



Laboratory-measured H₂SO₄-H₂O-NH₃ ternary homogeneous nucleation rates: Initial observations

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[1] We have measured nucleation rates of sulfuric acid-water-ammonia (H₂SO₄-H₂O-NH₃) ternary homogeneous nucleation (THN), with a fast flow nucleation reactor attached to two chemical ionization mass spectrometers (CIMSs) to measure H₂SO₄ and NH₃ concentrations simultaneously. Under our experimental conditions with a temperature of 288 K and RH from 4–42% and initial [H₂SO₄] in the 10⁸–10⁹ cm⁻³ range and [NH₃] from 10–50 ppbv ($\sim 2 \times 10^{11}$ – 1×10^{12} cm⁻³), the enhancement factor (*EF*) compared to the binary system ranges up to $\sim 1,000$ depending on [H₂SO₄], [NH₃] and RH; *EF* also exponentially increases with decreasing RH and decreasing initial [H₂SO₄]. The numbers of H₂SO₄ (9–10) and H₂O molecules (6–15) in the critical clusters are reduced in the presence of NH₃ [(6–8) and (4–10), respectively]; the number of NH₃ molecules in the critical clusters is smaller than 2, under our experimental conditions. **Citation:** Benson, D. R., M. E. Erupe, and S.-H. Lee (2009), Laboratory-measured H₂SO₄-H₂O-NH₃ ternary homogeneous nucleation rates: Initial observations, *Geophys. Res. Lett.*, 36, L15818, doi:10.1029/2009GL038728.

1. Introduction

[2] Nucleation is a gas-to-particle conversion process [Seinfeld and Pandis, 2006] and is a source of new aerosol particles. These newly formed particles have a high potential to grow to cloud condensation nuclei and hence have an important impact on the regional and global climate. The current nucleation parameterizations are hampered by high uncertainties because they are not vigorously tested by experiments. Field studies [Stanier et al., 2004; Weber et al., 1998] show that ammonia (NH₃) can be important for aerosol nucleation on the global and regional scale. Chemical analysis of atmospheric aerosols also demonstrates that these newly formed particles often contain ammonium sulfate, along with various oxygenated organic compounds [Smith et al., 2005, 2008]. While sulfuric acid-water-ammonia (H₂SO₄-H₂O-NH₃) ternary homogeneous nucleation (THN) is considered as the most important ternary nucleation system in the atmosphere, there is a large “hole” in the literature of laboratory studies for this NH₃-ternary nucleation system [Ball et al., 1999; Hanson and Eisele, 2002; Hanson and Lovejoy, 2006; Kim et al., 1998; Zhang et al., 2004].

[3] There are also large discrepancies amongst model predicted, laboratory measured, and atmospherically observed nucleation rates. The classical binary homogeneous nucleation (BHN) theories predict much lower nucleation rates compared to atmospheric observations [Vehkamäki et al., 2002]. Inclusion of NH₃ can enhance nucleation rates, but the THN theories with NH₃ also often over-predict the nucleation rates [Korhonen et al., 1999; Napari et al., 2002a] (e.g., even over ten orders of magnitude higher than those from BHN), with some exceptions [Antilla et al., 2005; Merikanto et al., 2007]. On the other hand, laboratory measured THN rates are only one to three orders of magnitude higher than the BHN rates [Ball et al., 1999; Hanson and Eisele, 2002; Hanson and Lovejoy, 2006; Kim et al., 1998; Zhang et al., 2004]. Whereas the laboratory studies show that THN rates increase with RH [Ball et al., 1999; Kim et al., 1998], the THN theories predict that nucleation rates are independent of RH or even anti-correlated with RH [Napari et al., 2002a; Yu, 2006]. Density functional calculations also give contradictory predictions on whether or not NH₃ can stabilize small clusters containing H₂SO₄ and H₂O molecules [Ianni and Bandy, 1999; Kurten et al., 2007]. While ammonia can enhance BHN nucleation rates, aerosol modeling studies show that with the amount of NH₃ (e.g., up to 100 pptv) typically used in the THN calculations, THN cannot explain atmospheric observations and other condensable organic species are also required in THN calculations [Kulmala et al., 2000]. In fact, THN parameterizations include NH₃ only in the range from 0–100 pptv and for NH₃ higher than 100 pptv, the NH₃ effects in the THN models become “saturated” [Merikanto et al., 2007]. However, atmospheric NH₃ concentrations in the troposphere are typically at the sub-ppbv or ppbv level [Nowak et al., 2007]. There are high uncertainties on exactly how much NH₃ is needed to effectively enhance BHN rates; this is in part because NH₃ concentrations are not directly measured in laboratory experiments [Ball et al., 1999; Kim et al., 1998; Zhang et al., 2004].

[4] Recently, we have built a laboratory nucleation setup to study H₂SO₄-H₂O binary homogeneous nucleation (BHN), by producing H₂SO₄ vapor from the SO₂ + OH → HSO₃ reaction at in-situ and by measuring low concentration of H₂SO₄ directly [Benson et al., 2008; Young et al., 2008]. Here, we present laboratory observations of NH₃-THN rates as a function of aerosol precursor concentrations (NH₃, H₂SO₄ and RH), using a similar approach by simultaneously measuring nucleation precursors. The numbers of H₂SO₄, NH₃, and H₂O molecules in the critical clusters are also derived from these observations. Nucleation enhancement factors (*EF*) induced by NH₃ are investigated, by comparing with BHN rates measured under similar experimental conditions. The present study provides a direct

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Table 1. Summary of the Experimental Conditions and Results^a

Data Used	CPC	RH (%)	SO ₂ source	[SO ₂] (ppmv)	Initial [H ₂ SO ₄] (10 ⁸ cm ⁻³)	Initial [NH ₃] (ppb)	Particle number (10 ³ cm ⁻³)	J (cm ⁻³ s ⁻¹)	EF	$n_{H_2SO_4}$	n_{H_2O}	n_{NH_3}
Figure 1a	Butanol	23–33	1 ppm	0.020–0.1	1.5–6.3	20	0.002–79.8	0.1–3,190	2.4–18	6–7.8	N/A	N/A
Figure 1b	Butanol	18–42	1 ppm	0.025–0.1	1.9–6.3	20	0.001–79.8	0.04–3,190	4.0–49	N/A	4.1–14.6	N/A
Figure 2a	Butanol	23–33	1 ppm	0.020–0.1	1.5–6.3	20	0.002–79.8	0.1–3,190	2.4–18	N/A	N/A	N/A
	Butanol	4–13	100 ppm	5–10	10–54	20	0.0004–243	0.02–14,020	1.4–994	N/A	N/A	N/A
Figure 2b	Butanol	18–33	1 ppm	0.050–0.1	2.4–6.3	20	0.012–79.8	0.5–3,190	2.3–16.2	N/A	N/A	N/A

^aInitial [H₂SO₄] and [NH₃] are measured at the beginning of nucleation reactor by two CIMSs simultaneously. Particle numbers are measured with butanol- or water-CPC at the end of the nucleation reactor. EF , enhancement factor by NH₃ in the nucleation reactor, is the ratio of nucleation or NH₃-THN over that of BHN under the same experimental conditions. $n_{H_2SO_4}$, n_{H_2O} , n_{NH_3} are numbers of H₂SO₄, H₂O, and NH₃ molecules in critical clusters derived from Figure 1; shown here are the values for THN studies. Total flow rate is 10 liters per minute (corresponding to residence time of 10 s).

comparison with our previous BHN studies [Benson *et al.*, 2008; Young *et al.*, 2008].

2. Experiments

[5] The experimental setup used to study THN with NH₃ is shown in Figure S1 (auxiliary material¹). This setup is based on the previous experimental design used for H₂SO₄-H₂O BHN studies in our lab [Benson *et al.*, 2008; Young *et al.*, 2008], with the addition of a second CIMS to measure [NH₃]. The system consists of five main regions: (i) a photolysis region where OH radicals are produced from the photodissociation of H₂O vapor using a UV lamp ($\lambda < 185$ nm), (ii) a mixing region, where SO₂, O₂ and NH₃ gases are introduced and where H₂SO₄ vapor forms from the SO₂ + OH reaction, (iii) a temperature-regulated nucleation region (fast flow reactor), (iv) an H₂O-based ultrafine condensation particle counter (UWCPC, TSI 3786) as well as a butanol-based ultrafine condensation particle counter (UCPC, TSI 3776), and (v) two chemical ionization mass spectrometers (CIMSs) to simultaneously measure initial [H₂SO₄] and [NH₃]. Figure S2 also shows the detailed configuration and dimension of the flow reactor with regard to production of aerosol precursors (OH and H₂SO₄) and mixing. Experimental conditions used in this study are summarized in Table 1.

[6] We produce H₂SO₄ vapor from the SO₂ + OH → HSO₃ reaction, as it occurs in the atmosphere and similarly to previous nucleation studies [Benson *et al.*, 2008; Berndt *et al.*, 2005; Young *et al.*, 2008]. OH is produced from water UV absorption and the typical OH concentrations are in the 10⁹–10¹⁰ cm⁻³ range [Young *et al.*, 2008]. This H₂SO₄-CIMS has been described elsewhere [Benson *et al.*, 2008; Eisele and Tanner, 1993; Young *et al.*, 2008]. Briefly, to detect H₂SO₄, NO₃⁻ ions are used as reagents. Our CIMS currently can detect H₂SO₄ as low as 2 × 10⁵–6 × 10⁵ cm⁻³. In the present study, we provide the initial [H₂SO₄] measured by CIMS at the beginning of the nucleation reactor, as opposed to the residual [H₂SO₄] at the end of the nucleation reactor we previously reported [Benson *et al.*, 2008; Young *et al.*, 2008]; because aerosol precursors, especially sulfuric acid, have substantial wall losses [Young *et al.*, 2008; Benson *et al.*, 2008], in the present study, we provide aerosol precursor concentrations measured at the end of nucleation reactor, which do not need these wall loss corrections. Mass conservation of sulfuric acid in the particle vs. gas phase has been discussed in elsewhere [Benson *et al.*, 2008; Young *et al.*, 2008].

[7] The NH₃-CIMS is based on Nowak *et al.* [2007]. This NH₃-CIMS instrument is identical to the H₂SO₄-CIMS mentioned above, except with a different ion-molecule reaction in a low pressure ionization region (~20 Torr). Protonated clusters of ethanol are used as ion reagents for NH₃ detection [Nowak *et al.*, 2007]. Whereas the H₂SO₄-CIMS detection limit depends on the CIMS sensitivity, the NH₃-CIMS detection limit ultimately depends on its background signals, which are extremely sensitive to the sampled NH₃ concentrations. Dealing with this background NH₃ is a challenge in nucleation experiments. Air from the nucleation reactor is brought in through one of two ports. One port is used for measurements of NH₃ from the nucleation reactor while the second port is used to deliver air through an NH₃ scrubber (Perma Pure Inc.) containing phosphoric acid that removes NH₃ from the sampled air to determine the instrumental background. A three way valve is actuated pneumatically to rotate and switch the sampled airflow between the two ports. We use an NH₃ standard gas, after dilution with pure nitrogen blown from liquid nitrogen (these nitrogen gases contain much lower impurity of NH₃ than the bottled standard nitrogen gases), to calibrate NH₃ concentrations. For ambient NH₃ measurements, our CIMS background signals typically range from 0.5–1 ppbv and the sensitivity of NH₃ detection is approximately 3 Hz/ppbv; under these conditions, we can measure NH₃ down to 50 pptv from ambient air (J. Li *et al.*, Correlation of aerosol nucleation and growth rates with H₂SO₄ and NH₃ concentrations: Atmospheric observations, manuscript in preparation, 2009). For the flow tube studies, the background NH₃ signals (likely generated from deionized water) range from 0–1.3 ppbv for RH ranging from 0–50%. NH₃ effects on nucleation are significant only after [NH₃] > 1 ppbv and therefore, we think that the effects of background NH₃ on the BHN results are not important under our experimental conditions.

[8] We have previously characterized the nucleation zone with a simple nucleation model based on the measured H₂SO₄ and aerosol size distributions [Young *et al.*, 2008]; these simulations show that nucleation takes place in the first half of the nucleation reactor. Nucleation rates shown here have taken into account the nucleation zone as well as particle stability, as shown by Young *et al.* [2008]. That is, the reported nucleation rates in the present study are 2.5 times lower than the ratios of particle number concentrations over the residence time in the nucleation reactor. We also have determined the wall loss of H₂SO₄ using numerical calculations from H₂SO₄ diffusion coefficients [Hanson

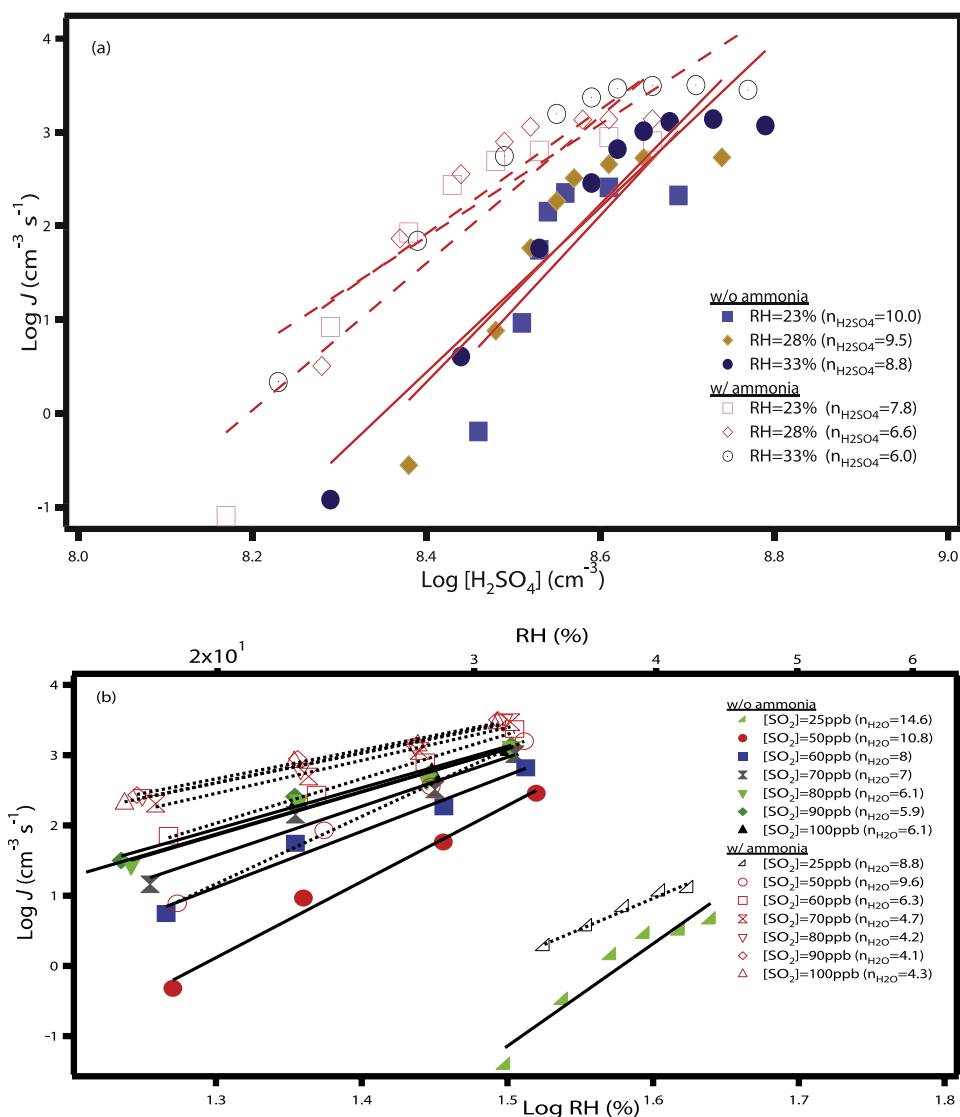


Figure 1. The measured nucleation rates for H₂SO₄-H₂O-NH₃ THN at 288 K as a function of (a) the initial [H₂SO₄], and (b) RH. The initial [NH₃] = 20 ppbv ($4.6 \times 10^{10} \text{ cm}^{-3}$) for THN experiments shown; the measured nucleation rates for H₂SO₄-H₂O BHN are also included, in comparison with the THN results. Background [NH₃] < 0.1 ppbv in the nucleation reactor with low RH, and NH₃ effects on nucleation are significant only after [NH₃] > 1 ppbv under the typical experimental conditions. Solid lines are fits to the experimental data. Detailed experimental conditions are shown in Table 1.

and Eisele, 2000] and also by measuring the initial and residual H₂SO₄ with two CIMSs simultaneously [Young *et al.*, 2008]. Wall loss factor of H₂SO₄ is about 1.7, under the typical experimental conditions used in this study. NH₃ wall loss is considered to be negligible compared to H₂SO₄, based on our atmospheric observations of NH₃ and H₂SO₄ with CIMSs (Li *et al.*, manuscript in preparation, 2009).

3. Results

[9] The measured nucleation rates, J , as a function of H₂SO₄ and RH in the absence or presence of NH₃ are shown in Figure 1. The total flow in the reactor is maintained at 10 liters per minute corresponding to residence time of 10 seconds. J values range from 2×10^{-2} – $1.4 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ depending on RH (4–42%) and the initial [H₂SO₄] (in the 10^8 – 10^9 cm^{-3} range), with higher J values in the presence of NH₃ than in the absence of NH₃.

[10] For the binary system, the numbers of H₂SO₄ molecules in the critical clusters ($n_{H_2SO_4}$) are obtained from slopes of linear fits of $\text{Log } J$ vs. $\text{Log } [H_2SO_4]$, based on multicomponent nucleation theories [Kashchiev, 1982; McGraw and Zhang, 2008; Nellas *et al.*, 2006]; $n_{H_2SO_4}$ range from 9–10, increasing as RH decreases. The numbers of H₂O molecules in the critical clusters (n_{H_2O}), obtained in a similar manner, range from 6–15. These results are consistent with our previous BHN studies [Benson *et al.*, 2008; Young *et al.*, 2008]. For the THN results shown in Figures 1a and 1b, 20 ppb of [NH₃] is used to result in a significant increase in particle number concentration, compared to the binary system. Similarly to the BHN case, in the NH₃-THN case, the $n_{H_2SO_4}$ values (6–8) are smaller at higher RH and n_{H_2O} (4–10) are also smaller at higher [SO₂] (and therefore higher [H₂SO₄]). In the presence of NH₃,

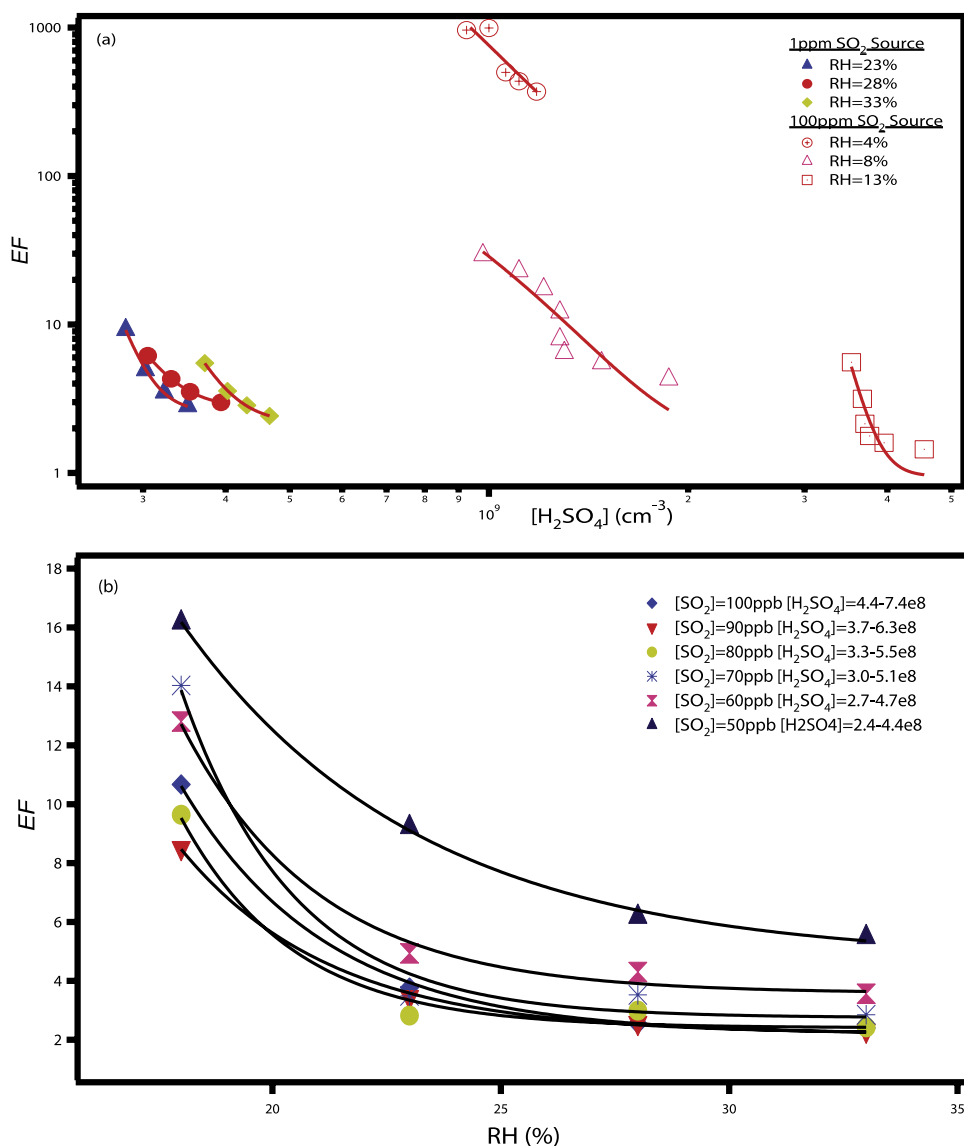


Figure 2. Measured enhancement factors (EF) of nucleation by NH_3 in THN compared to BHN, as a function of (a) initial $[\text{H}_2\text{SO}_4]$ and (b) RH. For the THN studies, $[\text{NH}_3] = 20$ ppbv. Detailed experimental conditions are shown in Table 1.

however, both $n_{\text{H}_2\text{SO}_4}$ and $n_{\text{H}_2\text{O}}$ become smaller than in the case without NH_3 , indicating that NH_3 indeed reduces nucleation barriers for H_2SO_4 and H_2O . This trend is consistent with the *Ball et al.* [1999] and *Kim et al.* [1998] studies. The numbers of NH_3 molecules in the critical clusters (n_{NH_3}) are also estimated to be about 0–2, with values increasing as RH or $[\text{H}_2\text{SO}_4]$ decreases.

[11] Enhancement factor (EF) is defined as the ratios of the measured CPC particle number concentration in NH_3 -THN vs. that in BHN under similar experimental conditions. Figure 2 shows the measured EF values as a function of H_2SO_4 and RH. EF ranges from 2–1,000 depending on the RH (4–33%) and $[\text{H}_2\text{SO}_4]$ (in the 10^8 – 10^9 cm⁻³ range). The solid lines in Figures 2a and 2b represent an exponential fit to the EF values and this shows that EF increases exponentially with decreasing RH and $[\text{H}_2\text{SO}_4]$. Laboratory observations by *Ball et al.* [1999] and *Kim et al.* [1998] and THN parameterizations by *Napari et al.* [2002a] have also indicated higher enhancement factors at lower RH and

lower $[\text{H}_2\text{SO}_4]$. The measured EF values increase linearly with $[\text{NH}_3]$ from the 1–50 ppbv range.

4. Discussions and Conclusion

[12] The main conclusion of our laboratory observations is that H_2SO_4 plays important roles in atmospheric nucleation even in the presence of NH_3 . Our observations also show that NH_3 enhances nucleation rates of H_2SO_4 and H_2O exponentially with decreasing H_2SO_4 and RH, at the initial $[\text{H}_2\text{SO}_4]$ 10^8 – 10^9 cm⁻³ range and RH from 4–42% and for $[\text{NH}_3]$ at the ppbv or tenth ppbv level. Under these experimental conditions, EF reaches up to $\sim 1,000$ at lower $[\text{H}_2\text{SO}_4]$ and RH; but no significant NH_3 effects are observed in our experiments for $[\text{NH}_3] < 1$ ppbv. This result is different from *Ball et al.* [1999] who have made NH_3 -THN laboratory observations at 295 K and $[\text{H}_2\text{SO}_4]$ in the 10^{10} – 10^{11} cm⁻³ range and RH 5% and 15%. Their observations showed NH_3 enhancement of nucleation rate

up to 3 orders of magnitude for even a low [NH₃] of 0.08 ppbv and 0.17 ppbv. There are three main differences in the experimental methods used in our study and by *Ball et al.* [1999]. First, we produce H₂SO₄ vapor from the SO₂ + OH reaction, whereas *Ball et al.* [1999] have used liquid H₂SO₄ solutions. Also, the nucleation zone [H₂SO₄] was about 10¹⁰ to 10¹¹ cm⁻³ in the *Ball et al.* [1999] study, which is 2 to 3 orders of magnitude higher than the initial [H₂SO₄] measured in this study. In addition, we measure [NH₃] directly with CIMS, whereas the *Ball et al.* [1999] study did not measure NH₃ and noted large uncertainties in estimation of NH₃. It is unclear at present, however, what causes this difference in the minimum [NH₃] needed to have the NH₃ ternary effect ($EF > 1$) between these two studies. Experiments are currently under taken to investigate the possible enhancement by NH₃ (<1 ppbv) at low [H₂SO₄], as our studies have shown that NH₃ effects are more pronounced at lower H₂SO₄ and RH. On the other hand, new particle formation from NH₃/SO₂/H₂O/air mixture by ionizing irradiation showed that with SO₂ and NH₃ at the ppmv level, a moderate EF (2–4) of nucleation rate was seen in the presence of NH₃ [*Kim et al.*, 1998], more similarly to our results, although the precursor concentrations used by *Kim et al.* [1998] were much higher than ours in general.

[13] Another important finding of our observations is that THN rates are a sensitive function of RH and this result has an important atmospheric implication. Our observations show that $n_{H_2SO_4}$ and n_{H_2O} values in THN (and BHN) are smaller at higher RH and higher H₂SO₄, as expected from nucleation theories. However, these THN parameterizations also often show that n_{H_2O} is close to zero [*Merikanto et al.*, 2007; *Napari et al.*, 2002a, 2002b] (that is, THN rates are insensitive to RH); this is inconsistent with our experiments where n_{H_2O} ranges from 4–10. Our studies also show that EF exponentially decreases with increasing RH (and [H₂SO₄]).

[14] Although our observations show that $n_{H_2SO_4}$ and n_{H_2O} are reduced in the presence of NH₃, the $n_{H_2SO_4}$ (6–8) values in THN measured from our laboratory studies are still much larger than 1–2, reported from the most of atmospheric observations [*Kulmala et al.*, 2004]. Our observations are also different from molecular cluster studies with CIMS [*Hanson and Eisele*, 2002] that showed THN critical clusters contain only two H₂SO₄ molecules (and one NH₃). Further experiments are needed to fully investigate these differences.

[15] One of the purposes of laboratory studies is to provide experimental data to test and constrain nucleation theories. Our laboratory-measured EF values are not as significant as those reported from previous THN parameterizations [*Napari et al.*, 2002b] which showed significant EF (up to ten orders of magnitude) in NH₃-THN compared to BHN; [NH₃] used in these models also ranged from 0–100 pptv, much lower than those used in our experiments (ppbv). Later parameterizations by *Antilla et al.* [2005] and *Merikanto et al.* [2007] have reduced this huge EF for [NH₃] from 0–1,000 pptv, by considering formation of ammonium bisulfate clusters. These newer THN parameterizations showed that in order to produce a nucleation rate of 1 cm⁻³ s⁻¹ for an [H₂SO₄] of less than 10⁹ cm⁻³, RH of 50%, and temperature of 288 K, the required [NH₃] is at least 1 ppbv.

[16] The H₂SO₄-H₂O-NH₃ THN is one of the most important atmospheric nucleation systems, but laboratory observations on this potentially important system are currently sparse. Our studies provide an important initial understanding of atmospheric ternary nucleation involving NH₃ from the experimental viewpoint, by providing nucleation rates together with constrained aerosol precursor concentrations. But many important aerosol nucleation questions remain, including EF by NH₃ at lower [H₂SO₄] (10⁵–10⁷ cm⁻³) and temperature effects on NH₃-THN. Also, it is still open if NH₃ can explain atmospheric nucleation and what is the role of NH₃ as compared to organic compounds for aerosol nucleation. Future studies are required to experimentally examine these critical atmospheric science questions.

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