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Ternary homogeneous nucleation of H_2SO_4 , NH_3 , and H_2O under conditions relevant to the lower troposphere

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Ternary homogeneous nucleation (THN) of H_2SO_4 , NH_3 and H_2O has been used to explain new particle formation in various atmospheric regions, yet laboratory measurements have failed to reproduce atmospheric observations. Here, we report laboratory observations of THN made under conditions relevant to the lower troposphere (H_2SO_4 of 10^6 – 10^7 cm^{-3} , NH_3 of 0.08–20 ppbv, and 288 K). Our observations show that NH_3 can enhance atmospheric H_2SO_4 aerosol nucleation and the enhancement factor (EF) in nucleation rate due to NH_3 increases linearly with increasing NH_3 and increases exponentially with decreasing H_2SO_4 and RH. The critical clusters of ternary homogeneous nucleation contain 3–5 molecules of H_2SO_4 , 1–4 molecules of H_2O , and only 1 molecule of NH_3 . The composition of H_2SO_4 and H_2O in critical clusters and the threshold of H_2SO_4 concentrations required for the unit nucleation rate both do not vary in the presence and absence of NH_3 . These observations can be directly used to improve aerosol nucleation models to correctly assess how man-made SO_2 and NH_3 affect aerosol formation and CCN production at the global scale.

1 Introduction

Nucleation (gas to particle conversion) is one of the most important atmospheric processes that directly control the number concentrations of aerosol particles and thus can affect global climate, air quality and human health. Nucleation 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 (40%) 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; Sipila et al., 2010; Young et al., 2008) have shown that sulfuric acid (H_2SO_4) is the main nucleation precursor, but the role of other ternary species such as ammonia (NH_3) and organic compounds is unclear.

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Chemical composition analysis of nanometer size particles made at various loca-
tions has shown these newly formed particles contain sulfate, ammonium and various
organic compounds including amines (Smith et al., 2008, 2009). Global atmospheric
aerosol model calculations also suggested that in a wide range of the troposphere and
the lower stratosphere, nucleation rates 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 explained by THN for many years
(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 over-predicts nucleation rates of THN over binary homogeneous nucleation
(BHN) of H₂SO₄ and H₂O. This THN parameterization includes the NH₃ range from
0–100 pptv and for NH₃ greater than 100 pptv, it assumes that there is no effect on the
nucleation rate except for H₂SO₄ less than 10⁶ cm⁻³, while atmospherically observed
NH₃ are typically at the sub-ppbv and ppbv level (Erupe et al., 2010; Nowak et al.,
2006). Later THN parameterizations included the effects of stable ammonium bisul-
fate (NH₄HSO₄) formation (Antilla 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).

At present, the exact amount of NH₃ needed to enhance nucleation rates 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. These
limited observations have shown that at such high concentrations of H₂SO₄, NH₃ of
ppbv or sub-ppbv can increase nucleation rates up to 3 orders of magnitude, although
often the enhancement factors (EF; defined as the ratio of nucleation rates in THN vs.
in BHN) due to NH₃ are around one order of magnitude.

In the present laboratory study, we present laboratory observations of homogeneous nucleation involving, H_2SO_4 , NH_3 , and H_2O . Experiments were performed at H_2SO_4 of 10^6 – 10^7 cm^{-3} , NH_3 of 0.08–2.6 ppbv (except only one occasion where 20 ppbv NH_3 was used), RH of 6–40% and 288 K, in a temperature- and RH-controlled fast flow nucleation reactor.

2 Experiments

Our nucleation experimental setup was described in detail in (Benson et al., 2008, 2009; Young et al., 2008). Briefly, the system consists of five main sections: (i) a photolysis region where OH radicals are produced from the photodissociation of H_2O vapor with a UV lamp ($\lambda < 185$ nm), (ii) a mixing region where the trace gases (SO_2 , O_2 , and N_2) are introduced into the flow tube and where H_2SO_4 is also produced from the $\text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3$ Reaction (R1, 2.0×10^{-11} $\text{cm}^3 \text{s}^{-1}$) at a local source (as opposed to continuously formed in the nucleation reactor), (iii) a double jacket, fast flow nucleation reactor (RH- and temperature-controlled), (iv) two chemical ionization mass spectrometers (CIMSs) to measure H_2SO_4 and NH_3 at the beginning of the nucleation reactor, and (v) a CPC (TSI 3786), which is connected to the end of the nucleation reactor, to measure particle number concentrations for >3 nm particles.

There are also several improvements in the current nucleation setup. We have 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 (WLF) of H_2SO_4 (1.5–4 now vs. 2–360 previously), by using large size inner diameters and by introducing trace species from the center of the flow reactor under high flow. H_2SO_4 concentrations are changed by changing OH with an iris beam splitter to control the UV beam; previously, H_2SO_4 was changed by changing SO_2 (Benson et al., 2008, 2009; Young et al., 2008). In addition, RH values are changed by adding water vapor at the downstream end after the production of H_2SO_4 , to allow independent changes in RH in the nucleation reactor and OH (thus H_2SO_4) concentrations.

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The detection scheme for the H₂SO₄-CIMS is based on NO₃⁻ + H₂SO₄ → HNO₃ + HSO₄⁻ (R2, 2.3 × 10⁻⁹ cm³ s⁻¹) at atmospheric pressure (Benson et al., 2008, 2009; Eisele and Tanner, 1993; Erupe et al., 2010; Young et al., 2008). NH₃ is detected in another CIMS using protonated ethanol ions as the reagent based on NH₃ + (CH₃CH₂OH)H⁺ → NH₄⁺ + CH₃CH₂OH (R3, 2.0 × 10⁻⁹ cm³ s⁻¹) at a lower pressure (20 torr) (Benson et al., 2008, 2009, 2010; Erupe et al., 2010; Nowak et al., 2006; Young et al., 2008). One issue that must be taken into account in the nucleation experiments is the amount of NH₃ that comes from the flow tube system, which most likely originated from water vapor (Nowak et al., 2006). This background NH₃, measured with CIMS, increased linearly with RH in the flow tube, but for RH from 6–40%, the NH₃ from water vapor in the flow tube was ~20–100 pptv.

3 Results

Figure 1a shows the measured nucleation rate (*J*) as a function of initial [H₂SO₄] for different RH values with and without NH₃. The total flow through the reactor was 10.3 lpm (2.8 lpm through the nucleation region and 7.5 lpm to the two CIMSs), corresponding to a residence time through the nucleation region of 240 s. *J* values varied from 3 × 10⁻³–2 × 10² cm⁻³ s⁻¹ for RH values 9–16% and initial [H₂SO₄] from 2 × 10⁶–2 × 10⁷ cm⁻³ and in general, was 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 unit *J* (1 cm⁻³ s⁻¹) was at the 10⁶ cm⁻³ range, which is one of the main findings of the present study.

From a plot of Log *J* vs. Log [H₂SO₄], one can obtain the number of H₂SO₄ molecules in the critical cluster (*n*_{H₂SO₄}) if saturation ratios of other components are constant, based on the first nucleation theorem (Kashchiev, 1982; McGraw and Zhang, 2008). The derived *n*_{H₂SO₄} was 3–5 for both BHN and THN cases. Unlike (Benson et al., 2009) in which *n*_{H₂SO₄} increased with decreasing RH, there was no clear trend in *n*_{H₂SO₄} as

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110 a function of RH. The $n_{\text{H}_2\text{SO}_4}$ values only slightly decreased (reduced by 0.04 to 0.4 molecules) for THN compared to BHN for the same RH.

Figure 1b shows the measured $\text{Log } J$ vs. Log RH for BHN and THN with NH_3 (20 ppbv). J varied from 3×10^{-3} – $3 \times 10^1 \text{ cm}^{-3} \text{ s}^{-1}$ for RH values 6–40%, initial $[\text{H}_2\text{SO}_4]$ in the range of 3×10^6 – $7 \times 10^6 \text{ cm}^{-3}$ and at a residence time of 120 s, and was usually higher in the presence of NH_3 than without it. In both the BHN and THN cases, the H_2SO_4 threshold to produce the unit J was again at the 10^6 cm^{-3} range. The slope of $\text{Log } J$ vs. Log RH , which is the same as the number of water molecules ($n_{\text{H}_2\text{O}}$) in critical clusters, was 1–4 and only slightly reduced in the presence of NH_3 . Thus, under these experimental conditions, there was also no change in the composition of H_2SO_4 and H_2O molecules in critical clusters in the presence and absence of NH_3 .

120 Figure 1c shows the measured J vs. NH_3 at H_2SO_4 of $8.2 \times 10^6 \text{ cm}^{-3}$, NH_3 from 0.08–0.80 ppbv, RH of 8 %, and a residence time of 170 s. At NH_3 from 0.08–1 ppbv, J varied from 0.2 – $2 \text{ cm}^{-3} \text{ s}^{-1}$. The slope of $\text{Log } J$ vs. $\text{Log } \text{NH}_3$ was nearly one, indicating that there is only one molecule of NH_3 present in the critical clusters, consistent with the above result that $n_{\text{H}_2\text{SO}_4}$ and $n_{\text{H}_2\text{O}}$ values did not change in BHN and THN (Fig. 1a and b).

130 By comparing the measured nucleation rates in THN vs. BHN taken under similar experimental conditions, enhancement factors (EF) were derived. EF values were usually lower than 10 for H_2SO_4 from 2×10^6 – $2 \times 10^7 \text{ cm}^{-3}$, NH_3 from 1.22–2.6 ppbv, RH from 6–16% and residence times of 60–240 s (Fig. 2a). Similarly to (Benson et al., 2009), EF was in general higher for lower H_2SO_4 (Fig. 2a) and lower RH (Fig. 2b) and higher at higher NH_3 (Fig. 2c).

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4 Discussions

Our observations show that the onset H_2SO_4 for nucleation to occur ($J = 1 \text{ cm}^{-3} \text{ s}^{-1}$) is on the order of 10^6 cm^{-3} with or without NH_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 H_2SO_4 of 10^6 – 10^8 cm^{-3} . On the other hand, BHN parameterizations typically require H_2SO_4 of 10^9 cm^{-3} or higher (Vehkamäki et al., 2002). Recent laboratory studies have shown that nucleation can occur at $[\text{H}_2\text{SO}_4]$ as low as 10^6 cm^{-3} (Berndt et al., 2005, 2008; Metzger et al., 2010; Sipilä et al., 2010). However, only two studies so far have shown the power dependence of J on $[\text{H}_2\text{SO}_4]$ of one (Metzger et al., 2010) or two (Sipilä et al., 2010), as found from atmospheric observations. (Sipilä et al., 2010) used a newly developed particle detector that measures particles down to 1.5 nm and also incorporated a longer residence time in the nucleation reactor and a continuous source of H_2SO_4 production in the nucleation reactor. (Metzger et al., 2010) added organic compounds (i.e. trimethylbenzene) in the H_2SO_4 aerosol nucleation, but used a regular TSI CPC 3025 to detect particles.

In the present study, we found the threshold of $10^6 \text{ cm}^{-3} \text{H}_2\text{SO}_4$ and the slope of J vs. H_2SO_4 between 3–5 for both BHN and NH_3 -THN cases, using the same instrument used in field studies to measure particles (TSI CPC 3876). While we used a longer residence time (60–240 s) in the nucleation region, H_2SO_4 was also produced in a local source. The slopes (3–5, as compared to 1–2) found in BHN are, however, thermodynamically consistent with quantum chemical calculations which show that a monomer or dimer of H_2SO_4 would spontaneously evaporate and is difficult to form critical clusters by themselves (Lovejoy et al., 2004; McGraw and Weber, 1998; McGraw and Zhang, 2008).

One of the main principles of THN is that it could explain nucleation occurring at lower $[\text{H}_2\text{SO}_4]$ 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 H_2SO_4 for nucleation was similar for BHN and THN. It was usually on the same order of magnitude and at

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most only about half of the value found in BHN, implying that while THN can occur at lower H₂SO₄, any enhancement with 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 (Fig. 2). These observation results may be consistent with density functional calculations which show that NH₃ can lower the Gibbs free energy of H₂SO₄–H₂O clusters under actual atmospheric conditions, but the amount of such clusters would be also negligible due to the required temperatures and NH₃ (Kurten et al., 2007).

Our results show that the $n_{\text{H}_2\text{SO}_4}$ and $n_{\text{H}_2\text{O}}$ values were reduced under THN compared to BHN, but $n_{\text{H}_2\text{SO}_4}$ and $n_{\text{H}_2\text{O}}$ both were also very similar in BHN and THN cases. For example, the $n_{\text{H}_2\text{SO}_4}$ value was reduced only by a fraction of a molecule (0.04 to 0.4 molecules). Thus, while the nucleation rate was enhanced, an addition of NH₃ did not drastically change the H₂SO₄ and H₂O composition of the critical clusters under atmospheric 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. This difference may be due to much longer nucleation times used in this study (60–240 s) or much lower H₂SO₄ concentrations used here (10⁶–10⁷ cm⁻³). The estimated n_{NH_3} was only one, which is consistent with cluster measurements by (Hanson and Eisele, 2002) and this unit value also explains the small reduction in $n_{\text{H}_2\text{SO}_4}$ and $n_{\text{H}_2\text{O}}$ in THN than in BHN. This low n_{NH_3} value 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,

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190 1–10 ppbv, and 10^3 – 10^5 cm⁻³, respectively (McMurry et al., 2005). And, the present
experimental conditions fall within these observational results. (McMurry et al., 2005)
also showed the slope of particle concentration vs. NH₃ is nearly one (McMurry et al.,
2005), similar to the present study showing that n_{NH_3} is only one. Another study made
195 in Kent, Ohio crossing four different seasons showed the threshold of H₂SO₄ is around
 10^6 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
measurements 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 for the unit J is 10^6 cm⁻³,
200 with NH₃ from 0.08–2.6 ppbv at 288 K. In comparison, the threshold in the THN param-
eterization is, for example, [H₂SO₄] of 10^9 cm⁻³ for NH₃ of 1 ppbv at 273 K (Merikanto
et al., 2007) (Fig. 3). A similar [H₂SO₄] threshold is also required in the BHN param-
eterization (Vekhamaki et al., 2002) (Fig. 3). We also used our typical experimental
205 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.

5 Conclusions

Our laboratory observations show that both the BHN and THN thresholds are 10^6 cm⁻³
210 H₂SO₄ and the slope of J vs. H₂SO₄ (that is, $n_{\text{H}_2\text{SO}_4}$) is 3–5, $n_{\text{H}_2\text{O}}$ is 1–4, using the
same particle instruments (TSI CPC 3876) used in field studies. The slope of J vs.
NH₃ (n_{NH_3}) was only one for THN. Nucleation enhancement factors by NH₃ varied
depending on H₂SO₄, RH and residence times, but was for most time <10. These
results imply that nucleation can be enhanced by NH₃, but H₂SO₄ is still the main nu-
215 cleation 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 Kent field observations.

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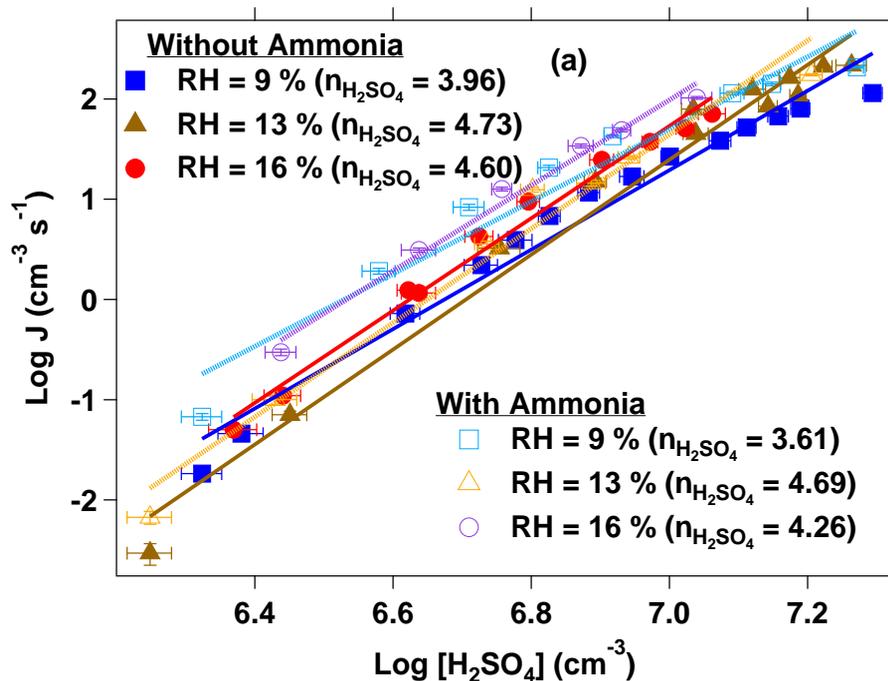


Fig. 1a. The measured $\text{Log } J$ vs. $\text{Log } [\text{H}_2\text{SO}_4]$ for binary (filled symbols) and ammonia-ternary nucleation (open symbols) at RH = 9% (squares), 13% (triangles), 16% (circles). Solid lines show the linear fitting curve of the data. These data are for a 240 s residence time. $\text{NH}_3 = 1.20$ ppbv for THN. The horizontal and vertical bars indicate one standard deviation of H_2SO_4 concentration and nucleation rate; the solid or dashed lines show the linear fitting curve of the data.

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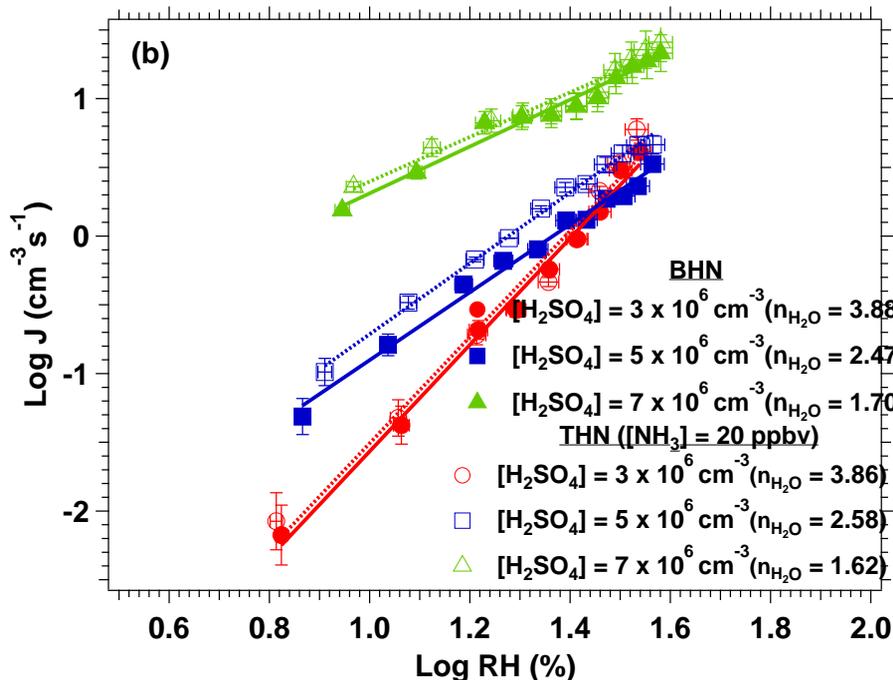


Fig. 1b. Graph of Log J vs. Log RH. The number of water molecules in the critical cluster is 1–4. This number is slightly reduced in the presence of ammonia (20 ppbv). The total flow through the reactor is 13.1 lpm (5.6 lpm through the nucleation region and 7.5 lpm to the two CIMSs), corresponding to a residence time through the nucleation region of 120 s. J varies from 3×10^{-3} – 3×10^1 cm⁻³ s⁻¹ for RH values 6–40% and initial [H₂SO₄] in the range of 3×10^6 – 7×10^6 cm⁻³ and is usually higher in the presence of NH₃ than without it. In both the BHN and THN cases, the H₂SO₄ threshold to produce the unit J (1 cm⁻³ s⁻¹) is at the 10⁶ cm⁻³ range.

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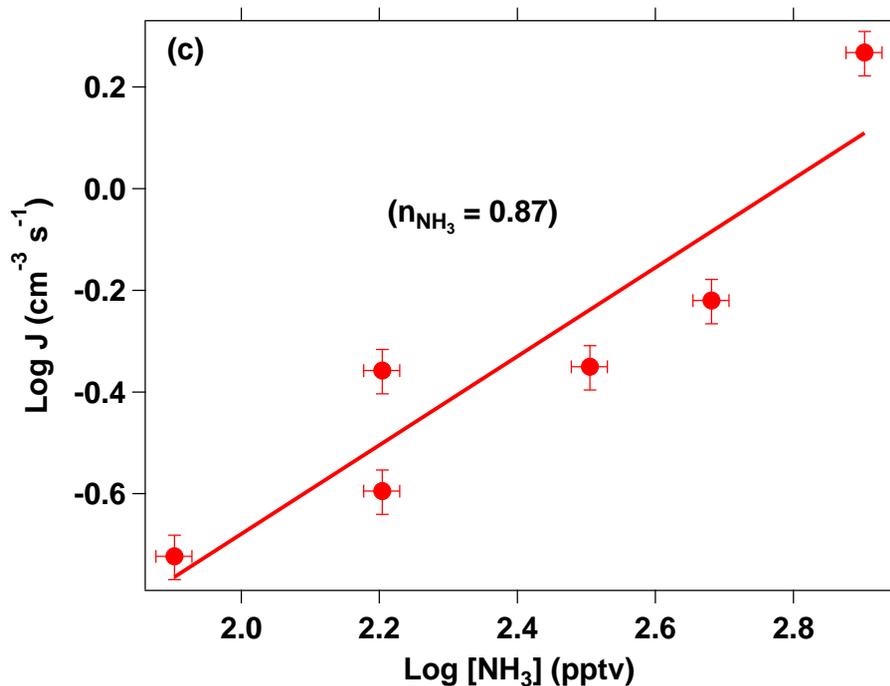


Fig. 1c. The measured $\text{Log } J$ vs. $\text{Log}[\text{NH}_3]$ for THN experiments. $\text{RH} = 8\%$. $\text{H}_2\text{SO}_4 = 8.2 \times 10^6 \text{ cm}^{-3}$. Residence time = 170 s. The solid line shows the linear fitting curve of the data.

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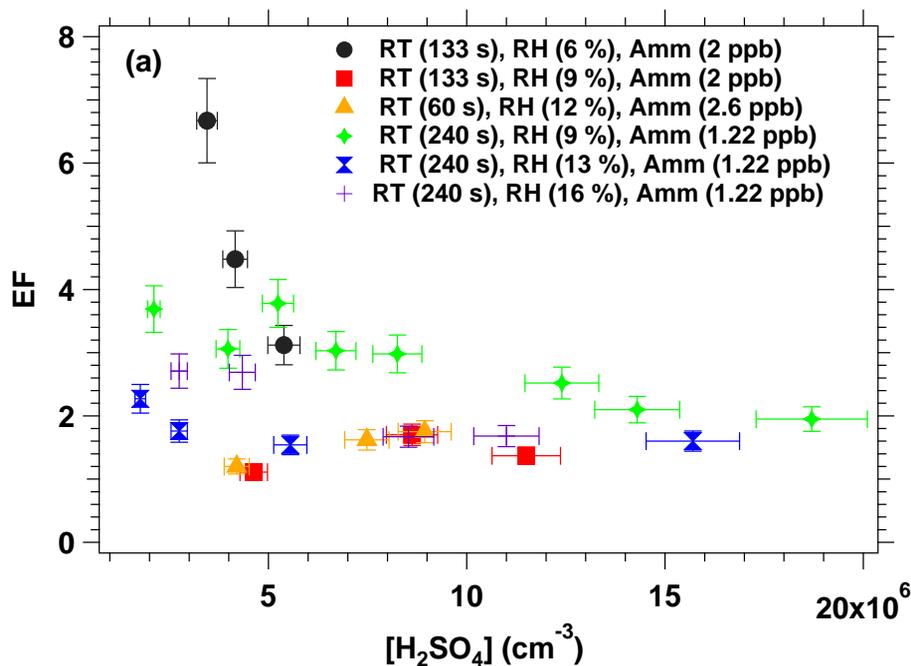


Fig. 2a. The measured nucleation enhancement factor (EF) as a function of $[\text{H}_2\text{SO}_4]$. RH = 6–16%. $[\text{NH}_3]$ = 1.22–2.6 ppbv. Residence time = 60–240 s.

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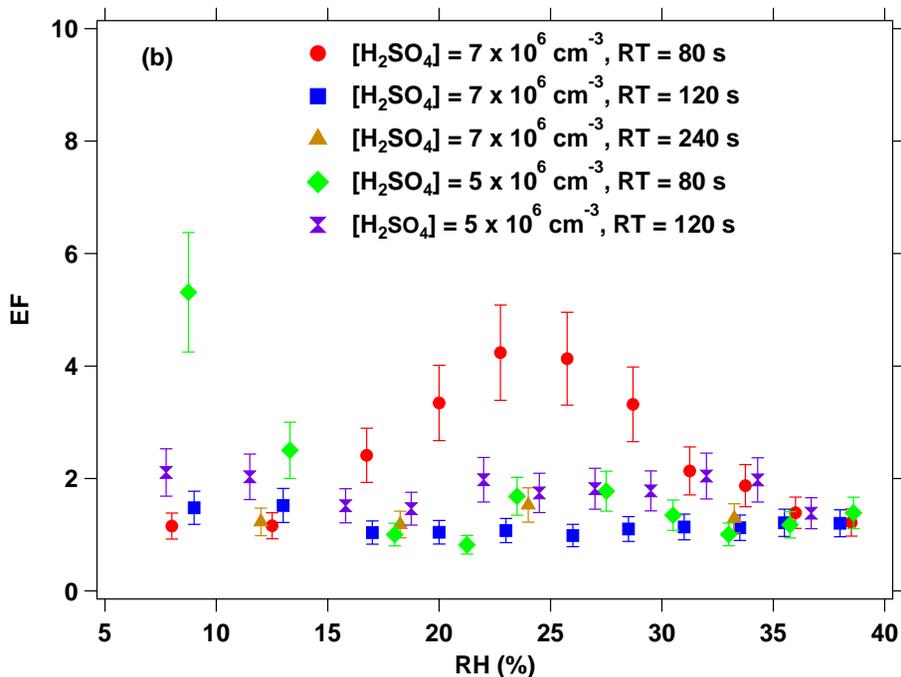


Fig. 2b. The measured nucleation enhancement factor (EF) as a function of RH. EF is defined as the ratio of nucleation rates in the NH_3 ternary homogeneous nucleation vs. rates in the binary homogeneous nucleation. $[\text{H}_2\text{SO}_4] = 5 \times 10^6 - 7 \times 10^6 \text{ cm}^{-3}$. RH = 7–39%. $[\text{NH}_3] = 20 \text{ ppbv}$. Residence time = 80–240 s.

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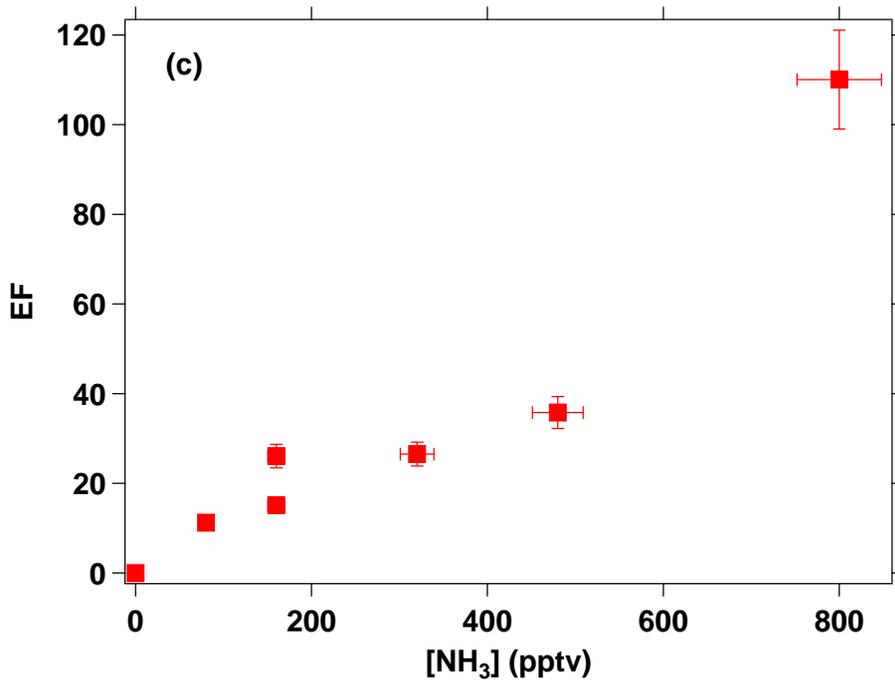



Fig. 2c. The measured nucleation enhancement factor (EF) as a function of NH₃ mixing ratio. RH = 8%. [H₂SO₄] = $8.2 \times 10^6 \text{ cm}^{-3}$. Residence time = 170 s.

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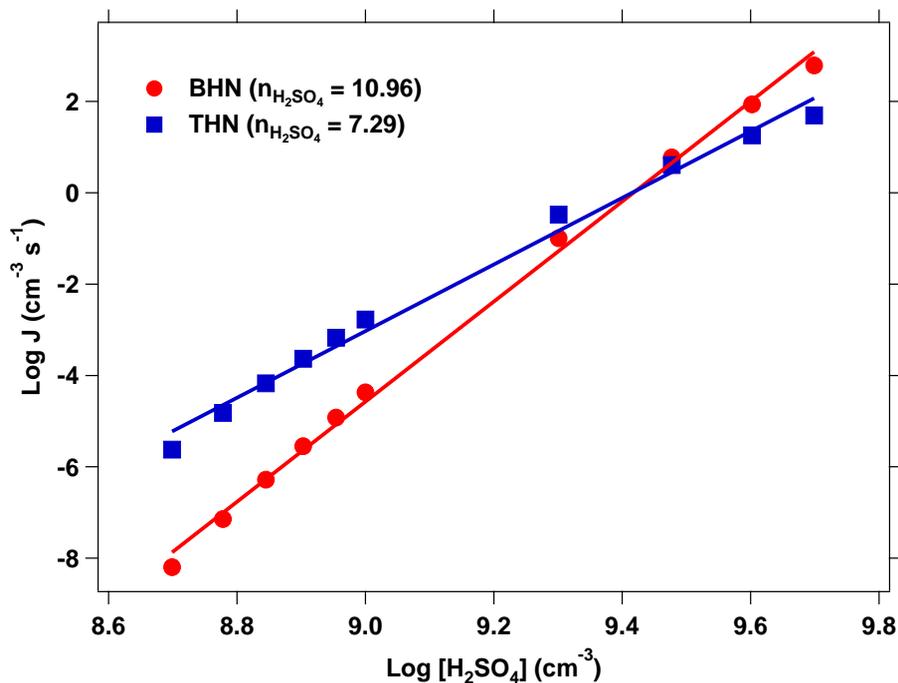


Fig. 3. Log J vs. Log $[H_2SO_4]$ based on predictions by (Vehkamäki et al., 2002) (BHN) and (Merikanto et al., 2007) (THN). The parameters are a temperature of 288 K, RH of 40% and NH_3 concentration of 100 pptv (for THN only).

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