Photolytically-Generated Sulfuric Acid and Particle Formation: Dependence on Precursor Species

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Abstract. Size distributions of particles formed from sulfuric acid (H₂SO₄) and water vapor in a Photolytic Flow Reactor (PhoFR) were measured with a nano-particle mobility sizing system. Experiments with added ammonia and dimethylamine were also performed. H₂SO₄ was synthesized from HONO, sulfur dioxide, and water vapor, initiating OH oxidation by HONO photolysis. For standard reactant flows and conditions, 296 K, 52 % relative humidity, and a ~40 s residence time, the calculated concentration of H₂SO₄ peaked at 1.2x10¹⁰ cm⁻³, measured particle mean diameter was ~6 nm and total number density was ~10⁴ cm⁻³. Measured distributions were influenced by molecular clusters at small sizes, less than or equal to 2 nm diameter, but were generally dominated by large particles that are roughly log-normal with mean diameters ranging up to 12 nm and a relatively constant lnσ of ~0.3. Particle number density and their mean size depended on relative humidity, HONO concentration, illumination, and SO₂ level. Particle formation conditions were stable over many months. Addition of single-digit pmol/mol mixing ratios of dimethylamine led to very large increases in number density. Ammonia at levels up to 2000 pmol/mol showed that NH₃ is less effective than dimethylamine at producing particles. A two-dimensional simulation of PhoFR reveals that H₂SO₄ scales with HONO and its level builds along the length of the flow reactor. Experimentally, particle growth scaled with HONO, in accord with model-predicted H₂SO₄ levels. Additional comparison between experiment and model indicates that reaction of HO₂ with SO₂ could be a significant source of H₂SO₄ in this experiment. The effects of potential contaminants on particle formation rates near room temperature are addressed and provide context in comparisons with previous experiments. The added-base experimental results provide support for previously published dimethylamine-H₂SO₄ cluster thermodynamics but do not support previously published ammonia-sulfuric acid thermodynamics.

1 Introduction

Particle formation in the atmosphere has long been studied (McMurry et al. 2005; Kulmala et al. 2004) to ascertain potential impacts on health (Nel 2005) and on climate processes (IPCC 2013). For example, nano-particles (characterized as < 10 nm in diameter) can have special health effects as their small size allows for efficient transport into lung tissue (Kreyling et al. 30
2006). They also influence climate by growing to sizes large enough to affect radiative forcing and the properties of clouds. Despite numerous and wide-ranging studies devoted to understanding new particle formation, mechanisms and nucleation rates applicable to many regions of the atmosphere remain uncertain.

Sulfuric acid-driven nucleation is a prime source of nanoparticles in the atmosphere (Kuang et al. 2012; Sipilä et al. 2010) thus it is the starting point for many laboratory studies. Previous work on particle nucleation in the binary (water-sulfuric acid) system (Kirkby et al. 2011; Ball et al. 1999; Zollner et al. 2012; Ehrhart et al. 2016; Yu et al. 2017) have concluded that binary nucleation can be significant at low temperatures such as at high latitudes and in the upper troposphere. The sulfuric acid/water binary system also serves as an important baseline diagnostic for comparing experimental results. Finally, nanoparticle growth by sulfuric acid and water vapors is of interest as well as uptake of oxidized organic compounds by acidic nanoparticles. Good knowledge of the formation and stability of binary nano-particles is needed to understand their subsequent growth via other compounds.

Previous laboratory studies of nucleation in the binary system diverge widely, especially for results taken at or near room-temperature, and experimental details may significantly affect results. For example, does it matter if \( \text{H}_2\text{SO}_4 \) is provided by a bulk or photolytic source or from which photolytic precursor: \( \text{O}_3 \), \( \text{H}_2\text{O}_2 \), \( \text{H}_2\text{O} \), etc. (Sipilä et al. 2010; Berndt et al. 2008; Laaksonen et al. 2008)? What are the limitations imposed by particle detector characteristics as well as cluster/particle wall losses (McMurry 1983; Kurten et al. 2015)? How well-determined are the concentrations of \( \text{H}_2\text{SO}_4 \) (Sipilä et al. 2010; Jokinen et al. 2018)?

A prime concern is whether contaminants are present at abundances significant enough to influence particle formation rates. For example, Zollner et al. (2012) argued that a \( 10^{-14} \) mixing ratio of methylamine could have affected their binary system measurements; Glasoe et al. (2015) carried this argument further and estimated that contaminant dimethylamine mixing ratios were less than \( 10^{-15} \). Kirkby et al. (2011) and more recently Kurten et al. (2016) estimate ammonia contaminant levels of 4-to-10 pptv \( \text{NH}_3 \) for their experiments performed at 292 - 298 K. Recently, Yu et al. (2017) reported upper limits for \( \text{NH}_3 \) and dimethylamine of 23 and 0.5 pmol/mol (pptv), respectively. Impurity dimethylamine at this level would very likely overwhelm binary system nucleation which underscores the importance of assessing potential contaminants.

Here we describe an apparatus and results from experiments on the formation of sulfuric acid nanoparticles from photolytically-generated sulfuric acid vapor (the \( \text{OH} + \text{SO}_2 \) photochemistry initiated with HONO photolysis at ~350-to-370 nm). Although nitrous acid is considered an important contributor to OH radical formation in many situations (Sörgel et al. 2011), little has been done to understand its photolysis that leads to sulfuric acid formation and new particle formation. We also studied the effects of adding ammonia or dimethylamine; both are known to greatly enhance particle production rates (Almeida et al. 2013; Glasoe et al. 2015; Yu, McGraw, and Lee 2012; Ortega et al. 2012; Nadykto and Yu 2011). Finally, the experimental results are compared to simulations of the flow reactor that couple the flow with photo-chemical kinetics and an acid-base particle formation scheme.
2 Methods

The Photolytic Flow Reactor (PhoFR) is a vertically-aligned cylindrical glass tube with an inner diameter of 5.0 cm, a length of ~130 cm, a volume of approximately 2.5 L and topped with a 23 cm conical glass piece with several flow inlets (Fig. 1a). In the course of this work, a Teflon screen was positioned between the cone and the flow reactor to calm the jetting from the inlets. A ~ 105 cm portion of PhoFR is jacketed and kept at a constant temperature, typically 296 K, by circulation of thermostated water. The main flow of gas was nitrogen from a liquid nitrogen gas-pack and the total flow rate was 2.9 sLpm (standard L / min, 273 K and 1 atm). The flow contained small amounts of SO$_2$ and HONO, typically a few and 0.02 mol/mol (ppmv), respectively, and up to several % water vapor; relative humidity was set by sending a portion of the flow over a heated water reservoir and then through a thermostated, vertically-aligned tube that removed excess water vapor. Total pressure was slightly above ambient, ~0.98 atm; gauge pressure was monitored continuously and it was typically 0.001 atm. The oxygen level from the liquid nitrogen, stated to be 10 ppmv or less, was apparently sufficient for the subsequent oxidation chemistry - noting little differences in particle size additions upon adding several % O$_2$ to the flow.

Entering gas flows were monitored and set by mass flow meters under computer control. Typical flows for baseline conditions in sLpm or sccm (standard cm$^3$ / min, 273 K, 1 atm) were dry gas at 1.4 sLpm, fully humidified air at 1.5 sLpm, HONO-laden (~15 ppmv, µmol/mol) N$_2$ flow at 4.2 sccm, and SO$_2$-laden flow at 32 sccm (1500 ppmv SO$_2$-in-N$_2$). These baseline conditions help diagnose the long term stability of the system. The baseline number densities of SO$_2$ and HONO in the flow reactor (accounting for dynamic dilution) are 4x10$^{14}$ and 6x10$^{11}$ cm$^{-3}$, respectively. The conical top section and the bottom 20 cm where aerosol was sampled were not insulated or thermo-regulated.

The SO$_2$-in N$_2$ mixture (Minneapolis Oxygen) was reported (Liquid Technologies Corporation, EPA Protocol) to contain 1500 ppmv SO$_2$ +/- 10%. Water vapor was taken from a gently heated ~500 mL volume of deionized water (Millipore) that also contained a few grams of concentrated sulfuric acid to suppress potential base contamination from the bulk water. This humidified flow then passed through 80 cm of vertically-aligned Teflon tubing (~6.2 mm ID) held at the temperature of the flow reactor.

Photolyte HONO was continuously produced (Febo et al. 1995) by flowing nitrogen laden with ~15 ppmv HCl vapor into a small (25 mL) round-bottom flask containing 1-2 grams of powdered NaONO(s), held at 40-50°C (Fig. 1b). HONO vapor and co-product NaCl(s) are produced in a classic double-displacement reaction. The powder could be very slowly mixed with a small (1 cm long) stir bar and results generally did not depend on whether the powder was stirred. Periodic gentle shaking of the flask usually led to only temporary changes in particle number densities.

The HONO level exiting the generator is likely to be equal to the HCl level entering it. The HCl-generator and a water vapor pre-saturator were temperature-controlled at typically 20 °C. A saturated (~6 m, molal) NaCl aqueous solution in the pre-saturator yields a relative humidity of 76 % in the flow: a stable amount of water vapor stabilizes the solution in the HCl-generator, which contains a solution with a 2-to-1 mole ratio for NaCl to H$_2$SO$_4$. The HCl-generator solution was prepared initially with concentrations of 3.5 m NaCl and 1.75 m H$_2$SO$_4$ and calculations (Wexler and Clegg, 2002; Friese and Ebel,
result in an HCl vapor pressure of $9.3 \times 10^{-6}$ atm. UV absorption measurements to determine the HONO level in this flow are described in the Supplement and results indicate that the source has a HONO level of about $1.5 \times 10^{-5}$ atm. This suggests that the HCl-generator’s HCl vapor pressure is slightly larger than the calculated value. While the water vapor pre-saturator minimized loss of water from the HCl-generator, small temperature differences between these two vessels can introduce variability and possibly a bias.

Four black lights that have a UVA spectral irradiance centered at 360 nm illuminated about a 115 cm length of the jacketed flow reactor from a distance of about 15 cm from the reactor center. A rough estimate of the fluence ($5 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$) indicates a photolysis rate of approximately $10^{-3}$ s$^{-1}$ for HONO. Described in the Supplement is an experiment where production of methylvinylketone and methacrolein from the oxidation of isoprene was monitored, yielding an estimate (along with the 15 ppmv HONO level discussed above) for the HONO photolysis rate of $8 \times 10^{-4}$ s$^{-1}$.

H$_2$SO$_4$ is formed via (i) OH produced via HONO photolysis, (ii) OH addition to SO$_2$, (iii) H-atom abstraction by O$_2$ and (iv) reaction of SO$_3$ with H$_2$O molecules (Lovejoy et al.) The HO$_2$ and NO radicals generated in this process can react together and generate an additional OH radical. When SO$_2$ is present at a few ppmv, the dominant loss for OH is OH $+$ SO$_2$: a pseudo-first-order loss rate coefficient is given by $[\text{SO}_2] \times k_{\text{OH}+\text{SO}_2} = 4 \times 10^{14}$ cm$^3$ s$^{-1}$ = 8.9 $\times 10^{-13}$ cm$^3$ s$^{-1}$ = 360 s$^{-1}$. With this SO$_2$ baseline level, OH reacts with HONO only about 1% of the time: an OH first-order loss rate coefficient is ~3 s$^{-1}$, from $[\text{HONO}] \times k_{\text{OH}+\text{HONO}} = 5 \times 10^{11}$ cm$^3$ s$^{-1}$. For low SO$_2$ levels, loss of OH due to reaction with HONO can be significant.

H$_2$SO$_4$ levels build as the flow moves down the reactor, forming H$_2$SO$_4$ molecular clusters and these clusters grow into stable particles. These particles accumulate enough material, primarily H$_2$SO$_4$ and H$_2$O, to grow to several nm in diameter.

Growth due to OH or HO$_2$ uptake followed by reaction with absorbed SO$_2$ may also contribute to growth. Particles were sampled on axis at the exit of the flow reactor, about 120 cm from the conical inlet, with a custom-built mobility-sizing and counter system designed for nanometer-sized particles. Briefly, size-classified particles (Am-241 charger and a TSI 3085 nanoDMA) were detected with a diethyleneeglycol (DEG), sheathed condensation particle counter (CPC) in tandem with a butanol-based CPC (Jiang et al. 2011). This system is denoted ‘DEG system’ in this study. The DEG CPC was operated with a saturator temperature of 57°C, a condenser temperature of 20°C, 0.36 L/min condenser flow and 0.07 L/min capillary flow. The nanoDMA was operated with 2 L/min aerosol-in and monodispersed-out flows and a 13 L/min sheath flow, as in Glasoe et al.

For a few experiments, ammonia or dimethylamine as trace gases were added through a port at the top of the flow reactor. Their sources were permeation tubes, and 100s and single-digit pptv levels could be set by either single- or double-stage, respectively, dynamic dilution systems (Freshour et al. 2014; Glasoe et al. 2015). Ammonia was used in the single-dilution system and dimethylamine was dedicated for use in the double-dilution system. Permeation rates were determined periodically by re-directing the base-laden flow through an acidic solution and monitoring the change in pH over time (Freshour et al., 2014).
2.1 Model

The 2-dimensional model of the flow reactor incorporating the photochemical kinetics of H$_2$SO$_4$ formation was built on a previous model of acid-base molecular cluster formation which was fully corroborated against a commercial computational fluid dynamics simulation (Hanson et al. 2017). The flow profile can be set to either plug or fully-developed laminar, clusters up to ten H$_2$SO$_4$ and base molecules can be simulated. The 2D model here incorporates the detailed photochemistry in our experiment, from the production of OH through its reactions with SO$_2$ as well as with HO$_2$, NO, NO$_2$, HONO, HNO$_3$, H$_2$O$_2$ etc. The acid and base species and all molecular clusters as well as OH are lost on the walls limited only by diffusion. The model reacts, convects and diffuses all reactants and products and yields the abundance of H$_2$SO$_4$ molecular clusters, the largest clusters are then correlated to the abundance of experimentally determined particles (Panta et al. 2012; Hanson et al. 2017). Coagulation is only crudely implemented, but these cluster-cluster interactions are not significant for most of the conditions of the present work. Also, the largest clusters can be grown to very large sizes via uptake of H$_2$SO$_4$ (and H$_2$O) assuming no loss. Further analysis of cluster growth and loss processes, including growth-only for clusters larger than 10 H$_2$SO$_4$ molecules, is presented in the Supplement. Ammonia or dimethyl amine could be included at a trace level with the flow entering the simulated reactor whereupon acid-base clustering commences and thus particle formation (note that base is also lost to the wall, limited by diffusion). The photochemistry is described in detail in the Supplement and the acid-base clustering reactions are described in detail in Hanson et al. 2017 along with thermodynamic schemes for clusters of the bases with sulfuric acid (those used here are primarily the NH3_I and DMA_I schemes from that work.)

3 Results and Discussion

3.1 Particle formation evaluation.

The stability of particle formation conditions over several months is demonstrated by presenting the number and the average size of particles for baseline conditions. In the next section, the modeled photochemistry for baseline conditions is presented to provide baseline particle formation conditions within PhoFR. Here, we also discuss how the size distributions were analyzed. In subsequent sections, these analytical devices will be applied to the results of experiments where reactant levels were varied.

Shown in Figure 2 are results over a 4 month period for baseline conditions: 52 % relative humidity (RH), 296 K, total flow of 2.9 sLpm, and a flow of N$_2$ through the HONO source, Q$_{N_2}$, of 4.2 sccm. The data was binned according to the flow of the SO$_2$ mixture, Q$_{SO_2}$, either 4 sccm or > 20 sccm. The abundance of HONO is 20 ppbv and SO$_2$ is either 2 ppmv or >10 ppmv. Fig. 2a shows the total particle number density, N$_p$, and Fig. 2b shows representative particle size distributions - corrected for size-dependent diffusion losses in CPC transport and inlet lines. N$_p$ was determined by summing the particle concentrations with D$_p$ of ~2.4 nm and larger. The two smallest diameter concentrations are not included because they have large
uncertainties due to large corrections applied to low count rates; furthermore, a mobility diameter of 2.4 nm is a local minimum for most of the size distributions.

The measured size distributions are governed by the interplay between the spatial distribution of \([\text{H}_2\text{SO}_4]\), whether base is added, and the nature of potential contaminant species. For example, the small- and the middle-sized particles decrease considerably between Feb. 23rd and May 15th (Fig. 2b) which is probably due to a decrease in particle-enhancing contaminants. Yet the concentrations of the largest particles are comparable in these two data sets: in other words, the leading edges of the distributions are similar. The largest particles must originate at the top of the reactor, having the highest overall exposure to \(\text{H}_2\text{SO}_4\). These so-called leading-edge particles are the focus of our analysis.

The leading-edge particles are greatly enhanced when base was added, whether ammonia or dimethylamine. In these cases, the leading-edge particles are prominent in the distributions and are described by log-normals (see the distributions presented below). The leading-edge volume-mean diameters for the added-base experiments are similar to those of the no-added base distributions. So we propose that the leading-edge particles are indicative of the nucleation conditions at the top of PhoFR.

In the Supplement is more discussion of the leading-edge mode of the particle size distributions, plots of modeled distributions and experimental leading-edge mode diameters (\(D_{le}\)) over time.

The high \(\text{SO}_2\) data (Fig. 2a) exhibits an \(N_p\) that averages about 2x10⁴ cm⁻³ since late February; also the leading edge of the size distributions (Fig. 2b), fit to log-normal functions, indicate mode diameters of about 6 nm with \(\ln\sigma\) values of ~0.35. The large drop in \(N_p\) on the 23rd of February is due to a Teflon mesh (ultrasonically cleaned and soaked overnight in a dilute sulfuric acid solution) placed between the cone and the flow reactor. The mesh limits backstreams from the illuminated section that may introduce \(\text{H}_2\text{SO}_4\) and thus nucleation in the cone. Ever since this big drop in \(N_p\), a trend in \(N_p\) can be discerned in Fig. 2a that is consistent with the changes with time of the size distributions in Fig. 2b. On the other hand, mode diameters (presented in the Supplement) indicate that \(D_{le}\) is roughly constant from January to May.

Since changes in \(D_{le}\) are small or negligible, the growth conditions in PhoFR must be stable during this 4-month time period. The cumulative exposure of particles to \(\text{H}_2\text{SO}_4\) as they travel down PhoFR is constant, indicating that the UV flux and reactant concentrations are also. The decrease in large particle numbers during this time likely indicates an increase in the purity of the system, for example a decrease in contaminant base levels entering the flow reactor. An increase in the cleanliness of the system could also be due to acid buildup on surfaces, potentially binding base-emitting contaminants. The changes in the distributions over 2.5 months (Fig.2b) are due to decreases in particles in the middle of the distribution. Based on their size, these particles were nucleated downstream of where the leading edge particles are. The flow reactor wall may accumulate enough acid that may tie up a purported contaminant responsible for the mid-sized particles.

### 3.1.1 Simulated reactant distributions

Shown in Fig. 3 are the results of a simulation using the 2D model that shows centerline concentrations of the gas-phase species and two molecular clusters. In order of abundance at the end of the reactor: On the left axis, \(\text{H}_2\text{SO}_4\), \(\text{NO}_2\), \(\text{NO}\), \(\text{HO}_2\), \(\text{H}_2\text{O}_2\), \(\text{HO}_2\text{NO}_2\) and \(\text{NH}_3\); and on the right axis, \(\text{OH}\), \((\text{H}_2\text{SO}_4)_2\text{NH}_3\) and 100 times the SA₈ cluster abundance. This simulation
was performed with [HONO] = 5x10^{11} \text{ cm}^{-3}, simulating an experiment with Q_4 = 4 \text{ sccm}. These conditions are close to those for the size distributions depicted in Fig. 2b.

Sulfuric acid rises steadily and reaches 1.2x10^{10} \text{ cm}^{-3} by the end of the lighted section that extends from 0 to 110 cm. NH_3 was introduced at the inlet at a level of 70 pptv which drops with axial distance due to wall loss: its concentration drops to \sim 20 \% of the inlet value by 40 cm. The effect of added base on particle formation is primarily at the top of the reactor despite the lowest sulfuric acid abundances there. The remaining 2/3 of the reactor has the highest sulfuric acid levels: over the distance 40 to 125 cm, [H_2SO_4] averages about 8x10^{9} \text{ cm}^{-3}.

This crude partitioning of the reactor is somewhat arbitrary but it provides a point of view for discussing the experimental results. Furthermore, this point of view is congruent with the experimental finding that a large particle mode at the leading edge of the size distributions is discernible, especially so when base was added. So although clusters are formed and particles are nucleated along the length of the reactor, we seek to explain only the largest of them.

With this perspective, we can estimate the growth of the leading-edge particles due to their accumulating H_2SO_4 and H_2O (assuming no evaporation) as they traverse the bottom 2/3 of the flow reactor. Using centerline values, an increase in particle diameter of 4.8 nm is estimated as they travel from 40 to 125 cm, using the bulk approximation to calculate the increase in diameter (Verheggen and Mozurkewich, 2002; Wexler and Clegg, 2002). Modeled particles that contain up to 250 H_2SO_4 molecules yield particle size distributions in agreement with this estimate from bulk properties (see the Supplement).

The behavior of the truncated clusters shown in Fig. 3 provides some justification for partitioning the reactor into a top 1/3 and a bottom 2/3. The abundance of (H_2SO_4)_2NH_3 peaks at about 50 cm indicating that nucleation involving base has reached its peak. The accumulation cluster (that was allowed to build up at 8 SA molecules but no further and with no SA evaporation) tells a similar story regarding this partitioning where its abundance levels off in the lower section of the reactor. Its behavior in the middle of the reactor, a lag in its abundance profile compared to the SA \_NH_3 cluster, indicates that some catching up is needed to grow the clusters to 8 SA molecules. The increase in the abundance of these clusters with Z reaches a maximum near 60 cm. This indicates that the partitioning is a decent rhetorical tool for discussing the results and for drawing broad conclusions.

### 3.2 Variation of Np, Dp with [reactant]

#### 3.2.1 Variation of HONO with no added base.

Depicted in Fig. 4a are representative particle size distributions as a function of N_2 flow through the HONO source, Q_4, a proxy for HONO abundance. Q_4 was varied from 1.6 to 5.3 sccm while the abundances of the other reactants were held constant. The size distributions are strongly dependent on HONO over this range, with concentrations increasing by a factor of \simten at small sizes and the large particle abundance by a hundred-fold. Log-normal distributions are also shown as the dashed lines in the figure with leading-edge mode diameter D_{le} and ln\sigma noted in the legend. The log-normals shown in the
Figure were not those from the fitting procedure (see the Supplement for more discussion of the fitting procedure) because two of the fits failed. For a consistent presentation, lnσ was fixed and each log-normal was adjusted visually to best cover the four or five points nearest the peak of each distribution. Np (Fig. 4b) and the volume-mean diameter of the leading edge mode, Dv,le (Fig. 4c) are plotted vs. Q4 and Np has a power-dependence on Q4 of about 4 while Dv,le increases linearly over most of this range.

It is reasonable to assume that the HONO concentration in PhoFR is linearly proportional to Q4, the nitrogen flow through the HONO source. The data in Fig. 4c shows that Dv,le scales approximately linearly with Q4 up to about 7 sccm, suggesting that particles exposure to H2SO4 is also linear over this range. The departure from linearity is noticeable in Fig. 4c and is probably affected by the inability of the fitting process (see Supplement) to yield leading edge log-normal distributions at low values of Q4 (indeed about half failed for Q4 ≤ 2.2 sccm) and scavenging of H2SO4 by particle surface area at the large Np that develops at high number densities and large sizes when Q4 is 8 to 10 sccm.

A power dependence of 5 for Np on H2SO4 was exhibited for the H2SO4-H2O binary system (Zollner et al. 2012) which is somewhat larger than that exhibited in Fig. 4b; other bulk experiments have power dependencies on H2SO4 that range up to ~20 (Wyslouzil et al. 1991; Viisanen et al. 1997). Yet the CLOUD experiment (Kurten et al. 2016), also with photolytic generation of H2SO4, shows a power dependency of 3.7 at 292 K for [H2SO4] concentrations from 3x10^8 to 1.5x10^9 cm^-3. An ammonia-contaminant abundance of 4 pptv was stated to apply to those results.

Experimental results (Glasoe et al. 2015; Almeida et al. 2013) show that power dependencies on H2SO4 are affected when a base is present. The presence of an impurity base compound probably affected our experimental results. It may be due to two sources: (i) contaminant entering with the flows and (ii) contaminant emanating from internal surfaces. The added base experiments have more discussion on this topic but we note here that our system is slowly cleaning up over time.

Particles grow due to uptake of H2SO4 and H2O: the estimate from the H2SO4 profile from the model simulation discussed above suggests an increase in diameter of about 4.8 nm for a Q4 of 4.0 sccm. The data in Fig. 4c show that the volume mean diameter is about 6 nm at this HONO level, which is consistent with that estimate. The agreement improves considering that nascent particles must attain a certain size to become stable, roughly 1.3 nm diameter or larger (large enough such that evaporation becomes negligible). There is also a 0.3 nm difference between mobility and volume/mass diameters. Presented in the Supplement are simulated particle size distributions for Q4= 2 sccm that peak at 3.7 nm in good agreement with measurements.

### 3.2.2 SO2

Particle size and number density were found to depend on SO2 abundance. Shown in Figs. 5 (a) and (b) are plots of Np and Dv,le (volume mean diameter of the leading-edge mode) vs. the flow rate of the SO2 mixture, Q1. HONO source flow rate Q4 was 4.2 sccm for this data. Despite its scatter, the data show the SO2 level affects both the number of large particles and their size, Dv,le; both increase with [SO2] and begin to level-off at high [SO2]. This behavior is expected as the SO2 abundance must be high enough to ensure it scavenges all of the OH and beyond that there should not be much effect.
However, a set of simulations that includes a reaction between HO$_2$ and SO$_2$ are shown as the lines in Figs. 5. Note that a level of 70 pptv of NH$_3$ entering the flow reactor was included. The simulated size is given by the growth estimate from the simulated H$_2$SO$_4$ profile plus an initial size of 1 nm and the mobility-diameter to mass-diameter offset of 0.3 nm (de La Mora et al.) The experimental results show increases with SO$_2$ that are roughly in line with the model simulations. Without a reaction between HO$_2$ and SO$_2$, the model shows small increases in N$_p$ (40 % vs. 250 % with the reaction) and size (10% vs. 20 % with the reaction) as SO$_2$ was increased from 2 to 16 pptv.

The simulation assumed a value of 3x10$^{-17}$ cm$^3$/s for $k_{HO2+SO2}$. There are disagreements in whether HO$_2$ reacts with SO$_2$ as well as potential end products (Chen et al. 2014; Kurten et al. 2011); we assumed H$_2$SO$_4$ and OH. Published values for this rate coefficient range from upper limits of 1x10$^{-18}$ cm$^3$/s (Graham et al. 1979) and 2x10$^{-17}$ cm$^3$/s (Burrows et al. 1979), to a value of 8x10$^{-16}$ cm$^3$/s (Payne et al. 1973). A heterogeneous reaction occurring in the particles involving SO$_2$ would help explain the dependence of $D_{V,le}$ on SO$_2$ abundance while leaving N$_p$ undisturbed.

The dependencies upon SO$_2$ were much smaller when minute amounts of dimethylamine were included in the model. Low levels of (0.003 pptv) dimethylamine gave simulated N$_p$ in the 10$^4$ cm$^{-3}$ range but at this level its ability to influence the change in N$_p$ with H$_2$SO$_4$ was limited due to being scavenged by clusters. This was also observed in simulations where HONO was varied in the presence of 0.005 pptv dimethylamine (see the Supplement). This suggests that a potential contaminant in our system is not a strong nucleator like dimethylamine.

### 3.2.3 Added ammonia.

Shown in Fig. 6 is the number of large particles vs. HONO flow rate taken with and without NH$_3$ addition. The level of added NH$_3$ when fully mixed and without any loss to the wall would be 230 pptv. With data for nominal conditions for comparison, the effect of 230 pptv NH$_3$ on the number of large particle abundance is significant, about a factor of 5, a factor that does not significantly depend on the level of HONO and thus H$_2$SO$_4$ present in the flow reactor. Variation of $D_{le}$ as HONO was varied is shown in the Supplement and adding base results in an increase of $D_{le}$ of about 20%. The shift in the distributions to slightly larger sizes could be due to particle formation occurring slightly upstream of that in the absence of added NH$_3$. Nevertheless, the leading-edge mode of the size distributions are distinct in Fig. 6(b): even the lowest Q$_4$ in 6(b) can be fit by a log-normal function.

Previous work has shown large increases in N$_p$ when ammonia was added to a (nominally clean) binary sulfuric acid-water nucleating system. For example Ball et al. (1999), Zollner et al. (2012), and Glasoe et al. (2015) observed factors of 10-to-1000, ~1000, and 10$^6$ for ammonia levels of a few pptv, 25 pptv, and 55 pptv, respectively. Kuerten et al. (2016) presented the CLOUD experiment data in a comprehensive manner and showed that a factor of about 100 increase in particle production was observed upon addition of several hundred pptv NH$_3$ at 292 K and an [H$_2$SO$_4$] = 1.5x10$^8$ cm$^{-3}$.

Simulations are shown in the Supplement with two different NH$_3$ levels (70 and 300 pptv) that mimicked the Np vs. Q$_4$ data remarkably well (70 pptv NH$_3$ for the no-added base and 300 for the added base case). Dimethylamine levels at 0.003 pptv yielded N$_p$ in the range of the experiment base suggesting that very small amounts of a contaminant can influence binary
nucleation experiments. An amide may be consistent with the experiment: it is intermediate in strength (Glasoe et al. 2015), stronger than ammonia but not so strong that scavenging could be a major loss process.

3.2.4 Variation of $N_p$ with added NH$_3$ level.

Shown in Figs. 7 are the total number of particles plotted as a function of added NH$_3$ levels for a fixed amount of HONO: (a) $Q_4 = 4.3$ sccm and (b) $Q_4 = 2.2$ sccm. The red squares at nominally zero NH$_3$ represent the range of data obtained without added base. There are large effects on $N_p$ due to the addition of NH$_3$ at the top of the reactor, up to a factor of ten for both sets of data. At high NH$_3$ levels (or prolonged exposure) particles counts rose dramatically. This is demonstrated in the Supplement with measurements on days when 2000 pptv NH$_3$ was added.

The large variability in Figs. 7 mirrors the underlying variability in $N_p$ without added NH$_3$ (Figs. 4b and 5a). Yet, within the scatter of the measurements the dependence of $N_p$ upon NH$_3$ can be approximated as linear. This is a smaller dependence than the 1.6 power dependence found in the bulk-source experiments of Glasoe et al. (2015). A linear dependence is similar to other photolytic H$_2$SO$_4$ production experiments, the flow reactor experiments of Benson et al. (2011) and Berndt et al. (2010), and the 292 K CLOUD chamber experimental results (Kuerten et al. 2016; Kirkby et al. 2011).

Simulated $N_p$ are shown in Fig. 7a for two different thermodynamic schemes (Hanson et al., 2017); both clearly indicate a stronger dependence on NH$_3$ than is exhibited in the experimental results. Failure to mimic the experimental results can be due in part to poor representation of the actual flow in the simulations, however inaccurate thermodynamics are probably the dominant contributor. We had concluded (Hanson et al., 2017) that NH$_3_\text{II}$ was better than NH$_3_\text{I}$ based on comparisons to the experimental data of Glasoe et al. (2015). The comparison shown in Fig. 7a indicates that neither satisfactorily represents the full range of the data with NH$_3_\text{II}$ having particularly overly strong binding free-energies while, relatively speaking, NH$_3_\text{I}$ is a better approximation of the NH$_3$-H$_2$SO$_4$ cluster binding energies for the present conditions.

3.2.5 Water variation and addition of dimethyl amine.

Shown in Fig. 8 are the $N_p$ and $D_{le}$ vs. humidity, calculated from the flow rate of the humidified nitrogen. Total flow rate, HONO, and SO$_2$ levels were kept constant; the humidified flow rate was varied from 0.5 to 2.4 sLpm. Although the overall data is phenomenologically exponential (see the fit in the figure), over limited ranges the data exhibits power dependencies. The power dependence of $N_p$ on RH is between 4 and 6 while $D_{le}$ varies from 5 nm to about 10 nm; there appears to be a rise in both above 80 % RH. A strong dependence of the number of particles on RH is expected for the binary sulfuric acid water nucleating system, and the power dependence here lies at the low end of range (5-to-9) reported by Zollner et al. A set of data with 2-to-5 ppt dimethyamine added is shown as the diamonds. There is much less water dependence (approximately linear) when dimethyamine is present which is consistent with theoretical notions (Almeida et al. 2013; Henschel et al. 2016). This indicates that clusters that lead to large particles are not particularly sensitive to H$_2$O when dimethyl amine is present, because the amine is a much better base than H$_2$O and nucleation associated with a strong acid-
base interaction is preferred. This postulate has been elucidated in previous publications (e.g. Kurten et al. 2008; Coffman and Hegg 1995).

Supposing there is dimethylamine-type base contaminant in the putatively base-free experiments (solid squares), it clearly does not reach the single digit pptv level for baseline 52 % RH conditions. Indeed, as shown in the Supplement, simulated particle number densities with a level of 0.003 pptv dimethylamine entering the flow reactor were consistent with the 52% RH, Q_4=4 sccm results. A set of simulations were run from 0.005 up to 2 pptv dimethylamine and predicted N_p scaled linearly with base level. At the 2 pptv level, an N_p of about 10^7 cm^{-3} was predicted while experimental N_p is 3x10^6 cm^{-3}. Note that an N_p at the 10^7 cm^{-3} level will be significantly affected by coagulation which is not well captured in the simulations.

3.2.6 Variations of dimethylamine and HONO.

Shown in Fig. 9 are measured size distributions with varying levels of added dimethylamine. The effect on the number of particles is large and even the smallest particles (mobility diameter of 1.7 nm) increased by about 3 orders of magnitude. The zero-added base data between these runs might be affected by dimethylamine holdover but this appears to be small: the N_p are within a factor of two of the Q_4=2.2 sccm data in Fig. 4a. It is clear that more dimethylamine leads to more particles, with N_p increasing approximately linearly with dimethylamine abundance. Note that the leading edge of the distributions is clearly the dominant mode for these conditions. The D_le does not change significantly with the amount of added dimethylamine (see the legend for values of D_le and lnσ_le).

Depicted in Fig. 10 are results from an experiment where HONO, Q_4, was varied (and thus H_2SO_4) in the presence of 2 pptv (+100/-50%) dimethylamine. Interestingly, the number of particles is not particularly sensitive to H_2SO_4 above Q_4= 2.7 sccm while their size is linearly dependent on Q_4. The model indicates a leveling off in the calculated N_p as Q_4 increases (see the Supplement) which appears to be due to scavenging of the amine by particles. Another contributing factor to an insensitivity of particle number concentrations to H_2SO_4 is particle-particle collisions. A rough estimate of these effects, assuming a coagulation rate coefficient of 2x10^{-9} cm^3/s, for an N_p of 4x10^6 cm^{-3} is 2x10^{-9} (4x10^6)^2 = 3x10^4 cm^{-3} s^{-1}; multiplying by a 30 s residence time and roughly 1x10^6 cm^{-3} would coagulate. This rough estimate suggests the effect should be properly evaluated, particularly for the data presented in Fig. 9. Note also that these are small sets of data and for Fig. 10 base was added at a level that challenges the lower range of the dynamic dilution system. Model simulations with DMA_I thermodynamics (Hanson et al. 2017) at Q_4 = 2 sccm with dimethylamine at levels of 5 and 10 pptv predict N_p of 5x10^6 cm^{-3} and 1x10^7 cm^{-3}, respectively. These compare favorably with the measured N_p at 5 and 10 pptv of 2.5 and 5 x10^6 cm^{-3}, respectively. The modeled values would be reduced with a proper treatment of particle-particle collisions. Nonetheless, the thermodynamic scheme DMA_I yields cluster concentrations that are consistent with the measured N_p and its trends with dimethylamine level. Scheme DMA_I was able to mimic the dimethylamine-H_2SO_4 data of Glasoe et al., tying that data to the present data.
Since effects due to adding dimethylamine at the single-digit pptv level are large, it would be desirable to experimentally investigate amine additions at lower levels. With the current dynamic dilution system base additions at levels lower than a few pptv are swamped by the precision uncertainty in flowmeter readings. More results from these types of experiments await further improvement in the dimethylamine delivery system.

3.3 Comparison to previous results.

A number of previous results are compiled along with the present measurements in Fig. 11 for nominally base-free conditions. The present results are assigned the simulated H$_2$SO$_4$ value in the center of the reactor and at 30 cm into the illuminated region. The nucleation rate J was taken to be $N_p$ divided by the time the center of the flow travels from 20 to 40 cm, 4 s. This time is presumed to apply for the nominally clean conditions here. On the other hand, with base added intentionally, significant nucleation may also occur in the 0 to 20 cm region where base abundance is high. Uncertainties in J are probably on the order of a factor of 2. Uncertainty in H$_2$SO$_4$ is about a factor of two, based on the calculated values at 15 and 60 cm, which are $-49$ and $+106$ %, resp., from the 30 cm value. The radial profile of H$_2$SO$_4$ at 30 cm axial distance is flat from the center out to a radius of 1.7 cm.

The previous experimental data in Fig. 11 were taken over a range of temperatures, 288 to 300 K, and relative humidities, 2.3 to 75 % RH; conditions indicated in the legend. The present results extrapolate to rates that are in fair agreement with Benson et al. 2009 and much of the CLOUD data set (Kirkby et al. 2011; Kurten et al. 2016) except for the 40 % RH at 298 K data. The bulk-source H$_2$SO$_4$ data reported by Zollner et al. is included for reference; it was corrected from 38% RH to 52 % RH, increasing by about a factor of 5 using a RH$^5$ dependency. The difference between the bulk-source and present photolytic H$_2$SO$_4$ is about 4 orders of magnitude; the Kurten et al. (2016) 40 % RH data is closest to this set of bulk data, within about two orders of magnitude.

There is apparent agreement of several data sets for H$_2$SO$_4$ concentrations of $10^8$ to $10^9$ cm$^{-3}$; our lowest J (and the extrapolation of our data, dotted line), Yu et al. (2017), Benson et al. (2009), Kurten et al. (2016) and Kirkby et al. (2012) but it is complicated by the wide range of relative humidities: 2.3 % RH up to 75 % RH. Lack of experimental water dependencies and assessment of base-levels makes drawing conclusions fraught with difficulty. Nonetheless, it is interesting that the dependencies of J on sulfuric acid level are similar in many of these studies. This suggests there is an underlying similarity in particle formation conditions such as contaminant identity and level (which seems unlikely) or the critical cluster’s H$_2$SO$_4$-content is not particularly sensitive to the type or abundance of the contaminant.

4 Summary

We presented a new experimental apparatus for studying particle formation involving photolytically-formed H$_2$SO$_4$ vapor and results show the system is reproducible and responds to changes in water, HONO and SO$_2$ concentrations largely as expected. Modeled particle formation rates could be made congruous with experimental observations by including either
dimethylamine at a level of $3 \times 10^{-15}$ mole fraction or NH$_3$ at a level of $\sim 10^{-10}$ mole fraction. Also, the dependence of $N_p$ on SO$_2$ level was best explained by a reaction between HO$_2$ and SO$_2$ that yields (ultimately) H$_2$SO$_4$ and OH with a rate coefficient of $3 \times 10^{-17}$ cm$^3$/s.

Comparison of the present results to other photolytic H$_2$SO$_4$ experiments yields several suppositions. Their divergence from the bulk-source data of Zollner et al. suggests these experiments are not clean enough and/or they are subject to an unknown reaction or photochemistry. The similarity of the present results to those of Benson et al. (2009), Kirkby et al. (2011), Kurten et al. (2016) and Yu et al. (2017) suggests a common element that affects nucleation beyond what bulk-source H$_2$SO$_4$ experiments reveal. The outlier results of Berndt et al. (2010, 2014) and Benson et al. (2011) may suffer from relatively high level of contaminants: Berndt et al. (2014) suggested that a pptv-level of amine could have been present in their experiment.

As can be seen in Fig. 11, there is a remarkable agreement of the H$_2$SO$_4$ power dependencies for Kirkby et al. (2011), Yu et al. (2017), and the present results. This may be due to a similarly-sized critical cluster across these studies.

Side products from photolytic generation of H$_2$SO$_4$ that enhance nucleation were suggested by Berndt et al. (2008), however, Sipila et al. (2010) found no difference between nucleation rates whether H$_2$SO$_4$ was produced photolytically or taken from a bulk source. Since then, the Sipila et al. (2010) nucleation rates have been seen to be many orders of magnitude too high for the putative binary system (i.e., extrapolation of the present results, the Zollner et al. (2012) bulk-liquid data, results from the CLOUD experiment (Kirkby et al., Kurten et al. 2017) and Yu et al. (2017)). Since the Sipila et al. (2010) data largely overlaps the Benson et al. (2011) and Berndt et al. (2014) data, it probably also suffers from amine contaminants at the pptv-level.

The total particle number strongly depended on relative humidity with RH$^4$ and RH$^6$ power relationships over RH ranges of 15 to 35 % and 40 to 77%, respectively. The CLOUD 298 K data reported by Kurten et al. (2017) shows a power dependency of 4 on RH from 40 to 75 % at 298 K in rough agreement with the present results. Yu et al. reported a nucleation rate that depended linearly on RH that seems to be out of line with these other data sets.

A nearly linear dependence of $N_p$ on added NH$_3$ was found which is also reflected in several other studies (Kirkby et al., Kurten et al., Benson et al.). This departs from the bulk-liquid experiments of Glasoe et al. who report a 1.6 NH$_3$-power dependency and the ACDC model predicts a power dependency of 2 to 3 (Kurten et al., 2017), albeit at lower H$_2$SO$_4$. At constant NH$_3$, we found power dependencies on H$_2$SO$_4$ for $N_p$ of about 3.5 which is close to that found by Glasoe et al. (2015) and somewhat larger than the CLOUD data (H$_2$SO$_4$-power dependency of 2.6.) A linear dependence on ammonia is consistent with nucleation initiated by sulfamic acid, as outlined by Lovejoy and Hanson (1996).

The model simulations with NH$_3$-H$_2$SO$_4$ thermodynamic schemes NH$_3$ _I and NH$_3$ _II (Hanson et al. 2017) resulted in $N_p$ that exceeded experiment for a large set of conditions. With the simulations serving as a bridge between these two experiments, we conclude that the present experimental data and the Glasoe et al. NH$_3$-H$_2$SO$_4$ results do not agree. Glasoe et al. discussed the discrepancies between their NH$_3$-H$_2$SO$_4$ results and those of Ball et al. and Zollner et al., but now, since the Glasoe et al. data are higher than the latter two as well as for much of the present results, we conclude that the Glasoe et al. NH$_3$ results are biased high. Finally, the putative agreement between Glasoe et al. and the 292 K 4 pptv NH$_3$ data from
CLOUD (demonstrated in Fig. 4 of Kurten et al. 2016) should not be a validation of these two sets of NH$_3$-H$_2$SO$_4$ nucleation rates.

In hindsight we can postulate a possible avenue for an amine contamination in the Glasoe et al. ammonia experiments: several amino-compounds were studied in succession with the same dynamic dilution system and ammonia experiments were performed in between amine experiments. Measurements in the ammonia-sulfuric acid system would be most vulnerable to the presence of small amounts of holdover amines. Note that in the present experimental setup, there were separate dynamic dilution systems for ammonia and for dimethylamine. Additions of dimethylamine resulted in large abundances of particles which limited the range of conditions we were able to study. The number densities are such that a model with proper treatments of coagulation and cluster-cluster collisions is needed to fully interpret the results. Nonetheless, the experimental results are in decent agreement with model simulations using the dimethylamine thermodynamic scheme (DMA$_I$, Hanson et al., 2017) that best captured the Glasoe et al. (2015) dimethylamine-H$_2$SO$_4$ experimental results. We found low RH dependencies when dimethylamine was added in line with expectations but it should be emphasized that the linearity of the RH dependence of N$_p$ is a preliminary finding and coagulation effects on these N$_p$ values need to be investigated with a proper coagulation simulation.

Atmospheric implications of the present work are of a qualitative nature. The current work suggests that nucleation rates in the NH$_3$-H$_2$SO$_4$ system are still uncertain and need further experimental investigation. Furthermore, we conclude that the nucleation rate expression eq. 3 of Glasoe et al. (2015) likely overestimates nucleation in the ammonia-sulfuric acid system. On the other hand, as alluded to in the previous paragraph, the current work is consistent with the Glasoe et al. dimethylamine-H$_2$SO$_4$ results. Also, the much-predicted low RH dependency for dimethylamine-H$_2$SO$_4$ nucleation finds experimental corroboration here. Finally, even if the reaction of HO$_2$ with SO$_2$ occurs with a rate coefficient of 1x10$^{-16}$ cm$^3$ s$^{-1}$, it is probably an insignificant source of atmospheric hydroxyl radicals and oxidized sulfur compounds.

In the future, a series of measurements of particles with added dimethylamine at fractional pptv levels are planned to better determine H$_2$SO$_4$ and amine dependencies. We also plan to study the relative humidity dependence of ammonia-induced H$_2$SO$_4$ nucleation as well as variations of temperature on both amine- and ammonia-addition nucleation. In the long term, the system developed here will be used in particle growth studies where nm-diameter particles prepared in the Glasoe et al. apparatus are directed through PhoFR along with target organic compounds.

**Data availability.** All data presented in this manuscript are available by contacting the authors.

**Author contribution.**

HA and JV built the particle detector and performed preliminary experiments, MA helped design and carry out experiments, SM carried out added-NH$_3$ experiments and helped with the manuscript, JK helped develop the photochemical module, and DH developed and ran the simulations, developed and carried out experiments and prepared the manuscript with contributions from all co-authors. The authors declare that they have no conflict of interest.
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References


Fig. 1 (a) PhoFR schematic and (b) HONO source. The average flow velocity of 2.8 cm/s yields an average residence time in PhoFR of approximately 45 s. The concentrations listed in (b) are in molal (mole per kg H$_2$O).
Fig. 2. (a) Number of large particles for baseline HONO ($Q_0 = 4.2$ sccm; $[\text{HONO}] = 5 \times 10^{11} \text{ cm}^{-3}$) plotted vs. time for two different SO$_2$ levels, equivalent to 2 and $>10$ ppmv. (b) Measured size distributions for the high SO$_2$ conditions just after the mesh was installed, Feb. 23rd, and late in the time period depicted in (a).
Fig. 3. Model simulation for [HONO] = 5x10^{11} cm^{-3}, [SO_2] = 4x10^{14} cm^{-3}. Concentrations of NO through H_2SO_4 are plotted on the left axis; concentrations of OH, and the (H_2SO_4)_nNH_3 and (H_2SO_4)(NH_3)_1,2,3 clusters on the right axis (the latter clusters were summed over NH_3 content and multiplied by 100). These simulations are equivalent to experimental conditions of Q_4 = 4.0 sccm, Q_1 = 32 sccm and added NH_3 at 70 pptv. The lighted section is from 0 to 110 cm. At 110 cm HONO photolysis ceases and [OH] (right axis) drops to a level supplied by HO_2 + NO.
Fig. 4. (a) Measured size distributions as a function of $Q_4$, the flow rate through the HONO generator. Log-normal distributions manually fitted to the leading edge are shown as the dashed lines. Note that raw count rates at the smallest size for the three lowest $Q_4$ are roughly $0.1 \text{s}^{-1}$ and, statistically, they are not significantly different. This is slightly above the background count rate of $\sim 0.05 \text{s}^{-1}$. (b) Number of large particles as a function of $Q_4$, the HONO-laden flow rate. RH was 52%, $T = 296$ K, and $[\text{SO}_2] > 2.5 \times 10^{14} \text{cm}^{-3}$. For reference, $Q_4 = 4$ scm results in a modeled value of $\sim 4 \times 10^9 \text{cm}^{-3}$ for $\text{H}_2\text{SO}_4$ at $Z = 35$ cm and $R = 0$ (the center of the reactor; see Fig. 3.) (c) Volume mean diameter of the particles in the leading edge of the particle distributions, $D_{\text{V,le}} = D_{\text{le}} \cdot \exp(1.5 \ln \sigma)$. $D_{\text{le}}$ and $\ln \sigma$ from those distributions that had a local minimum between the smallest particles and the peak at large diameters and thus were able to be fit.
Fig. 5 (a) Number of large particles and (b) volume mean diameter of the leading edge mode plotted vs. flow rate of SO$_2$ mixture. $Q_4$, the HONO-source flow rate, was 4.2 sccm which results in roughly 5x10$^{11}$ cm$^{-3}$ [HONO] in PhoFR. For reference, an SO$_2$ mixture flow rate of 32 sccm results in a [SO$_2$] of 4x10$^{14}$ cm$^{-3}$ in PhoFR (about 16 pptv). The orange lines are model values for $N_p$ and size with 70 pptv NH$_3$ entering the flow reactor and a k3x5 (HO$_2$ + SO$_2$) rate coefficient of 3x10$^{-17}$ cm$^3$/s. The simulated size has 1.3 nm (to take into account initial cluster size of ~1 nm and the mobility to mass size difference of 0.3 nm, de La Mora et al.) added to the growth due to H$_2$SO$_4$ exposure as discussed above.
Fig. 6 (a) \(N_p\) vs. \(Q_4\) (i.e., HONO) and (b) particle size distributions with \(NH_3\) present. In (b), the log-normal parameters are listed in the legend and were obtained from a fitting procedure except for the \(Q_4 = 1.61\) sccm data.
Fig. 7. Variation of $N_p$ with added NH$_3$ for $Q_4$ of (a) 4.3 sccm and (b) 2.2 sccm. Simulated Np are shown in (a) for NH3_I and NH3_II thermodynamics. The range of measured $N_p$ without added base are shown as the squares.
Fig. 8. Variation of (a) $N_p$ and (b) $D_{V,le}$ with RH in % (RH determined by the fraction of flow through the water saturator, $Q_4$). $Q_4$ was 4.2 sccm and $Q_1 > 20$ sccm. Plot (a) also shows data with dimethyl amine added: at 2 pptv (filled diamonds) and data at a lower $Q_4 = 2.1$ sccm and dimethyl amine at 5 pptv. In (b) a linear fit is shown as the dashed line (phenomenological) while the solid line is the diameter increase based on water uptake using bulk values for the density and mass fraction of H$_2$SO$_4$ as a function of RH (Wexler and Clegg, 2002).
Fig. 9 Size distributions as a function of added dimethyl amine.

Fig. 10. Size distributions as a function of HONO level.
Fig. 11: Comparison of results from previous work (all photolytic H$_2$SO$_4$ production except Zollner et al., 2012) for nominally clean conditions. RH color-coding was applied to the points and temperatures are indicated in the legend.