

Ternary homogeneous nucleation of H₂SO₄, NH₃, and H₂O under conditions relevant to the lower troposphere

D. R. Benson, J. H. Yu, A. Markovich, and S.-H. Lee

Kent State University, Department of Chemistry, Kent, Ohio 44240, USA

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Abstract. Ternary homogeneous nucleation (THN) of H₂SO₄, NH₃ and H₂O has been used to explain new particle formation in various atmospheric regions, yet laboratory measurements of THN have failed to reproduce atmospheric observations. Here, we report first laboratory observations of THN made under conditions relevant to the lower troposphere ([H₂SO₄] of 10⁶–10⁷ cm⁻³, [NH₃] of 0.08–20 ppbv, and a temperature of 288 K). Our observations show that NH₃ can enhance atmospheric H₂SO₄ aerosol nucleation and the enhancement factor (EF) in nucleation rate (*J*) due to NH₃ (the ratio of *J* measured with vs. without NH₃) increases linearly with increasing [NH₃] and increases with decreasing [H₂SO₄] and RH. Two chemical ionization mass spectrometers (CIMS) are used to measure [H₂SO₄] and [NH₃], as well as possible impurities of amines in the nucleation system. Aerosol number concentrations are measured with a water condensation counter (CPC, TSI 3786). The slopes of Log *J* vs. Log [H₂SO₄], Log *J* vs. Log RH, and Log *J* vs. Log [NH₃] are 3–5, 1–4, and 1, respectively. These slopes and the threshold of [H₂SO₄] required for the unity nucleation vary only fractionally in the presence and absence of NH₃. These observations can be used to improve aerosol nucleation models to assess how man-made SO₂ and NH₃ affect aerosol formation and CCN production at the global scale.

events have been observed in a wide range of atmospheric regions (Kulmala et al., 2004). These newly formed particles further grow by condensation and coagulation and can contribute to a large fraction (15–55 %) of CCN concentrations at the global scale (Merikanto, 2009), but the nucleation mechanisms are not well understood. Atmospheric observations (Erupe et al., 2010; Kulmala et al., 2004; McMurry et al., 2005) and laboratory studies (Benson et al., 2008; Berndt et al., 2005; Sipilä et al., 2010; Young et al., 2008) have shown that sulfuric acid (H₂SO₄) is the main nucleation precursor, but the role of other ternary species such as ammonia (NH₃) and organic compounds is not well understood.

Chemical composition analysis of nanometer size particles made at various locations has shown these newly formed particles contain sulfate, ammonium and various organic compounds including amines (Smith et al., 2008, 2010). Global atmospheric aerosol model calculations also suggested that in a wide range of the troposphere and the lower stratosphere, nucleation rates (*J*) can be predicted by the ternary homogeneous nucleation (THN) of H₂SO₄, NH₃, and H₂O (Lucas and Akimoto, 2006). Especially in the eastern US, new particle formation has been successfully explained by NH₃-THN (Gaydos et al., 2005; Jung et al., 2006; Stanier et al., 2004). The above mentioned modeling predictions were based on Napari et al. (2002)'s THN parameterization, which also predicts *J* values for many orders of magnitude higher than binary homogeneous nucleation (BHN) of H₂SO₄ and H₂O. This THN parameterization includes the [NH₃] range from 0–100 pptv (1 pptv ≈ 2 × 10⁷ cm⁻³) and for [NH₃] greater than 100 pptv, it assumes that there is no effect on *J* except for [H₂SO₄] less than 10⁶ cm⁻³, while atmospherically observed [NH₃] are typically at the sub-ppbv and ppbv level (Erupe et al., 2011; Nowak et al., 2006). Later THN parameterizations included the effects of stable ammonium bisulfate formation (Anttila et al., 2005; Merikanto et al., 2007) to match the available laboratory THN observations in the NH₃ range from 0–170 pptv (Ball et al., 1999); but these

1 Introduction

Particle nucleation (gas to particle conversion) is one of the important atmospheric processes that directly control the number concentrations of aerosol particles and thus can affect global climate, air quality and human health. Nucleation



Correspondence to: S.-H. Lee
(slee19@kent.edu)

parameterizations also fail drastically due to overestimation of the degree of proton transfer from bulk liquid properties (Vehkamäki, 2010).

At present, the exact [NH₃] needed to enhance *J* over BHN and the magnitude of enhancement in nucleation due to NH₃ are both uncertain, mostly because there are only a very limited number of laboratory studies of NH₃-THN (Ball et al., 1999; Benson et al., 2009; Berndt et al., 2010; Hanson and Eisele, 2002; Kim et al., 1998). To produce particles, these experiments also used [H₂SO₄] > 10⁸ cm⁻³, two to three orders of magnitude higher than typical atmospheric concentrations (10⁵–10⁷ cm⁻³) (Erupe et al., 2010; McMurry et al., 2005). These limited observations have shown that at such high [H₂SO₄], [NH₃] of ppbv or sub-ppbv can increase *J* up to 3 orders of magnitude, although often the enhancement factors (EF) due to NH₃ are around only one order of magnitude.

Laboratory studies of nucleation are challenging due to technical limitations and the experimental results are often not reproducible between different studies. It is also unclear how different experimental techniques and parameters affect nucleation results. The different experimental parameters include the method to produce H₂SO₄ vapor (with the SO₂ + OH → HSO₃ Reaction (R1) at in-situ or vaporization from liquid H₂SO₄ samples; a point or continuous source in the nucleation reactor), determination of aerosol precursor concentrations (e.g., [H₂SO₄] are measured with mass spectrometry or calculated from the estimated [SO₂] and [OH] in the nucleation reactor), estimation of wall loss of aerosol precursors and nucleation time in the nucleation reactor, and particle detection with different cutting sizes. The detection efficiencies in particle counters are important for experiments made at low [H₂SO₄], since the majority of particles often may not grow sufficiently large enough to be detected with 100 % detection efficiency. Additionally, direct detection of gas phase precursors is also critical because nucleation is a non-linear process so *J* is extremely sensitive to precursor concentrations (Lee et al., 2003; Seinfeld and Pandis, 2006).

There are also several technical limitations in laboratory nucleation studies. For example, in BHN studies that usually use water vapor to produce different RH values in the nucleation reactor, it is usually assumed that ternary species do not exist in the nucleation system, but in fact NH₃ impurities are unavoidable, because even highly purified water contains some amounts of NH₃ as impurities (Benson et al., 2010; Nowak et al., 2006). Depending on the material used in the nucleation reactor, the effects of such impurity NH₃ can be also different. Experimental tests have shown that whereas adsorption of NH₃ is most effective on stainless steel material, NH₃ adsorption is minimal on fluorinated ethylene propylene (FEP) or perfluoroalkoxy (PFA) Teflon surfaces (Benson et al., 2010; Neuman et al., 2003; Nowak et al., 2002, 2006; Yokelson et al., 2003). Such impurities are one of the major limitations of nucleation studies, especially considering that NH₃ can increase nucleation of H₂SO₄ aerosols

(Ball et al., 1999; Benson et al., 2009, 2010; Berndt et al., 2010). It is also possible that amines can co-exist with NH₃, as they both have similar sources (Ge et al., 2010). And, amines can also enhance H₂SO₄ aerosol nucleation similarly to NH₃ (Berndt et al., 2010; Erupe et al., 2011).

Here, we present laboratory observations of homogeneous nucleation involving, H₂SO₄, NH₃, and H₂O, for the first time, made under conditions typically relevant to the lower troposphere. Experiments were made at [H₂SO₄] of 10⁶–10⁷ cm⁻³, [NH₃] of 0.08–2.6 ppbv (except only one occasion where 20 ppbv NH₃ was used), RH of 6–40 % and 288 K, in a temperature- and RH-controlled fast flow nucleation reactor. All aerosol precursors were also simultaneously and directly measured with CIMS to provide more constrained precursor concentrations needed for nucleation. Prior to the present study, possible impurities of NH₃ and amine concentrations present in a nucleation system have never been quantified in laboratory studies. The present study also discusses the effects of various experimental parameters on homogeneous nucleation observation results, especially in terms of growth rate (GR) estimated under low [H₂SO₄] conditions. There is another companion paper by Erupe et al. (2011), where we show the effects of trimethylamine on H₂SO₄ nucleation and our results show that trimethylamine acts in a strikingly similar manner as NH₃.

2 Experiments

The nucleation experimental setup was described in detail in Benson et al. (2008, 2009) and Young et al. (2008). Briefly, as shown in Fig. 1, the system consists of five main sections: (i) a photolysis region where OH radicals are produced from the photodissociation of H₂O vapor with a UV lamp ($\lambda < 185$ nm), (ii) a mixing region where the trace gases (SO₂, O₂, and N₂) are introduced into the flow tube and where H₂SO₄ is also produced from the following reaction:



at a local source, (iii) a double jacket, fast flow nucleation reactor (RH- and temperature-controlled), (iv) two chemical ionization mass spectrometers (CIMSs) to measure [H₂SO₄] and [NH₃] at the beginning of the nucleation reactor, and (v) a water CPC (TSI 3786) connected to the end of the nucleation reactor to measure particle number concentrations of particles.

There are also several improvements in the current nucleation setup. First, we have re-designed a new nucleation reactor with larger size diameters (13 cm now vs. 2.54 or 5.08 cm previously) based on Donahue et al. (1996) to significantly reduce wall loss factors (WLFs; the ratios of [H₂SO₄] at the beginning vs. at end of the nucleation reactor) of H₂SO₄ (1.5–4 now vs. 2–360 previously; Benson et al., 2008, 2009; Young et al., 2008), by using large size inner diameters and by introducing trace species from the center

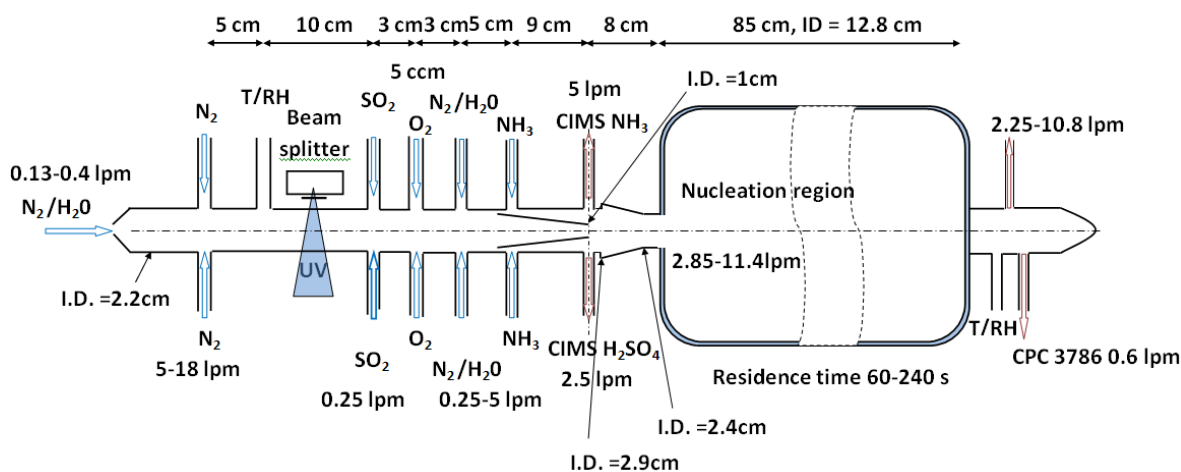


Fig. 1. A flow reactor used in KSU aerosol nucleation setup. All [H₂SO₄] and [NH₃] reported in this study were measured at the entrance of the nucleation reactor. Trimethylamine was also measured with CIMS based on a similar ion chemistry used in NH₃ measurements (Erupe et al., 2011). For wall loss studies, we used two CIMSs at the entrance and the end of the nucleation reactor, to simultaneously measure H₂SO₄ (Fig. 2b).

of the flow reactor under high flow; this design is described in detail below in this section. [H₂SO₄] were changed by changing [OH] with an iris beam splitter to control the UV beam; previously, [H₂SO₄] was changed by changing [SO₂] (Benson et al., 2008, 2009; Young et al., 2008). In addition, RH values were changed by adding water vapor at the downstream end after the production of H₂SO₄, to allow independent changes in RH in the nucleation reactor and [OH] (thus [H₂SO₄]).

H₂SO₄ vapor is produced only via Reaction (R1) (rate limiting step; rate constant $k_1 = 8.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$; Finlayson-Pitts and Pitts, 2000) and the following two subsequent reactions:

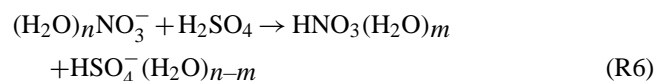


OH radicals were produced from UV dissociation of water vapor; this allows for an ozone-free system and hence provides an advantage compared to other studies where OH was produced from ozone photolysis (Berndt et al., 2005, 2006; Sipilä et al., 2010). [OH] were also directly measured from UV photon flux measurements. This method also allows for a minimal-hydrocarbon system compared to other methods where the OH titration method was used with various hydrocarbon compounds (Berndt et al., 2005, 2006). H₂SO₄ vapor was produced at a local source at the beginning of the nucleation reactor as opposed to a continuous source in the nucleation reactor, but this fact would not affect the measured J values, because the amount of H₂SO₄ molecules used by nucleation is typically much smaller than those lost on the wall and left in the gas phase (Benson et al., 2008; Young et al., 2008).

[H₂SO₄] were detected with CIMS, using the following ion-molecule reaction:



at atmospheric pressure, using ²¹⁰Po as the ion source and HNO₃ gases as reagent (Benson et al., 2008, 2009; Eisele and Tanner, 1993). The rate constant of Reaction (R5) (k_5) is $2.32 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ with a factor of 2 uncertainties (Viggiano et al., 1997); the ion-molecule reaction time was 0.1 s. As discussed in Erupe et al. (2010), it is also possible that in the ion molecule reaction region, NO₃⁻ ions make clusters, such as NO₃⁻(HNO₃)_m, where $m = 1, 2, 3, \dots$ etc., and NO₃⁻(H₂O)_n, and $n = 1, 2, 3, \dots$ etc. Laboratory measurements have showed that these clusters also react with H₂SO₄ to produce HSO₄⁻-containing clusters (Viggiano et al., 1997):



But their reaction rates, k_6 and k_7 , are all approximately $1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, very similar to k_5 (Viggiano et al., 1997). A collision dissociation chamber (CDC) was also used to effectively dissociate these clusters in our CIMS. Therefore, the presence of possible clusters of ion reagents would not affect the CIMS sensitivity. This is the case for the gas phase H₂SO₄ detection, but for the measurements of atmospheric neutral or charged clusters containing H₂SO₄, these ion reagent clusters can affect the mass peak identification and the instrument sensitivity of individual H₂SO₄ clusters sampled from ambient air. As shown in Young et al. (2008), calibrations of H₂SO₄ with OH have shown that

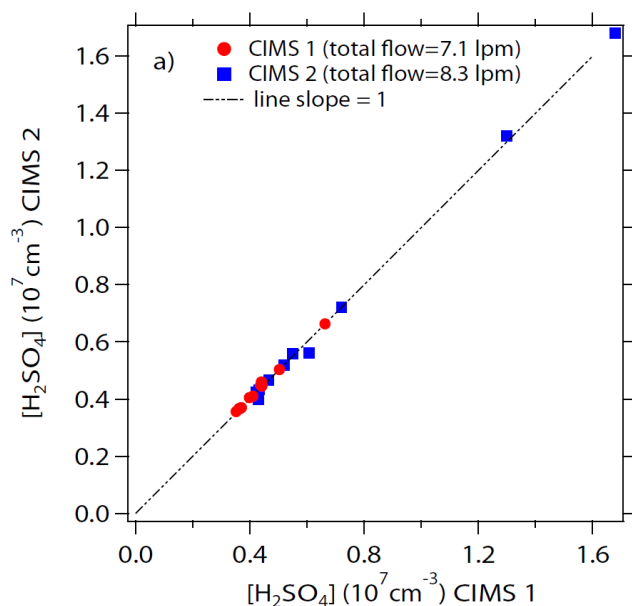


Fig. 2a. The measured [H₂SO₄] with two CIMSs at the beginning of the nucleation reactor. RH = 14 %. Dashed line shows the linear fitting of the data.

the CIMS measures all free-H₂SO₄ molecules produced in the gas phase. Figure 2a also shows the [H₂SO₄] measured with two CIMSs in the nucleation reactor, demonstrating that the two CIMSs give the similar results within <3 % in the 10⁶ cm⁻³ range.

The detection limit of H₂SO₄-CIMS was 2 × 10⁵ cm⁻³ and the uncertainty associated with our ambient measurements was estimated to be about 60 % at maximum (Erupe et al., 2010). In our previous studies (Benson et al., 2008; Young et al., 2008), we reported the residual [H₂SO₄] (measured at the end of the nucleation reactor) and further used the calculated WLFs to indicate the [H₂SO₄] range in the nucleation reactor. Here, we make a correction that these initial [H₂SO₄] should be a factor of 4.6 lower (due to the 2.3 times lower *k*₃ and the 2 times lower ion molecule reaction time due to different flow rates used) than the reported values, but this error does not affect the main conclusions of these previous papers, because of the high WLFs (up to 360).

[NH₃] were measured with another CIMS (Benson et al., 2010), using protonated ethanol ions as reagent based on:



at a lower pressure (20 torr); *k*₈ = 2.0 × 10⁻⁹ cm³ s⁻¹ (Nowak et al., 2006). One of the major technical challenges of measuring these sticky base molecules is to efficiently reduce the “CIMS background” signals, which are different by definition from impurity background concentrations in the nucleation reactor, and these background signals must be taken into account, as discussed in detail in Benson et al. (2010). The CIMS sensitivity for NH₃ was about 3–

4 Hz pptv⁻¹ for >1 MHz of reagent ion signals, with 30 % uncertainties. The estimated detection limit was ~45 pptv (3σ) for 1 min integration time.

The [NH₃] was measured only before the nucleation region (Fig. 1). But there were no significant losses from where NH₃ was introduced to where it was measured. Figure 1 shows where all the gases are added. If we added NH₃ to the port labeled N₂/H₂O (before the flow is centered) the NH₃ was the same as if we added it directly before the NH₃-CIMS inlet. To minimize adsorption and desorption of NH₃ (Benson et al., 2010; Neuman et al., 2003; Nowak et al., 2002, 2006, 2007; Yokelson et al., 2003), the entire experimental setup was built exclusively by FEP or PFA Teflon, without any metal materials. We have also used nitrogen gases vaporized from liquid nitrogen, which has the lowest [NH₃] impurities, <~20 pptv (Nowak et al., 2007). The impurity NH₃ gases in the system, very likely originated from deionized water, were systematically determined with CIMS as a function of RH in the system [NH₃] from water vapor increased linearly with RH in the flow tube, and was below 100 pptv for RH from 6–40 %. These values are actually similar to [NH₃] found in some remote areas (Dentener and Crutzen, 1994).

There are also possible amine impurities in deionized water, as ion exchange resins typically used for water purification often contain trimethylamine which is covalently bonded to polymer backbone of the resin to form the strong anion exchange site (for example, http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0032/0901b803800326ca.pdf?filepath=liquidseps/pdfs/noreg/177-01837.pdf&fromPage=GetDoc). We also have tried to measure possible impurities of amines in the system with CIMS based on the ion chemistry shown by Erupe et al. (2010), which is similar to Reaction (R8). Our preliminary investigations show trimethylamine (the most abundant atmospheric amine compound) of <85 pptv in the nucleation reactor at RH of 6 %, but more systematic experiments are required in the future for different types of amines under different RH conditions with higher CIMS sensitivities. Due to the presence of such impurities of NH₃ (<100 pptv, or <2 × 10⁹ cm⁻³) and amines (e.g., trimethylamine <85 pptv, or <1.7 × 10⁹ cm⁻³), strictly speaking, the BHN system referred in the present study is not the absolute BHN system and is rather a “pseudo” BHN system.

Our previous setup had residence times up to 77 s (Benson et al., 2008, 2009; Young et al., 2008), and recently we have redesigned the nucleation reactor (Fig. 1) to increase the range of residence times (50–240 s). The new nucleation reactor was designed to reduce wall loss of aerosol precursors significantly, by using a larger diameter size (I.D. of 12.8 cm now vs. 2.54 or 5.08 cm previously (Benson et al., 2008, 2009) and by introducing trace gases from the center of the flow tube with fast flows (Fig. 1), based on Donahue et al. (1996). The combination of the large diameter and high flows effectively minimizes the chances for gas phase molecules to travel from the center of the flow tube to the

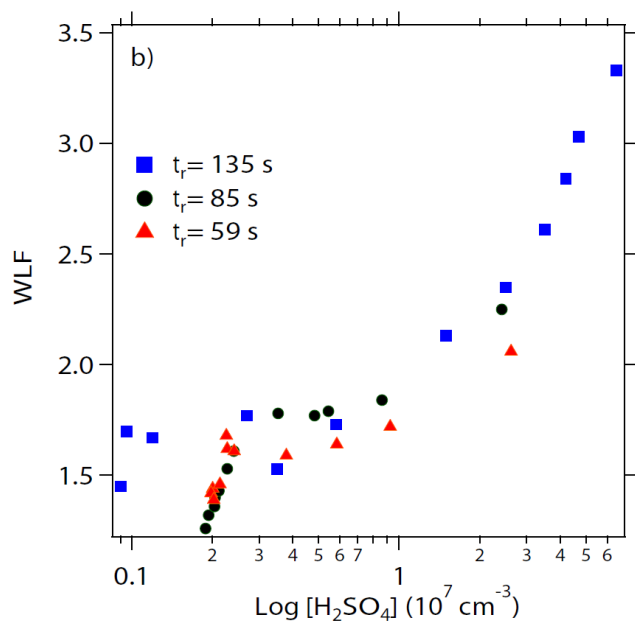


Fig. 2b. The measured WLF with two CIMSs located at the beginning (initial [H₂SO₄]) and end of the nucleation reactor (residual [H₂SO₄]) as a function of initial [H₂SO₄]. WLF is the ratio of initial to residual [H₂SO₄]. RH = 20 %.

wall. To examine how this “cone-shaped” tube (I.D. 1 cm at the end of the cone) would affect the CIMS measurements near the entrance of the nucleation reactor, we have compared [H₂SO₄] and particle concentrations in the reactor with and without this “cone-shaped” tube, and the differences were only about 20 %.

WLFs were measured by two CIMSs located at the beginning and end of the nucleation reactor. The measured WLFs were <4 (Fig. 2b), significantly lower than those in the previous experiments (up to 360) (Benson et al., 2008; Young et al., 2008). The measured values within the estimated WLFs from a diffusion limited process (Young et al., 2008), but were also dependent on the initial [H₂SO₄] and increased with increasing the initial [H₂SO₄]. It is also possible that inhomogeneous air mixing was present in the nucleation reactor which could affect our WLF measurements. In the future, we plan to investigate flow dynamics in the air mixing region and the nucleation reactor, in order to understand how different flow conditions affect nucleation experimental conditions.

The cutting sizes of the water CPC at different detection efficiencies are 3 nm (100 % detection efficiency), 2.3 nm (50 %), 2 nm (25–30%) and 1.8 nm (~10%), (http://www.tsi.com/uploadedFiles/Product_Information/Literature/Spec_Sheets/3786_2980291.pdf). Using these nucleation times and the measured total particle number concentrations measured by CPC, we derived J . Therefore, it is possible that the slopes of Log J vs. Log [H₂SO₄] were

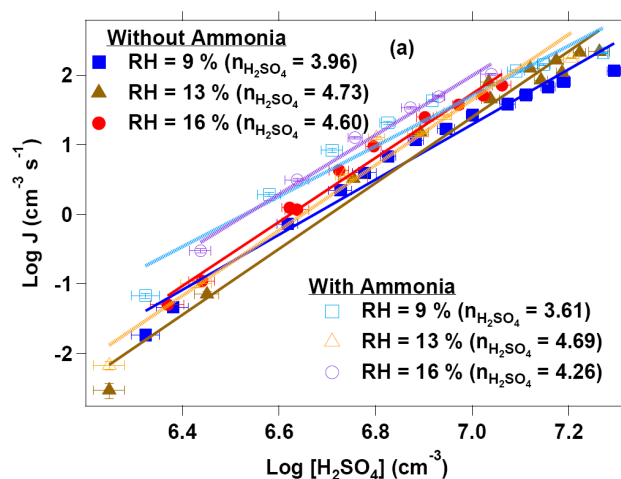


Fig. 3a. The measured Log J vs. Log [H₂SO₄] for BHN (filled symbols) and NH₃-THN (open symbols) at RH = 9 % (squares), 13 % (triangles), 16 % (circles). [NH₃] = 1.20 ppbv for THN. The horizontal and vertical bars indicate one standard deviation of [H₂SO₄] and J ; the solid or dashed lines show the linear fitting curve of the data.

overestimated due to lower detection efficiencies of CPC for particles smaller than 2 nm, because at higher [H₂SO₄], more particles grow and are detected by CPC.

3 Results

Figure 3a shows the measured J as a function of initial [H₂SO₄] for different RH values with and without introducing NH₃ gases (1.2 ppb). The total flow through the reactor was 10.3 lpm, corresponding to a residence time through the nucleation region of 240 s. J values varied from 3×10^{-3} – 2×10^2 cm⁻³ s⁻¹ for RH values 9–16 % and initial [H₂SO₄] from 2×10^6 – 2×10^7 cm⁻³. In general, J were higher in the presence of NH₃ (1.2 ppbv) than in the absence of it. However, in both BHN and THN cases, the [H₂SO₄] threshold to produce the unity J (1 cm⁻³ s⁻¹) was at the 10⁶ cm⁻³ range, which is one of the main conclusions of the present study. The slope of Log J vs. Log [H₂SO₄] was 3–5 for both BHN and THN cases. Unlike Benson et al. (2009), in which the slope increased with decreasing RH, there was no clear trend in the slope as a function of RH. This slope only slightly decreased (reduced by 0.04 to 0.4 molecules) for THN compared to BHN for the same RH.

Figure 3b shows the measured Log J vs. Log RH for BHN and THN with NH₃ (20 ppbv). J varied from 3×10^{-3} – 3×10^1 cm⁻³ s⁻¹ for RH values 6–40 %, initial [H₂SO₄] in the range of 3×10^6 – 7×10^6 cm⁻³ and at a residence time of 120 s, and was usually higher in the presence of NH₃ than without it. The slope of Log J vs. Log RH was 1–4 and only slightly reduced in the presence of NH₃. Thus, under these experimental conditions, there were also no substantial

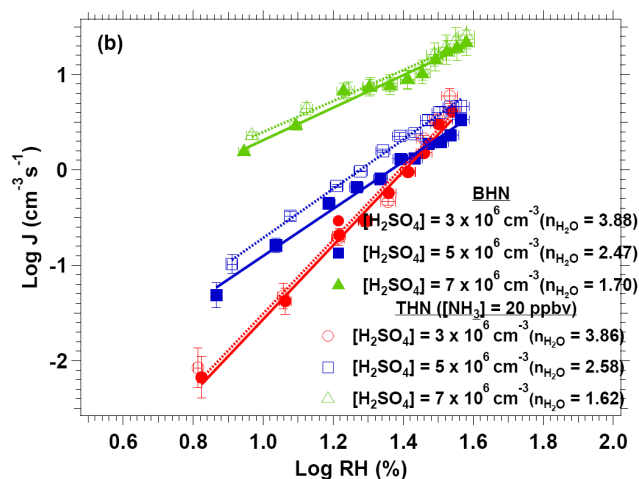


Fig. 3b. Log J vs. Log RH. $[\text{NH}_3] = 20$ ppbv. The total flow through the reactor is 13.1 lpm (5.6 lpm through the nucleation region and 7.5 lpm to the two CIMSSs), corresponding to a residence time through the nucleation region of 120 s.

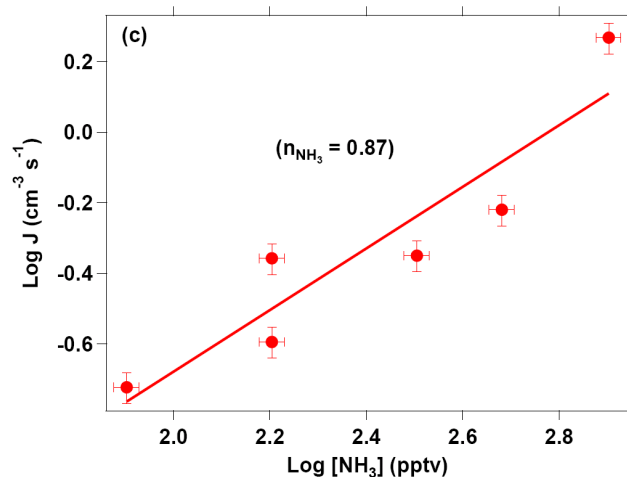


Fig. 3c. The measured Log J vs. Log $[\text{NH}_3]$ for THN experiments. RH = 8%. $[\text{H}_2\text{SO}_4] = 8.2 \times 10^6 \text{ cm}^{-3}$. Residence time = 170 s.

changes in the composition of H₂SO₄ and H₂O molecules in critical clusters in the presence and absence of NH₃.

Figure 3c shows the measured Log J vs. Log $[\text{NH}_3]$ at $[\text{H}_2\text{SO}_4]$ of $8.2 \times 10^6 \text{ cm}^{-3}$, $[\text{NH}_3]$ from 0.08–0.80 ppbv, RH of 8%, and a residence time of 170 s. At $[\text{NH}_3]$ from 0.08–1 ppbv, J varied from 0.2–2 $\text{cm}^{-3} \text{ s}^{-1}$. The slope of Log J vs. Log $[\text{NH}_3]$ was nearly one, indicating that there is only one molecule of NH₃ present in the critical clusters, consistent with the above result that the slopes of Log J vs. Log $[\text{H}_2\text{SO}_4]$ and Log J vs. Log RH did not change in BHN and THN (Fig. 3a and b).

To understand the effects of residence time on the slope of Log J vs. Log $[\text{H}_2\text{SO}_4]$, we also compared data taken at different residence times (thus nucleation times) using different

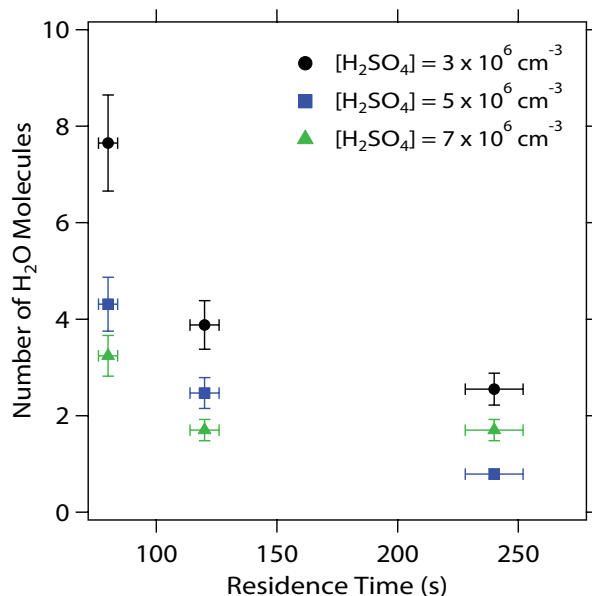


Fig. 4. The $n_{\text{H}_2\text{O}}$ values (derived from Log J vs. Log RH) as a function of residence time and $[\text{H}_2\text{SO}_4]$. The horizontal and vertical bars indicate one standard variation in residence time and $n_{\text{H}_2\text{O}}$.

diameters of the nucleation reactors (not shown). We found that at shorter residence times the slopes were higher and J values were lower at similar $[\text{H}_2\text{SO}_4]$. For low $[\text{H}_2\text{SO}_4]$, increasing residence time can enhance J , because longer residence times would allow more particles grow from critical clusters to the measurable sizes by CPC (measuring particles > 1.8 nm at which the TSI 3876 detection efficiency is $\sim 10\%$). On the other hand, for high $[\text{H}_2\text{SO}_4]$, increasing residence time would decrease J , because H₂SO₄ molecules may be lost by the competitive scavenging process on the tube wall and on aerosol surfaces. As a result, the slope should be smaller at a long residence time than at a short residence time. That is, depending on different residence times and different levels of $[\text{H}_2\text{SO}_4]$, either nucleation or scavenging can be dominant, as discussed in Young et al. (2008), and such competing processes are reflected in different slopes taken at different residence times. The same trend was also observed for the slope of Log J vs. Log RH and the slope also decreased with increasing residence time (Fig. 4). Additionally, the slope of Log J vs. Log $[\text{H}_2\text{SO}_4]$ was also affected by low detection efficiencies of CPC for particles smaller than 2 nm, as discussed in the following section.

By comparing the measured J in THN vs. BHN taken under similar experimental conditions, EF was derived. EF values were usually lower than one order of magnitude for $[\text{H}_2\text{SO}_4]$ from 2×10^6 – $2 \times 10^7 \text{ cm}^{-3}$, $[\text{NH}_3]$ from 1.22–2.6 ppbv, RH from 6–16% and residence times of 60–240 s (Fig. 5a). Similarly to Benson et al. (2009), EF was in general higher for lower $[\text{H}_2\text{SO}_4]$ (Fig. 5a), lower RH (Fig. 5b) and higher at higher NH₃ (Fig. 5c).

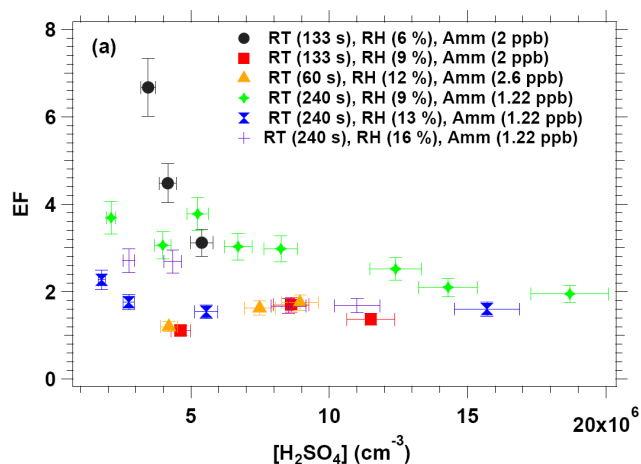


Fig. 5a. The measured EF as a function of [H₂SO₄]. [NH₃] = 1.22–2.6 ppbv. RH = 6–16 %. Residence time = 60–240 s.

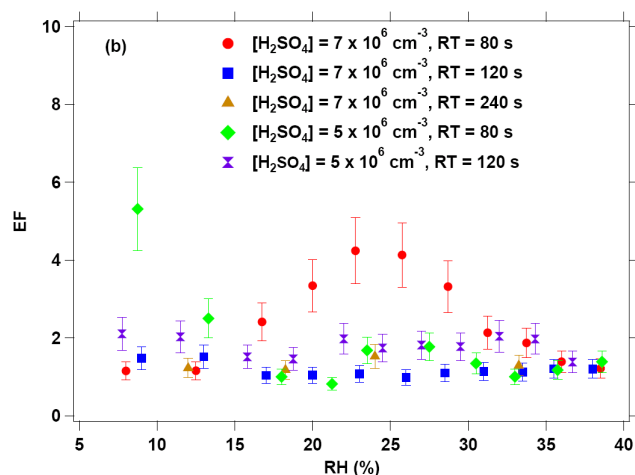


Fig. 5b. The measured EF as a function of RH. [H₂SO₄] = 5 × 10⁶–7 × 10⁶ cm⁻³. [NH₃] = 20 ppbv. RH = 7–39 %. Residence time = 80–240 s.

4 Discussions

4.1 Growth Rates (GR)

The TSI 3876 (water CPC) cutting size with 10 % detection efficiency is ~ 1.8 nm (http://www.tsi.com/uploadedFiles/Product_Information/Literature/Spec_Sheets/3786_2980291.pdf). We have tested this detection efficiency with a particle size magnifier (PSM, Airmodus A09) (Vanhanen et al., 2011). Our results indicate that CPC measures 2 nm particles with detection efficiency of ~ 25 % (consistent with the above online spec sheet), while PSM has 85 % detection efficiency at this size. CPC also measures a noticeable amount of particles of 1.8 nm (e.g., 50–100 cm⁻³). By measuring particle number concentrations with PSM at different saturator flow rates (thus different cutting sizes in PSM) and different [H₂SO₄] (thus different mode sizes of the particles generated), we also found that these particles in the nucleation reactor are all smaller than 2 nm, with the majority smaller than 1.8 nm.

Kulmala et al. (2007) have suggested critical cluster sizes to be from 1–2 nm. Considering that the critical cluster size is 1.5 nm and the produced particles in our nucleation reactor are smaller than 1.8 nm, we derived GR to be than 7.7 nm h⁻¹ (residence time of 240 s in Fig. 3a). If critical size is 1.7 nm, then the GR is less than 2.6 nm h⁻¹. These GR values are well within the range of GR (1–20 nm h⁻¹), for example, measured in a less polluted US continental environment at similar [H₂SO₄] used in the present study (Erupe et al., 2010). A GR of 1 nm h⁻¹ is estimated by condensation of [H₂SO₄] of 1.5 × 10⁷ cm⁻³ (Nieminen et al., 2010) based on the kinetic regime condensation theory and accommodation coefficient of H₂SO₄ of unity. Considering an uncertainty of 60 % in H₂SO₄ detection by CIMS and an additional 20 % uncertainty in [H₂SO₄] due to the cone shaped inlet, a GR

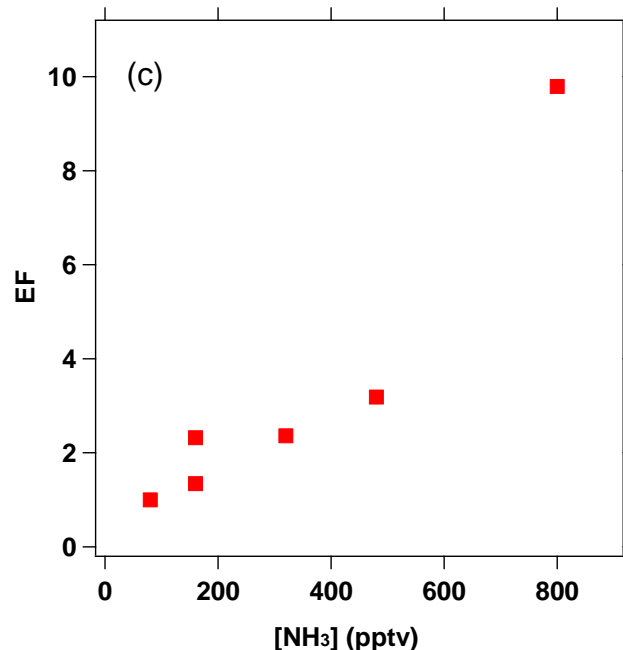


Fig. 5c. The measured EF as a function of [NH₃]. [H₂SO₄] = 8.2 × 10⁶ cm⁻³. RH = 8 %. Residence time = 170 s.

of 1.8 nm h⁻¹ is possible under the CIMS-reported [H₂SO₄] of 1 × 10⁷ cm⁻³. By further considering the effects of base molecules on growth (additional 10 % discussed below), this estimated GR (1.8 nm h⁻¹) would become ~ 2 nm h⁻¹, as the upper limit. Coagulation of cluster size particles is negligible. This upper limit of GR value is quite close to the GR of 2.6 nm h⁻¹ estimated above from our observations. Similarly high GR was also found in other laboratory studies (Berndt et al., 2005, 2006), in which particles were detected with TSI 3776 (the same detection efficiencies as TSI 3786) at [H₂SO₄] of 7 × 10⁶ cm⁻³ and a residence time of 290 s (they

reported J of 0.3–0.4 cm⁻³ s⁻¹); therefore, these reported experimental conditions imply GR was around 4 nm h⁻¹. Below we examine the possible factors that can contribute to the measured GR in our system.

Assuming that newly nucleation H₂SO₄ particles were fully neutralized by NH₃, GR will only increase with a factor of 1.1. Similarly, amines (organic base compounds) also will not significantly contribute to the GR. GR is ultimately determined by H₂SO₄ vapor (in the absence of condensable organic compounds), whereas NH₃/amines and water can only co-condense on newly formed particles to maintain thermodynamic equilibrium with the vapor phase. Pryor et al. (2011) and Zhang et al. (2009) have shown that tens or hundreds of pptv of NH₃ actually cannot explain the elevated GR. So it is unlikely that the possible impurities of NH₃ or amines present in the system can explain the GR estimated in our nucleation reactor.

We have also ruled out the major effects of organic compounds on the GR. In our system, we did not introduce any organic compounds. However, there may be still some trace level of hydrocarbons (and carbon monoxide) gases from the highly purified gas bottles, but they would be rapidly scavenged by OH radicals. Within very short reaction times (<0.1 s in our system; Young et al., 2008), hydrocarbons do not produce highly oxidized low volatility compounds to condense on particles and even there are some higher generations of oxidation products, their concentrations are too low to affect aerosol growth in the system. We have also made additional tests to investigate the effects of organics, by introducing different functional groups of organic compounds at the ppbv to hundreds of ppbv level, but these organic compounds did not produce particles. For example, in the presence of isoprene at the sub-ppbv level, there was no effect on nucleation of H₂SO₄, but when isoprene concentrations increased to ppbv level, nucleation was abruptly suppressed because isoprene scavenges OH rapidly, similarly to (Kiendler-Scharr et al., 2009) plant chamber study. Erupe et al. (2011) have also discussed the effects of oxidation products of trimethylamine with OH; the amine oxidation products did not produce particles (implying that nucleation enhancement was likely due to formation of salts, rather than due to amine oxidation products).

4.2 THN effects

There are also differences, especially in the threshold of H₂SO₄ and the slope, between the current and the early THN study (Benson et al., 2009). The main difference between the two studies is the flow reactor used for nucleation experiments. Because the flow reactor is much larger in the present study (I.D. 12.8 cm vs. 5.08 cm previously), we had much higher residence times in the current study (up to 240 s) with the current setup. The difference in residence times will cause the slopes to be different so the behavior with respect to relative humidity may also be altered. As for the dif-

ferences in EF, in the previous study (Benson et al., 2009) it was shown that EFs increase exponentially with decreasing H₂SO₄ and the same trend was also found in the present study. From these results, one would expect that EFs in the current study should actually be higher due to lower [H₂SO₄] used. However, because of the differences between these two studies (including larger I.D. for the nucleation region and higher residence times), direct extrapolation between the studies is inconclusive. It seems only when all conditions are the same that EFs are higher for lower H₂SO₄. These results also imply that, due to matrix effects of experimental conditions on nucleation, one should be extremely cautious when directly comparing different studies.

Our observations show that the onset H₂SO₄ for nucleation to occur ($J = 1$ cm⁻³ s⁻¹) is on the order of 10⁶ cm⁻³. Atmospheric observations (Birmili et al., 2000; Erupe et al., 2010; Kulmala et al., 2004; McMurry et al., 2005; Weber et al., 1999) have shown that nucleation occurs at [H₂SO₄] of 10⁶–10⁸ cm⁻³. In the present study, we found the threshold of 10⁶ cm⁻³ [H₂SO₄] and the slope of Log J vs. Log [H₂SO₄] between 3–5 for both BHN and NH₃-THN cases, when using TSI 3876. While we used a longer residence time (60–240 s) in the nucleation region, H₂SO₄ was also produced in a local source. These slopes were likely affected by different cuttings sizes in TSI 3876, which can measure only a fraction of 1.8–2 nm particles as discussed in the above section. Sipilä et al. (2010)'s PSM measurements have showed that the slope was only 1–2, due to higher detection efficiencies for 1–2 nm particles in PSM. Based on these slopes, Sipilä et al. (2010) have concluded that the critical clusters contain only 1–2 H₂SO₄ molecules. However, it is difficult to understand, from the thermodynamics viewpoint, how monomer (gas phase molecule) or small size dimers of H₂SO₄ can act as critical clusters, since they would not spontaneously condense to grow larger.

It has been also common practice to compare the slope of Log J vs. Log [H₂SO₄] obtained in the laboratory studies with those from field studies (Metzger et al., 2010; Sipilä et al., 2010). But there is a difference in the methods used to make these slopes in the laboratory studies and field observations. The atmospherically derived slopes are usually from ensemble data obtained at various RH and temperatures and different saturation ratios of possible ternary precursors (which are unknown currently). On the other hand, laboratory values are derived from the data taken under a constant temperature and RH, and presumably in the absence of, or at least in the possibly lowest amount of, ternary species in the binary case. Such a difference has been neglected when comparing the slopes derived from field and laboratory studies. A more rigorous approach directly applying the first nucleation theorem, in which which nucleation rates can be sorted out under the same temperature and the same supersaturation ratios of other nucleation precursors, for atmospheric observations is needed to better understand the chemical composition of the critical clusters in the atmosphere.

One of the main principles of THN is that it could explain nucleation occurring at lower [H₂SO₄] where BHN would fail (Weber et al., 1998). As shown by the present study and others (Ball et al., 1999; Benson et al., 2009), the threshold H₂SO₄ for nucleation was similar for BHN and THN. It was usually on the same order of magnitude and at most only about half of the value found in BHN, implying that while THN can occur at lower [H₂SO₄], any enhancement by NH₃ would not be large enough to shift the threshold value. Most EF values were largest at three orders of magnitude for [H₂SO₄] from 10⁸–10¹⁰ cm⁻³ (Ball et al., 1999; Benson et al., 2009). As shown in the present study, when [H₂SO₄] (10⁶–10⁷ cm⁻³) and [NH₃] (0.08–2.6 ppbv) were one or three orders of magnitude lower than in these cited studies, the EF values were mostly <10 (Figs. 3 and 5).

Our results show that the slope of Log *J* vs. Log [H₂SO₄] and Log *J* vs. Log RH were reduced under THN than in BHN, but the both slopes were also very similar in the BHN and THN cases. For example, the Log *J* vs. Log [H₂SO₄] slope was reduced only by a fraction of a molecule (0.04 to 0.4 molecules). Thus, while the *J* was enhanced, an addition of NH₃ did not drastically change the H₂SO₄ and H₂O composition of the critical clusters under atmospherically relevant conditions. These results are different from previous studies (Ball et al., 1999; Benson et al., 2009) which showed that the critical cluster contains 2–3 less molecules of H₂SO₄ in the presence of NH₃.

The slope of Log *J* vs. Log [NH₃] derived from the present study was only one, which is consistent with cluster measurements by Hanson and Eisele (2002). And, this unity value also explains the small reduction in the slope of Log *J* vs. Log [H₂SO₄] and Log *J* vs. Log RH in THN than in BHN. This low slope in Log *J* vs. Log [NH₃] may also imply that NH₃ actually acts rather as a catalysis agent and is less physically incorporated into the cluster formation itself during the THN process. It is also possible that there is an energy reduction due to the exothermic heat released from the acid-base neutralization reaction between H₂SO₄ and NH₃, so that even only one molecule of NH₃ is sufficient to reduce the Gibbs free energy for critical cluster formation.

Field studies of new particle formation made in Atlanta, Georgia in the summer 2002 showed that [H₂SO₄], [NH₃] and particle concentrations are approximately 10⁶–10⁸ cm⁻³, 1–10 ppbv, and 10³–10⁵ cm⁻³, respectively (McMurry et al., 2005). And, the precursor concentrations used in the present laboratory experiments fall within these observation results. McMurry et al. (2005) also showed the slope of logarithms of particle concentration vs. [NH₃] is nearly one (McMurry et al., 2005), similar to the present study showing that the slope of Log *J* vs. Log [NH₃] is only one. Another study made in Kent, Ohio crossing four different seasons showed the threshold of [H₂SO₄] is around 10⁶ cm⁻³, even when NH₃ was at the sub-ppbv level (Erupe et al., 2010). While our laboratory observations also fall within the observation results taken in Kent, the Kent mea-

surements had a nearly constant NH₃ level (sub-ppbv) over different seasons, so it was difficult to use these data to quantitatively test the *J* vs. [NH₃] relationship.

Our laboratory observations show the threshold of [H₂SO₄] needed for the unity *J* is order of 10⁶ cm⁻³, with [NH₃] from 0.08–2.6 ppbv at 288 K. In comparison, the threshold in the THN parameterization is, for example, [H₂SO₄] of 10⁹ cm⁻³ for [NH₃] of 1 ppbv at 273 K (Merikanto et al., 2007). A similar [H₂SO₄] threshold is also required in the BHN parameterization (Vehkamäki et al., 2002). We also used our typical experimental conditions of [H₂SO₄], [NH₃], RH and temperature used in the present study, but the THN parameterization (Merikanto et al., 2007) did not produce particles. As discussed in Erupe et al. (2010), this THN parameterization also did not reproduce atmospheric observations made in Kent.

Since the [H₂SO₄] threshold (10⁶ cm⁻³) found in BHN or THN (with sub-ppbv NH₃, commonly found in the atmosphere) is well within the typical atmospheric conditions (Erupe et al., 2010), one would expect that aerosol nucleation should take place instantly under most atmospheric conditions. But in the atmosphere, even at [H₂SO₄] of 10⁷ cm⁻³, nucleation often does not occur with low surface areas of pre-existing aerosols (Erupe et al., 2010). These results open an important atmospheric question which requires future studies to answer: under what atmospheric conditions does new particle formation actually not occur?

While impurities of NH₃ or amines in the nucleation system have become increasingly recognizable for laboratory studies, this has become to a question whether BHN process is less important than previously thought. While this question remains to be examined in the future, our THN with NH₃ (this study) and trimethylamine (Erupe et al., 2011), together with other laboratory studies (Berndt et al., 2005; Sipilä et al., 2010), strongly imply that H₂SO₄ is still the main aerosol nucleation precursor. There is also another important aspect that one should take into account in homogeneous nucleation studies. Even if the system has multiple chemical species, it cannot be simply assumed that nucleation would take place through THN or multicomponent processes; rather it depends on several conditions including how much these ternary species are present in the system, and sometimes nucleation can take place solely via BHN even in the presence of ternary species (McGraw and Zhang, 2008). A laboratory study has also shown that different mechanisms may occur with the same aerosol precursors, under different experimental conditions (Kim et al., 1998). A typical atmospheric example would be the upper troposphere and lower stratosphere; even when there are many other chemical species in the gas phase, ion induced nucleation dominates in this region (Lee et al., 2003), because of low temperatures and high ion production rates by cosmic rays. While nucleation takes place nearly everywhere in the atmosphere, it is essential to understand how different nucleation processes co-exist in the same condition and when a certain nucleation

process dominates under different atmospheric conditions. A universal nucleation mechanism which can be applied to all atmospheric conditions would unlikely exist, because of the diverse chemical, physical, meteorological and dynamics conditions found in the real atmosphere.

5 Conclusions

Our laboratory observations show that both the BHN and THN thresholds are $10^6 \text{ cm}^{-3} \text{ H}_2\text{SO}_4$ and the slope of Log J vs. Log [H₂SO₄] and Log J vs. Log RH are 3–5 and 1–4, respectively, when a CPC (TSI CPC 3876). The slope of Log J vs. Log [NH₃] is only one for THN. EF by NH₃ varies depending on [H₂SO₄], [NH₃], RH and residence times, but was for most time <10. To our knowledge, this is first time that NH₃-THN laboratory studies were made under conditions relevant to the lower troposphere. Our results reinforce that nucleation can be enhanced by NH₃, but H₂SO₄ is still the main nucleation precursor responsible for new particle formation in the atmosphere. While our laboratory study could reproduce atmospheric observations made in Atlanta (McMurry et al., 2005) and Kent (Erupe et al., 2010), the current THN parameterization (Antilla et al., 2005; Merikanto et al., 2007) fails to produce particles under conditions used in our laboratory study and those found in the Kent field observations (Erupe et al., 2010).

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