁻¹.

3. Results and discussion

Uptake of NH₃, DMA and their mixtures into H₂SO₄ particles were conducted at 10% and 50% RH. Single component uptake served as the base case for comparison. Additional experiments with H₂C₂O₄ at 10 and 70% RH were conducted at a gas ratio of 0.5 only and are discussed in Sect. 3.3. A summary of all the experimental conditions is given in Table 1.

The uptake of alkaline gases into acidic droplets involves a series of inter-related processes including gas phase diffusion, immediate reaction of gas molecules colliding with the aerosol surface (Eq. 1a and b) or adsorption and dissolution (Eq. 2a and b), followed by further liquid phase diffusion and proton transfer in the bulk particle (Eq. 3a and b) (Swartz et al., 1999; Kulmala and Wagner, 2001; Davidovits et al., 2006; Pöschl et al., 2007; Kolb et al., 2010).



The above equations and related reaction steps indicate a strong acidity dependence, thus with increasing neutralization, the scope extent of DMA and NH₃ uptake may change. Here, the extent of (stoichiometric) neutralization of the particles is defined as the number of moles of alkaline species over moles of acidic species, $X = (\text{DMAH} + \text{NH}_4)/\text{SO}_4$ or $X = (\text{DMAH} + \text{NH}_4)/\text{C}_2\text{O}_4$ and is hereafter referred to as the neutralization ratio. In the course of the uptake experiments, the neutralization ratio ranged from highly acidic ($X = 0$) to neutral ($X = 2$). But-However, not all equilibrated particles were completely neutralized, as will be further discussed in Sect. 3.4.

3.1 Single gas uptake

At 50% RH, the uptake of NH₃ fully neutralized the H₂SO₄ droplets within 2 hours, forming aqueous (NH₄)₂SO₄ droplets (Fig. 1, grey diamonds). At 10% RH, NH₃ uptake (Fig. 1, open diamonds) was similar to that at 50% RH initially, until X exceeded 1.1, where crystallization significantly retarded the subsequent uptake. The continued increase in particulate NH₄⁺ even after crystallization indicates that crystalline acidic particles were still susceptible to uptake, but imposed bulk diffusion limitations that retarded the uptake. Neutralization was not complete within the measured period of 15 hours.

Uptake of DMA at the mixing ratio of 0.15 ppm (Fig. 1, triangles) was significantly slower than that at 1 ppm (Fig. 1, squares). Like the initial uptake of NH₃, DMA uptake did not differ significantly between 10% and 50% RH, until approaching equilibrium at DMAH/SO₄ ratios of 1.5±0.1 at 10% RH, and 1.7±0.1 (DMA_{0.15ppm}) and 1.9±0.1 (DMA_{1ppm}) at 50% RH (Table 1, X_{equil}). There was no indication of phase change in these particles even at 10% RH. This is consistent with earlier studies, where secondary and tertiary methyl and ethyl-ammonium sulfates were described as hygroscopic, non-crystallizing salts at RH ≤ 10% (Qiu and Zhang, 2012; Chan and Chan, 2013; Chu et al., 2015). Furthermore, these studies showed that upon drying of synthesized DMAS droplets (DMAH/SO₄ ratios = 2) with amine-free air, DMA evaporated from the particles, leading to a final DMAH/SO₄ ratio of 1.5 at < 3% RH (Chan and Chan, 2013; Chu et al., 2015). In our experiment, the same equilibrium DMAH/SO₄ ratio of 1.5 was established at 10% RH, despite a continuous supply of DMA gas.

Particles exposed to 1 ppm of DMA at 10% RH were more neutralized initially with $X_{\text{max-neutral}} = 1.7 \pm 0.1$ (Table 1,) and then equilibrated to lower X_{equil} of 1.5 ± 0.1 (Table 1). Some of the initially absorbed DMA molecules had re-partitioned into the gas phase despite the presence of DMA gas in the surrounding atmosphere. The phenomenon of re-volatilization is further discussed in Sect. 4.

5 3.2 DMA-NH₃ co-uptake

Figure 2 depicts the temporal profiles of DMAH/SO₄, NH₄/SO₄ and X at the different gas ratios and RH. At 10% RH particles solidified during the experiment (Fig. 2a and b, indicated by crosshatched areas) and needed 2 to > 18 hours (for 0.5_{10%} and 0.1_{10%}, respectively) to completely neutralize sulfate. Upon reaching neutralization, NH₃ had almost completely displaced the DMAH absorbed earlier from the solid particles. The phase transition and DMAH displacement at 10% RH will be further discussed in Sect. 3.2.3 and 3.2.4.

At 50% RH SO₄²⁻ was completely neutralized (Fig. 2c and d) within 1-2 hours. Neutralization in droplets was followed by a partial displacement of NH₄ by DMA, reaching a final equilibrium composition enriched in DMAH (Sect. 3.2.2). The results show that the DMAH/NH₄ ratios varied substantially during uptake before stable compositions were reached. In the following, we will discuss the dependence of gas uptake on the phase state and neutralization ratio of the particles.

3.2.1 Uptake into liquid acidic droplets

Figure 3 displays the changes in the DMAH/NH₄ ratios as a function of time for the four co-uptake experiments. For the first measurement point under each condition, the DMAH/NH₄ ratio (Table 2, t_{initial}) was close to the gas phase DMA/NH₃ ratio (indicated by grey bands in Fig. 3), implying that initially both gases partitioned equally effectively into highly concentrated H₂SO₄. For instance, in panels a and b the DMAH/NH₄ ratios in the acidic droplets were 0.07 ± 0.01 and 0.43 ± 0.04 , comparable to gaseous DMA/NH₃ ratios of 0.07 and 0.46, respectively. Starting from the second measured values, a clear decrease in DMAH/NH₄ ratios can be observed. Figure 4 compares the uptake of DMA and NH₃ in single and mixed gas experiments. The initial uptake trends of single gas and co-uptake did not deviate noticeably, confirming indicating- that DMA and NH₃ uptake took place independent of each other. Consequently, earlier reported uptake coefficients from single gas uptake NH₃ and DMA into sulfuric acid may be used for co-uptake analysis.

Swartz et al. (1999) measured the heterogeneous uptake of NH₃ into a chain of 70 wt% and 40 wt% H₂SO₄ droplets (equilibrated at 10% and 50% RH, respectively), and obtained gas phase diffusion-corrected uptake coefficients (γ_{NH_3}) of 0.8 and 1.0, respectively. The highly effective uptake into concentrated H₂SO₄ at pH < 0 was attributed to surface reactions, i.e., NH₃ molecules reacting with interfacial hydronium ions (H₃O⁺) without prior solvation (Swartz et al., 1999). As H₂SO₄ droplets in the present study have a solution pH ≤ -0.9 (Wexler and Clegg, 2002) at both 50% RH (43 wt% H₂SO₄) and 10% RH (64 wt% H₂SO₄), protonation without prior dissolution may take place for NH₃ in the first few minutes of uptake when pH is very low.

Wang et al. (2010) reported an uptake coefficient (γ_{DMA}) of about 0.03 for DMA uptake into concentrated H₂SO₄ of ≥ 62 wt% ($\leq 10\%$ RH) at 283 K. The coefficient is noticeably smaller than that of close to unity reported for NH₃ uptake into H₂SO₄ of similar acidity (Swartz et al., 1999). In the current study, NH₃ uptake into fresh H₂SO₄ droplets was not overwhelmingly dominant. However, as the uptake continued, the DMAH/NH₄ ratios decreased by 30-40% for all experimental conditions within the first 1-2 hours (Fig. 3 a-d), which indicates a preferential uptake of NH₃. Since the gas concentrations of both NH₃ and DMA were constant, it is likely that the decreasing particle acidity and increasing neutralization ratio caused this change.

To date no systematic study on the relevance of surface protonation has been conducted for DMA uptake. However the gas phase basicity of NH_3 and its derivatives (such as R_3N) have been shown to correlate well with the differential heats of chemisorption on acidic (zeolite) surfaces (Parrillo et al., 1993). Since DMA possesses a slightly higher gas phase basicity than NH_3 (Brauman et al., 1971; Parrillo et al., 1993), DMA gas molecules might, similar to NH_3 , have a high affinity to interfacial H_3O^+ . Surface protonation on fresh H_2SO_4 particles may thus be important for the initial uptake of both NH_3 and DMA, which could explain why the initial particle phase ratio is equal to the gas phase ratio.

~~Wang et al. (2010) reported an uptake coefficient (γ_{DMA}) of about 0.03 for DMA uptake into concentrated H_2SO_4 of ≥ 62 wt% ($\leq 10\%$ RH) at 283 K, which is noticeably smaller than the coefficient of close to unity reported for NH_3 uptake into H_2SO_4 of similar acidity (Swartz et al., 1999). In the current study, NH_3 uptake into fresh H_2SO_4 droplets was not overwhelmingly dominant. However, as the uptake continued, the DMA/ NH_4 ratios dropped by 30–40% for all experimental conditions within the first 1–2 hours (Fig. 3 a d), which indicates a preferential uptake of NH_3 . Since the gas concentrations of both NH_3 and DMA were constant, it is likely that the decreasing particle acidity and increasing neutralization ratio caused this change.~~

Swartz et al. (1999) reported a threshold $\text{pH} \leq 0$ for surface protonation to occur and a drop in γ_{NH_3} by one order of magnitude when the pH was increased to above zero. Hanson and Kosciuch (2003) observed a similar drop in γ_{NH_3} during the uptake of NH_3 into H_2SO_4 , when the solution approached ammonium bisulfate (NH_4HSO_4) composition. Using the *E-AIM* model (Wexler and Clegg, 2002, www.aim.env.uea.ac.uk/aim) we estimated that $n\text{H}_3\text{O}^+$ decreased by about 40% as the neutralization ratio increased from $X = 0$ (H_2SO_4 droplets) to 0.5. Once the particles were half neutralized ($X = 1$, bisulfate stoichiometry), the solution pH were estimated to exceed zero. Hence if we assume a similar threshold as reported by Swartz et al. (1999), surface protonation (Eq. 1a and b); ~~which can explain the comparable initial uptake of DMA and NH_3 ,~~ may no longer be relevant when particles approached bisulfate composition.

~~Figure 4 compares the uptake of DMA and NH_3 in single and mixed gas experiments. The uptake trends of single gas and co-uptake did not deviate noticeably, confirming that DMA and NH_3 uptake took place independent of each other.~~ Despite the increase in pH when neutralization ratios exceeded unity ($X = 1$), there were sufficient amounts of H_3O^+ to support the uptake of both gases. Hence, the presence of NH_3 gas molecules at 14 times higher concentration than DMA had little effect on the uptake of DMA into acidic particles. The same can be said for DMA, which seemed not to have influenced NH_3 partitioning into acidic droplets. This finding clearly differentiates the group of hydrophilic R_3N from more hydrophobic organics such as hexadecane, hexadecanol (Daumer et al., 1992) or typical atmospheric organic vapor (Liggio et al., 2011), which form an organic film that limits the access of NH_3 to the inorganic core.

The independent uptake of DMA and NH_3 at 10% RH prevailed until the particles underwent phase change (Fig. 4a and c, dotted lines). Once particles effloresced, a preferential uptake of NH_3 was observed, which resulted in a significant drop in DMAH/ NH_4 (Fig. 3a and b), as discussed in Sect. 3.2.3. At 50% RH the co-uptake of DMA and NH_3 was independent from each other until the particles reached complete neutralization ($X = 2.0$) (Fig. 4b and d, solid lines). Once neutralized, only DMA uptake continued (Fig. 4b) with concurrent displacement of NH_4^+ (Fig. 4d) as discussed [hereafternext](#).

3.2.2 Displacement of NH_4^+ from neutralized droplets

When approaching full neutralization, where both gases started to compete for limited available H_3O^+ ions, the DMAH/ NH_4 ratios in droplets of the 0.1_{50%} and 0.5_{50%} experiments started to increase (Fig. 3c and d, solid line). In solution DMA ($\text{pK}_a = 10.64$; Hall, 1957) is a stronger base than NH_3 ($\text{pK}_a = 9.21$), consequently it has a higher affinity for H_3O^+ than NH_3 does. Thus, while the fraction of DMA species gradually increased, some of the NH_4^+ dissociated (Eq. 3a, reverse reaction) and NH_3 was released back to the gas phase (Eq. 2a, reverse reaction).

Similar displacement of NH_4^+ by alkyl-amines has been reported for aqueous particles of ammonium bisulfate, chloride, oxalate and sulfate at 50 and 75% RH (Chan and Chan, 2012, 2013) and nitrate at 20% RH (Lloyd et al., 2009). Similarly, Lloyd et al. (2009) observed the displacement of NH_4^+ by trimethylamine (TMA) from water-coated NH_4NO_3 nanoparticles despite an excess of NH_3 gas ($n\text{TMA}_{(\text{g})}/n\text{NH}_{3(\text{g})} = 0.1$), although they did not report the quantity-percentage of NH_4^+ displaced. Their gas phase conditions were comparable to our experiment at 0.1_{50%}. In our experiment DMA was able to displace about 9% of the initially absorbed NH_4^+ (Table 2, $\chi_{\text{NH}_4^+}$). The equilibrium DMAH/ NH_4 ratio in the 0.1_{50%} condition-experiment was 0.18 ± 0.02 (Table 2, t_{equil}), which indicates an enhancement of DMA by a factor of 2-3 in the particle phase compared to the gas phase. Particles under-in the 0.5_{50%} conditions-experiment equilibrated at a DMAH/ NH_4 ratio of 1.77 ± 0.13 , hence 3-4 times higher than the gas ratio; by the time a stable particle composition was established, with 50% of the initially absorbed NH_4^+ was displaced (Table 2). Yet it should be noted that equilibrated particles at 0.5_{50%} possessed a neutralization ratio of only $X = 1.8 \pm 0.1$, hence the particle was incompletely neutralized (see Sect. 3.4) despite the presence of 1.9 ppm NH_3 and 0.9 ppm DMA in the surrounding gas phase.

The experimental equilibrium DMA/ NH_3 and DMAH/ NH_4 ratios (Table 2, t_{equil}) were compared with calculations using the *E-AIM* Model (Model II, 296 ± 1 K, no solid formation; Wexler and Clegg, 2002). Measured equilibrium DMAH/ SO_4 , NH_4/SO_4 were used as input parameters. The *E-AIM* predicted DMA/ NH_3 gas ratios that would equilibrate over particles lay in our experiments with DMA/ NH_3 of to be 0.14 and 0.01, and hence below the experimental DMA/ NH_3 gas ratios of 0.49 and 0.07. Considering the entire uptake process, the modelled result would These results imply that *E-AIM* would predict DMAH/ NH_4 even larger than our reserved ratios simply a more intensive displacement of NH_4^+ by DMA and stronger enrichment of DMA relative to NH_3 species in the particle phase compared to the gas phase. Yet, the experimental findings They are also qualitatively consistent with the *E-AIM* modeled values and consistent with earlier simulations by Barsanti et al., (2009), who reported that DMAH/ NH_4 in submicron acetic acid droplets can be significantly larger than their gas phase ratio, even if gas concentrations of NH_3 dominated DMA by one to three order of magnitudes.

Thus, in the current study we provide Our measurements are experimental evidence that DMA preferentially partitions into neutralized liquid sulfate particles over NH_3 , due to its stronger basicity/alkalinity. DMA then partially displaces NH_4^+ from neutralized aqueous particles even when the NH_3 gas concentration is one order of magnitude greater than the DMA gas concentration.

3.2.3 Phase transition and uptake into solid acidic particles

NH_3 (single gas) uptake into H_2SO_4 at 10% RH decelerated noticeably when the NH_4/SO_4 ratio exceeded 1.1 (Fig. 5, filled triangles). A comparable retardation occurred in the co-uptake experiments 0.1_{10%} and 0.5_{10%}, but at NH_4/SO_4 ratios of about 1.5 (Fig. 5a and b, open triangles).

We used Raman microscopy (Chu et al., 2015) to further investigate the slowdown-retardation of the reactions and possible changes in the physical state for the single uptake of NH_3 (Fig. 6) and the co-uptake experiment 0.5_{10%} (Fig. 7). Note that each sample was composed of several hundreds of closely packed-deposited droplets deposited on a substrate. The droplets were not expected to reach the same cation-to-sulfate stoichiometry, nor exhibit phase transitions at the exact same time. For the acquisition of in-situ Raman signals, we selected individual particles just before and right after phase transition, and in crystalline state, to represent the phase change process.

During the single gas uptake of NH_3 into H_2SO_4 droplets at 10% RH, crystallization occurred within the first 60 min. As shown in Fig. 6, during efflorescence of acidic droplets (Fig. 6, spectra 2 and 3) the HSO_4^- characteristic bands at 590 cm^{-1} and

1035 cm^{-1} (Dawson et al., 1986; Lund Myhre et al., 2003) transformed to doublets at 579/609 cm^{-1} and 1013/1043 cm^{-1} of solid particles (Fig. 6, spectra 2 and 3), suggesting the formation of crystalline NH_4HSO_4 (Dawson et al., 1986; Colberg et al., 2004). As uptake continued, a gradual shift towards $(\text{NH}_4)_2\text{SO}_4$ was indicated by an increase in the SO_4^{2-} stretching mode 975 cm^{-1} and a decrease in the HSO_4^- band at 579 cm^{-1} (Fig. 6, spectrum 4). The retarded diffusion of NH_3 from the surface to the interior of the crystals is likely to have limited the uptake, explaining why the spectra did not fully resemble $(\text{NH}_4)_2\text{SO}_4$ (Fig. 6, spectrum 5) within the measured period.

Efflorescence was also observed for the co-uptake of NH_3 and DMA at 10% RH. Under 0.5_{10%} conditions, most particles experienced the first morphological change after 40–60 min of uptake, forming fairly spherical solids with long lined patterns (Fig. 7, yellow rectangular). Raman spectral analysis of particles that had only just transitioned from liquid to solid phase state (Fig. 7, spectrum 3) showed an emerging SO_4^{2-} band at 984 cm^{-1} . Meanwhile the HSO_4^- frequencies near 590 cm^{-1} and 1030 cm^{-1} in the droplet (Fig. 7, spectrum 2) shifted towards 597 cm^{-1} and 1043 cm^{-1} in the solid particle (Fig. 7, spectrum 3) but both remained single broad peaks, without signs of scissoring as observed for bisulfate from NH_3 single gas uptake (Fig. 6, spectra 3 and 4). The observed features more closely resemble the spectral characteristics of letovicite $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (Colberg et al., 2004) than those of NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$.

~~The d~~During NH_3 -DMA co-uptake the absorbed DMAH^+ seems to have suppressed ~~the precipitation of NH_4HSO_4~~ ~~precipitation~~ in particles with a composition of $1.1 < \text{NH}_4/\text{SO}_4 < 1.5$, so that the phase change started only at a NH_4/SO_4 around 1.5 (Fig. 5a and b). It can be seen from the 0.1_{10%} experiment (Fig. 5a) that this suppression of NH_4HSO_4 precipitation ~~also even~~ occurred ~~if at the~~ ~~DMAH/ NH_4 at the time of phase change was~~ as low as 0.05 ~~at the time of phase change~~ (Table 2, t_{pc}), ~~hence even if the concentration of DMA species was low compared to the amount of NH_3 species present in the particle~~. Since $\text{R}_3\text{NH}/\text{NH}_4$ ratios in ambient samples near emission sites can be up to 0.23 (Sorooshian et al. 2008), ~~Since, and with~~ DMAH^+ ~~as is~~ the most frequently detected aminium ion in aerosols (Müller et al., 2009; Rehbein et al., 2011; Hu et al., 2015; Youn et al., 2015), ~~Since, and with~~ DMAH^+ ~~as is~~ the most frequently detected aminium ion in aerosols (Müller et al., 2009; Rehbein et al., 2011; Hu et al., 2015; Youn et al., 2015), DMAH/NH_4 ratios in aerosols can possibly reach ≥ 0.05 and ~~thus could change~~ ~~thus DMA can affect~~ the crystallization behavior of $\text{NH}_4\text{-H-SO}_4$ -salts in atmospheric particles. ~~Furthermore, by~~ ~~By~~ retaining the particles of a composition of $1.1 < \text{NH}_4/\text{SO}_4 < 1.5$ at 10% RH in liquid phase, the presence of DMA species accelerated the uptake of NH_3 compared to single gas NH_3 uptake where crystallization retarded the uptake into particles with $\text{NH}_4/\text{SO}_4 > 1.1$.

After the NH_4 - DMAH -mixed particles crystallized, the uptake of NH_3 continued at a slower pace (Figure 5a and b), while DMA was no longer absorbed and the DMAH/NH_4 ratio ~~started continued~~ to decrease (Fig. 3a). In earlier reports of single gas R_3N uptake (where R_3N might be methylamine, DMA, TMA or triethylamine), R_3N (in the absence of NH_3) were observed to effectively adsorb onto NH_4HSO_4 surfaces in a coated flow reactor (Qiu et al., 2011). In the presence of NH_3 in our experiments, however, DMA was not taken up by acidic crystalline particles. Liu et al. (2012) reported steric effects to influence the uptake effectiveness of primary, secondary and tertiary methyl-amines into solid citric and humic acid measured in a Knudsen cell reactor, where smaller R_3N molecules are more effectively absorbed than larger ones. A similar effect of steric hindrance may have caused the preferential uptake of the smaller NH_3 molecules over DMA in our experiments. Besides steric reasons, the release of ~~more~~ lattice enthalpy during the formation of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{SO}_4$ may have made the uptake of NH_3 also thermodynamically favorable.

DMAH/NH_4 ratios at the time of neutralization (t_{neutral}) reached 0.032 ± 0.001 for the 0.1_{10%} condition and 0.19 ± 0.01 for the 0.5_{10%} condition (Table 2), showing a slight enrichment of NH_4^+ in the particle over the gas phase.

3.2.4 Displacement of DMAH⁺ from solid neutralized particles

After reaching full neutralization, both Raman spectral analysis and IC results of solid particles indicated a gradual reduction of ~~DMAH⁺-DMA species~~ and increase of ~~NH₄⁺-NH₃ species~~ in the particle phase, which is also reflected in decreasing DMAH/NH₄ ratios in Fig. 3a and b.

5

~~At 10–20 minutes after the phase transition, DMAH⁺-NH₄⁺-mixed particles experienced a second morphological change to a polycrystalline structure (Fig. 7, grey rectangular, spectrum 4). Raman spectra of these particles showed a slowly vanishing HSO₄⁻ band at 1043 cm⁻¹. and However, a significant decrease in the full width at half maximum (FWHM) of the increase in the SO₄²⁻ band at 980 cm⁻¹, which indicates the (full) crystallization of sulfate (Lee et al., 2008), was only observed hours after the morphology change (Fig. 7, spectrum 4). We suspect that the observed morphological changes are related to the formation of a (NH₄)₂SO₄ shell structure due to DMAH⁺ displacement by NH₃. DMAH⁺ was subsequently slowly displaced from the particle core, which eventually led to the formation of crystalline (NH₄)₂SO₄ with only traces of DMAH⁺ left inside the particles, as revealed by IC analysis.~~

10

It is interesting to note, that the DMAH/NH₄ ratios of equilibrated particles for 0.5_{10%} and 0.1_{10%} were both 0.02 (Table 2). Even if the NH₃ gas concentration is only twice of that of DMA, NH₃ can almost completely displace DMAH⁺ from the solid particle.

15

Since different gas mixtures resulted in similar particle composition, calculations by *E-AIM* based on these equilibrated particle compositions yielded similar gas phase DMA/NH₃ ratios for the 0.1_{10%} and 0.5_{10%} experiments of 0.57 and 0.32, with an uncertainty of up to 40% due to strong temperature sensitivity. The modelled results are qualitatively in agreement with the experimental results, confirming that despite considerable amounts of DMA in the gas phase, the equilibrated solid sulfate particle would predominantly contain NH₃ species.

20

Overall it can be concluded that, for DMA-NH₃ co-uptake, NH₃ is favorably absorbed into acidic liquid particles, except for very concentrated H₂SO₄, where DMA and NH₃ seem to partition similarly effectively. Unless the particles either crystallize or are close to full neutralization, DMA and NH₃ in general do not influence each other's uptake and act as if they were the only gas present.

25

For uptake into neutralized particles, DMA is favorably absorbed into liquid neutral particles due to its stronger basicity leading to partial NH₄⁺ displacement depending on gas phase NH₃ concentration; NH₃ is favorably taken up into solid neutral particles and can almost completely displace DMAH⁺ due to the thermodynamically favorable formation of (NH₄)₂SO₄ crystals and steric reasons.

30

3.3 Uptake into oxalic acid particles

We performed additional experiments with H₂C₂O₄ to further elucidate the influence of phase state on the co-uptake process. H₂C₂O₄ is a model organic acid frequently detected in ambient aerosols (Kawamura and Ikushima, 1993; Decesari et al., 2000; Yao et al., 2003; Yu et al., 2005; Müller et al., 2009). Efflorescence of aqueous supermicron H₂C₂O₄ particles occurs at 51.8%-56.7% RH, forming anhydrous solids (Peng et al., 2001). We chose to examine the co-uptake of DMA and NH₃ into initially solid and initially liquid particles, respectively, at 10% and 70% RH, respectively.

35

Figure 8 compares the co-uptake into H₂C₂O₄ and H₂SO₄ particles at DMA/NH₃ = 0.5. Within the first hour of uptake into solid H₂C₂O₄ particles at 10% RH (Fig. 8a, inverted triangles), the neutralization ratio increased to $X = 0.3$. In the subsequent 15 hours, no further major increase was not observed, suggesting that the gas uptake into anhydrous H₂C₂O₄ particles

40

was incomplete and may have been limited to adsorption on the surface and outer layers of the particles. DMAH/NH₄ ratios (Figure 8b) stayed roughly constant ~~decreased from initially 0.26±0.05 during the first four hours of uptake to 0.17±0.04 after 14-15 h (Table 2), despite a relatively constant overall neutralization ratio (X = 0.3). Some of the initially adsorbed DMA molecules were displaced by NH₃.~~

5

The uptake at 70% RH ~~starting with H₂C₂O₄ droplets~~ was monitored under the microscope for subsequent phase changes (Fig. S2). Within 15 minutes of uptake, liquid particles transformed into round, irregularly patterned solids, suggesting that the uptake of even small amounts of gas caused a phase change in these H₂C₂O₄ particles. The formation of ammonium salts via the uptake of NH₃ has earlier been shown to decrease the hygroscopicity of H₂C₂O₄ particles and ~~influence change~~ their phase state (Peng and Chan, 2001; Ma et al., 2013). We found that prior to phase change, a ring of small satellites formed around the droplets. This observation can be most plausibly explained by ~~a the~~ pinning effect caused by ~~the~~ fast evaporation of the solvent from a droplet deposited on a substrate (Deegan et al., 1997). Similar halo formation has been described for other atmospheric particles (Hamacher-Barth et al., 2016) ~~but yet~~, we believe that this effect does not have a ~~significant~~ impact on the general uptake observations here. The co-uptake trends into solidified H₂C₂O₄ particles ~~at of the ox0.5_{70%} conditions~~ ~~experiments~~ were comparable to those of 0.5_{10%} and 0.5_{50%} into H₂SO₄ (Fig. 8b8a), indicating that the solids formed during phase change (dashed lines, Fig. 8) did not retard the uptake and that diffusion inside the particle bulk was not a limiting factor of the uptake. In fact, the particles ~~were~~ almost completely neutralized within the first hour of reaction. Similar observations have been reported by Li et al. (2015), who investigated NH₃ uptake into submicron organic particles produced from oxidation of isoprene, a precursor gas of H₂C₂O₄ (Ervens et al., 2014). Li et al. (2015) showed that even at RH down to <5%, NH₃ uptake was not restricted by diffusion. Unlike the co-uptake into partially neutralized H₂SO₄ particles at 10% RH, where DMA uptake discontinued once the particles formed solids, uptake of DMA into solid, partially neutralized H₂C₂O₄ particles remained effective.

10
15
20

Within two hours of uptake, the solid particles of ox0.5_{70%} experienced a morphological change and transformed into crystals (Fig. S2). Concurrently, the DMAH/NH₄ ratios dropped from 0.34 to <0.1 (Table 2, t_{equil}), showing that NH₃ can displace DMAH⁺ from neutralized oxalate particles, which may trigger the transformation to a crystalline morphology. Final particle morphologies show a ~~centered~~ particle with a monoclinic or orthorhombic crystal structure, a shape typical of ammonium oxalate (Blake and Clegg, 2009), ~~and surrounded by~~ small residuals of the satellite particles (Fig. S2).

25

3.4 Stability of reaction products and re-volatilization of NH₃ and DMA

As shown in Sect. 3.1, single gas DMA uptake into H₂SO₄ equilibrated ~~with at~~ incompletely neutralized droplets at both 10% and 50% RH with X_{equil} between 1.5 ~~and~~ -1.9 (Table 1). ~~Temporal profiles of the DMA uptake of 1ppm at 10% RH show that DMAH/SO₄ ratios peaked after 4-5 hours (Fig. 1), reaching X_{max-neutral} of 1.7±0.1 before DMA partially re-volatilized and particles equilibrated with a more acidic composition of X_{equil} = 1.5±0.1 (Table 1). When placing equilibrated samples into~~ Under amine-free atmosphere, the neutralization ratio ~~of these equilibrated particles~~ decreased ~~further~~ to X_{N2} = 1.2±0.2 at 10% RH and X_{N2} = 1.7±0.2 at 50% RH, as a result of DMA evaporation ~~from these particles~~ (Table 1). Similar degassing of methyl and ethyl-amines from synthesized salts has been reported in earlier studies (Chan and Chan, 2013; Chu et al., 2015; Lavi et al., 2015).

30

35

To ~~examine-summarize~~ the influence of NH₄⁺ ~~on-in~~ the volatilization of DMA from particles and the formation of partially neutralized equilibrated droplets, we compared co-uptake experiments 0.5_{10%} and 0.5_{50%} to single gas uptake DMA_{1ppm10%}, DMA_{1ppm50%}. Figure 9 illustrates the maximum neutralization, equilibrium and composition of particles exposed to RH-conditioned N₂ atmosphere for the four mentioned experiments.

40

~~Particles in In~~ co-uptake experiments, particles reached full neutralization (Fig. 9d and j). The total cation content in particles at 10% RH at the time of neutralization was ~~comprised of~~ > 80% NH_4^+ (Fig. 9d). When approaching equilibrium, DMAH^+ was displaced by NH_3 and the NH_4^+ content increased to 98% (Fig. 9e). Although the cation composition had changed, no decrease in X beyond the margin of error was observed (Fig. 9d to e). ~~When, even when the~~ particles were exposed to pure N_2 (Fig. 9f), the particle composition did not change due to the formation of a stable crystal. At 50% RH, DMA partially displaced NH_4^+ from neutralized particles, with an increase in DMAH/SO_4 from 0.7 at the point of maximum neutralization (Fig. 9j) to 1.3 at equilibrium (Fig. 9k). Accompanying the increase in DMAH^+ was a ~~drop decrease~~ in the total neutralization ratios from $X = 2$ to about $X = 1.8$ (Fig. 9j to k), indicating that more NH_3 has degassed than was replaced by DMA. Hence while re-volatilization of DMA was responsible for the decrease in X ~~under for~~ $\text{DMA}_{1\text{ppm}50\%}$ ~~conditions~~, degassing of NH_3 could be responsible for the decrease in X neutralization ratios in co-uptake experiments. Once exposed to N_2 , even more NH_3 evaporated from DMAH-NH_4 mixed particles (Fig. 9k to l), which further increased the acidity of these particles.

It should be noted, that the degassing of NH_3 was negligible for particles of the 0.1_{50%} condition (Fig. 2c). At the point of maximum neutralization they contained large amounts of NH_4^+ and a DMAH/NH_4 ratio below 0.1, which seems to have prevented re-volatilization.

Under exposure to N_2 , ~~X decreased in~~ DMAH-NH_4 mixed particles that were originally in liquid phase state and contained large amounts of DMAH^+ (Fig. 9b, h, k) ~~exhibited a decrease in X~~ , reflecting that the equilibrium compositions of these droplets were sensitive to changes in DMA and NH_3 gas concentrations.

4. Summary and Conclusions

The co-uptake of DMA and NH_3 into H_2SO_4 and $\text{H}_2\text{C}_2\text{O}_4$ particles was investigated at different RH and DMA/NH_3 gas ratios. The stoichiometric neutralization ratio and physical state of the particles were the two major factors influencing DMA and NH_3 uptake.

In the uptake into fresh, very acidic H_2SO_4 droplets at 10% and 50% RH, both DMA and NH_3 partitioned effectively, leading to a DMAH/NH_4 ratio comparable to the DMA/NH_3 gas ratio. Subsequently, the DMAH/NH_4 ratio decreased as NH_3 uptake was faster. The uptake of DMA and that of NH_3 were independent of each other because of the availability of abundant acids, as long as the particles did not reach neutralization nor undergo phase change. This result may explain why the highest particulate R_3NH^+ mass concentrations are detected in acidic aerosols ~~with at~~ low NH_4/SO_4 ratios (Youn et al., 2015).

In fully neutralized droplets at 50% RH, the limited availability of H_3O^+ ions for acid-base reactions led to a partial displacement of NH_4^+ by the stronger base DMA. This process yielded equilibrium particle compositions enriched in DMAH^+ by up to four times the gas phase ratio. It also potentially explains DMA partitioning into the neutralized condensed phase despite excess NH_3 (Sorooshian et al., 2008; Lloyd et al., 2009; Rehbein et al., 2011; VandenBoer et al., 2011). When NH_4 is present in neutralized DMAH -rich sulfate droplets, DMA from the gas phase can displace NH_4 from droplets, and prompt additional NH_3 to evaporate to form non-neutralized particles. Hence, the presence of DMAH can prevent aqueous sulfate particles from full neutralization. In our experiments NH_3 re-volatilization happened at DMAH/NH_4 ratio of above 0.5, which is at the upper end of DMAH/NH_4 measured in atmospheric particles (Sorooshian et al., 2008; VandenBoer et al., 2011; Youn et al., 2015).

At 10% RH, the phase changed from liquid to solid during uptake. This instantly inhibited further DMA uptake, while NH₃ uptake continued. Once the particles were fully neutralized, NH₃ displaced DMAH⁺ from crystal structures and finally formed (NH₄)₂SO₄ with little residual ~~NH₄~~DMAH⁺, regardless of the DMA gas concentrations in the surrounding.

5 H₂C₂O₄ particles at 70% RH were initially liquid, but transformed into non-crystalline solids after absorbing small amounts of DMA and NH₃. Subsequent uptake was similar to that of liquid sulfate particles. The formation of solid, partially neutralized H₂C₂O₄ particles did not hinder DMA uptake. Fully neutralized oxalate particles then crystallized upon displacement of DMAH⁺ by NH₃, similar to the displacement of DMAH⁺ from crystalline sulfate particles. Anhydrous H₂C₂O₄ at 10% RH was rather inert and took up small amounts of DMA and NH₃, presumably by adsorption only.

10

In solid neutralized particles, NH₃ uptake is sterically and thermodynamically favored to form (NH₄)₂SO₄ or ammonium oxalate crystals by displacing DMAH⁺. Hence, once ambient aerosols are in solid state, they are unlikely to take up R₃N, even when R₃N and NH₃ gas concentrations are of the same magnitude.

15

~~In the absence of NH₄⁺, DMA partially evaporated from DMAH⁺-rich sulfate droplets. However, in the more common scenarios where NH₄⁺ is present, DMA can displace NH₄⁺ from neutral droplets, and cause additional NH₃ to evaporate and form non-neutralized particles. Hence, the presence of DMAH⁺ can prevent aqueous sulfate particles from full neutralization. In our experiments NH₃ re-volatilization required DMAH/NH₄ ratio of about 0.5, which is at the upper end of DMAH/NH₄ measured in atmospheric particles (Sorooshian et al., 2008; VandenBoer et al., 2011; Youn et al., 2015).~~

20

The DMA and NH₃ gas concentrations and sulfate neutralization ratios used in the present study are high and are only likely in the vicinity of emission sources or in emission plumes (Sorooshian et al., 2008; Ge et al., 2011). Under such conditions, particle neutralization ratios are likely to be high (Sorooshian et al., 2008), and NH₃ and amines compete for particulate H₃O⁺ ions, where DMA can displace NH₄⁺ in liquid and NH₃ can displace DMAH⁺ in solid particles. Although laboratory experiments have shown that in the absence of NH₃, DMA could partially displace NH₄⁺ from solid ammonium salts including (NH₄)₂SO₄ and NH₄NO₃ (Lloyd et al., 2009; Qiu and Zhang, 2012; Chan and Chan, 2012, 2013), this scenario is unlikely under atmospheric conditions with abundant NH₃.

25

In this study, we used DMA as a proxy for atmospherically relevant R₃N. As different R₃N and their sulfate and oxalate salts possess different hygroscopic and crystallization properties (Qiu and Zhang, 2012; Clegg et al., 2013; Chan and Chan, 2013; Chu et al., 2015; Sauerwein et al., 2015) which can all influence uptake behavior, the findings here obtained may not be generalizable to all short-chain aliphatic amine compounds. ~~It should also be mentioned that particle size may affect the particle composition as a result of the uptake, as well as the crystallization of the particle. It should also be mentioned that particle size may affect the gas uptake kinetics, as well as the crystallization behavior of the particle. When applying the results of this study to submicron particles, one may expect a considerably faster uptake and thus changes in DMAH/NH₄ ratios in acidic particles. Yet the overall trends of displacement reactions based on phase state and neutralization ratio as well as crystallization inhibition by DMAH are considered applicable to particles of smaller size. Nevertheless,~~ the observed results may be most relevant to aerosols larger than 1 μm, which were found in the atmosphere to have the highest R₃NH/NH₄ ratio (VandenBoer et al., 2011; Youn et al., 2015). To improve our understanding of the mechanisms governing the simultaneous exchange of NH₃ and R₃N between the gas and particle phases, particle size dependence should be investigated in the future.

30

35

Acknowledgements

This work was supported by the Research Grants Council of the Hong Kong Special Administrative Region, China (GRF grant no. 600112 and 16300214).

References

- 5 Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359–363, 2013.
- 10 Angelino, S., Suess, D. T., and Prather, K. A.: Formation of Aerosol Particles from Reactions of Secondary and Tertiary Alkylamines: Characterization by Aerosol Time-of-Flight Mass Spectrometry, *Environ. Sci. Technol.*, 35, 3130–3138, 2001.
- 15 Behera, S. N., Sharma, M., Aneja, V. P., and Balasubramanian, R.: Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies, *Environ. Sci. Pollut. Res.*, 20, 8092–8131, 2013.
- 20 Blake, A. J. and Clegg, W.: *Crystal structure analysis: Principles and practice*; edited by William Clegg, 2nd ed., International Union of Crystallography book series, 13, Oxford University Press, Oxford, 2009.
- Bonner, O. D.: Osmotic and activity coefficients of methyl-substituted ammonium nitrates at 298.15 K, *J. Chem. Eng. Data*, 26, 148–149, 1981.
- 25 Brauman, J. I., Riveros, J. M., and Blair, L. K.: Gas-phase basicities of amines, *J. Am. Chem. Soc.*, 93, 3914–3916, 1971.
- Breitmaier, E. and Jung, G.: *Organische Chemie: Grundlagen, Stoffklassen, Reaktionen, Konzepte, Molekülstrukturen*; 129 Tabellen, 5., überarb. Aufl., Thieme, Stuttgart, New York, XVIII, 1000 S., 2005.
- Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Amine exchange into ammonium bisulfate and ammonium nitrate nuclei, *Atmos. Chem. Phys.*, 10, 3495–3503, 2010a.
- 30 Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Size-dependent reactions of ammonium bisulfate clusters with dimethylamine, *J. Phys. Chem. A*, 114, 11638–11644, 2010b.
- Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Amine reactivity with charged sulfuric acid clusters, *Atmos. Chem. Phys.*, 11, 8735–8743, 2011.
- Chan, L. P. and Chan, C. K.: Displacement of Ammonium from Aerosol Particles by Uptake of Triethylamine, *Aerosol Sci. Tech.*, 46, 236–247, 2012.
- 35 Chan, L. P. and Chan, C. K.: Role of the aerosol phase state in ammonia/amines exchange reactions, *Environ. Sci. Technol.*, 47, 5755–5762, 2013.
- Chu, Y., Sauerwein, M., and Chan, C. K.: Hygroscopic and phase transition properties of alkyl aminium sulfates at low relative humidities, *Phys. Chem. Chem. Phys.*, 17, 19789–19796, 2015.
- 40 Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ at Tropospheric Temperatures, *J. Phys. Chem. A*, 102, 2137–2154, 1998.

- Clegg, S. L., Qiu, C., and Zhang, R.: The deliquescence behaviour, solubilities, and densities of aqueous solutions of five methyl- and ethyl-aminium sulphate salts, *Atmos. Environ.*, 73, 145–158, 2013.
- Colberg, C. A., Krieger, U. K., and Peter, T.: Morphological Investigations of Single Levitated H₂SO₄ /NH₃ /H₂O Aerosol Particles during Deliquescence/Efflorescence Experiments, *J. Phys. Chem. A*, 108, 2700–2709, 2004.
- 5 Daumer, B., Niessner, R., and Klockow, D.: Laboratory studies of the influence of thin organic films on the neutralization reaction of H₂SO₄ aerosol with ammonia, *J. Aerosol Sci.*, 23, 315–325, 1992.
- Davidovits, P., Kolb, C. E., Williams, L. R., Jayne, J. T., and Worsnop, D. R.: Mass accommodation and chemical reactions at gas-liquid interfaces, *Chem. Rev.*, 106, 1323–1354, 2006.
- Dawson, B. S. W., Irish, D. E., and Toogood, G. E.: Vibrational spectral studies of solutions at elevated temperatures and pressures. 8. A Raman spectral study of ammonium hydrogen sulfate solutions and the hydrogen sulfate-sulfate equilibrium, *J. Phys. Chem.*, 90, 334–341, 1986.
- 10 Dawson, M. L., Perraud, V., Gomez, A., Arquero, K. D., Ezell, M. J., and Finlayson-Pitts, B. J.: Measurement of gas-phase ammonia and amines in air by collection onto an ion exchange resin and analysis by ion chromatography, *Atmos. Meas. Tech.*, 7, 2733–2744, 2014.
- 15 Decesari, S., Facchini, M. C., Fuzzi, S., and Tagliavini, E.: Characterization of water-soluble organic compounds in atmospheric aerosol: A new approach, *J. Geophys. Res.*, 105, 1481–1489, 2000.
- Deegan, R. D., Bakajin, O., Dupont, T. F., Huber, G., Nagel, S. R., and Witten, T. A.: Capillary flow as the cause of ring stains from dried liquid drops, *Nature*, 389, 827–829, 1997.
- Ervens, B., Sorooshian, A., Lim, Y. B., and Turpin, B. J.: Key parameters controlling OH-initiated formation of secondary organic aerosol in the aqueous phase (aqSOA), *J. Geophys. Res. Atmos.*, 119, 3997–4016, 2014.
- 20 Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part I. A review, *Atmos. Environ.*, 45, 524–546, 2011.
- Hall, H. K.: Correlation of the Base Strengths of Amines 1, *J. Am. Chem. Soc.*, 79, 5441–5444, 1957.
- Hamacher-Barth, E., Leck, C., and Jansson, K.: Size-resolved morphological properties of the high Arctic summer aerosol during ASCOS-2008, *Atmos. Chem. Phys.*, 16, 6577–6593, 2016.
- 25 Hansen, M. J., Adamsen, A. P. S., and Feilberg, A.: Recovery of odorants from an olfactometer measured by proton-transfer-reaction mass spectrometry, *Sensors*, 13, 7860–7871, 2013.
- Hanson, D. and Kosciuch, E.: The NH₃ Mass Accommodation Coefficient for Uptake onto Sulfuric Acid Solutions, *J. Phys. Chem. A*, 107, 2199–2208, 2003.
- Healy, R. M., Evans, G. J., Murphy, M., Sierau, B., Arndt, J., McGillicuddy, E., O'Connor, I. P., Sodeau, J. R., and Wenger, J. C.: Single-particle speciation of alkylamines in ambient aerosol at five European sites, *Anal. Bioanal. Chem.*, 407, 5899–5909, 2015.
- 30 Hu, Q., Yu, P., Zhu, Y., Li, K., Gao, H., and Yao, X.: Concentration, Size Distribution, and Formation of Trimethylammonium and Dimethylammonium Ions in Atmospheric Particles over Marginal Seas of China*, *J. Atmos. Sci.*, 72, 3487–3498, 2015.
- 35 Huntzicker, J. J., Cary, R. A., and Ling, C.-S.: Neutralization of sulfuric acid aerosol by ammonia, *Environ. Sci. Technol.*, 14, 819–824, 1980.
- Jen, C. N., McMurry, P. H., and Hanson, D. R.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, *J. Geophys. Res. Atmos.*, 119, 7502–7514, 2014.
- Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, 27, 2227–2235, 1993.
- 40 Kolb, C. E., Cox, R. A., Abbatt, J. P. D., Ammann, M., Davis, E. J., Donaldson, D. J., Garrett, B. C., George, C., Griffiths, P. T., Hanson, D. R., Kulmala, M., McFiggans, G., Pöschl, U., Riipinen, I., Rossi, M. J., Rudich, Y., Wagner, P. E., Winkler, P. M., Worsnop, D. R., and O'Dowd, C. D.: An overview of current issues in the uptake of atmospheric trace gases by

- aerosols and clouds, *Atmos. Chem. Phys.*, 10, 10561–10605, 2010.
- Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petaja, T., Sipila, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Jarvinen, E., Aijala, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkila, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin, R. L. 3., Duplissy, J., Vehkamäki, H., Back, J., Kortelainen, A., Riipinen, I., Kurten, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, *Science*, 339, 943–946, 2013.
- Kulmala, M. and Wagner, P. E.: Mass accommodation and uptake coefficients – a quantitative comparison, *J. Aerosol Sci.*, 32, 833–841, 2001.
- 10 Kurtén, T., Loukonen, V., Vehkamäki, H., and Kulmala, M.: Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia, *Atmos. Chem. Phys.*, 8, 4095–4103, 2008.
- Kürten, A., Bergen, A., Heinritzi, M., Leiminger, M., Lorenz, V., Piel, F., Simon, M., Sitals, R., Wagner, A., and Curtius, J.: Observation of new particle formation and measurement of sulfuric acid, ammonia, amines and highly oxidized molecules using nitrate CI-API-TOF at a rural site in central Germany, *Atmos. Chem. Phys. Discuss.*, 1–47, 2016.
- 15 Lavi, A., Segre, E., Gomez-Hernandez, M., Zhang, R., and Rudich, Y.: Volatility of atmospherically relevant alkylammonium carboxylate salts, *J. Phys. Chem. A*, 119, 4336–4346, 2015.
- Lee, A. K. Y., Ling, T. Y., and Chan, C. K.: Understanding hygroscopic growth and phase transformation of aerosols using single particle Raman spectroscopy in an electrodynamic balance, *Faraday Discuss.*, 137, 245–263, 2008.
- Li, Y. J., Liu, P., Gong, Z., Wang, Y., Bateman, A. P., Bergoend, C., Bertram, A. K., and Martin, S. T.: Chemical Reactivity and Liquid/Nonliquid States of Secondary Organic Material, *Environ. Sci. Technol.*, 49, 13264–13274, 2015.
- 20 Liggio, J., Li, S.-M., Vlasenko, A., Stroud, C., and Makar, P.: Depression of ammonia uptake to sulfuric acid aerosols by competing uptake of ambient organic gases, *Environ. Sci. Technol.*, 45, 2790–2796, 2011.
- Liu, Y., Ma, Q., and He, H.: Heterogeneous uptake of amines by citric acid and humic acid, *Environ. Sci. Technol.*, 46, 11112–11118, 2012.
- 25 Lloyd, J. A., Heaton, K. J., and Johnston, M. V.: Reactive uptake of trimethylamine into ammonium nitrate particles, *J. Phys. Chem. A*, 113, 4840–4843, 2009.
- Lund Myhre, C. E., Christensen, D. H., Nicolaisen, F. M., and Nielsen, C. J.: Spectroscopic Study of Aqueous H₂SO₄ at Different Temperatures and Compositions: Variations in Dissociation and Optical Properties, *J. Phys. Chem. A*, 107, 1979–1991, 2003.
- 30 Ma, Q., He, H., and Liu, C.: Hygroscopic properties of oxalic acid and atmospherically relevant oxalates, *Atmos. Environ.*, 69, 281–288, 2013.
- Macaskill, J. B. and Bates, R. G.: Osmotic and activity coefficients of monomethyl-, dimethyl-, and trimethylammonium chlorides at 25°C, *J. Solution Chem.*, 15, 323–330, 1986.
- Mäkelä, J. M., Yli-Koivisto, S., Hiltunen, V., Seidl, W., Swietlicki, E., Teinilä, K., Sillanpää, M., Koponen, I. K., Paatero, J., Rosman, K., and Hämeri, K.: Chemical composition of aerosol during particle formation events in boreal forest, *Tellus B*, 53, 2001.
- 35 McMurry, P. H., Takano, H., and Anderson, G. R.: Study of the ammonia (gas)-sulfuric acid (aerosol) reaction rate, *Environ. Sci. Technol.*, 17, 347–352, 1983.
- Müller, C., Iinuma, Y., Karstensen, J., van Pinxteren, D., Lehmann, S., Gnauk, T., and Herrmann, H.: Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands, *Atmos. Chem. Phys.*, 9, 9587–9597, 2009.
- 40 Olenius, T., Kupiainen-Maatta, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Free energy barrier in the growth of sulfuric acid-ammonia and sulfuric acid-dimethylamine clusters, *J. Chem. Phys.*, 139, 84312, 2013.

- Parrillo, D. J., Gorte, R. J., and Farneth, W. E.: A calorimetric study of simple bases in H-ZSM-5: A comparison with gas-phase and solution-phase acidities, *J. Am. Chem. Soc.*, 115, 12441–12445, 1993.
- Peng, C. and Chan, C. K.: The water cycles of water-soluble organic salts of atmospheric importance, *Atmos. Environ.*, 35, 1183–1192, 2001.
- 5 Peng, C., Chan, M. N., and Chan, C. K.: The Hygroscopic Properties of Dicarboxylic and Multifunctional Acids: Measurements and UNIFAC Predictions, *Environ. Sci. Technol.*, 35, 4495–4501, 2001.
- Pöschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions – Part 1: General equations, parameters, and terminology, *Atmos. Chem. Phys.*, 7, 5989–6023, 2007.
- Pratt, K. A., Hatch, L. E., and Prather, K. A.: Seasonal Volatility Dependence of Ambient Particle Phase Amines, *Environ. Sci. Technol.*, 43, 5276–5281, 2009.
- 10 Qiu, C., Wang, L., Lal, V., Khalizov, A. F., and Zhang, R.: Heterogeneous reactions of alkylamines with ammonium sulfate and ammonium bisulfate, *Environ. Sci. Technol.*, 45, 4748–4755, 2011.
- Qiu, C. and Zhang, R.: Physicochemical properties of alkylaminium sulfates: hygroscopicity, thermostability, and density, *Environ. Sci. Technol.*, 46, 4474–4480, 2012.
- 15 Rehbein, P. J. G., Jeong, C.-H., McGuire, M. L., Yao, X., Corbin, J. C., and Evans, G. J.: Cloud and fog processing enhanced gas-to-particle partitioning of trimethylamine, *Environ. Sci. Technol.*, 45, 4346–4352, 2011.
- Robacker, D. C. and Bartelt, R. J.: Solid-Phase Microextraction Analysis of Static-Air Emissions of Ammonia, Methylamine, and Putrescine from a Lure for the Mexican Fruit Fly (*Anastrephaludens*), *J. Agric. Food Chem.*, 44, 3554–3559, 1996.
- Rovelli, G., Miles, R. E. H., Reid, J. P., and Clegg, S. L.: Hygroscopic Properties of Aminium Sulphate Aerosols, *Atmos. Chem. Phys. Discuss.*, 1–32, 2016.
- 20 Sauerwein, M., Clegg, S. L., and Chan, C. K.: Water Activities and Osmotic Coefficients of Aqueous Solutions of Five Alkylaminium Sulfates and Their Mixtures with H₂SO₄ at 25 °C, *Aerosol Sci. Tech.*, 49, 566–579, 2015.
- Schade, G. W. and Crutzen, P. J.: Emission of aliphatic amines from animal husbandry and their reactions: Potential source of N₂O and HCN, *J. Atmos. Chem.*, 22, 319–346, 1995.
- 25 Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and McMurry, P. H.: Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, *Proc. Natl. Acad. Sci. U.S.A.*, 107, 6634–6639, 2010.
- Smith, J. N., Dunn, M. J., VanReken, T. M., Iida, K., Stolzenburg, M. R., McMurry, P. H., and Huey, L. G.: Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth, *Geophys. Res. Lett.*, 35, 2008.
- 30 Sorooshian, A., Murphy, S. M., Hersey, S., Gates, H., Padro, L. T., Nenes, A., Brechtel, F. J., Jonsson, H., Flagan, R. C., and Seinfeld, J. H.: Comprehensive airborne characterization of aerosol from a major bovine source, *Atmos. Chem. Phys.*, 8, 5489–5520, 2008.
- Swartz, E., Shi, Q., Davidovits, P., Jayne, J. T., Worsnop, D. R., and Kolb, C. E.: Uptake of Gas-Phase Ammonia. 2. Uptake by Sulfuric Acid Surfaces, *J. Phys. Chem. A*, 103, 8824–8833, 1999.
- 35 Tao, Y., Ye, X., Jiang, S., Yang, X., Chen, J., Xie, Y., and Wang, R.: Effects of amines on particle growth observed in new particle formation events, *J. Geophys. Res. Atmos.*, 121, 324–335, 2016.
- VandenBoer, T. C., Petroff, A., Markovic, M. Z., and Murphy, J. G.: Size distribution of alkyl amines in continental particulate matter and their online detection in the gas and particle phase, *Atmos. Chem. Phys.*, 11, 4319–4332, 2011.
- 40 Wang, L., Lal, V., Khalizov, A. F., and Zhang, R.: Heterogeneous chemistry of alkylamines with sulfuric acid: implications for atmospheric formation of alkylaminium sulfates, *Environ. Sci. Technol.*, 44, 2461–2465, 2010.
- Wexler, A. S. and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H⁺ NH₄⁺ Na⁺ SO₄²⁻ NO₃⁻ Cl⁻ Br⁻ and H₂O, *J. Geophys. Res.*, 107, 2002.

- Yao, X., Lau, A. P., Fang, M., Chan, C. K., and Hu, M.: Size distributions and formation of ionic species in atmospheric particulate pollutants in Beijing, China: 2—dicarboxylic acids, *Atmos. Environ.*, 37, 3001–3007, 2003.
- Yeung, M. C., Lee, A. K. Y., and Chan, C. K.: Phase Transition and Hygroscopic Properties of Internally Mixed Ammonium Sulfate and Adipic Acid (AS-AA) Particles by Optical Microscopic Imaging and Raman Spectroscopy, *Aerosol Sci. Tech.*, 43, 387–399, 2009.
- You, Y., Kanawade, V. P., Gouw, J. A. de, Guenther, A. B., Madronich, S., Sierra-Hernández, M. R., Lawler, M., Smith, J. N., Takahama, S., Ruggeri, G., Koss, A., Olson, K., Baumann, K., Weber, R. J., Nenes, A., Guo, H., Edgerton, E. S., Porcelli, L., Brune, W. H., Goldstein, A. H., and Lee, S.-H.: Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS), *Atmos. Chem. Phys.*, 14, 12181–12194, 2014.
- 10 Youn, J.-S., Crosbie, E., Maudlin, L. C., Wang, Z., and Sorooshian, A.: Dimethylamine as a major alkyl amine species in particles and cloud water: Observations in semi-arid and coastal regions, *Atmos. Environ.*, 122, 250–258, 2015.
- Yu, J. Z., Huang, X.-F., Xu, J. H., and Hu, M.: When Aerosol Sulfate Goes Up, So Does Oxalate: Implication for the Formation Mechanisms of Oxalate, *Environ. Sci. Technol.*, 39, 128–133, 2005.
- 15 Zheng, J., Ma, Y., Chen, M., Zhang, Q., Wang, L., Khalizov, A. F., Yao, L., Wang, Z., Wang, X., and Chen, L.: Measurement of atmospheric amines and ammonia using the high resolution time-of-flight chemical ionization mass spectrometry, *Atmos. Environ.*, 102, 249–259, 2015.

Table 1: Experimental conditions including relative humidity (RH), gas mixing ratios, the maximum neutralization ratios ($X_{\text{max neutral}}$) and neutralization ratios of equilibrated particles (X_{equil}), and the neutralization ratios of equilibrated particles exposed to N_2 for about 5 hours (X_{N_2}).

Experiment	Particle composition	RH	[DMA]	[NH ₃]	Neutralization ratio ^a		
		%	(ppm)		$X_{\text{max neutral}}^{\text{b}}$	X_{equil}	X_{N_2}
NH ₃ ,1.9ppm,10%	H ₂ SO ₄ (aq)	10		1.94 ± 0.13			
NH ₃ ,1.9ppm,50%	H ₂ SO ₄ (aq)	50		1.93 ± 0.12	2.0 ± 0.1	2.0 ± 0.1	
DMA _{0.15} ppm,10%	H ₂ SO ₄ (aq)	10	0.16 ± 0.02		1.5 ± 0.1	1.5 ± 0.1	1.2 ± 0.2
DMA _{0.15} ppm,50%	H ₂ SO ₄ (aq)	50	0.16 ± 0.02		1.7 ± 0.1	1.7 ± 0.1	1.7 ± 0.2
DMA ₁ ppm,10%	H ₂ SO ₄ (aq)	10	1.00 ± 0.11		1.7 ± 0.1	1.5 ± 0.1	1.2 ± 0.1
DMA ₁ ppm,50%	H ₂ SO ₄ (aq)	50	1.00 ± 0.11		1.9 ± 0.1	1.9 ± 0.1	1.7 ± 0.1
0.1 10%	H ₂ SO ₄ (aq)	10	0.14 ± 0.01	1.89 ± 0.04	2.0 ± 0.1	2.0 ± 0.2	2.0 ± 0.4
0.1 50%	H ₂ SO ₄ (aq)	50	0.14 ± 0.01	1.89 ± 0.04	2.0 ± 0.1	2.0 ± 0.2	1.9 ± 0.1
0.5 10%	H ₂ SO ₄ (aq)	10	0.89 ± 0.03	1.93 ± 0.13	2.0 ± 0.1	1.9 ± 0.2	1.9 ± 0.2
0.5 50%	H ₂ SO ₄ (aq)	50	0.89 ± 0.04	1.83 ± 0.04	2.0 ± 0.1	1.8 ± 0.1	1.7 ± 0.2
ox0.5 10%	H ₂ C ₂ O ₄ (s)	10	0.89 ± 0.04	1.82 ± 0.03	0.3 ± 0.1	0.3 ± 0.1	
ox0.5 70%	H ₂ C ₂ O ₄ (aq)	70	0.96 ± 0.00	1.86 ± 0.01	1.9 ± 0.2	1.9 ± 0.2	

- 5 ^aThe neutralization ratio is defined as the number of moles of alkaline species over moles of acidic species, $X = (\text{DMAH} + \text{NH}_4) / \text{SO}_4$ or $X = (\text{DMAH} + \text{NH}_4) / \text{C}_2\text{O}_4$. ^b For co-uptake experiments $X_{\text{max neutral}}$ describes the maximum neutralization ratio of particles before reaching equilibrium.

Table 2: Comparison of DMA/NH₃ (gas) molar ratios at different RH and DMAH/NH₄ (particle) ratios at different times (t), as well as the displacement percentage (χ) for DMAH⁺ (10% RH) and NH₄⁺ (50% RH) are given.

Experiment	RH	DMA/ NH ₃	DMAH/NH ₄				Displacement percentage ^e	
	%		$t_{\text{initial}}^{\text{a}}$	t_{pc}^{b}	$t_{\text{neutral}}^{\text{c}}$	$t_{\text{equil}}^{\text{d}}$	χ_{DMAH^+}	$\chi_{\text{NH}_4^+}$
0.1 _{10%}	10	0.07 ± 0.01	0.07 ± 0.01	0.05 ± 0.01	0.03 ± 0.00	0.02 ± 0.00	42%	
0.1 _{50%}	50	0.07 ± 0.01	0.08 ± 0.01		0.07 ± 0.01	0.18 ± 0.02		9%
0.5 _{10%}	10	0.46 ± 0.04	0.43 ± 0.04	0.27 ± 0.01	0.19 ± 0.01	0.02 ± 0.00	89%	
0.5 _{50%}	50	0.49 ± 0.02	0.34 ± 0.02		0.51 ± 0.04	1.77 ± 0.13		50%
ox0.5 _{10%}	10	0.49 ± 0.02	0.25 ± 0.03		0.25 ± 0.03	0.17 ± 0.04		
ox0.5 _{10%}	70	0.52 ± 0.52	0.34 ± 0.02	0.34 ± 0.02	0.26 ± 0.01	0.09 ± 0.02		

^a t_{initial} indicates the time of the first measurement (10-15 min); ^b t_{pc} indicates the time when the majority of particles changed from liquid to solid phase, ^c t_{neutral} indicates the time when particles reached (maximum) neutralization, ^d t_{equil} indicates the time when the particle composition reached equilibrium, ^e The displacement percentage χ_{DMAH^+} denotes n_{DMAH^+} per particle at time t_{pc} over time t_{equil} ; $\chi_{\text{NH}_4^+}$ denotes $n_{\text{NH}_4^+}$ per particle at time t_{neutral} over t_{equil} ;

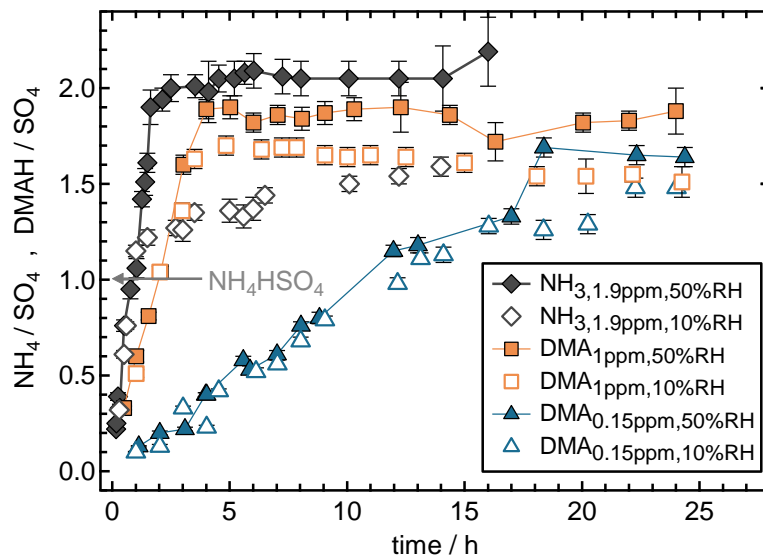


Figure 1: Single gas uptake of NH_3 (1.9 ppm) and DMA (1 ppm and 0.15 ppm) into H_2SO_4 , at 10% and 50% RH. $\text{NH}_4^+/\text{SO}_4$ and DMAH/SO_4 denote molar ratios of NH_3 or DMA species to total sulfate species in the particle.

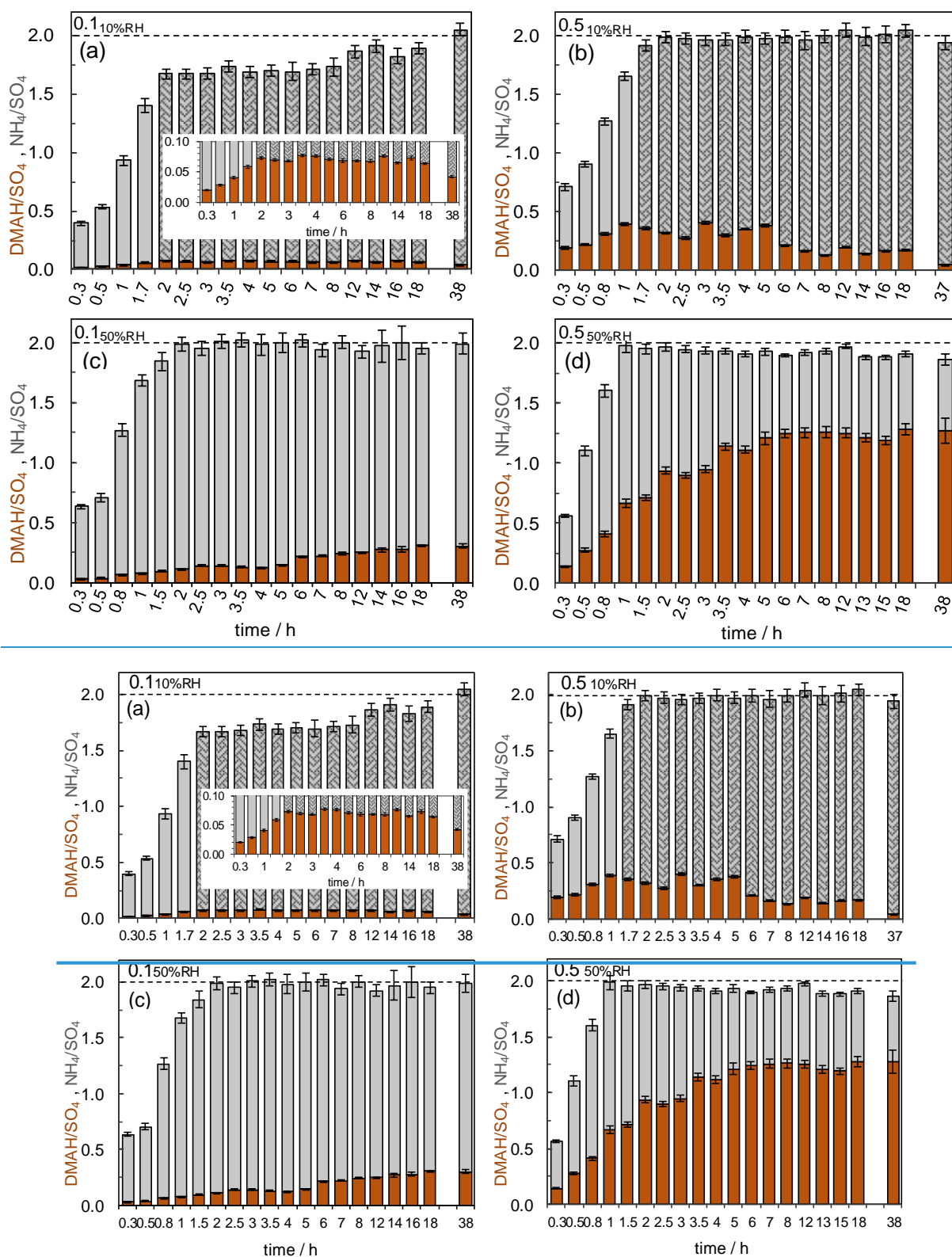
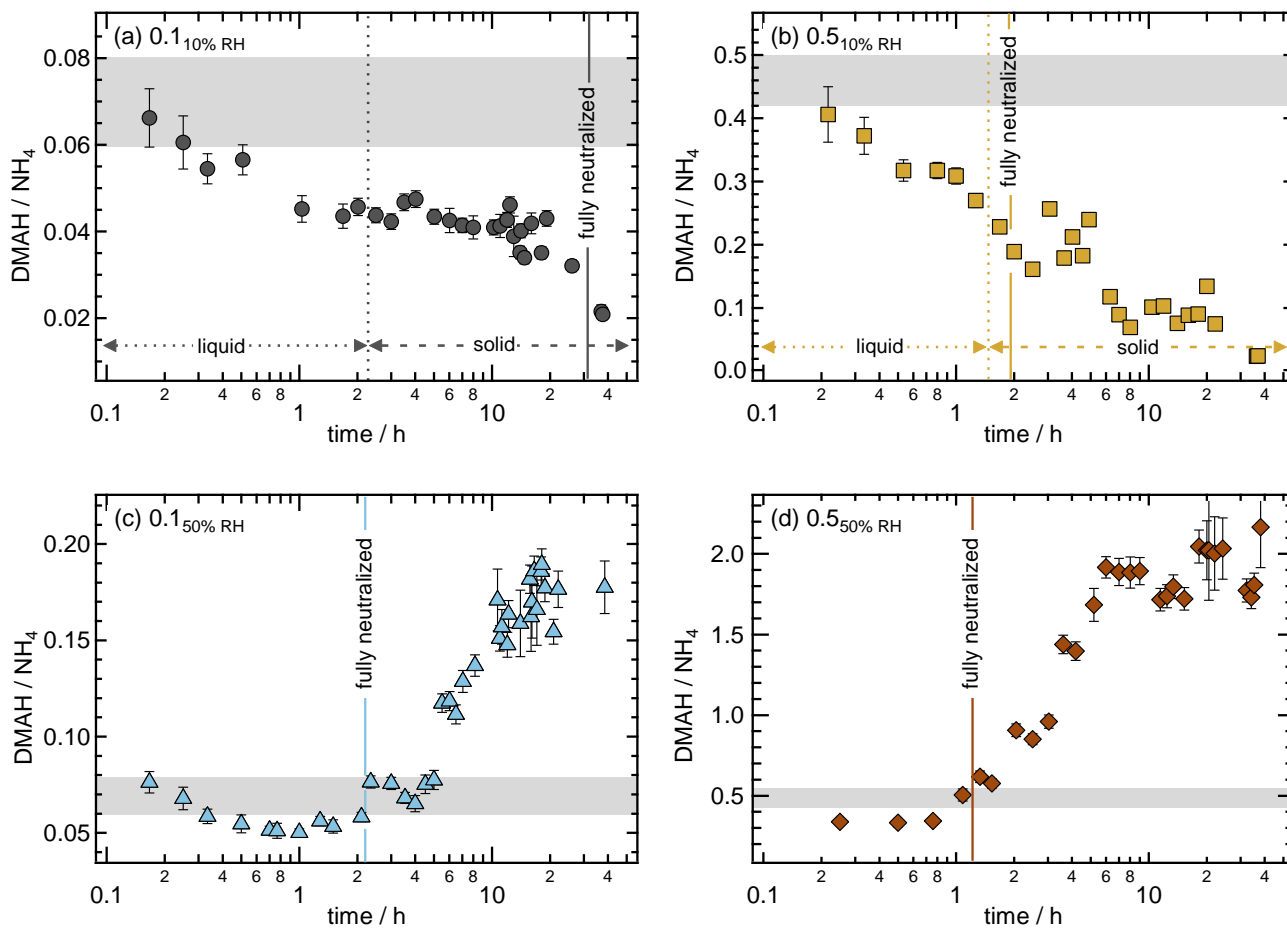


Figure 2: DMA- NH_3 co-uptake of DMA and NH_3 into H_2SO_4 as a function of time: a) $\text{DMA}/\text{NH}_3 = 0.07$ at 10% RH (0.1_{10%}), b) $\text{DMA}/\text{NH}_3 = 0.46$ at 10% RH (0.5_{10%}), c) $\text{DMA}/\text{NH}_3 = 0.07$ at 50% RH (0.1_{50%}), and d) $\text{DMA}/\text{NH}_3 = 0.49$ at 50% RH (0.5_{50%}). A value of two indicates complete neutralization of H_2SO_4 . Contributions of DMAH^+ (brown) and NH_4^+ (grey) to the neutralization are shown as molar ratios (DMAH/SO_4 and NH_4/SO_4). Crosshatched NH_4^+ bars indicate that the majority of particles underwent phase transition from liquid to solid. The inner graph in Fig. 2a is a magnified view of the DMAH^+ -fraction.



5 **Figure 3: Particulate DMAH/NH₄ molar ratios as a function of time for DMA- NH₃ co-uptake at a) DMA/NH₃ = 0.07 at 10% RH (0.1_{10%}), b) DMA/NH₃ = 0.46 at 10% RH (0.5_{10%}), c) DMA/NH₃ = 0.07 at 50% RH (0.1_{50%}), and d) DMA/NH₃ = 0.49 at 50% RH (0.5_{50%}). DMA/NH₃ gas molar ratios (including uncertainties) are indicated by the grey bands. Dashed vertical lines indicate that the majority of particles underwent phase transition from liquid to solid. Solid vertical lines indicate that particles reached a neutralization ratio of two. Uncertainties from ion chromatography analysis are displayed on the vertical axis unless they are smaller than the symbols.**

10

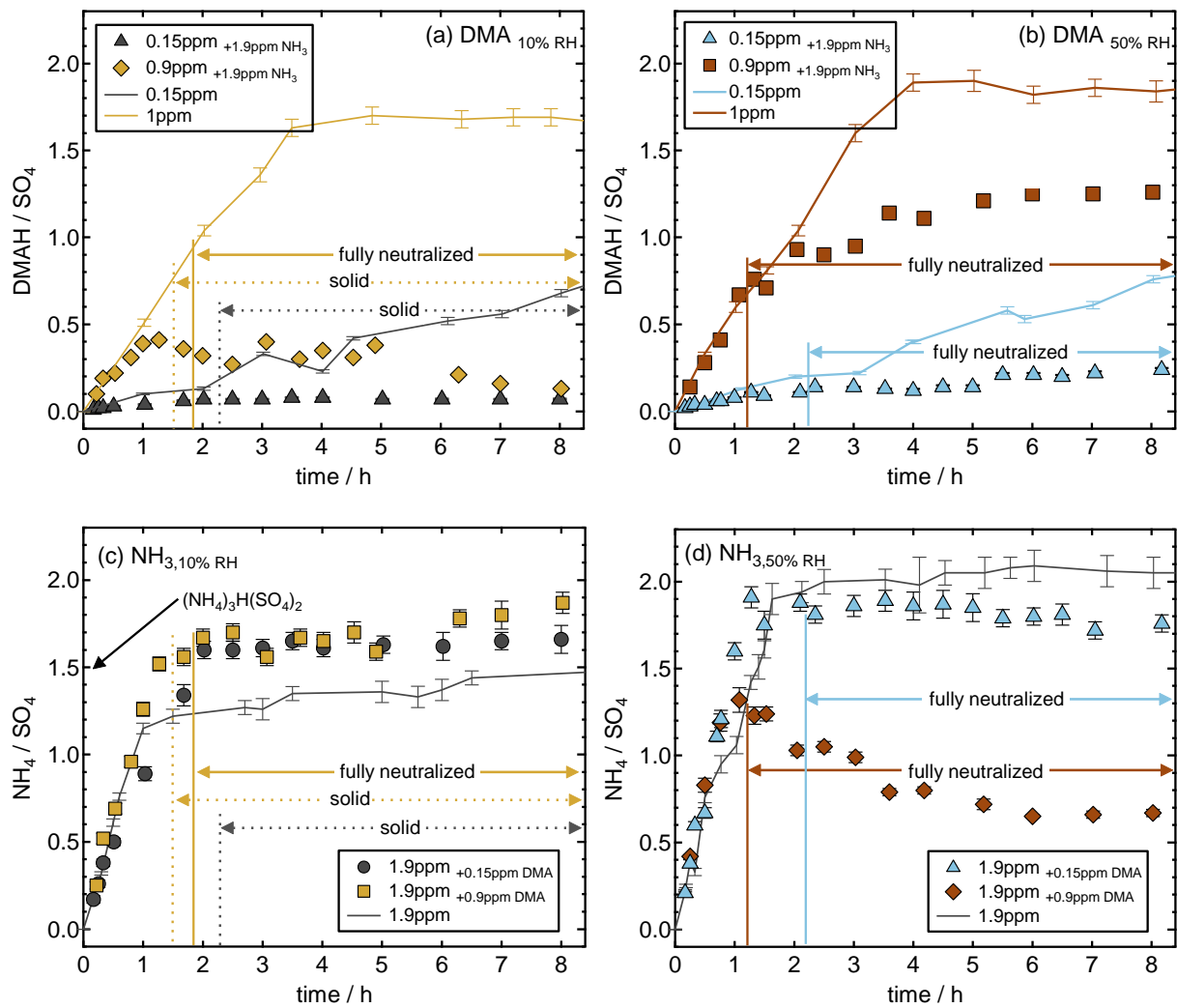


Figure 4: Comparison of particulate DMAH/SO₄ (a, b) and NH₄/SO₄ (c, d) in single gas uptake (line) vs. DMA- NH₃ co-uptake (symbols) into H₂SO₄ at 10% RH (a,c) and 50% RH (b, d), in the first 8 hours of reaction. Dashed vertical lines indicate phase transition of the majority of particles. Solid vertical lines indicate that particles reached a neutralization ratio of two. Uncertainties from ion chromatography analysis are displayed on the vertical axis unless they are smaller than the symbols.

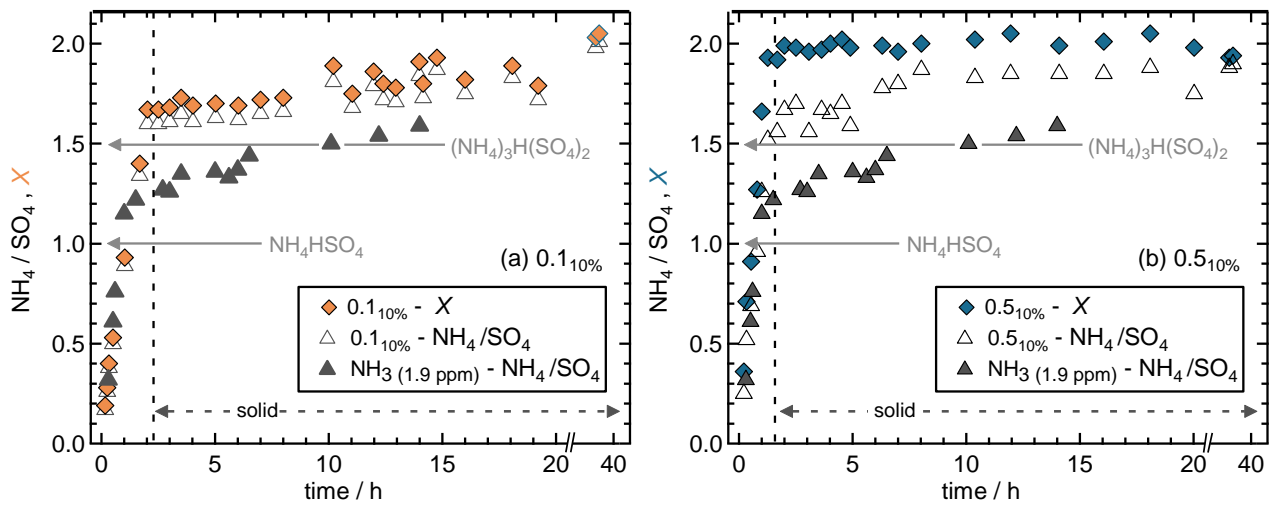


Figure 5: Comparison of particulate NH_4/SO_4 in single gas uptake (filled triangles) vs. DMA-- NH_3 co-uptake (open triangles) experiments at 10% RH into H_2SO_4 : a) $\text{DMA}/\text{NH}_3 = 0.07$, and b) $\text{DMA}/\text{NH}_3 = 0.46$. Diamonds denote the net-uptake neutralization ratio (X) in co-uptake experiments. Error bars are omitted for clarity.

5

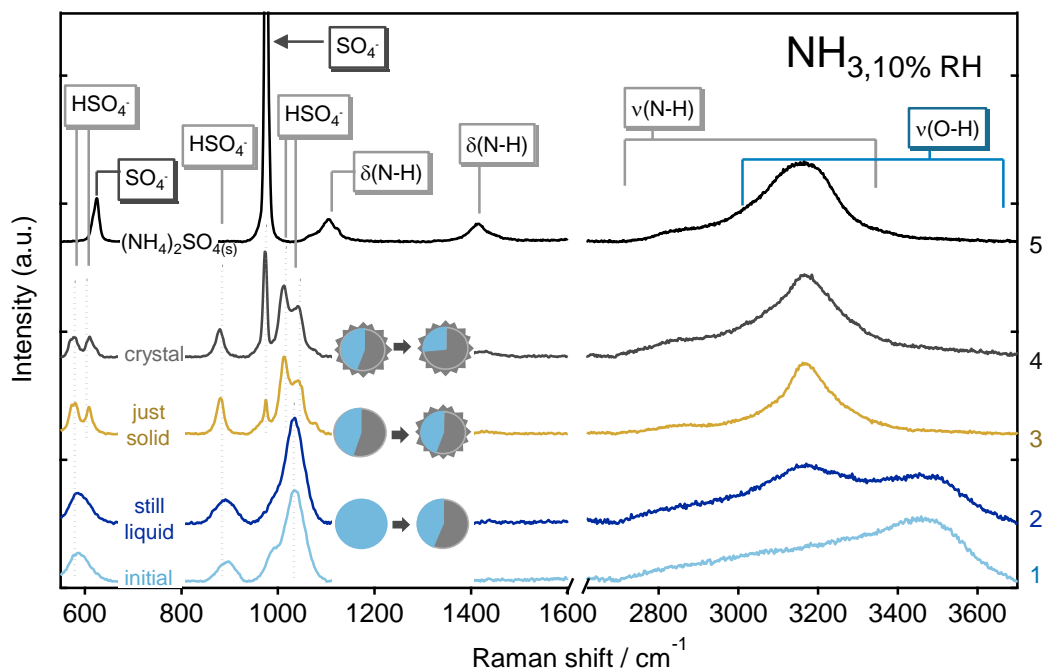


Figure 6: Raman spectra of selected particles representing different phase states during uptake of NH_3 into H_2SO_4 at 10% RH. A spectrum of crystalline $(\text{NH}_4)_2\text{SO}_4$ is added for reference. Sketches indicate the cation composition range (as inferred from IC measurements) of particles when the spectra were recorded; grey denotes NH_4^+ and blue denotes H_3O^+ (HSO_4^-).

5

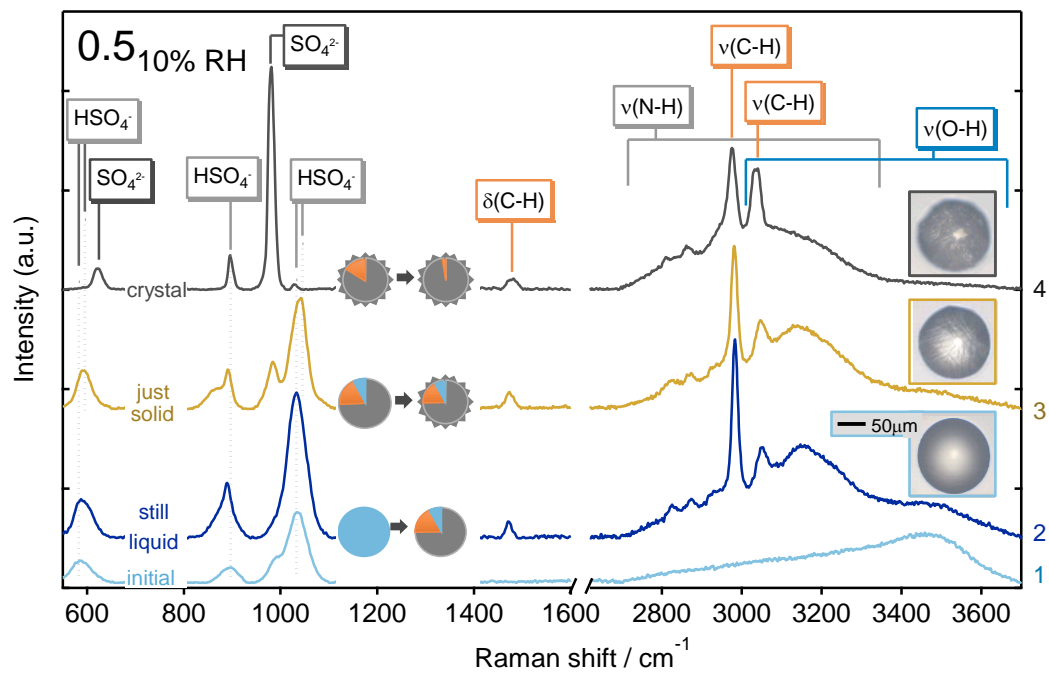


Figure 7: Raman spectra and morphological changes of selected particles during DMA- NH₃ co-uptake into H₂SO₄ at 10% RH at a DMA/NH₃ molar ratio of 0.46 (0.5_{10%}). Sketches indicate the cation composition range (as inferred from IC measurements) of particles when the spectra were recorded. Orange denotes DMAH⁺, grey denotes NH₄⁺, and blue denotes H₃O⁺ (HSO₄⁻).

5

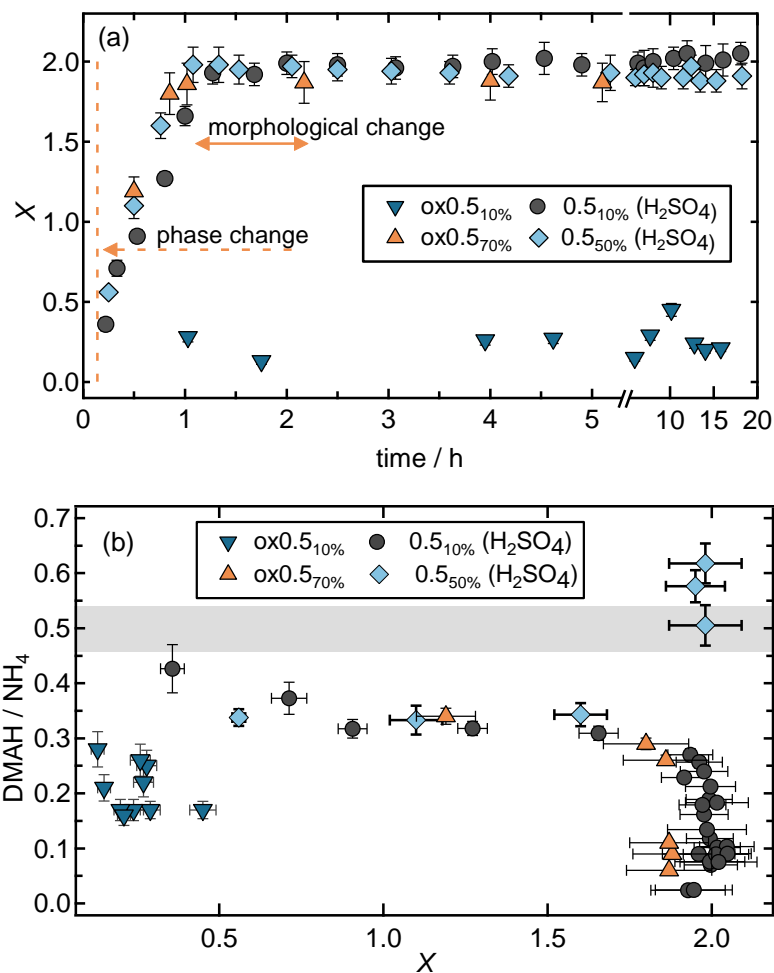


Figure 8: DMA-NH₃ co-uptake at DMA/NH₃ gas molar ratios of 0.5 (given in Table 1) into sulfuric and oxalic acid particles at 10%, 50% and 70% RH. a) Neutralization ratios as a function of time. The vertical dotted line indicates that the majority of oxalic acid particles at 70% RH underwent phase transition from liquid to solid; the vertical solid line indicates the morphological transformation of oxalic acid particles from a non-crystalline to a crystalline morphology at 70% RH. b) DMAH/NH₄ ratios as a function of particle neutralization ratio; the shaded area indicates the gas phase molar ratio of DMA/NH₃ (including uncertainties).

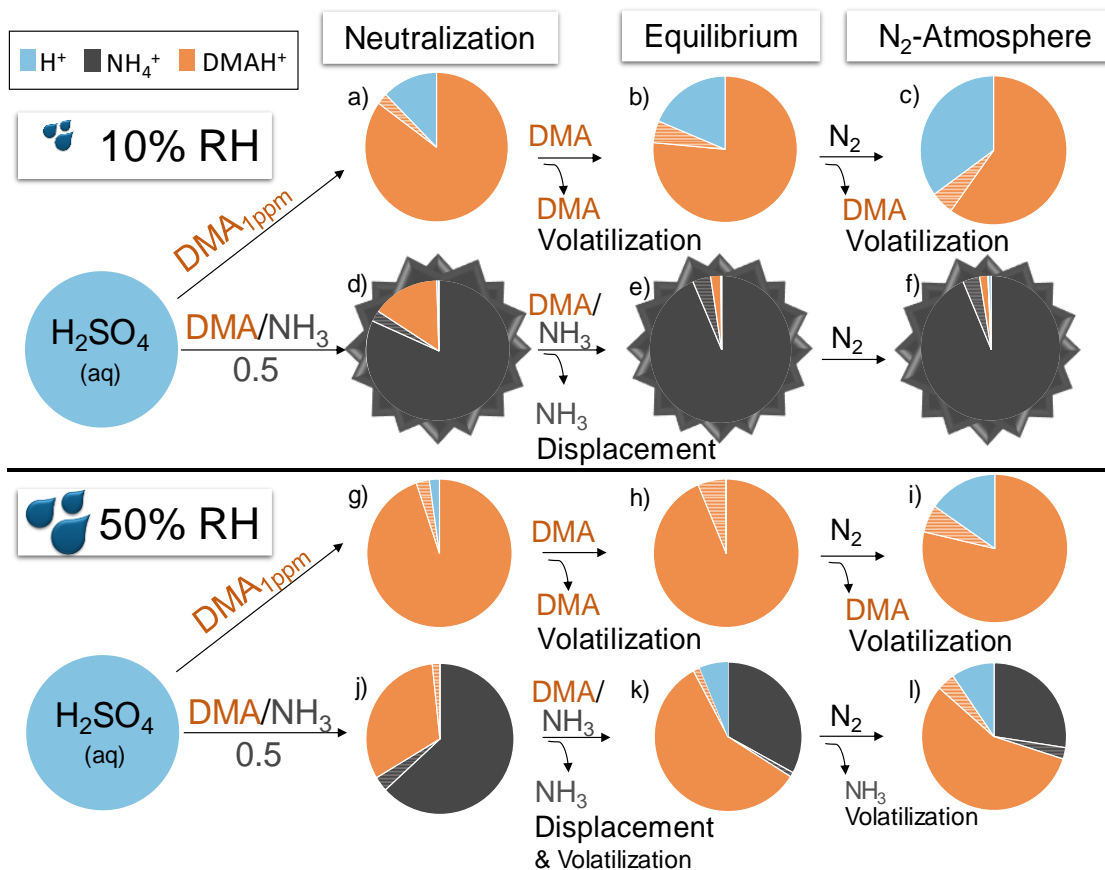


Figure 9: Particle neutralization ratios and the proportion of each cation at maximum neutralization (first column), equilibrium (second column), and after exposure of equilibrated particles to N₂ gas (third column). Color scheme: orange represents DMAH⁺, grey represents NH₄⁺, shaded areas indicate uncertainty of the respective species, and blue represents H₃O⁺ (HSO₄⁻). Stars around pie charts indicate that particles were crystalline solids. Concentrations of DMA and NH₃ are shown in Table 1.