



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

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Abstract. Heterogeneous uptake is one of the major mechanisms governing the amounts of short-chain alkylamines and ammonia (NH_3) 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 NH_3 into sulfuric and oxalic acid particles at gaseous DMA/ NH_3 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 show that the particulate dimethylaminium/ammonium molar ratios ($\text{DMAH}^+/\text{NH}_4^+$) changed substantially during the uptake process, which was severely influenced by the extent of neutralisation and the particle phase state. In general, DMA uptake and NH_3 uptake into concentrated H_2SO_4 droplets were initially similarly efficient, yielding $\text{DMAH}^+/\text{NH}_4^+$ ratios that were similar to DMA/ NH_3 ratios. As the co-uptake continued, the $\text{DMAH}^+/\text{NH}_4^+$ gradually dropped due to a preferential uptake of NH_3 into partially neutralised acidic droplets. At 50 % RH, once the sulfate droplets were neutralised, the stronger base DMA displaced some of the ammonium absorbed earlier, leading to $\text{DMAH}^+/\text{NH}_4^+$ ratios up to four times higher than the corresponding gas phase ratios. However, at 10 % RH, crystallisation of partially neutralised sulfate particles prevented further DMA uptake, while NH_3 uptake continued and displaced DMAH^+ , forming almost pure ammonium sulfate. Displacement of DMAH^+ by NH_3 has also been observed in neutralised, solid oxalate particles. The results can explain why $\text{DMAH}^+/\text{NH}_4^+$ ratios in ambient liq-

uid aerosols can be larger than DMA/ NH_3 , despite an excess of NH_3 in the gas phase. An uptake of DMA to aerosols consisting of crystalline ammonium salts, however, is unlikely, even at comparable DMA and NH_3 gas phase concentrations.

1 Introduction

NH_3 and short-chain alkylamines (R_3N) gases are frequently detected in the atmosphere. Total emissions of NH_3 largely dominate those of R_3N (Schade and Crutzen, 1995). The characteristic ambient mixing ratios of NH_3 and R_3N are of 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 R_3N such as agricultural and industrial activities also release NH_3 (Behra et al., 2013). Hence, elevated R_3N gas concentrations are likely accompanied by enhanced concentrations of NH_3 (Schade and Crutzen, 1995; Zheng et al., 2015). Despite the 2 to 3 orders of magnitude difference in gas phase concentration, particle phase aminium-to-ammonium ($\text{R}_3\text{NH}^+/\text{NH}_4^+$) molar ratios of up to 0.2 have been detected. For instance, average $\text{R}_3\text{NH}^+/\text{NH}_4^+$ molar ratios were measured: 0.0045–0.17 in $\text{PM}_{1.8}$ in urban and rural continental air masses over urban and rural sites in Ontario, Canada (VandenBoer et al., 2011), 0.02 in $\text{PM}_{1.0}$ 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 R_3NH/NH_4 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 replace NH_4^+ from ammonium-sulfuric acid clusters (Bzdek et al., 2010a, b) 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, 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 aerosols, as well as in marine aerosols (Müller et al., 2009; VandenBoer et al., 2011; Youn et al., 2015). These aminium 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 aminium 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 R_3NH/NH_4 molar ratios. A second peak of R_3NH/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-aminium 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 aminium sulfates remain in 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 R_3NH/NH_4 ratio are consequently less acidic and could absorb more water than ammonium sulfate ($(NH_4)_2SO_4$), 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, b, 2011; Wang et al., 2010; Qiu et al., 2011; Chan and Chan, 2012) into acidic particles, none have been written 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, aminium R_3NH^+ ions can still dominate NH_4^+ in 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 an 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 period and phase state identification as well as 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 neutralisation and the change in phase state on the uptake behaviour 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 the ability to form a non-crystallising DMAS droplet even at low RH (Chan and Chan, 2013) and a 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 set-up (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 analysed 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, the system was conditioned for several hours to minimise wall losses of either one or both gases prior to the uptake experiment (see Supplement for detailed descriptions). A schematic of the experimental set-up is shown in Fig. S1 in the Supplement.

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.

A 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 $\text{H}_2\text{C}_2\text{O}_4$. We abbreviate these experimental conditions for uptake into H_2SO_4 as 0.1₁₀ %, 0.5₁₀ %, 0.1₅₀ % and 0.5₅₀ %, and for uptake into $\text{H}_2\text{C}_2\text{O}_4$ as ox0.5₁₀ % and ox0.5₇₀ %. Four 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 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 % H_2SO_4 or highly concentrated $\text{H}_2\text{C}_2\text{O}_4$ were prepared from ultrapure water (18.2 M Ω) and concentrated H_2SO_4 (97 wt %, Acros Organics, titrated against standardised NaOH) or $\text{H}_2\text{C}_2\text{O}_4$ powder (99 %, Aldrich). For each experiment, a few millilitres of the solution were drawn into a piezoelectric particle generator (MicroFab Tech., Inc.). 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 N_2

($\sim 1000 \text{ cm}^3 \text{ min}^{-1}$) 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 the films took place inside a glove bag (GLOVEBAG, Glas Col®) to avoid exposure of the samples to room air and humidity levels.

2.3 Particle analysis

For each condition, the experiment was repeated at different time intervals to complete one time series. The samples were removed from the cell and submerged in $\sim 12 \text{ mL}$ 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).

IC yields total values for DMA and NH_3 species, and hence the distribution between molecules and ions in the samples could not be determined. In the following we use DMAH to represent $n\text{NH}_2(\text{CH}_3)_2^+ + n\text{NH}(\text{CH}_3)_2$ and NH_4 to represent $n\text{NH}_4^+ + n\text{NH}_3$ 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 $\text{SO}_4 = n\text{H}_2\text{SO}_4 + n\text{HSO}_4^- + n\text{SO}_4^{2-}$, and the total oxalate is indicated by C_2O_4 . Molar ratios in the particle phase are accordingly denoted by DMAH / NH_4 , DMAH / SO_4 and NH_4 / SO_4 , while gaseous molar ratios are denoted by DMA / NH_3 .

DMAH concentrations of the first measurement points for particles in the 0.1₁₀ % and 0.1₅₀ % conditions lie at the lower end of the IC calibration range. A conservative estimation of uncertainty up to 15 % for these values would decrease the DMAH / NH_4 ratio by 0.02, which has negligible impacts on the observed trends and values. The uncertainties 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.

After 35–38 h, 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 N_2 atmosphere for > 5 h prior to IC analysis to further investigate their compositional stability in an amine- and ammonia-free environment.

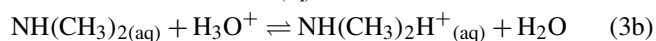
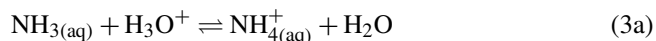
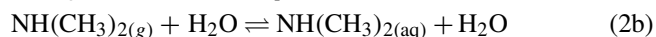
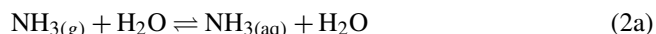
Furthermore, uptake experiments at 0.5₁₀ % and of NH_3 at 10 % RH were repeated with particles of 60–200 μm in size in flow cells equipped with a quartz window to track alterations in chemical composition and concurrent morphological changes with a Raman microscope (Renishaw RM series) as described by 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 interrelated 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 neutralisation, the extent of DMA and NH₃ uptake may change. Here, the extent of (stoichiometric) neutralisation 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 neutralisation ratio. In the course of the uptake experiments, the neutralisation ratio ranged from highly acidic ($X = 0$) to neutral ($X = 2$). However, not all equilibrated particles were completely neutralised, as will be further discussed in Sect. 3.4.

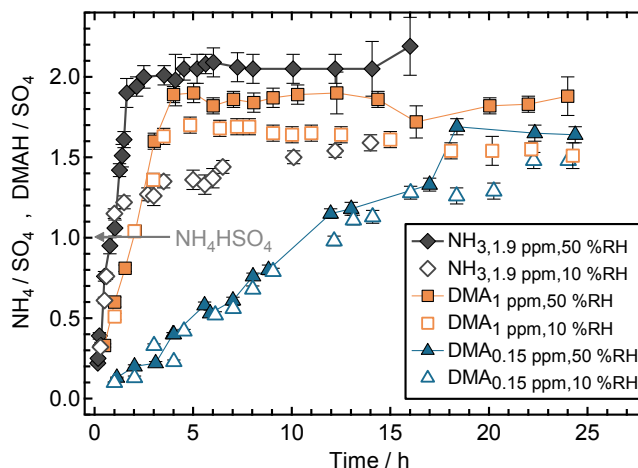


Figure 1. Single-gas uptake of NH₃ (1.9 ppm) and DMA (1 and 0.15 ppm) into H₂SO₄, at 10 and 50 % RH. NH₄ / SO₄ and DMAH / SO₄ denote molar ratios of NH₃ or DMA species to total sulfate species in the particle.

3.1 Single-gas uptake

At 50 % RH, the uptake of NH₃ fully neutralised the H₂SO₄ droplets within 2 h, 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 crystallisation significantly retarded the subsequent uptake. The continued increase in particulate NH₄, even after crystallisation, indicates that crystalline acidic particles were still susceptible to uptake, but imposed bulk diffusion limitations that retarded the uptake. Neutralisation was not complete within the measured period of 15 h.

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 it approached equilibrium at DMAH / SO₄ ratios of 1.5 ± 0.1 at 10 % RH, and 1.7 ± 0.1 (DMA_{0.15} ppm) and 1.9 ± 0.1 (DMA₁ ppm) 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-aminium sulfates were described as hygroscopic, non-crystallising salts at RH ≤ 10 % (Qiu and Zhang, 2012; Chan and Chan, 2013; Chu et al., 2015). Furthermore, these studies showed that upon drying synthesised 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.

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

Experiment	Particle composition	RH	[DMA]	[NH ₃]	Neutralisation ratio ^a		
		%	(ppm)		X_{\max}^b neutral	X_{equil}	X_{N_2}
NH ₃ , 1.9 ppm, 10 %	H ₂ SO ₄ (aq)	10		1.94 ± 0.13			
NH ₃ , 1.9 ppm, 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	

^a The neutralisation 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_{\max} neutral describes the maximum neutralisation 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 ^c	
			t_{initial}^a	t_{pc}^b	t_{neutral}^c	t_{equil}^d	χ_{DMAH}	χ_{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 ₇₀ %	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) neutralisation. ^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} ; χ_{NH_4} denotes n_{NH_4} per particle at time t_{neutral} over t_{equil} .

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 h (for 0.5₁₀ % and 0.1₁₀ %, respectively) to completely neutralise sulfate. Upon reaching neutralisation, 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 SO₄^{2−} was completely neutralised (Fig. 2c and d) within 1–2 h. Neutralisation in droplets was followed by a partial displacement of NH₄ by DMA, reaching a final equi-

librium 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 neutralisation 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 effec-

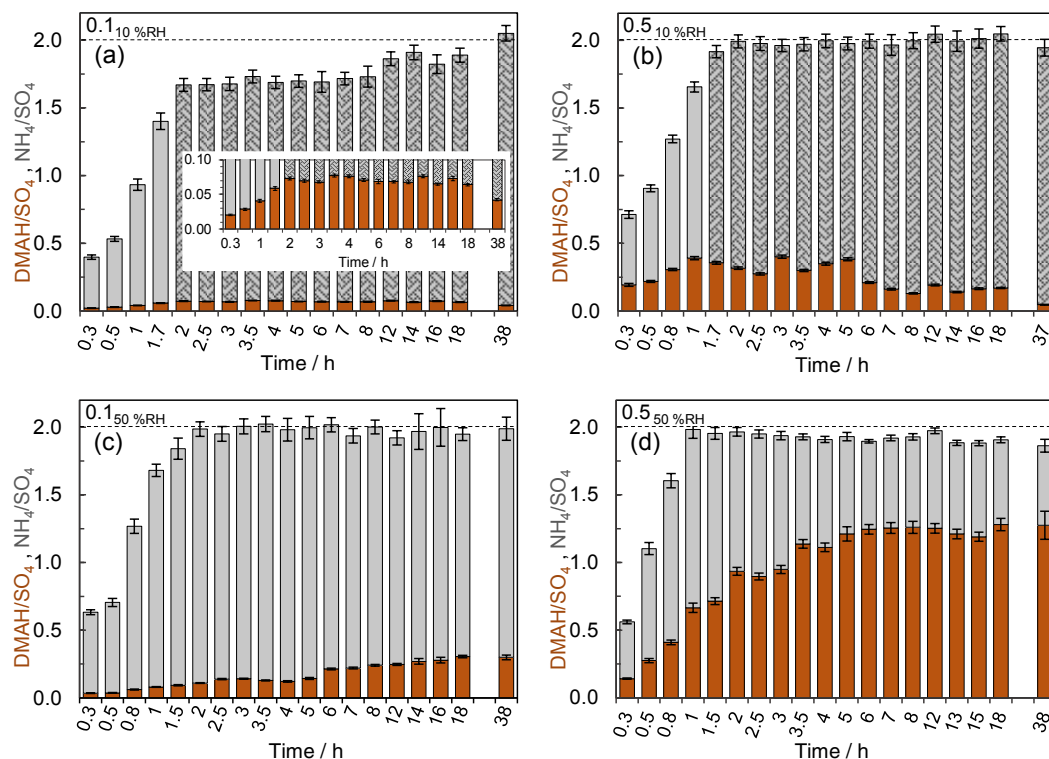


Figure 2. Co-uptake of DMA and NH_3 into H_2SO_4 as a function of time: (a) $\text{DMA} / \text{NH}_3 = 0.07$ at 10 % RH ($0.1_{10\%}$), (b) $\text{DMA} / \text{NH}_3 = 0.46$ at 10 % RH ($0.5_{10\%}$), (c) $\text{DMA} / \text{NH}_3 = 0.07$ at 50 % RH ($0.1_{50\%}$) and (d) $\text{DMA} / \text{NH}_3 = 0.49$ at 50 % RH ($0.5_{50\%}$). A value of two indicates complete neutralisation of H_2SO_4 . Contributions of DMAH (brown) and NH_4 (grey) to the neutralisation are shown as molar ratios ($\text{DMAH} / \text{SO}_4$ and $\text{NH}_4 / \text{SO}_4$). Crosshatched NH_4 bars indicate that the majority of particles underwent phase transition from liquid to solid. The inner graph in (a) is a magnified view of the DMAH fraction.

tively into highly concentrated H_2SO_4 . For instance, in panels a and b the $\text{DMAH} / \text{NH}_4$ ratios in the acidic droplets were 0.07 ± 0.01 and 0.43 ± 0.04 , comparable to gaseous DMA / NH_3 ratios of 0.07 and 0.46, respectively. Starting from the second measured values, a clear decrease in $\text{DMAH} / \text{NH}_4$ 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.

Swartz et al. (1999) measured the heterogeneous uptake of NH_3 into a chain of 70 and 40 wt % H_2SO_4 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 H_2SO_4 at $\text{pH} < 0$ was attributed to surface reactions, i.e. NH_3 molecules reacting with interfacial hydronium ions (H_3O^+) without prior solvation (Swartz et al., 1999). As H_2SO_4 droplets in the present study have a solution $\text{pH} \leq -0.9$ (Wexler and Clegg, 2002) at both 50 % RH

(43 wt % H_2SO_4) and 10 % RH (64 wt % H_2SO_4), protonation without prior dissolution may take place for NH_3 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 H_2SO_4 of ≥ 62 wt % (≤ 10 % RH) at 283 K. The coefficient is noticeably smaller than that of close to unity reported for NH_3 uptake into H_2SO_4 with similar acidity levels (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 $\text{DMAH} / \text{NH}_4$ ratios decreased by 30–40 % for all experimental conditions within the first 1–2 h (Fig. 3a–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 neutralisation 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.,

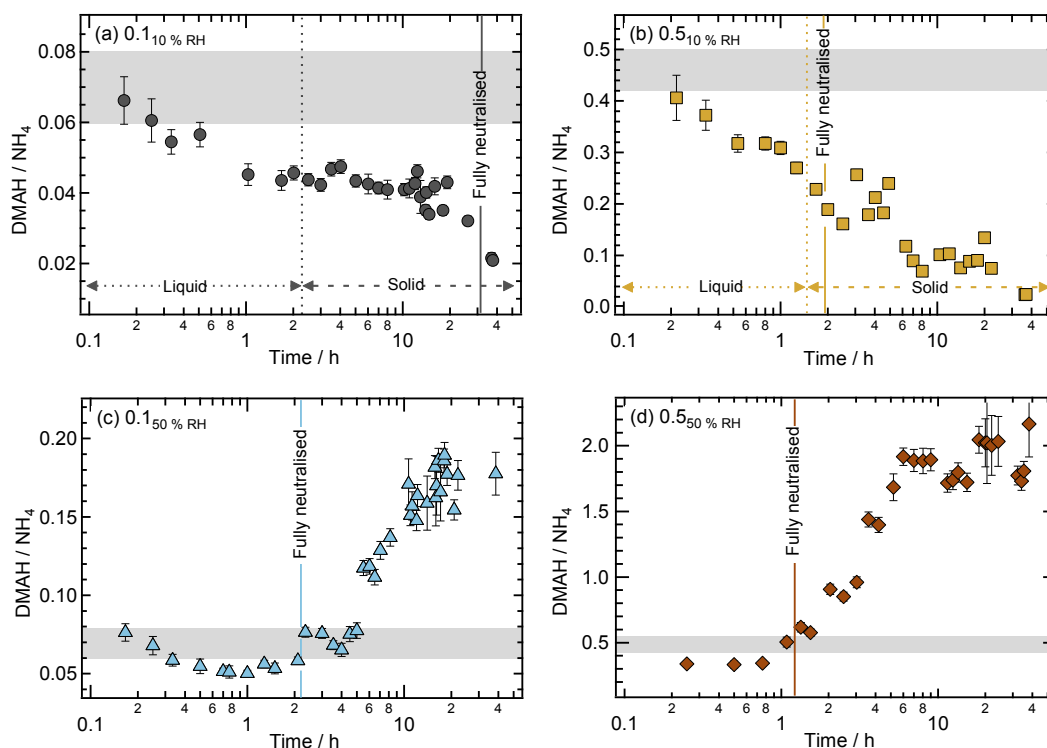


Figure 3. Particulate DMAH/NH₄ molar ratios as a function of time for DMA–NH₃ co-uptake at (a) DMA/NH₃ = 0.07 at 10 % RH (0.1₁₀ %), (b) DMA/NH₃ = 0.46 at 10 % RH (0.5₁₀ %), (c) DMA/NH₃ = 0.07 at 50 % RH (0.1₅₀ %) and (d) DMA/NH₃ = 0.49 at 50 % RH (0.5₅₀ %). DMA/NH₃ gas molar ratios (including uncertainties) 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 neutralisation ratio of two. Uncertainties from ion chromatography analysis are displayed on the vertical axis unless they are smaller than the symbols.

1993), DMA gas molecules might, similarly to NH₃, have a high affinity to interfacial H₃O⁺. Surface protonation on fresh H₂SO₄ particles may thus be important for the initial uptake of both NH₃ and DMA, which could explain why the initial particle phase ratio is equal to the gas phase ratio.

Swartz et al. (1999) reported a threshold of pH ≤ 0 for the occurrence of surface protonation and a drop in γ_{NH₃} by 1 order of magnitude when the pH was increased to above zero. Hanson and Kosciuch (2003) observed a similar drop in γ_{NH₃} during the uptake of NH₃ into H₂SO₄, when the solution approached ammonium bisulfate (NH₄HSO₄) composition. Using the E-AIM model (Wexler and Clegg, 2002, www.aim.env.uea.ac.uk/aim) we estimated that *n*H₃O⁺ decreased by about 40 % as the neutralisation ratio increased from *X* = 0 (H₂SO₄ droplets) to 0.5. Once the particles were half neutralised (*X* = 1, bisulfate stoichiometry), the solution pH was estimated to exceed zero. Hence, if we assume a similar threshold to the one reported by Swartz et al. (1999), surface protonation (Eq. 1a and b) may no longer be relevant when particles approached bisulfate composition.

Despite the increase in pH when neutralisation ratios exceeded unity (*X* = 1), there were sufficient amounts of H₃O⁺ to support the uptake of both gases. Hence, the presence of NH₃ gas molecules at a concentration 14 times higher

than DMA had little effect on the uptake of DMA into acidic particles. The same can be said for DMA, which seemed to not have influenced NH₃ partitioning into acidic droplets. This finding clearly differentiates the group of hydrophilic R₃N from more hydrophobic organics such as hexadecane, hexadecanol (Daumer et al., 1992) or typical atmospheric organic vapour (Liggio et al., 2011), which form an organic film that limits the access of NH₃ to the inorganic core.

The independent uptake of DMA and NH₃ at 10 % RH prevailed until the particles underwent phase change (Fig. 4a and c, dotted lines). Once particles effloresced, a preferential uptake of NH₃ was observed, which resulted in a significant drop in DMAH/NH₄ (Fig. 3a and b), as discussed in Sect. 3.2.3. At 50 % RH the uptakes of DMA and NH₃ were independent from each other until the particles reached complete neutralisation (*X* = 2.0) (Fig. 4b and d, solid lines). Once neutralised, only DMA uptake continued (Fig. 4b) with concurrent displacement of NH₄ (Fig. 4d), as discussed next.

3.2.2 Displacement of NH₄ from neutralised droplets

When approaching full neutralisation, where both gases started to compete for limited available H₃O⁺ ions, the DMAH/NH₄ ratios in droplets of the 0.1₅₀ % and 0.5₅₀ %

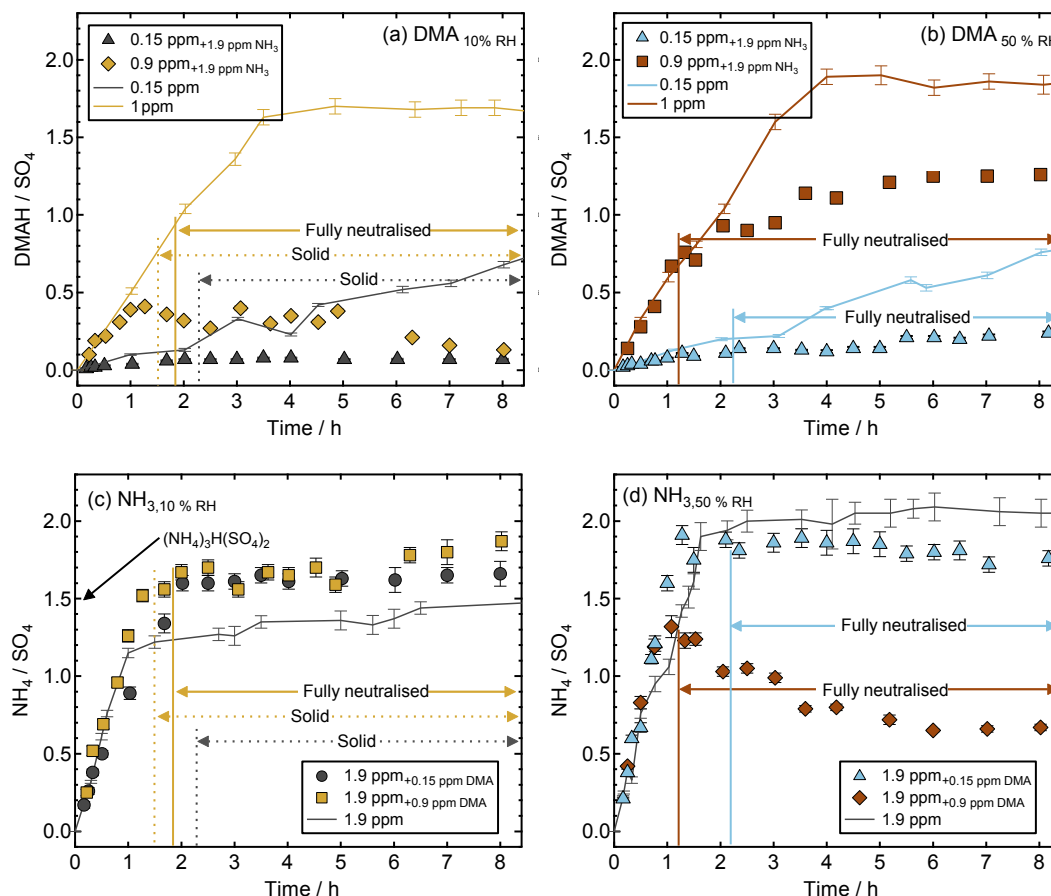


Figure 4. Comparison of particulate DMAH / SO₄ (a, b) and NH₄ / SO₄ (c, d) in single-gas uptake (line) vs. DMA-NH₃ co-uptake (symbols) into H₂SO₄ at 10 % RH (a, c) and 50 % RH (b, d), in the first 8 h of reaction. Dashed vertical lines indicate phase transition of the majority of particles. Solid vertical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

experiments started to increase (Fig. 3c and d, solid line). In solution, DMA ($pK_a = 10.64$; Hall, 1957) is a stronger base than NH₃ ($pK_a = 9.21$). Consequently it has a higher affinity for H₃O⁺ than NH₃ does. Thus, while the fraction of DMA species gradually increased, some of the NH₄ dissociated (Eq. 3a, reverse reaction) and NH₃ was released back to the gas phase (Eq. 2a, reverse reaction).

Similar displacement of NH₄ by alkylamines 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). Lloyd et al. (2009) observed the displacement of NH₄ by trimethylamine (TMA) from water-coated NH₄NO₃ nanoparticles despite an excess of NH₃ gas ($nTMA_{(g)} / nNH_{3(g)} = 0.1$), although they did not report the percentage of displaced NH₄. Their gas phase conditions were comparable to our experiment at 0.15₅₀%. In our experiment DMA was able to displace about 9 % of the initially absorbed NH₄ (Table 2, χ_{NH_4}). The equilibrium DMAH / NH₄ ratio in the 0.15₅₀% 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 in the 0.5₅₀% experiment equilibrated at a DMAH / NH₄ ratio of 1.77 ± 0.13 ; hence they are 3–4 times higher than the gas ratio, with 50 % of the initially absorbed NH₄ displaced (Table 2). Yet it should be noted that equilibrated particles at 0.5₅₀% possessed a neutralisation ratio of only $X = 1.8 \pm 0.1$; hence the particle was incompletely neutralised (see Sect. 3.4) despite the presence of 1.9 ppm NH₃ and 0.9 ppm DMA in the surrounding gas phase.

The experimental equilibrium DMA / NH₃ and DMAH / NH₄ 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 / SO₄, NH₄ / SO₄ were used as input parameters. The E-AIM-predicted DMA / NH₃ gas ratios that would equilibrate over particles in our experiments are 0.14 and 0.01, and hence below the experimental DMA / NH₃ gas ratios of 0.49 and 0.07. These results imply that E-AIM would predict DMAH / NH₄ to be even larger

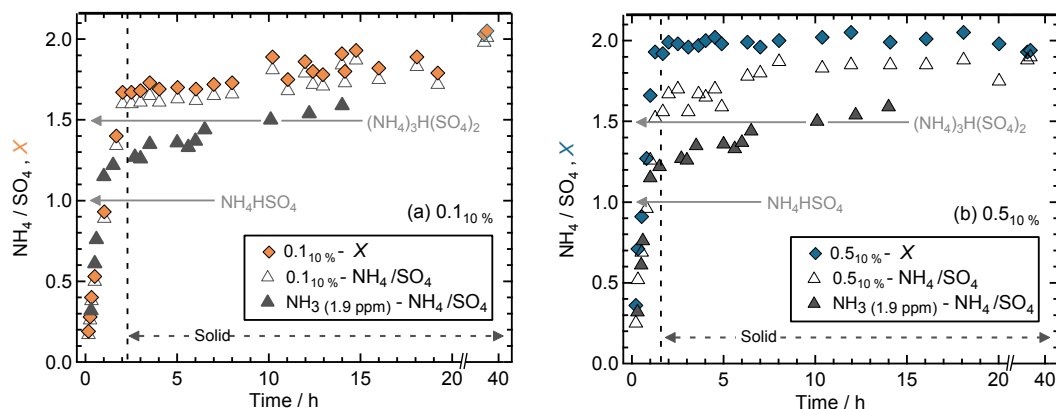


Figure 5. Comparison of particulate $\text{NH}_4 / \text{SO}_4$ in single-gas uptake (filled triangles) vs. DMA- NH_3 co-uptake (open triangles) experiments at 10 % RH into H_2SO_4 : (a) DMA / $\text{NH}_3 = 0.07$, and (b) DMA / $\text{NH}_3 = 0.46$. Diamonds denote the neutralisation ratio (X) in co-uptake experiments. Error bars are omitted for clarity.

than our reserved ratios. They are also 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 1 to 3 orders of magnitude.

Our measurements are experimental evidence that DMA preferentially partitions into neutralised liquid sulfate particles over NH_3 due to its stronger basicity. DMA then partially displaces NH_4 from neutralised aqueous particles even when the NH_3 gas concentration is 1 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 $\text{NH}_4 / \text{SO}_4$ ratio exceeded 1.1 (Fig. 5, filled triangles). A comparable retardation occurred in the co-uptake experiments 0.1₁₀% and 0.5₁₀%, but at $\text{NH}_4 / \text{SO}_4$ ratios of about 1.5 (Fig. 5a and b, open triangles). We used Raman microscopy (Chu et al., 2015) to further investigate the 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 0.5₁₀% (Fig. 7). Note that each sample was composed of several hundreds of closely deposited droplets deposited on a substrate. The droplets were not expected to reach the same cation-to-sulfate stoichiometry, nor exhibit phase transitions at exactly the same time. For the acquisition of in situ Raman signals, we selected individual particles just before and right after phase transition to represent the phase change process.

During the single-gas uptake of NH_3 into H_2SO_4 droplets at 10 % RH, crystallisation 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 and 1035 cm^{-1} (Dawson et al., 1986; Lund Myhre

et al., 2003) transformed to doublets at 579/609 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 0.5₁₀% 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 rectangle). 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 and 1030 cm^{-1} in the droplet (Fig. 7, spectrum 2) shifted towards 597 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 $(\text{NH}_4)_2\text{SO}_4$.

During NH_3 -DMA co-uptake the absorbed DMAH seems to have suppressed the precipitation of NH_4HSO_4 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 $\text{NH}_4 / \text{SO}_4$ around 1.5 (Fig. 5a and b). It can be seen from the 0.1₁₀% experiment (Fig. 5a) that this suppression of NH_4HSO_4 precipitation even occurred at DMAH / NH_4 as low as 0.05 at the time of phase change (Table 2, t_{pc}). $\text{R}_3\text{NH} / \text{NH}_4$ ratios in ambient samples near emission sites can be up to 0.23 (Sorooshian

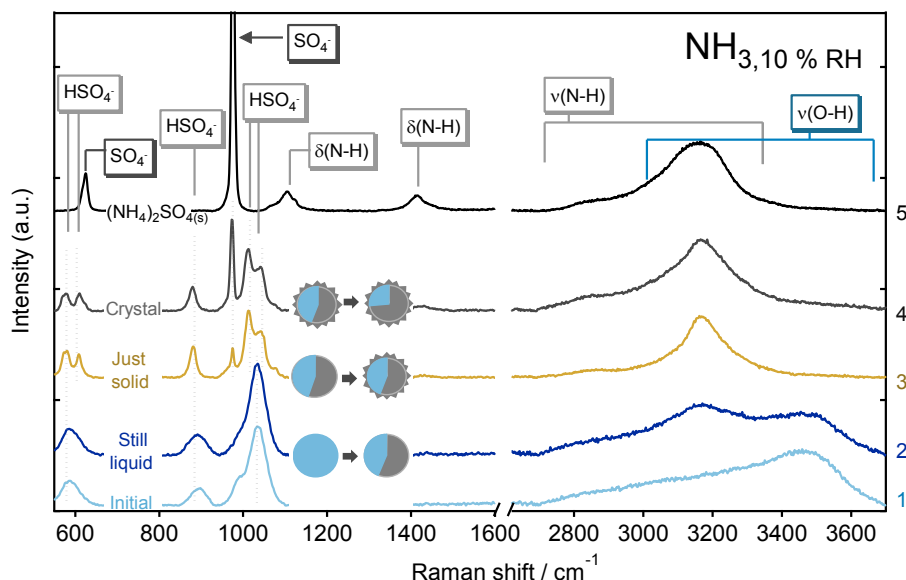


Figure 6. Raman spectra of selected particles representing different phase states during uptake of NH_3 into H_2SO_4 at 10 % RH. A spectrum of crystalline $(\text{NH}_4)_2\text{SO}_4$ is added for reference. Sketches indicate the cation composition range (as inferred from IC measurements) of particles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

et al., 2008). Since DMAH 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 DMA can affect the crystallisation behaviour of NH_4 –H– SO_4 -salts in atmospheric particles. Furthermore, 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 crystallisation retarded the uptake into particles with $\text{NH}_4 / \text{SO}_4 > 1.1$.

After the NH_4 –DMAH-mixed particles crystallised, the uptake of NH_3 continued at a slower pace (Fig. 5a and b), while DMA was no longer absorbed and the DMAH/ NH_4 ratio 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 that steric effects influence the uptake effectiveness of primary, secondary and tertiary methylamines 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 also made the uptake of NH_3 thermodynamically favourable.

DMAH/ NH_4 ratios at the time of neutralisation (t_{neutral}) reached 0.032 ± 0.001 for the 0.1₁₀% condition and 0.19 ± 0.01 for the 0.5₁₀% 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 neutralised particles

After reaching full neutralisation, both Raman spectral analysis and IC results of solid particles indicated a gradual reduction of DMAH and increase of NH_4 in the particle phase, which is also reflected in decreasing DMAH/ NH_4 ratios in Fig. 3a and b. At 10–20 min after the phase transition, DMAH– NH_4 -mixed particles experienced a second morphological change to a polycrystalline structure (Fig. 7, grey rectangle, spectrum 4). Raman spectra of these particles showed a vanishing HSO_4^- band at 1043 cm^{-1} , and a significant increase in the SO_4^{2-} band at 980 cm^{-1} , which indicates the (full) crystallisation of sulfate (Lee et al., 2008). We suspect that the observed morphological changes are related to the formation of a $(\text{NH}_4)_2\text{SO}_4$ shell structure due to DMAH displacement by NH_3 . DMAH was subsequently slowly displaced from the particle core, which eventually led to the formation of crystalline $(\text{NH}_4)_2\text{SO}_4$ with only traces of DMAH left inside the particles, as revealed by IC analysis. It is interesting to note that the DMAH/ NH_4 ratios of equilibrated particles for 0.5₁₀% and 0.1₁₀% were both 0.02 (Table 2). Even if the NH_3 gas concentration is only twice that of DMA, NH_3 can almost completely displace DMAH from the solid particle.

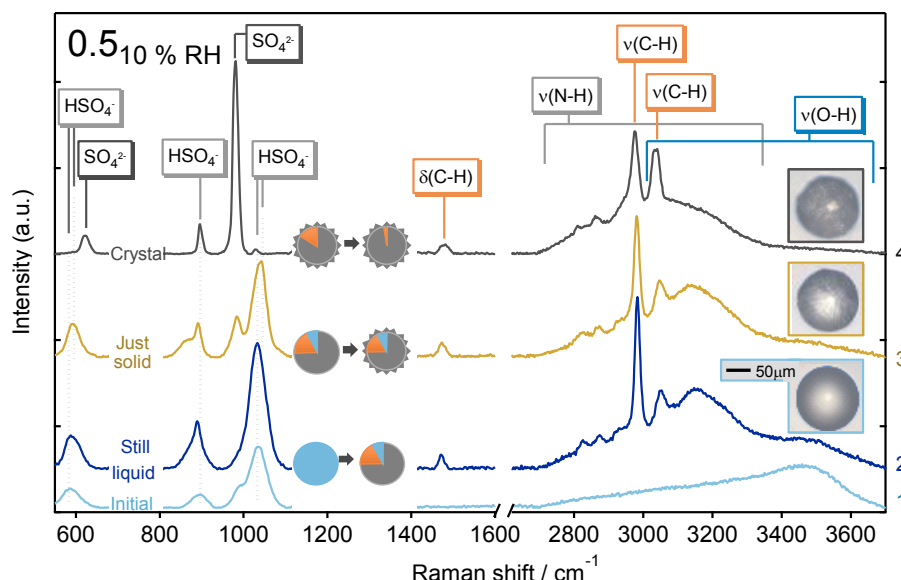


Figure 7. Raman spectra and morphological changes of selected particles during DMA–NH₃ co-uptake into H₂SO₄ at 10 % RH at a DMA / NH₃ molar ratio of 0.46 (0.5₁₀ %). Sketches indicate the cation composition range (as inferred from IC measurements) of particles when the spectra were recorded. Orange denotes DMAH, grey denotes NH₄, and blue denotes H₃O⁺ (HSO₄[−]).

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 0.1₁₀ % and 0.5₁₀ % 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 NH₄.

Overall it can be concluded that, for DMA–NH₃ co-uptake, NH₃ is favourably absorbed into acidic liquid particles, except for very concentrated H₂SO₄, where DMA and NH₃ seem to partition similarly effectively. Unless the particles either crystallise or are close to full neutralisation, DMA and NH₃ in general do not influence each other's uptake and each act as if they were the only gas present. For uptake into neutralised particles, DMA is favourably absorbed into liquid neutral particles due to its stronger basicity, leading to partial NH₄ displacement depending on gas phase NH₃ concentration. NH₃ is favourably taken up into solid neutral particles and can almost completely displace DMAH due to the thermodynamically favourable formation of (NH₄)₂SO₄ crystals and its steric properties.

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; Dece-

sari 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 at 10 and 70 % RH, respectively.

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 neutralisation ratio increased to $X = 0.3$. In the subsequent 15 h, a further major increase was not observed, suggesting that the gas uptake into anhydrous H₂C₂O₄ particles was incomplete and may have been limited to adsorption on the surface and outer layers of the particles. The DMAH / NH₄ ratio (Fig. 8b) stayed roughly constant.

The uptake at 70 % RH was monitored under the microscope for subsequent phase changes (Fig. S2). Within 15 min 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 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 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 we believe that this effect does not have a significant im-

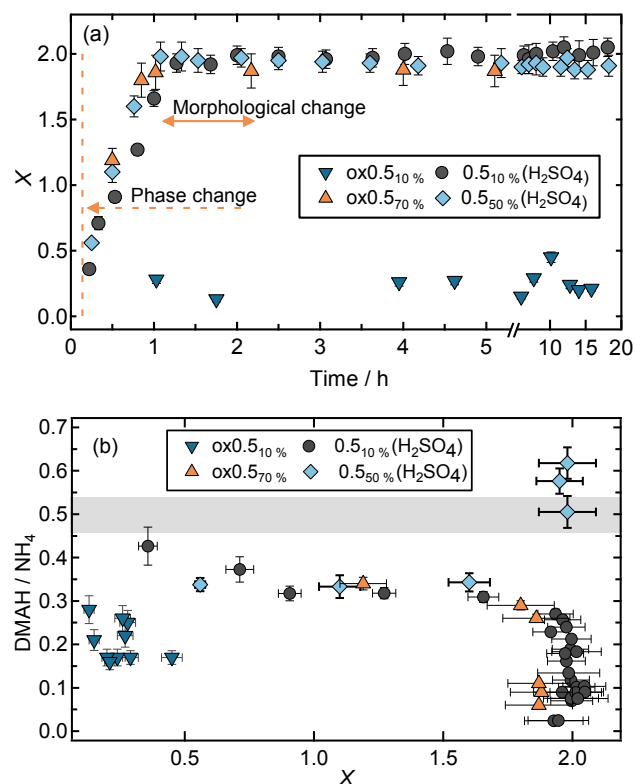


Figure 8. DMA–NH₃ co-uptake at DMA / NH₃ gas molar ratios of 0.5 (Table 1) into sulfuric and oxalic acid particles at 10, 50 and 70 % RH. (a) Neutralisation ratios as a function of time. The vertical dotted line indicates that the majority of oxalic acid particles at 70 % RH underwent phase transition 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 neutralisation ratio; the shaded area indicates the gas phase molar ratio of DMA / NH₃ (including uncertainties).

pact on the general uptake observations here. The co-uptake trends into solidified H₂C₂O₄ particles of the ox0.5₇₀ % experiments were comparable to those of 0.5₁₀ % and 0.5₅₀ % into H₂SO₄ (Fig. 8a), indicating that the solids formed during phase change (dashed line,) 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 neutralised 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 neutralised H₂SO₄ particles at 10 % RH, in which DMA uptake discontinued once the particles formed solids, the uptake of DMA into solid, partially neutralised H₂C₂O₄ particles remained effective.

Within 2 h of uptake, the solid particles of ox0.5₇₀ % 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 neutralised oxalate particles, which may trigger the transformation to a crystalline morphology. Final particle morphologies show a particle with a monoclinic or orthorhombic crystal structure, a shape typical of ammonium oxalate (Blake and Clegg, 2009), surrounded by small residuals of the satellite particles (Fig. S2).

3.4 Stability of reaction products and revolatilisation of NH₃ and DMA

As shown in Sect. 3.1, single-gas DMA uptake into H₂SO₄ equilibrated at incompletely neutralised droplets at both 10 and 50 % RH with X_{equil} between 1.5 and 1.9 (Table 1). Under amine-free atmosphere, the neutralisation 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). Similar degassing of methyl and ethyl-amines from synthesised salts has been reported in earlier studies (Chan and Chan, 2013; Chu et al., 2015; Lavi et al., 2015).

To summarise the influence of NH₄ in the volatilisation of DMA from particles and the formation of partially neutralised equilibrated droplets, we compared co-uptake experiments 0.5₁₀ % and 0.5₅₀ % to single-gas uptake DMA_{1 ppm 10 %}, DMA_{1 ppm 50 %}. Figure 9 illustrates the maximum neutralisation, equilibrium and composition of particles exposed to RH-conditioned N₂ atmosphere for the four mentioned experiments. In co-uptake experiments, particles reached full neutralisation (Fig. 9d and j). The total cation content in particles at 10 % RH at the time of neutralisation was > 80 % NH₄ (Fig. 9d). When approaching equilibrium, DMAH was displaced by NH₃ and the NH₄ 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 the particles were exposed to pure N₂ (Fig. 9f), the particle composition did not change due to the formation of a stable crystal. At 50 % RH, DMA partially displaced NH₄ from neutralised particles, with an increase in DMAH / SO₄ from 0.7 at the point of maximum neutralisation (Fig. 9j) to 1.3 at equilibrium (Fig. 9k). Accompanying the increase in DMAH was a decrease in the total neutralisation ratio from $X = 2$ to about $X = 1.8$ (Fig. 9j to k), indicating that more NH₃ has degassed than was replaced by DMA. Hence while revolatilisation of DMA was responsible for the decrease in X for DMA_{1 ppm 50 %}, degassing of NH₃ could be responsible for the decrease in X in co-uptake experiments. Once exposed to N₂, even more NH₃ evaporated from DMAH–NH₄ mixed particles (Fig. 9k to l), which further increased the acidity of these particles. It should be noted that the degassing of NH₃ was negligible for particles of the 0.1₅₀ % condition (Fig. 2c). At the point of maximum

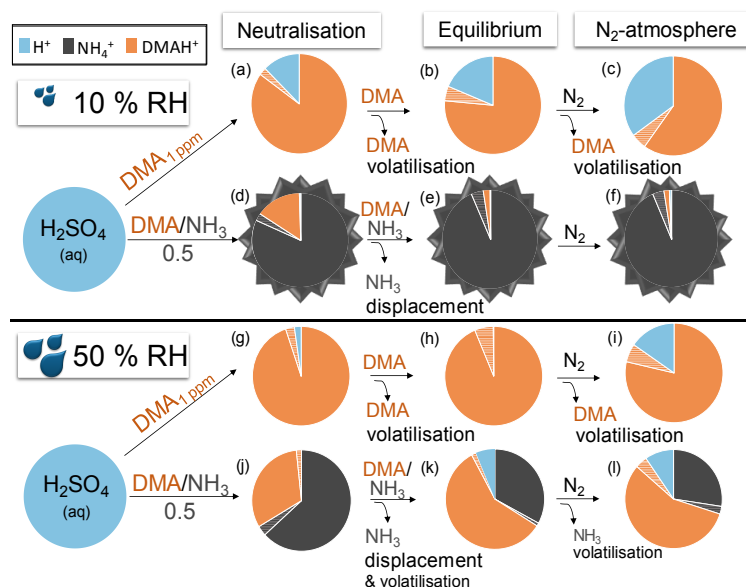


Figure 9. Particle neutralisation ratios and the proportion of each cation at maximum neutralisation (first column), equilibrium (second column) and after exposure of equilibrated particles to N_2 gas (third column). Colour scheme: orange represents DMAH, grey represents NH_4 , shaded areas indicate uncertainty of the respective species and blue represents H_3O^+ (HSO_4^-). Stars around pie charts indicate that particles were crystalline solids. Concentrations of DMA and NH_3 are shown in Table 1.

neutralisation, they contained large amounts of NH_4 and a DMAH/ NH_4 ratio below 0.1, which seems to have prevented revolatilisation. 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 the sensitivity of the equilibrium compositions of these droplets 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 $H_2C_2O_4$ particles was investigated at different RH and DMA/ NH_3 gas ratios. The stoichiometric neutralisation ratio and physical state of the particles were the two major factors influencing DMA and NH_3 uptake.

During 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 uptakes of DMA and NH_3 were independent of each other because of the availability of abundant acids, as long as the particles did not reach neutralisation nor undergo phase change. This result may explain why the highest particulate R_3NH^+ mass concentrations are detected in acidic aerosols at low NH_4 / SO_4 ratios (Youn et al., 2015).

In fully neutralised droplets at 50 % RH, the limited availability of H_3O^+ ions for acid-base reactions led to a par-

tial 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 neutralised 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 neutralised 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-neutralised particles. Hence, the presence of DMAH can prevent aqueous sulfate particles from full neutralisation. In our experiments NH_3 revolatilisation 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 NH_3 uptake continued. Once the particles were fully neutralised, NH_3 displaced DMAH from crystal structures and finally formed $(NH_4)_2SO_4$ with little residual DMAH, regardless of the DMA gas concentrations in the surrounding.

$H_2C_2O_4$ particles at 70 % RH were initially liquid, but transformed into non-crystalline solids after absorbing small amounts of DMA and NH_3 . Subsequent uptake was similar to that of liquid sulfate particles. The formation of solid, partially neutralised $H_2C_2O_4$ particles did not hinder DMA uptake. Fully neutralised oxalate particles then crystallised upon displacement of DMAH by NH_3 , similarly to the displacement of DMAH from crystalline sulfate particles. An-

hydrous $\text{H}_2\text{C}_2\text{O}_4$ at 10 % RH was rather inert and took up small amounts of DMA and NH_3 , presumably by adsorption only.

In solid neutralised particles, NH_3 uptake is sterically and thermodynamically favoured to form $(\text{NH}_4)_2\text{SO}_4$ or ammonium oxalate crystals by displacing DMAH. Hence, once ambient aerosols are in a solid state, they are unlikely to take up R_3N , even when R_3N and NH_3 gas concentrations are of the same magnitude.

The DMA and NH_3 gas concentrations and sulfate neutralisation 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 neutralisation ratios are likely to be high (Sorooshian et al., 2008), and NH_3 and amines compete for particulate H_3O^+ ions, where DMA can displace NH_4 in liquid and NH_3 can displace DMAH in solid particles. Although laboratory experiments have shown that in the absence of NH_3 DMA could partially displace NH_4 from solid ammonium salts including $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 (Lloyd et al., 2009; Qiu and Zhang, 2012; Chan and Chan, 2012, 2013), this scenario is unlikely under atmospheric conditions with abundant NH_3 .

In this study, we used DMA as a proxy for atmospherically relevant R_3N . As different R_3N and their sulfate and oxalate salts possess different hygroscopic and crystallisation 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 behaviour, the findings obtained here may not be generalisable to all short-chain aliphatic amine compounds. Additionally, organic coatings are commonly found on the surface of inorganic aerosols (Mochida et al., 2002). The role of such coating in the heterogeneous uptake of amines warrants further studies (Chu and Chan, 2017). It should also be mentioned that particle size may affect the gas uptake kinetics, as well as the crystallisation behaviour 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 neutralisation ratio as well as crystallisation inhibition by DMAH are considered applicable to particles of smaller size. Nevertheless, the observed results may be most relevant to aerosols larger than $1\text{ }\mu\text{m}$, which were found in the atmosphere to have the highest $\text{R}_3\text{NH}/\text{NH}_4$ ratio (Vanden-Boer et al., 2011; Youn et al., 2015). To improve our understanding of the mechanisms governing the simultaneous exchange of NH_3 and R_3N between the gas and particle phases, particle size dependence should be investigated in the future.

Data availability. Data are available upon request from the corresponding author.

The Supplement related to this article is available online at doi:10.5194/acp-17-6323-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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