

Response to RC1: 'Review of Tiszenkel et al.', Anonymous Referee #1, 03 Feb 2019

The article is nicely written, relevant literature is cited and the shortcomings of the current study (mainly related to the experimental setup) are discussed appropriately. However, I don't think the study brings anything new to the current scientific literature. The temperature effects on nucleation and early growth have already been discussed extensively in the previous study from partly the same author group (Yu et al. 2017), as well as in the studies from the CLOUD community.

Response 1: We appreciate the reviewer's helpful comments. In our revision, we elaborate on the following three points that stress the new material that this study brings to the scientific literature. By adding these new analysis and discussions, the manuscript has improved significantly.

- 1) *The TANGENT apparatus: CLOUD (Kurten et al., 2016, Duplissy et al., 2016, Kirkby et al., 2011) and Yu 2017's experiments focus on nucleation and growth of sub-3 nm particles in a consistent environment. In this study, due to the unique experimental setup allowed by TANGENT, we are examining nucleation and further growth independently, which has not yet been published. For example, the experiments in Figures 6 and 7 are unique to this study and require the TANGENT experimental setup to accomplish.*
- 2) *Temperature effects on growth: very few studies exist that elaborate on temperature effects on growth of newly formed particles (Skrabalova et al., 2014, Yu et al., 2017). The TANGENT experimental setup allows for unique experiments where conditions for nucleation can vary in temperature, allowing for study of subsequent growth of particles formed at a variety of temperature conditions. The experiments undertaken in this study illustrate that new and unique experimental design.*
- 3) *Parameter space: This study contributes more measurement data of nucleation and growth rates in a wide parameter space of temperature and RH conditions, compared to Yu et al., 2017.*
- 4)

Given that the current study lacks crucial information about the cluster composition and measurements of base organic contaminations in their system (thus relying on many assumptions based on comparison to the previous literature), there is little value in the few additional data points and speculations that are presented.

Response 2: We understand the limitations of the experimental measurements available to us for this study. We have made the revised manuscript more robust based on the three points in response 1 by including a more thorough discussion section with a broader scope of applications of this data (Specifically the applicability of this data to the marine boundary layer and polluted megacities, Section 3.2, page 11 and 12), additional literature review (specifically the growth effects of bases present in the system as well as a discussion of cluster composition, section 3.2, page 10 and 11), and additional data (Fig 7).

Given their high nucleation and growth rates for each sulfuric acid concentrations in the nucleation tube, I agree with the authors, that the nucleation mechanism is most probably ternary, i.e. involving ammonia and/or amines. However, the authors have not measured the cluster composition at the end of the nucleation tube, which, most probably, critically affects the survival of the nucleated clusters in warmer temperatures (what they intended to study and which is presented as one of the main conclusions).

Response 3: We agree. We have added a more thorough discussion of chemical composition to the discussion section (Section 3.2, page 11) in order to account for the question of chemical composition affecting survivability. By doing so, we found that the possible chemical composition that we estimated based on CLOUD studies are actually consistent with high GR in FT-2, which we also believe in large part are enhanced by base-multicomponent effects proposed by (Lehtipalo et al. 2018).

Also, only one pair of temperatures (FT-1, FT-2) is presented, so we don't actually get any information about the effect of temperature on the survival and further growth of these unknown clusters.

Response 4: This is a good point. We have created a new figure (Figure 7 in manuscript) with FT-1 and FT-2 both at the same temperature to serve as a contrast to the temperature gradient seen in Figure 6. This data is intended to address the shortcoming of the previous draft that did not show the effects of nucleation temperature on survival and growth of newly formed particles. By including this new figure, the revised manuscript shows more clearly the temperature effects on growth of the newly formed particles (Section 3.2, page 10).

The measured GRs at FT-2 are high, 15-23nm/h, so it is very hard for me to believe that they could be caused by SO₂ and O₃ only, especially as the particles are smaller than 2nm when they exit the nucleation tube. Rather, it seems possible (as the authors also mention) that organic contaminants (which were not measured) could affect the growth either directly and/or by participating in forming sulfuric acid. This would also explain the observed nucleation in the growth tube.

Response 5: We recognize that these measured GRs are high. To that end, we have deduced three possibilities for these high growth rates: organic contaminants leading to growth by HOMs as parameterized by Trostl 2016, multicomponent growth as parameterized by Lehtipalo 2018, and cluster/cluster collisional growth as shown by Lehtipalo 2016 (Section 3.2, page 10-11).

The possible effect of bases on growth of sub-3nm particles, found in several recent studies, is not discussed here at all. Therefore, I don't think that there is enough justification to speculate on unknown heterogeneous reactions causing the growth, as the authors claim in the abstract and conclusions.

Response: We included new refs. (Lehtipalo et al., 2018 and 2016; Stolzenburg et al., 2018) that we unfortunately overlooked previously. Our new analysis shows that it is very likely that the growth of the particles in these experiments included base stabilization as an important mechanism (Section 3.2, page 10-11). But we still believe that ozone and SO₂ also contribute to the additional nucleation in FT-2, and we added more discussion.

I'm looking forward to the final results of the TANGENT study, as I think there is potential to do more and get interesting results with this setup, but I don't think the initial results as presented here should warrant publication in ACP.

More specific comments: -The authors should give realistic uncertainly estimations for their results and think about the accuracy of the values presented. Especially figure 3 should have error bars, and it should be discussed what kind of error estimates this gives for the critical diameter and growth rates. -The calculation method of nucleation and growth rates should

explained better, as well as the meaning of the growth rate factor. The variables used in the equations (and where the values for them come from) should be explained.

5 *Response 7: Thank you – we agree and we have addressed them in the revised manuscript. We have elaborated on the calculation of nucleation and growth rates and have given a more complete definition of growth rate factor, with explicit definitions of all variables in equations (Section 2.2, page 6-7). Uncertainty analysis is also included in a new section (2.3, page 7) now.*

10

15

20

25

30

Response to RC2: 'Review of Tiszenkel et al, Temperature Effects on Sulfuric Acid Aerosol Nucleation and Growth: Initial Results from the TANGENT Study', Anonymous Referee #2, 14 Feb 2019

Scientific significance

New particle formation is a difficult and important problem, and there is currently a lack of diversity in the laboratory studies used to characterize it. Measurements from independent groups are to be encouraged. However, the current manuscript requires revision if it is to be suitable for ACP. At first glance, it is unclear how much new information it adds to Yu et al (2017), although the new results do become clearer with a very careful reading. The last part of the introduction should be expanded to explain how the new study differs.

Response 1: We thank the reviewer's for thoughtful comments. We agree that there was a lack of clarity in the original manuscript of the new elements of this study as it builds upon previous work, notably Yu et al 2017 which examined a similar parameter space in a similar setup. To that end, we have expanded both the introduction (Page 3, lines 8-22) and the discussion section (Section 3.2, final 2 paragraphs) to stress how this study, especially using the new TANGENT experimental setup, can contribute new findings to the literature.

The paper does not explicitly explain the point of the TANGENT apparatus, nor why it is an improvement on previous experimental setups, except via the sentence in the abstract that it allows nucleation and growth to be studied independently. This sentence should be revisited in the text with a better explanation for why this is an improvement on Yu et al (2017) where nucleation and growth rates are presented separately already. I appreciate that “separately” and “independently” are not the same, but this needs to be made more obvious in the paper text.

Response 2: We agree. In the revised manuscript, we added an expanded statement on the combination of FT-1 and FT-2 in the experimental setup section to clarify this further (Section 2.1, page 4 and 5). And in the results sections, we also included more data analysis of TANGENT results, and added discussion on the implications on the data. These TANGENT results are now presented in a separate section (Section 3.2) from FT-1 only results (now Section 3.1).

The lack of direct measurements of contaminant NH₃ and amines during the experiments is a serious shortcoming, as the concentrations of contaminants could differ markedly between 2017 and 2018 measurement periods. This shortcoming limits the quantitative usefulness of the results, and places high demands on the quality of the data analysis and presentation if the paper is to meet the ACP publication criteria.

Response 3: We make several assumptions in our data analysis with regard to ammonia and amine contamination. First, by ensuring that our experimental conditions, including using the same flow tubes, adhering to the same cleaning technique/schedule, using the same suppliers for any species added to the system, and running experiments with the same

precursors, we can still be confident that the contaminant levels should not have dramatically changed between 2017 and 2018.

- 5 *Second, 2017 ammonia and amine measurements were conducted both in the UD laboratory and in UAH's laboratory before transporting all instruments for the IOP, and the ammonia/amine readings in both environments were similar, showing ammonia and amine levels very close to the detection limit of the instrument (ranging from 1 to 40 pptv depending on the species being measured). This consistency between different environments leads us to believe that ammonia/amine measurements from the 2017 IOP can give us a good idea of measurements from the 2018 IOP experiments.*
- 10 In addition to explaining explicitly the benefits of their new setup, the authors should consider setting their paper apart by including in their figures a more detailed, quantitative comparison with other relevant literature, for example Duplissy et al (2016) or Dunne et al (2016). The authors could try to determine from published nucleation measurements what ammonia or amine concentration would be required to reproduce the new particle formation rates they measure.
- 15 *Response 4: A quantitative comparison with CLOUD data is an important aspect of this study. We modified Figure 4 with CLOUD data from Dunne et al (2016), using data points of neutral nucleation. We believe it is now clearer where this study results stand in the current knowledge of the field.*

- In order to make clear the usefulness of the TANGENT setup, the authors should explain explicitly and quantitatively how they can put several different concentrations of precursors in flow tube 2, or maintain them at different temperatures, and measure different growth rates, for a constant nucleation rate in flow tube 1.
- 20

- Response 5: We agree. As stated in response 2, the experimental setup section of the manuscript was expanded to specifically address the questions raised here. Specifically, we have addressed that FT-2 is kept at constant T and RH and only ozone was varied in FT-2. FT-1 was varied more diversely, with temperature, RH and SO₂ varied across experiments (Section 3.1). This had the effect of varying SO₂ in FT-2 after dilution. These experiments aimed to measure two effects in the system – the effect of changing temperature in the nucleation region as well as the effect of varying ozone in the growth region (Section 3.2).*
- 25

- This is exactly what is done in Figure 6 – which is excellent. However, the figure is presented in the text as describing the situation with different temperatures in the two flow tubes. While the temperatures in the flow tubes happened to be different in the measurement presented, the figure actually describes the effect of varying ozone, and no quantitative conclusion about the effect of temperature can be extracted from it.
- 30

- Response 6: Yes, we address this together with the following comment.*
- 35

To quantify the effect of temperature in flow tube 2, another figure is needed where the data in Figure 6 are compared to a corresponding measurement in which the two flow tubes are kept at the same temperature. More generally, the existing plots

show the parameter space of nucleation rate vs sulfuric acid, temperature and humidity is quite well explored, but this could have been achieved without the second flow tube and similar measurements were already published by Yu et al (2017). It would be useful to present more measurements where the conditions in the second flow tube are varied with those in the first tube fixed.

5

Response 7: We agree. We have prepared an additional figure, Figure 7 in the manuscript, that shows results from an experiment that was done with FT-1 and FT-2 at the same temperature. The discussion section was expanded to discuss the implications of the comparison between the results with a temperature gradient and the results with a uniform temperature throughout the system (Section 3.2, page 10). In short, by adding this new figure, we can see more clearly that the clusters can survive evaporation when they are transferred between different temperature regions.

10

Scientific quality

The measurements and calculations of nucleation rate use techniques which have been published previously. The experimental apparatus is described clearly. The quality of the data is therefore reasonably well-established, apart from the lack of measurements of contamination that I already mentioned. I have only a couple of outstanding questions. What are the temperature and RH dependences of the critical cluster size?

15

Response 8: The temperature dependence on critical cluster size was a linear correlation ($R^2 = 0.98$), going from 1.627 nm at 258 K to 1.651 nm at 297 K. However, considering an error of ± 0.2 nm in these measurements, it is indeed difficult to make a definitive conclusion. The RH dependence is more difficult to surmise as RH was difficult to control in the nucleation region, but the critical cluster diameter is negatively correlated with RH across the temperature range; for example, at 268 K the critical cluster diameter was calculated at 1.50 nm at 80% RH and 1.69 nm at 23% RH. Again, the amount of error makes this fairly inconclusive.

25 Why is critical cluster size equal to the diameter at $[H_2SO_4]=0$ (please add reference)?

Response 9: This assumption is based on the equation for growth rate factor used in Yu et al 2017. The equation used to calculate growth rate factor (that is, enhancement of the growth rate over 1 ppt H_2SO_4 leading to 1 nm h^{-1} growth), is:

$$k_G = \frac{\Delta D_{p,tr} \times 10^7 \text{ cm}^{-3}}{[H_2SO_4]_0} \frac{k_L}{1 - e^{-n k_L t_r}}$$

30 $\Delta D_{p,tr}$ represents the particle growth after nucleation; therefore when $\Delta D_{p,tr} = 0$, no growth has occurred past nucleation, and therefore the D_p at that point is the critical radius. In figure 3, the equation of the fit lines for each temperature is $D_p = \frac{\Delta D_{p,tr}}{\Delta [H_2SO_4]_0} ([H_2SO_4]) + b$. If $\Delta D_{p,tr} = 0$ then D_p represents the critical radius, which equals the y-intercept of the line. We have now included this clarification (Section 2.2, Page 6 and 7)

The survival of the particles in the second flow tube is clearly difficult to disentangle from the strange additional growth via sulfur dioxide and ozone.

Response 10: Indeed, the growth rates in FT-2 are high. We believe there are some heterogeneous process involving SO₂ and ozone are contributing to the additional nucleation and growth in FT-2. However, we do not understand these chemical mechanisms at present. Additionally, regarding to the growth, it seems that base contaminations in FT-2 are partially responsible, based on findings from Lehtipalo et al. (2018 and 2016) studies. We included this new discussion in Section 3.2.

I don't have any good ideas for why this nucleation happens, beyond the obvious speculations about unmeasured contamination. Could the SO₂+O₃ reaction be because of a contamination by alkaline material – metallic fragments for example, or enormously high amine or ammonia concentrations – which raise the pH to something like what is seen in sea spray aerosols or cloud droplets?

Response 11: The presence of transition metals in the experimental setup could indeed serve as a source for oxidation at higher pHs (Seinfeld and Pandis p.294): The funnels at the beginning and end of FT-2 were stainless steel. It is unclear how heterogeneous reactions of our precursor gases on the surface of the flow tube could impact the nucleation. However, the particles in this experiment are likely acidic as can be seen from cluster composition of base nucleation as shown in CLOUD experiments (Kirkby 2011; Almeida 2013). Lawler et al., 2016 also showed acidic chemical composition of nanoparticles with sulfuric acid and base nucleation. We added new discussions in Section 3.2 to address acidity of the particles.

Presentation quality

The written English is generally of good quality. There are a few missing articles “a” and “the” distributed through the text. The sentence “Larger mean diameters were detected under lower temperatures for a given [H₂SO₄]”, would imply the method used to determine the critical cluster size would give a larger critical cluster size for lower temperatures. It is clear from theory and from Figure 3 that this is not the case, so the sentence could be rephrased.

Response 12: We have fixed these errors.

Figures 3 and 4 need error bars, if possible, or at least a careful explanation of what the uncertainties are, what is in the noise and what is a real effect.

Response 13: We agree. And we added new Section 2.3 and discussed detailed error propagation analysis.

“Our results thus show that particles were observed at the end of the room temperature nucleation tube after they were initially nucleated at lower temperatures growth tube. These results can explain the presence of newly formed particles observed in

Amazon forests by (Wang et al., 2016),..... “ It is not clear that the second sentence follows from the first. The focus on the Amazon here and in the introduction and conclusion seems odd, since this is one of the few locations on Earth where nucleation may not be dominated by the sulfuric acid clustering that is the subject of this paper.

- 5 *Response 14: We agree that those two sentences in the original manuscript did not come together as clearly as we had intended, and that focusing on the Amazon is shortsighted considering our results. We have added some clarifying contents between the two sentences in the revised manuscript. We have addressed the focus on the Amazon boundary layer by broadening the scope of our study, discussing our results in the context of the marine boundary layer, where H₂SO₄ particle formation certainly occurs, as well as polluted megacities, where NPF occurs despite high pre-existing particle loads with abundant pollutant*
- 10 *species present such as SO₂ and O₃, as the conditions in FT-2 were during these experiments (Section 3.2). Regardless of the composition of the particles, studies of how particles evolve once they are transferred between environmental conditions represent an area of aerosol nucleation and growth that lacks laboratory study, and this manuscript represents experiments and observations that can initiate further investigation in this area.*
- 15 The demonstration that particles survive when the temperature increases is useful, however, and this enabled me to understand the reason for the TANGENT setup. The same mechanism that operates in the Amazon also operates in marine regions, where sulfuric acid nucleated in the upper troposphere survives to make CCN at cloud level (see recent papers by Lynn Russell’s group from the North Atlantic, or much earlier work by Tony Clarke and others).
- 20 *Response 15: We appreciate this comment. We have added a more thorough discussion of the implications of the results from TANGENT to Section 3.2, addressing marine boundary layer aerosol distributions as well as a more detailed description of how these results can help to explain new particle formation in areas such as polluted megacities where NPF occurs despite a high preexisting particle load.*

Temperature Effects on Sulfuric Acid Aerosol Nucleation and Growth: Initial Results from the TANGENT Study

Lee Tiszenkel¹, Chris Stangl², Justin Krasnomowitz², Qi Ouyang¹, Huan Yu³, Michael J. Apsokardu², Murray V. Johnston², Shan-Hu Lee^{1,4,*}

¹Department of Atmospheric Science, University of Alabama in Huntsville, Huntsville, AL

²Department of Chemistry and Biochemistry, University of Delaware, Newark, DE

³School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing, China

⁴Department of Environmental Science and Engineering, Fudan University, Shanghai, China

Correspondence to: Shan-Hu Lee (shanhu.lee@uah.edu)

Abstract. New particle formation (NPF) consists of two steps: nucleation and subsequent growth. At present, chemical and physical mechanisms that govern these two processes are not well understood. Here, we report initial results obtained from the TANGENT (Tandem Aerosol Nucleation and Growth Environment Tube) experiments. The TANGENT apparatus enables us to study these two processes independently. The present study focuses on the effects of temperature on sulfuric acid nucleation and further growth. Our results show that lower temperatures enhance both the nucleation and growth rate. However, under temperatures below 268 K the effects of temperature on the nucleation rate become less significant and the nucleation rate becomes less dependent on RH, indicating that particle formation takes place via barrierless nucleation at lower temperatures. We also examined the growth of newly formed particles under differing temperature conditions for nucleation and further growth. Our results show that newly nucleated clusters formed at low temperatures can indeed survive evaporation and grow in a warmer environment in the presence of SO₂ and ozone, strongly implying. These results also imply that some heterogeneous reactions involving nanoparticles affect nucleation and growth of newly formed particles.

1. Introduction

Atmospheric nanoparticles affect human health and air quality. Newly formed particles can contribute to approximately 30-70% of cloud condensation nuclei (CCN) in the atmosphere (Merikanto et al., 2009; Wang and Penner, 2009; Yu and Luo, 2009; Gordon et al., 2017). NPF takes place via two steps: initial nucleation (formation of critical clusters) and subsequent growth of nucleated clusters (Kulmala et al., 2013). At present, chemical and physical mechanisms that govern these two processes, as well as the identity of chemical precursors involved in these processes, are still not well understood (Zhang et al., 2012; Yu et al., 2017b). Current global models fail to represent NPF in the atmosphere for a wide range of temperature and RH conditions and for different emissions of biogenic and anthropogenic precursors due to a lack of observations. For example, models predict frequent NPF during the summer in mixed deciduous forests in the United States (Yu et al., 2015), while field observations show an absence of NPF in this region. NPF takes place via two steps: initial nucleation (formation of critical clusters) and subsequent growth of nucleated clusters (Kulmala et al., 2013). At present, chemical and physical mechanisms

that govern these two processes, as well as the identity of chemical precursors involved in these processes, are still not well understood (Zhang et al., 2012; Yu et al., 2017b). Current global models fail to represent NPF in the atmosphere for a wide range of temperature and RH conditions and for different emissions of biogenic and anthropogenic precursors due to a lack of observations. For example, models predict frequent NPF during the summer in mixed deciduous forests in the United States (Yu et al., 2015), while field observations show an absence of NPF in this region (Kanawade et al., 2011; Lee et al., 2016).

Also, current NPF theories are unable to explain the frequent NPF observed in extremely polluted megacities (Yu et al., 2017b; Kulmala et al., 2017).

Temperature and RH are the key thermodynamic properties of aerosol formation and growth (Seinfeld and Pandis, 2016). Nucleation rate (J) is a function of temperature and the Gibbs free energy barrier of cluster formation. At lower temperatures, Gibbs free energy barriers become lower and critical cluster diameters become smaller. Condensational species can affect aerosol growth differently at different temperatures because their saturation vapor pressures are dependent on temperature. For water, RH is the same as saturation ratio and chemical activity. Laboratory experiments of aerosol nucleation and growth as a function of temperature and RH remain limited, although these observations are critically needed in global models to correctly parameterize NPF under various altitude, latitude and seasonal conditions. Aerosol nucleation experiments are extremely challenging due to various experimental difficulties, including contamination of base compounds (Erupe et al., 2011; Yu et al., 2012). At present there is a lack of consistency between different experiments from different groups and even from the same groups using the same experimental setup. The lack of reproducibility and consistency of the nucleation experiments greatly hinders our understanding of nucleation mechanisms.

(Duplissy et al., 2016) conducted studies of binary homogeneous nucleation of sulfuric acid and water, with and without ions in the CLOUD (Cosmics Leaving OUTdoor Droplets) chamber at different temperatures ranging from 207 to 299 K and RH between 11% - 58%. At lower temperatures both ion nucleation and neutral binary nucleation are at the kinetic regime, while at higher temperatures J is strongly dependent on $[\text{H}_2\text{SO}_4]$, indicating there are high Gibbs free-energy barriers at these temperatures. At the nucleation regime, nucleation rates are strongly dependent on RH. Kürten et al. (2016) reported the temperature dependence of ternary nucleation in the CLOUD chamber, at the temperature from 208 to 298 K, $[\text{H}_2\text{SO}_4]$ between 10^5 and 10^9 cm^{-3} , and $[\text{NH}_3]$ up to ~ 1400 pptv. At 208 K, J reached the threshold of $1 \text{ cm}^{-3} \text{ s}^{-1}$ at a $[\text{H}_2\text{SO}_4]$ of $\sim 3 \times 10^6 \times 10^6 \text{ cm}^{-3}$ for the binary case, and at $[\text{H}_2\text{SO}_4]$ of $\sim 5 \times 10^5 \times 10^5 \text{ cm}^{-3}$ for the ternary case with $[\text{NH}_3]$ of 5 pptv. At 298 K, RH has strong effects on the measured J for both charged and neutral ternary nucleation, because the increase in RH could lead to a displacement of NH_3 from the stainless-steel walls in the CLOUD chamber and lead to an elevated NH_3 background level and consequently to higher J .

Laboratory experiments of growth rates (GR) of newly nucleated particles are very sparse. (Skrabalova et al., 2014) studied GR of newly formed particles in a flow tube at the temperature between 283 to 303 K and RH of 1% and 30%, designated as “dry” and “wet” conditions, respectively. $[\text{H}_2\text{SO}_4]$ was varied between $2 \times 10^8 \times 10^8 \text{ cm}^{-3}$ and $1.4 \times 10^{10} \times 10^{10} \text{ cm}^{-3}$. They found different effects of RH on GR ; at $[\text{H}_2\text{SO}_4]$ below 10^9 cm^{-3} , growth is promoted in drier conditions, whereas at $[\text{H}_2\text{SO}_4]$ higher than 10^9 cm^{-3} , growth favours wetter conditions. Yu et al. (2017a) performed flow tube experiments of sulfuric acid aerosol

nucleation, at the temperature from 248 to 313 K and RH from 1% to 79%, under minimal base concentrations ($[\text{NH}_3] < 23$ pptv, methylamine < 1.5 pptv, and dimethylamine < 0.52 pptv). This study provides for the first time the temperature and RH dependence of both J and GR . J shows the following dependence within the experimental conditions:

$$J = 10^{41.8} [\text{RA}]^3 [\text{RH}] e^{\frac{-2.4 \times 10^4}{T}}, \quad (1)$$

- 5 where RA is relative acidity (or saturation ratio) of sulfuric acid, and T temperature. Their results show that GR is independent of temperature below 290 K, but significantly decreases at temperatures above 290 K. RH has a moderate effect on GR .

At present, there is still no clear evidence from atmospheric observations that demonstrates “causal effects” of temperature and RH on NPF. Recent CLOUD studies have shown that oxygenated organics formed from BVOCs can grow newly nucleated particles in a wide range of tropospheric temperatures (Stolzenburg et al., 2018). This is because gas phase autooxidation reactions involved in the formation of HOMs usually have strong temperature dependencies, with higher reaction rates at higher temperatures (Frege et al., 2018), whereas nucleation is favoured at lower temperatures.

Another important perspective of temperature effects on NPF is the effects of temperature on evaporation of newly nucleated clusters and nanoparticles— that have undergone transport to differing temperature conditions for further growth. Boundary layer particle concentrations in the marine regions have been shown to be a result of sulfuric acid-driven nucleation of nanoparticles in the free troposphere as a result of oxidation of upwardly transported and oceanic dimethylsulfide. These particles then undergo downward transport to become reservoirs of nanoparticles in the boundary layer. This has been observed and modelled by several groups over the previous decades (Russell et al., 1994; Raes, 1995; Clarke, 1993).

The lack of local NPF events in Amazon forests has been a confounding observation for many years (Rizzo et al., 2018) and yet there are reservoirs of nuclei mode particles at the surface which do not form typical “banana” plots of aerosol size distributions observed elsewhere (Martin et al., 2016). Understanding the origin of these nuclei mode particles has been a subject of recent studies. (Wang et al., 2016) reported that while NPF does not take place in Amazon forests at the surface level during the dry and wet season, NPF takes place in the colder free troposphere; these newly formed particles can be transported down to the boundary layer to become a reservoir of nanoparticles at the surface. A subsequent question is whether newly nucleated clusters and nanoparticles in the free troposphere can survive evaporation during their transport to the warmer boundary region.

At present, the temperature effects on the growth of newly formed particles crossing different temperature regions have not been examined in a controlled laboratory environment. In order to address this shortcoming in laboratory experiments of this relatively common phenomenon, we have constructed the TANGENT apparatus, consisting of a temperature- and RH-controlled nucleation flow tube that permits study of gas-to-particle conversion over a wide parameter space. This nucleation region is connected to a room temperature growth tube where conditions for further growth of these nanoparticles can differ dramatically from those of their nucleation. With the suite of instruments monitoring precursor gases as well as particle size

[distributions from sub-3 nm up to CCN sizes at key areas of the flow apparatus, the critical processes that atmospheric nanoparticles undergo can be studied and parameterized with TANGENT.](#)

Here, we present the initial results of the TANGENT experiments conducted during the Intensive Observation Period (IOP) study in June and July 2018. In the present study, we report the temperature effects on J and GR of sub-2 nm particles in the nucleation tube. We also discuss how temperature differences in the nucleation and growth tube affect the potential evaporation of newly nucleated clusters while these clusters are transported from the colder to the warmer temperature region.

2. Methods

2.1 The TANGENT Experimental Setup

Figure 1 shows the schematic diagram of the TANGENT apparatus. The TANGENT consists of the two flow tubes (FT) to enable studies of nucleation (FT-1) and subsequent growth (FT-2). The nucleation tube was built by the University of Alabama in Huntsville, and the growth tube by University of Delaware. [TANGENT allows for nucleation to be observed as a separate process from growth; with a short residence time \(45 s\), precise temperature control, and the ability to produce \$H_2SO_4\$ at concentrations spanning \$10^6\$ to \$10^9\$ \$cm^{-3}\$, FT-1 is able to nucleate and monitor particles from precursor gases at a variety of conditions. After particles are nucleated in FT-1 where size distributions are recorded, particles are then transported to the growth tube \(FT-2\), where the particles undergo further growth at room temperature for a longer residence time \(4 min\) with the ability to precisely control other trace gases in the growth environment. According to our knowledge, this is the first flow tube experimental setup that allows for aerosol nucleation and growth processes to be investigated independently but at the same time.](#)

The experimental setup of the nucleation region (FT-1) was based on (Benson et al., 2009; Benson et al., 2008; Erupe et al., 2011; Young et al., 2008b; Yu et al., 2012; Yu et al., 2017a; Benson et al., 2011). It consists a photolysis region where H_2SO_4 is generated photochemically and monitored followed by a temperature-controlled nucleation tube. In the photolysis region, OH radicals were produced via photodissociation of water vapor in a quartz tube using a mercury lamp (Pen-Ray Model 11SC-1). The mercury lamp was located in a temperature-controlled enclosure filled with a constant nitrogen flow. UV intensity was adjusted with an aperture over the slit in the enclosure exposing the quartz tube to the UV lamp. UV intensity was monitored with a CsI phototube (Hamamatsu Model R5764) and picoammeter (Keithley 6732). Measurements of UV intensity were taken to ensure consistency between experimental trials. SO_2 , O_2 and N_2 gases were introduced to the flow tube immediately after the photolysis region. H_2SO_4 forms from the $SO_2 + OH$ reaction. Heating tape was applied to the H_2SO_4 production region to suppress nucleation prior to entering the temperature-controlled nucleation zone. The H_2SO_4 production region was monitored with a condensation particle counter (CPC, TSI 3776) and particle sizing magnifier (PSM, Airmodus A09) to ensure no particles were formed before the flow entered the nucleation region.

~~[H₂SO₄ concentrations at the beginning of the nucleation tube were measured with a nitrate-based chemical ionization mass spectrometer \(CIMS\) based on \(Eisele and Tanner, 1993\) continuously during the experiments. Calibration of \[H₂SO₄\] with](#)~~

~~the nitrate CIMS was described previously by (Young et al., 2008). The CIMS was operated with an inlet flow of 5.0 SLPM and an ion-molecule reaction time of 0.05 s. The lower limit of detection was calculated to be $\sim 1 \times 10^5 \text{ cm}^{-3}$. The overall uncertainty of the H_2SO_4 measurements was estimated at $\pm 60\%$.~~

H_2SO_4 concentrations at the beginning of the nucleation tube were measured with a nitrate-based chemical ionization mass spectrometer (CIMS) based on (Eisele and Tanner, 1993) continuously during the experiments. Calibration of $[\text{H}_2\text{SO}_4]$ with the nitrate-CIMS was described previously by (Young et al., 2008a). The CIMS was operated with an inlet flow of 5.0 SLPM and an ion-molecule reaction time of 0.05 s. The lower limit of detection was calculated to be $\sim 1 \times 10^5 \text{ cm}^{-3}$.

No base compounds were added, but base compounds were present in the flow tube as impurities likely generated from deionized water used for H_2SO_4 production and RH control (Erupe et al., 2011; Yu et al., 2012). NH_3 and amines were not measured during the 2018 IOP, but they were measured under very similar experimental conditions during the entire 2017 IOP with an ethanol-CIMS at the beginning of the nucleation tube (You et al., 2014; Yu and Lee, 2012). Detection limits of NH_3 /amines in our CIMS were pptv or sub-pptv with a 1-min integration, as previously discussed elsewhere (Benson et al., 2010; Erupe et al., 2011; You et al., 2014; Yu and Lee, 2012).

The nucleation tube is an 80 cm long Pyrex glass tube with an i.d. of 4.85 cm. The temperature of the nucleation tube was controlled with a circulating bath and a water-based potassium formate heat transfer fluid (Dynalene HC-50, Dynalene, Inc.) to adjust the temperature between 258 and 297 K. RH was adjusted by directing some of the dry nitrogen makeup flow through deionized water in a water bubbler. Thus, in our experimental setup, changes in RH in the nucleation tube did not affect the OH radical concentrations in the photolysis region. Temperature and RH probes (CS-215, Campbell Scientific) were used to monitor the conditions at the beginning of the photolysis region, as well as at the end of the nucleation region. An additional temperature and RH probe (Traceable, Fisher Scientific) was applied inside the nucleation tube to confirm the RH. Residence time in the nucleation region (FT-1) was 45 s.

~~Particle concentrations at the exit of FT-1 were measured with a PSM [Vanhanen et al., 2011].~~ Particle concentrations at the exit of FT-1 were measured with a PSM (Vanhanen et al., 2011). The PSM saturator flow was operated with a 240-step cycle between 0.1 - 0.9 SLPM at a rate of 1 s per step, giving saturator flow dependent cut-off sizes between 1.26 nm and 2.85 nm.

These cut-offs were resolved to six size bins in an inversion method based on (Lehtipalo et al., 2014), producing size distributions with six size bins: 1.26 - 1.53 nm, 1.53 - 1.79 nm, 1.79 - 2.06 nm, 2.06 - 2.32 nm, 2.32 - 2.59 nm, and 2.59 - 2.85 nm. Particle concentrations were also monitored with a scanning mobility particle sizer (SMPS) consisting of a differential mobility analyser (DMA, TSI 3080) and a CPC (TSI 3776). However, under the typical experimental conditions, particles above 3 nm in diameter did not appear even with the most favourable conditions for nucleation and growth (e.g., high $[\text{H}_2\text{SO}_4]$, high RH and low temperature).

During the experiments, $[\text{H}_2\text{SO}_4]$ was varied by adjusting the aperture on the mercury lamp housing (hence varying $[\text{OH}]$) at a fixed $[\text{SO}_2]$, allowing for a range of $[\text{H}_2\text{SO}_4]$ spanning roughly one order of magnitude for a given dilution of SO_2 . $[\text{H}_2\text{SO}_4]$ was further varied by adjusting the SO_2 dilution, allowing for measurements spanning $[\text{H}_2\text{SO}_4]$ of 10^6 to 10^9 cm^{-3} . The PSM

measurements showed that each experimental condition was “stabilized” typically after ~30 min for a specific set of [H₂SO₄], RH and temperature.

The photolysis and nucleation tubes were cleaned thoroughly with deionized water, citric acid solution and ethanol and allowed to dry for 24 hours while heated to 60 °C with pure N₂ flowing through the flow tube. Between experiments, the photolysis and nucleation tubes were continuously flushed with dry vaporized liquid nitrogen. A constant flow of N₂ was passed through the experimental apparatus at all times during the IOP to ensure that the conditions inside the tube would remain constant and there would be no intrusion of room air.

The nucleated clusters (smaller than 2 nm) were transported to the growth tube (FT-2) for further growth with an extended residence time (4 min). FT-1 and FT-2 were coupled with an 8-inch stainless steel tube with additional inlet ports for injection of ozone, zero air and SO₂. ~~The growth tube was described by~~ (Krasnomowitz et al., 2018; Stangl et al., 2018). ~~The growth tube was described by~~ (Krasnomowitz et al., 2019; Stangl et al., 2019). The growth tube consists of a 1.52 m long and 0.2 m i.d. fused quartz tube fitted with stainless steel funnels on each end that reduce the i.d. down to 0.051 m. The total volume of the tube and entrance and exit funnels is 52.4 L, giving a surface-to-volume ratio of 0.24 cm⁻¹. The 8-inch straight tube fitting allows carrier/reactant gases to enter the tube via an axial inlet port and continuous flow through the entire length of the reactor during the course of an experiment. The end of the tube was attached to an ozone monitor (Thermo Scientific 49i), a hygrometer (Traceable, Fisher Scientific), and an SMPS (TSI 3938, 3788).

FT-2 has several ports at the inlet to inject additional gases in to the system to observe their effects on further growth of freshly nucleated particles. Ozone was added to FT-2 using the calibration ozone generator on a Thermo Scientific 49i. Ozone was varied in FT-2 by adjusting the UV intensity of the calibration lamp. The residence time in FT-2 could be changed by varying the flow of zero air in to FT-2. During a typical experimental run using both FT-1 and FT-2, conditions would only be changed in FT-2, with temperature, RH and precursor species in FT-1 held constant throughout the entire experiment. The experiments undertaken in this study measured two effects in the system: the effect of changing temperature in the nucleation region as well as the effect of varying ozone (in the co-presence of SO₂) in the growth region.

2.2 Calculations of Nucleation (J) and Growth Rate (GR)

~~Calculations of J were made based on Yu et al., [2017].~~ Calculations of J were made based on (Yu et al., 2017a). Briefly, J was calculated according to the following approximation:

$$J_0 \approx N_{tot} \times n k_L, \quad (2)$$

where J_0 represents the nucleation rate corresponding to the initial sulfuric acid concentration ([H₂SO₄]₀) measured at the beginning of the nucleation tube, N_{tot} the total number concentration of particles detected at the end of the nucleation region, n the nucleation theorem power ~~determined by the linear fit between Log N_{tot} and Log [H₂SO₄]₀~~, and k_L the diffusion-limited, pseudo first-order wall loss coefficient (Hanson and Eisele, 2000). The nucleation theorem power n was experimentally determined for each set of experiments by the linear fit of Log N_{tot} vs. Log [H₂SO₄]₀. Our k_L was typically 0.01 s⁻¹. Eq. 2 allows us to obtain J_0 at different [H₂SO₄]₀ using n and N_{tot} of the formed clusters (all smaller than 2 nm in the present study).

To calculate GR , the critical cluster size was determined experimentally, with the critical cluster size corresponding to the y-intercept of the linear fit between the mean particle diameter, D_p , and the $[H_2SO_4]_0$ (e.g., Fig. 3). D_p was obtained using the inversion of the PSM size distribution measured at the end of FT-1. GR was calculated by the difference between the critical size and D_p divided by the nucleation time.

- 5 ~~The growth rate factor k_G , defined as the ratio of $GR/[H_2SO_4]$, was determined by the expression derived by (Yu et al., 2017):~~
~~The growth rate factor k_G is defined as the growth rate enhancement over 1 pptv H_2SO_4 causing 1 nm hr^{-1} of growth. The collision limited condensation of H_2SO_4 of 1 pptv contributes roughly 1 nm hr^{-1} of growth rate at a temperature of 298 K (Nieminen et al., 2011). Thus, the k_G is an indicator of the deviation of the actual growth rate compared to this conventional collision-limited GR . The k_G were determined by the expression derived by (Yu et al., 2017a):~~

$$10 \quad k_G = \frac{\Delta D_{p,tr} \times 10^7 \text{ cm}^{-3}}{[H_2SO_4]_0} \frac{k_L}{1 - e^{-nk_L t_r}}, \quad (3)$$

~~Where $\Delta D_{p,tr}$ represents the change in diameter over the residence time (t_r) in the nucleation tube (FT-1). $\frac{\Delta D_{p,tr}}{[H_2SO_4]_0}$ was experimentally determined by plotting from the slope of the D_p against vs. $[H_2SO_4]_0$ plot (e.g., Fig. 3), which gives a linear relationship. Thus, the k_G is the product of the slope and $\frac{k_L \times 10^7 \text{ cm}^{-3}}{1 - e^{-nk_L t_r}}$. can be calculated from n and k_L values. The k_G is the product of this slope and $\frac{k_L \times 10^7 \text{ cm}^{-3}}{1 - e^{-nk_L t_r}}$. Extrapolation to the y-axis of Figure 3 gives a value for the critical cluster diameter.~~

- 15 ~~$\Delta D_{p,tr} = 0$ for the critical cluster and thus $D_{p, critical}$ will be equal to the y-intercept of the linear fit of each data set.~~

2.3 Uncertainty analysis

~~The uncertainties in the J_0 calculation arise from uncertainties in CIMS H_2SO_4 measurements, measurements of particle concentrations in the PSM and the size inversion from PSM-measured number concentrations. The uncertainty in the H_2SO_4 CIMS is approximately 60% (Erupe et al., 2010; Eisele and Tanner, 1993; Benson et al., 2008; Benson et al., 2009; Kürten et al., 2012; Petäjä et al., 2009). The wall loss calculation has $\pm 7\%$ uncertainty (Hanson and Eisele, 2000). The measurement error in the PSM size distribution, based on the standard error calculated between run-to-run experiments under an identical condition, is $\pm 26\%$. The uncertainties in inversion of the particle diameter from the PSM measurement are estimated around 12% (or ± 0.2 nm) for inorganic particles in the size range observed in this experiment (Lehtipalo et al., 2014; Lehtipalo et al., 2016; Kulmala et al., 2013; Yu et al., 2017a). Propagation of the errors in sulfuric acid measurement, wall loss, and the PSM measurements results in an overall uncertainty of $\pm 65.5\%$ in the calculation of J_0 .~~

3. Results and Discussion

3.1. Nucleation and growth in FT-1

Table 1 shows the typical experimental conditions used in the FT-1 (nucleation tube) and FT-2 (growth tube) during the 2018 IOP study. In the nucleation tube, temperature was varied from 258 to 297 K and RH from 4% to 85%. $[H_2SO_4]$ spanned from

10^6 to 10^8 cm^{-3} , corresponding to RA of 10^{-5} to 10^{-2} . RA was calculated using the sulfuric acid saturation vapor pressures provided by (Vehkamäki et al., 2002). NH₃ and amine measurements not taken during this study, but they were undertaken during the 2017 IOP campaign using the same experimental apparatus, precursor gases and cleaning schedule as the 2018 campaign that is the concern of this study. The CIMS-measured NH₃ (during the 2017 IOP) was 14.2 ± 6.7 ppt (Fig. 2). Thus, the ratio of [NH₃]/[H₂SO₄] ranged from 0.6 to 268. According to (Schobesberger et al., 2015) and (Dunne et al., 2016), these ratios represent ternary nucleation and some nucleation in a transition regime between binary and ternary, when considering only the effects of NH₃ (without amines). Overall, the measured nucleation rates ranged from $10 - 10^5$ cm^{-3} at higher temperatures and lower [H₂SO₄] up to 10^5 cm^{-3} at lower temperatures and higher [H₂SO₄]. The observed *GR* ranged from 1 to 80 nm h^{-1} . The growth tube (FT-2) was kept at room temperature (297 K) and dry conditions (RH of 10%). SO₂ was added in the range from 100 ppbv to 5 ppmv and ozone from 0 to 248 ppbv.

Figure 3 shows the measured D_p with the PSM at the end of FT-1 as a function of the initial [H₂SO₄]₀ at the temperature between 258 and 297 K. [H₂SO₄]₀ was varied from 8×10^6 cm^{-3} to 7×10^7 cm^{-3} . The RH was kept in relatively narrow range between 20% and 30%. The y-intercept in Fig. 3 indicates the critical cluster diameter of was estimated to be between 1.67-1.68 nm, 7 nm depending on temperature, with lower temperatures resulting in smaller critical cluster diameters. However, since the PSM inversion that determines D_p has an uncertainty of ± 0.2 nm, it is difficult to discuss the temperature trends of the critical cluster diameter. This critical size is consistent with Kulmala et al. (2013) (Kulmala et al., 2013) and Almeida et al. (2013) (Almeida et al., 2013), which determined critical cluster diameters of 1.5 ± 0.3 nm and 1.7 nm, respectively. Larger mean diameters were detected under lower temperatures for For a given [H₂SO₄]₀, the mean D_p at the end of the 45 second residence time in FT-1 was larger for lower temperatures. Previously, (Glasoe et al., 2015; Yu et al., 2017a) have also shown increasing *GR* with increasing [H₂SO₄] from flow tube experiments. The slope of D_p vs. [H₂SO₄]₀ increased with each 10 degree decrease in temperature over the course of these experiments. Thus, the growth rate factor k_G also increased with subsequent temperature decreases (e.g., from 1.27 at 297 K to 12.6 at 258 K). These results indicate that lower temperatures promote the faster growth of particles due to the reduction in saturation vapor pressures of H₂SO₄ at lower temperatures.

Figure 4 shows the relationship of Log *J* vs. Log RA for different temperatures. Experiments were conducted at 10 K intervals, starting from 297 K down to 258 K for RH between 41% and 45%. Across all temperature and RH experiments conducted, in general, *J* values were shifted 2 to 3 orders of magnitude above previous literature values [Yu 2017, Brus 2011] of flow tube nucleation studies (Brus et al., 2010; Yu et al., 2017a) and 4 to 5 orders of magnitude above CLOUD measurements of H₂SO₄ nucleation as shown in the figure using CLOUD data from (Dunne et al., 2016). This upward shift was consistent across trials.

Based on our measured NH₃ and amine concentrations (Fig. 2), this upward shift is consistent with the nucleation rate enhancement due to synergistic effects of NH₃ concentrations on the order of 20 to 30 pptv, and dimethylamine concentrations on the order of 1 to 25 ppt reported by other studies (Glasoe et al., 2015). There was a consistent relationship between Log *J* and Log RA. Except for 288 K and 297 K, where the slope of Log *J* vs. Log RA was approximately 2, slope was 3 for all trials, with the best-fit lines shifting towards higher values of RA as temperature decreased. Hanson and colleagues provided comprehensive analysis of Log *J* vs. Log RA (or Log [H₂SO₄]) obtained from flow tube studies (Glasoe et al., 2015; Zollner et

al., 2012). In general, flow tube studies from various groups have shown slopes between 3-6 for the ternary system (Glasoe et al., 2015; Zollner et al., 2012; Brus et al., 2010; Berndt et al., 2014; Erupe et al., 2011; Yu et al., 2012; Hanson et al., 2017). Using the CLOUD experiments, (Dunne et al., 2016; Almeida et al., 2013; Kirkby et al., 2011) also showed the slope of 3 for the ternary system. This slope is consistent with the base-stabilization mechanism provided by (Chen et al., 2012; Jen et al., 2014; Jen et al., 2016) that the bottleneck clusters contain 3-4 H₂SO₄ molecules with at least one base molecule. It was previously believed that the slope of Log *J* vs. Log RA dictates the amount of H₂SO₄ molecules present in the critical cluster based on classical nucleation theory (CNT) (Kashchiev, 1982; McGraw and Zhang, 2008), which then would imply here that the critical cluster contains three H₂SO₄ molecules for the ternary system. However, more recent work by (Malila et al., 2013; Vehkamäki et al., 2012) (Malila et al., 2013; Vehkamäki et al., 2012) has shown that this conclusion may be an oversimplification of the mechanism of particle formation resulting from an application of CNT with an incomplete understanding of the free energy maxima and minima. As a result, there is caveat when the critical cluster composition is determined by the simple relationship between *J* and [H₂SO₄].

Figure 5 shows the measured *J* as a function of temperature for [H₂SO₄] between $2 \times 10^2 \times 10^7$ and $3 \times 10^3 \times 10^7$ cm⁻³ and RH between 15% to 45%. *J* increased with the decreasing temperature in the temperature range above 268 K. The higher *J* at lower temperatures is consistent with predictions from CNT (Seinfeld and Pandis, 2016) (Seinfeld and Pandis, 2016). However, a shift in slope is visible around 268 K, indicating that the dependence of *J* on temperature becomes less significant at low temperatures. The variation seen across RH at higher temperatures also becomes negligible below this temperature. Thus, these results indicate that at temperatures below 268 K, Gibbs free energy barriers are reduced significantly. This is consistent with (Duplissy et al., 2016) that (Duplissy et al., 2016) found barrierless particle formation at lower temperatures. As discussed above, the base contamination present in the conditions for this study resulted in elevated *J* values, which also resulted in this barrierless kinetic nucleation occurring at a relatively higher temperature.

3.2. TANGENT experiments: Further growth of clusters in FT-2:

In order to determine whether newly formed particles nucleated at lower temperatures can survive downward transport to warmer temperature conditions, we conducted experiments using two different temperature tests (Figs. 6 & 7): the first test had a much lower temperature in FT-1 (268 K) and than in FT-2 (297 K) and the second test had the same temperature (297 K) in both tubes. During the first test (Fig. 6) (The), the average particle concentration coming out of FT-1 was $2 \times 10^5 \times 10^5$ cm⁻³ with a median diameter of 1.909 nm at [H₂SO₄]₀ of $6 \times 10^2 \times 10^7$ cm⁻³ and RH of 10%. These newly formed particles were further mixed with an additional zero air flow at a 1:6 dilution. The [SO₂] was 83 ppbv and the ozone level was varied from 0 to 248 ppbv in FT-2. No particles were observed coming out of FT-2 when ozone was absent, indicating that SO₂ alone does not cause nucleation and growth of clusters. However, in the presence of ozone and SO₂, continuous nucleation and further growth of transported clusters took place in FT-2. The particle concentration measured at the end of FT-2 was closely correlated with the ozone concentration: the particle concentration ranged from $3 \times 10^3 \times 10^2$ cm⁻³ (with *D_p* of 2.8 nm) at the lowest ozone of 28 ppbv up to $5 \times 10^4 \times 10^4$ cm⁻³ (*D_p* of 3.4 nm) at the maximum ozone of 248 ppbv. Thus, the particle concentration in FT-

2 at the highest ozone was even greater than that coming out of FT-1 after dilution, indicating that a high ozone load resulted in additional nucleation and the further growth of clusters in FT-2. This could be the result of the remaining H_2SO_4 vapour passing through to FT-2, but we excluded this possibility. After considering wall loss in FT-1 and the 1:6 dilution FT-2, $[\text{H}_2\text{SO}_4]$ in FT-2 was estimated to be 1.15×10^6 cm^{-3} , which can result in J only on the order of $10^1 \text{ cm}^{-3} \text{ s}^{-1}$ at room temperature and the dry condition, as shown from the results obtained in FT-1 (e.g., Fig. 4). However, the measured formation rate (J) of particles in FT-2 was $190 \text{ cm}^{-3} \text{ s}^{-1}$, in contrast to this estimation. There was another possibility that ozone reacted with possible organic impurities in FT-2 to produce OH, which oxidized SO_2 to produce H_2SO_4 and nucleated in FT-2, but no organics were added in our experiments. It is not clear at present what is the cause of nucleation in FT-2 and this requires future study. However, it was clear that the co-presence of ozone and SO_2 was an important factor in preventing evaporation of newly formed particles and facilitated them to the further grow at the higher temperature. The overall GR of particles in FT-2 was from 14.9 to 23.1 nm h^{-1} , depending on the ozone concentration. These results may imply some heterogeneous reactions occurring on acidic sulfuric acid clusters, in a similar way to form sulphate from oxidation reactions of SO_2 on acidic particles as proposed by (Hung and Hoffmann, 2015).

The second test was conducted with FT-1 and FT-2 both at a constant temperature of 297 K (Fig. 7). FT-1 was held at a constant $[\text{H}_2\text{SO}_4]_0$ of $1.3 \times 10^8 \text{ cm}^{-3}$. The total particle concentration out of FT-1 for this experiment was $1.7 \times 10^5 \text{ cm}^{-3}$ with a mean diameter of 1.9 nm. Aside from the higher $[\text{H}_2\text{SO}_4]_0$, which was necessary to produce the same particle concentration in the higher temperature FT-1, particle count and mean diameter were similar to the experiment with a cold FT-1. However, the size distributions in Figure 6a and Figure 7a indicate that there were more particles in the higher diameter size bins when the temperature in FT-1 was lower. At the end of FT-2, particle concentration and size were again closely correlated with ozone concentration, ranging from $8.6 \times 10^1 \text{ cm}^{-3}$ ($D_p = 2.7 \text{ nm}$) at the lowest ozone concentration up to $2.3 \times 10^4 \text{ cm}^{-3}$ ($D_p = 3.8 \text{ nm}$) at the highest ozone load. These concentrations and sizes result in a growth rates ranging from 12.0 to 28.1 nm hr^{-1} , indicating that the growth the highest ozone concentrations was faster during the constant temperature experiment at. This was due to a greater concentration of smaller particles formed at higher $[\text{H}_2\text{SO}_4]_0$ in the second test.

Examining the contrast between Figure 6, we see notable effects of temperature gradient on the survival of particles to the end of FT-2. While the average size at the end of the nucleation tube was similar in each experiment ($D_p = 1.9 \text{ nm}$ with 268 K FT-1, $D_p = 1.9 \text{ nm}$ with 298 K FT-1), we can see from the size distributions in each experiment that the low-temperature FT-1 resulted in a greater concentration of particles in the larger size bins. These particles (once they are stabilized, e.g. by base compounds) are more thermodynamically stable and therefore have a greater ability to survive evaporation when transported to the warmer environment of FT-2. Particles formed in warmer environments have a greater energy barrier to overcome before they become stable enough to grow spontaneously (Lovejoy et al., 2004).

The additional nucleation occurring in FT-2 in the co-presence of SO_2 and ozone cannot be explained by the current knowledge. These results suggest some possible heterogeneous reactions involving SO_2 and ozone on acidic clusters. One possibility is the presence of alkaline species such as transition metal or high NH_3 /amine concentrations that could increase the pH of the particles, which can contribute to the production H_2SO_4 by SO_2 oxidation in the presence of ozone (Seinfeld and Pandis,

2016; Hung and Hoffmann, 2015). However, CLOUD studies have often found that particles nucleated in the presence of NH₃/amines remain acidic (Lawler et al., 2016). Understanding how SO₂ and ozone interact each other on the acidic nanoparticles to facilitate nucleation and growth will require future studies.

We also examined the additional effects of organics and base compounds on *GR* in FT-2. First, to see the effects of possible impurities of organics, we used the growth rate parameterization from (Tröstl et al., 2016):

$$GR = kD_p[HOM]^p \quad (4)$$

Solving Eq. 4 for [HOM] using our observed growth rates of 12.0 to 28.1 nm hr⁻¹, $D_p = 1.9$ nm, $k = 5.2 \times 10^{-11}$ and $p = 1.424$ (Tröstl et al., 2016) results in a [HOM] of 2.8 to 3.8 pptv necessary to account for these growth rates. The amount of monoterpene required to produce that amount of HOMs was calculated using equation 16 from Tröstl et al., 2016 solved for [MT]:

$$[MT] = \frac{[HOM] \cdot CS}{Y_1 k_1 [O_3]} \quad (5)$$

Using the yield of HOMs from ozonolysis of monoterpenes $Y_1 = 2.9\%$ (Kirkby et al., 2016), temperature dependent reaction rate of ozone and α -pinene $k_1 = 8.06 \times 10^{-17}$ (Khamaganov and Hites, 2001), and 10^{-3} for condensation sink (*CS*, calculated from size distributions in FT-2) it would require between 100 and 1000 ppbv of monoterpenes to account for that concentration of HOMs. These high concentrations were very unlikely to be present in FT-2 considering the rigorous cleaning of the TANGENT apparatus as well as the lack of added monoterpenes to the system.

Second, to see the possible multicomponent growth due to the presence of ammonia in the system, we utilized the parameterization of multicomponent growth from equation (4) of (Lehtipalo et al., 2018):

$$GR = k_1[H_2SO_4]^a + k_2[H_2SO_4]^b[NH_3]^c + k_3[Org]^d \quad (6)$$

Where k_1 and k_2 are 2.05×10^{-7} and 6.69×10^{-11} , respectively (Lehtipalo et al., 2018) and $a = b = c = d = 1$. Assuming [Org] = 0 for simplicity, and [H₂SO₄] and [NH₃] values from the temperature gradient experiment (1.15×10^6 cm⁻³ H₂SO₄, 14 ppt NH₃ estimated from 2017 IOP measurements), we should expect a *GR* of 0.24 nm hr⁻¹. However, this calculation only considers the presence of NH₃ in the system, when it is very likely that there were amines present at pptv levels (Fig. 2). (Glasoe et al., 2015) and (Yu et al., 2012) found synergistic effects on *GR* when both NH₃ and methylamine/dimethylamine are present that can enhance *GR* by 1 to 2 orders of magnitude, which would put these calculated *GR* values in range of the observed 23.1 nm hr⁻¹ *GR* seen in the FT-2.

Also, cluster-cluster collision in the presence of stabilizing base compounds such as trace amines that were present in TANGENT can enhance growth by an order of magnitude (Lehtipalo et al., 2016). Thus, it seems that the observed high *GR*s in FT-2 were at least in some part due to multicomponent effects of base compounds and cluster-cluster collisional growth effects on *GR*, in addition to potential heterogeneous processes discussed above.

The chemical composition of the particles nucleated and grown in this experiment is an element that is likely to have an influence on their stability, growth, and survivability in a different environment. We did not measure chemical composition of clusters and particles in the present study. However, we can surmise the chemical composition of the particles in this study

based on CLOUD studies that utilized API-TOF instruments (Duplissy et al., 2016; Kirkby et al., 2011; Kürten et al., 2014). These studies, conducted in similar precursor conditions of H₂SO₄ and NH₃/amines at pptv levels, found that pure H₂SO₄ clusters did not exist beyond dimers and trimers at the lowest temperatures; NH₃ or amines particles consisting of H₂SO₄ molecules clustered with ammonia molecules at ratios up to 1:1 were common. It thus can be expected that the particles in this study had a similar chemical composition, and the presence of bases in these newly formed particles was a critical factor for their survival and further growth. This chemical composition is also consistent with above analysis about the GR in the FT-2, derived from the multicomponent nucleation and growth processes by (Lehtipalo et al., 2018).

Our results ~~thus in the TANGENT setup using two different temperatures in FT-1 and FT-2~~ show that particles were observed at the end of the room temperature nucleation tube after they were initially nucleated at lower temperatures growth tube. ~~These results can,~~ which is similar to the experiments in which FT-1 was held at cold temperatures for particle formation before particles were transported and allowed to grow further in the warmer environment of FT-2. These results thus clearly demonstrate that indeed small clusters can survive evaporation when transported within different temperature regions. This is consistent with the mechanism of particle formation and downward transport in the marine boundary layer, where nucleation takes place by sulfuric acid formed in the free troposphere at cooler high altitudes before they are transported downwards to warmer conditions (Russell et al., 1994; Raes, 1995; Clarke, 1993). Our results can also help to explain the presence of newly formed particles observed in Amazon forests by (Wang et al., 2016), which concluded that the particle loads observed in the boundary layer could be the result of downward transport of particles formed in the colder free troposphere. ~~The results of our experiments thus confirm that particles can indeed nucleate at higher altitudes under colder temperatures and while transported downward to warmer surface sites, they can survive and grow further.~~

Also, these high GR and additional nucleation observed in FT-2 in the co-presence of SO₂ and ozone may be relevant to the frequent and strong NPF events observed in extremely polluted Chinese mega cities (Guo et al., 2014; Yao et al., 2018; Yu et al., 2017b). In these environments, there exists a high pre-existing particle load that would ordinarily suppress NPF by acting as condensation sink of newly formed particles. However, in these highly polluted areas NPF events are observed with some regularity, which cannot be explained by the current knowledge.

4. Conclusions and Implications

We have conducted experiments to study the temperature dependence of aerosol nucleation and growth using the TANGENT setup. This setup consists of two flow tubes which enable us to study nucleation and subsequent growth independently. In the nucleation tube, temperature was varied from 258 to 297 K and RH from 4% to 85%. [H₂SO₄] spanned 10⁶ to 10⁸ cm⁻³, which corresponds to RA of 10⁻⁵ to 10⁻². Based on the measured [NH₃] to [H₂SO₄] ratios, it was most likely that nucleation took place via the ternary process. The growth tube was kept at room temperature and the dry condition (RH of 10%). SO₂ was present at 100 ppbv to 5 ppmv and ozone at 0 to 248 ppbv.

Our results indicate that lower temperatures enhance both nucleation and growth rates as predicted by CNT. However, the temperature effects on nucleation rates become less important at lower temperatures (below 268 K), consistent with CLOUD studies (~~Duplissy et al., 2016~~)(Duplissy et al., 2016) which found that sulfuric acid nucleation takes place at the kinetic limit without a Gibbs free energy barrier when temperature was low. These results emphasize the importance of NH₃ and other ternary species at warmer temperatures, for example, especially in the conditions present in the boundary layer.

Our results demonstrate that clusters formed at lower temperatures, while being transported to warmer temperatures, can survive evaporation and even grow further in the presence of SO₂ and ozone. ~~Thus~~We are providing the first this laboratory experimental evidence that support the mechanism of downward transport of newly formed particles from the free troposphere to the marine boundary layer proposed by several field and modelling studies (Russell et al., 1994;Raes, 1995;Clarke, 1993). Similarly, based on our results, it is reasonable to conclude that the new particles formed in the free troposphere over the Amazon forest are transferred downward to the warmer surface to act as a reservoir of nuclei mode particles (~~Wang et al., 2016~~), though the mechanism of growth is different from the one studied here (SO₂ + ozone).

Our results also show that the further growth is strongly dependent on the ozone level, implying that some unknown heterogeneous reaction processes involving SO₂ and ozone on sulfuric clusters may play important roles in NPF. These results can open a new research avenue for future studies for better understanding the roles of heterogeneous reactions involving nanoparticles and the effects of SO₂ on the nanoparticle growth. At present, it is not known why NPF takes place with high frequency and strong magnitude in extremely polluted megacities in China under the conditions with exceedingly high loadings of pre-existing aerosol particles (Guo et al., 2014;Yao et al., 2018;Yu et al., 2017b). The heterogeneous reactions involving SO₂ on nanoparticles proposed here may provide some key insights into understanding the frequent nucleation and fast growth observed in these regions, where there are also very high concentrations of SO₂ and ozone.

Data Availability

All data of this work can be obtained from ~~L. Tiszenkel (lt0021@uah.edu)~~Lee Tiszenkel (lt0021@uah.edu) and Shanhu Lee (shanhu.lee@uah.edu).

Author Contributions

SL and MJ designed the experiments and LT, CS, JK, QO and MA carried them out. LT, QO and HY developed code used in the data analysis. LT, CS and QO performed the data analysis. LT and SL prepared the manuscript with contributions from all co-authors.

Acknowledgements

This work was supported by NSF Awards AGS-1649719 and AGS-1649694.

References

- 5 Almeida, J., Schobesberger, S., Kurten, A., Ortega, I. K., Kupiainen-Maatta, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurten, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppa, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petaja, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Trostl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359-363, 10.1038/nature12663
- 10 F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Trostl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359-363, 10.1038/nature12663
- 15 <http://www.nature.com/nature/journal/v502/n7471/abs/nature12663.html#supplementary-information>, 2013.
- Benson, D. R., Young, L. H., Kameel, R., and Lee, S. H.: Laboratory-measured sulfuric acid and water homogeneous nucleation rates from the $\text{SO}_2 + \text{OH}$ reaction, *Geophys. Res. Lett.*, 35, Doi:10.1029/2008GL033387, 10.1029/2008GL033387, 2008.
- Benson, D. R., Erupe, M. E., and Lee, S. H.: Laboratory-measured $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ ternary homogeneous nucleation rates: initial observations *Geophys. Res. Lett.*, 36, Doi:10.1029/2009GL038728, 10.1029/2009GL038728, 2009.
- 20 Benson, D. R., Al-Refai, M., and Lee, S.-H.: Chemical Ionization Mass Spectrometer (CIMS) for ambient measurements of Ammonia, *Atmos. Meas. Tech.*, 3, 1133-1162, 2010.
- Benson, D. R., Yu, J. H., Markovich, A., and Lee, S. H.: Ternary homogeneous nucleation of H_2SO_4 , NH_3 , and H_2O under conditions relevant to the lower troposphere, *Atmospheric Chemistry and Physics*, 11, 4755-4766, 10.5194/acp-11-4755-2011,
- 25 2011.
- Berndt, T., Sipilä, M., Stratmann, F., Petäjä, T., Vanhanen, J., Mikkilä, J., Patokoski, J., Taipale, R., Mauldin III, R. L., and Kulmala, M.: Enhancement of atmospheric $\text{H}_2\text{SO}_4 / \text{H}_2\text{O}$ nucleation: organic oxidation products versus amines, *Atmos. Chem. Phys.*, 14, 751-764, 10.5194/acp-14-751-2014, 2014.
- Brus, D., Hyvarinen, A. P., Viisanen, Y., Kulmala, M., and Lihavainen, H.: Homogenous nucleation of sulfuric acid and water mixture: experimental setup and first results, *Atmos. Chem. Phys.*, 10, 2631-2641, 2010.
- 30

- Chen, M., Titcombe, M., Jiang, J. K., Jen, C., Kuang, C. A., Fischer, M. L., Eisele, F. L., Siepmann, J. I., Hanson, D. R., Zhao, J., and McMurry, P. H.: Acid-base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer, *Proc. Natl. Acad. Sci. U. S. A.*, 109, 18713-18718, 10.1073/pnas.1210285109, 2012.
- Clarke, A. D.: Atmospheric nuclei in the Pacific mid-troposphere: their nature, concentration, and evolution *J. Geophys. Res.*, 5 98, 20633-20647, 1993.
- Dunne, E. M., Gordon, H., Kürten, A., Almeida, J., Duplissy, J., Williamson, C., Ortega, I. K., Pringle, K. J., Adamov, A., Baltensperger, U., Barmet, P., Benduhn, F., Bianchi, F., Breitenlechner, M., Clarke, A., Curtius, J., Dommen, J., Donahue, N. M., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Jokinen, T., Kangasluoma, J., Kirkby, J., Kulmala, M., Kupc, A., Lawler, M. J., Lehtipalo, K., Makhmutov, V., Mann, G., Mathot, S., Merikanto, J., 10 Miettinen, P., Nenes, A., Onnela, A., Rap, A., Reddington, C. L. S., Riccobono, F., Richards, N. A. D., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Sengupta, K., Simon, M., Sipilä, M., Smith, J. N., Stozkhov, Y., Tomé, A., Tröstl, J., Wagner, P. E., Wimmer, D., Winkler, P. M., Worsnop, D. R., and Carslaw, K. S.: Global atmospheric particle formation from CERN CLOUD measurements, *Science*, 354, 1119-1123, 2016.
- Duplissy, J., Merikanto, J., Franchin, A., Tsagkogeorgas, G., Kangasluoma, J., Wimmer, D., Vuollekoski, H., Schobesberger, 15 S., Lehtipalo, K., Flagan, R. C., Brus, D., Donahue, N. M., Vehkamäki, H., Almeida, J., Amorim, A., Barmet, P., Bianchi, F., Breitenlechner, M., Dunne, E. M., Guida, R., Henschel, H., Junninen, H., Kirkby, J., Kürten, A., Kupc, A., Määttänen, A., Makhmutov, V., Mathot, S., Nieminen, T., Onnela, A., Praplan, A. P., Riccobono, F., Rondo, L., Steiner, G., Tome, A., Walther, H., Baltensperger, U., Carslaw, K. S., Dommen, J., Hansel, A., Petäjä, T., Sipilä, M., Stratmann, F., Vrtala, A., Wagner, P. E., Worsnop, D. R., Curtius, J., and Kulmala, M.: Effect of ions on sulfuric acid-water binary particle formation: 20 2. Experimental data and comparison with QC-normalized classical nucleation theory, *J. Geophys. Res.*, 121, 1752-1775, 10.1002/2015JD023539, 2016.
- Eisele, F. L., and Tanner, D. J.: Measurements of gas phase concentrations of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, *J. Geophys. Res.*, 98, 9001-9010, 1993.
- Erupe, M. E., Benson, D. R., Li, J., Young, L. H., Verheggen, B., Al-Refai, M., Tahboub, O., Cunningham, V., Frimpong, F., 25 Viggiano, A. A., and Lee, S. H.: Correlation of aerosol nucleation rate with sulfuric acid and ammonia in Kent, Ohio: An atmospheric observation, *J. Geophys. Res.*, 115, Doi:10.1029/2010JD013942, DOI:10.1029/2010JD013942, 2010.
- Erupe, M. E., Viggiano, A. A., and Lee, S. H.: The effect of trimethylamine on atmospheric nucleation involving H_2SO_4 , *Atmos. Chem. Phys.*, 11, 4767-4775, 2011.
- Frege, C., Ortega, I. K., Rissanen, M. P., Praplan, A. P., Steiner, G., Heinritzi, M., Ahonen, L., Amorim, A., Bernhammer, A. 30 K., Bianchi, F., Brilke, S., Breitenlechner, M., Dada, L., Dias, A., Duplissy, J., Ehrhart, S., El-Haddad, I., Fischer, L., Fuchs, C., Garmash, O., Gonin, M., Hansel, A., Hoyle, C. R., Jokinen, T., Junninen, H., Kirkby, J., Kürten, A., Lehtipalo, K., Leiminger, M., Mauldin, R. L., Molteni, U., Nichman, L., Petäjä, T., Sarnela, N., Schobesberger, S., Simon, M., Sipilä, M., Stolzenburg, D., Tomé, A., Vogel, A. L., Wagner, A. C., Wagner, R., Xiao, M., Yan, C., Ye, P., Curtius, J., Donahue, N. M., Flagan, R. C., Kulmala, M., Worsnop, D. R., Winkler, P. M., Dommen, J., and Baltensperger, U.: Influence of temperature on

- the molecular composition of ions and charged clusters during pure biogenic nucleation, *Atmos. Chem. Phys.*, 18, 65-79, 10.5194/acp-18-65-2018, 2018.
- 5 Glasoe, W. A., Volz, K., Panta, B., Freshour, N., Bachman, R., Hanson, D. R., McMurry, P. H., and Jen, C.: Sulfuric acid nucleation: an experimental study of the effect of seven bases, *J. Geophys. Res.*, 120, 1933-1950, 10.1002/2014JD022730, 2015.
- Gordon, H., Kirkby, J., Baltensperger, U., Bianchi, F., Breitenlechner, M., Curtius, J., Dias, A., Dommen, J., Donahue, N. M., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Frege, C., Fuchs, C., Hansel, A., Hoyle, C. R., Kulmala, M., Kurten, A., Lehtipalo, K., Makhmutov, V., Molteni, U., Rissanen, M. P., Stozkhov, Y., Trostl, J., Tsagkogeorgas, G., Wagner, R., Williamson, C., Wimmer, D., Winkler, P. M., Yan, C., and Carslaw, K. S.: Causes and importance of new particle formation
- 10 in the present-day and preindustrial atmospheres, *J. Geophys. Res.-Atmos.*, 122, 8739-8760, 10.1002/2017jd026844, 2017.
- Guo, S., Hua, M., Zamor, M. L., Peng, J., Shang, D., Zheng, J., Du, Z., Wu, Z., Shao, M., Zeng, L., Molina, M. J., and Zhang, R.: Elucidating severe urban haze formation in China, *Proc. Nat. Acad. Sci.*, 49, 17373–17378, 2014.
- Hanson, D. R., and Eisele, F. L.: Diffusion of H_2SO_4 in humidified nitrogen: hydrated H_2SO_4 , *J. Phys. Chem.*, 104, 1715-1719, 2000.
- 15 Hanson, D. R., Bier, I., Panta, B., Jen, C. N., and McMurry, P. H.: Computational Fluid Dynamics Studies of a Flow Reactor: Free Energies of Clusters of Sulfuric Acid with NH_3 or Dimethyl Amine, *J. Phys. Chem. A*, 121, 3976-3990, 10.1021/acs.jpca.7b00252, 2017.
- Hung, H.-M., and Hoffmann, M. R.: Oxidation of gas-phase SO_2 on the surfaces of acidic microdroplets: Implications for sulfate and sulfate radical anion formation in the atmospheric liquid phase, *Environ. Sci. Technol.*, 49, 13768-13776, 2015.
- 20 Jen, C. N., McMurry, P. H., and Hanson, D. R.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, *J. Geophys. Res.*, 119, Doi: 10.1002/2014jd021592, 10.1002/2014jd021592, 2014.
- Jen, C. N., Zhao, J., McMurry, P. H., and Hanson, D. R.: Chemical ionization of clusters formed from sulfuric acid and dimethylamine or diamines, *Atmos. Chem. Phys.*, 16, 12513-12529, 10.5194/acp-16-12513-2016, 2016.
- Kanawade, V. P., Guenther, A. B., Jobson, B. T., Erupe, M. E., Pressely, S. N., Tripathi, S. N., and Lee, S. H.: Isoprene
- 25 suppression of new particle formation in a mixed deciduous forest, *Atmos. Chem. Phys.*, 11, 6013-6027, 2011.
- Kashchiev, D.: On the relation between nucleation work, nucleus size, and nucleation rate, *J. Phys. Chem.*, 76, 5098-5102, 10.1063/1.442808, 1982.
- Khamaganov, V. G., and Hites, R. A.: Rate Constants for the Gas-Phase Reactions of Ozone with Isoprene, α - and β -Pinene, and Limonene as a Function of Temperature, *The Journal of Physical Chemistry A*, 105, 815-822, 10.1021/jp002730z, 2001.
- 30 Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kurten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkila, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petaja, T., Schnitzhofer, R., Seinfeld, J. H., Sipila,

- M., Stozhkov, Y., Stratmann, F., Tome, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, *Nature*, 476, 429-433, <http://www.nature.com/nature/journal/v476/n7361/abs/nature10343.html#supplementary-information>, 2011.
- 5 Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Peräkylä, O., Piel, F., Petäjä, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A.
- 10 D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S., and Curtius, J.: Ion-induced nucleation of pure biogenic particles, *Nature*, 533, 521-526, 10.1038/nature17953, 2016.
- 15 Krasnomowitz, J. M., Apsokardu, M. J., Stangl, C. M., Lee, S., and Johnston, M. V.: Growth of ammonium sulfate seed particles in the Aitken mode size range by α -pinene ozonolysis, *Aerosol Sci. Technol.*, Under review, 2018.
- Krasnomowitz, J. M., Apsokardu, M. J., Stangl, C. M., Tiszenkel, L., Ouyang, Q., Lee, S., and Johnston, M. V.: Growth of Aitken mode ammonium sulfate particles by α -pinene ozonolysis, *Aerosol Science and Technology*, 53, 406-418, 10.1080/02786826.2019.1568381, 2019.
- 20 Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Järvinen, E., Äijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkilä, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin, R. L., Duplissy, J., Vehkamäki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurtén, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V. M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, *Science*, 339, 943-946, 10.1126/science.1227385, 2013.
- 25 Kulmala, M., Kerminen, V.-M., Petaja, T., Ding, A., and Wang, L.: Atmospheric gas-to-particle conversion: why NPF events are observed in megacities?, *Faraday Discussions*, Doi: 10.1039/C1036FD00257A, 10.1039/c6fd00257a, 2017.
- Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid, *The Journal of Physical Chemistry A*, 116, 6375-6386, 10.1021/jp212123n, 2012.
- 30 Kürten, A., Jokinen, T., Simon, M., Sipilä, M., Sarnela, N., Junninen, H., Adamov, A., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hakala, J., Hansel, A., Heinritzi, M., Hutterli, M., Kangasluoma, J., Kirkby, J., Laaksonen, A., Lehtipalo, K., Leiminger, M., Makhmutov, V., Mathot, S., Onnela, A., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L., Schobesberger, S., Seinfeld, J. H., Steiner, G., Tomé, A., Tröstl, J., Winkler, P. M., Williamson, C., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K. S., Kulmala, M.,

- Worsnop, D. R., and Curtius, J.: Neutral molecular cluster formation of sulfuric acid–dimethylamine observed in real time under atmospheric conditions, *Proc. Nat. Acad. Sci.*, 111, 15019–15024, 10.1073/pnas.1404853111, 2014.
- Kürten, A., Bianchi, F., Almeida, J., Kupiainen-Määttä, O., Dunne, E. M., Duplissy, J., Williamson, C., Barnet, P., Breitenlechner, M., Dommen, J., Donahue, N. M., Flagan, R. C., Franchin, A., Gordon, H., Hakala, J., Hansel, A., Heinritzi, M., Ickes, L., Jokinen, T., Kangasluoma, J., Kim, J., Kirkby, J., Kupc, A., Lehtipalo, K., Leiminger, M., Makhmutov, V., Onnela, A., Ortega, I. K., Petäjä, T., Praplan, A. P., Riccobono, F., Rissanen, M. P., Rondo, L., Schnitzhofer, R., Schobesberger, S., Smith, J. N., Steiner, G., Stozhkov, Y., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Wagner, P. E., Wimmer, D., Ye, P., Baltensperger, U., Carslaw, K., Kulmala, M., and Curtius, J.: Experimental particle formation rates spanning tropospheric sulfuric acid and ammonia abundances, ion production rates, and temperatures, *J. Geophys. Res.*, 121, 12377–12400, 10.1002/2015JD023908, 2016.
- Lee, S.-H., Uin, J., Guenther, A. B., Gouw, J. A. d., Yu, F., Nadykto, A. B., Herb, J., Ng, N. L., Koss, A., Brune, W. H., Baumann, K., Kanawad, V. P., Keutsch, F. N., Nenes, A., Olsen, K., Goldstein, A., and Qi, O.: Isoprene suppression of new particle formation: Potential mechanism and implications, *J. Geophys. Res.*, 121, Doi:10.1029/2016JD024844 10.1029/2016JD024844 2016.
- Lehtipalo, K., Leppä, J., Kontkanen, J., Kangasluoma, J., Franchin, A., Wimmer, D., Schobesberger, S., Junninen, H., Petäjä, T., Sipilä, M., Mikkilä, J., Vanhanen, J., Worsnop, D. R., and Kulmala, M.: Methods for determining particle size distribution and growth rates between 1 and 3 nm using the Particle Size Magnifier, *Boreal Environ. Res.*, 19, 215–236, 2014.
- Lehtipalo, K., Rondo, L., Kontkanen, J., Schobesberger, S., Jokinen, T., Sarnela, N., Kürten, A., Ehrhart, S., Franchin, A., Nieminen, T., Riccobono, F., Sipilä, M., Yli-Juuti, T., Duplissy, J., Adamov, A., Ahlm, L., Almeida, J., Amorim, A., Bianchi, F., Breitenlechner, M., Dommen, J., Downard, A. J., Dunne, E. M., Flagan, R. C., Guida, R., Hakala, J., Hansel, A., Jud, W., Kangasluoma, J., Kerminen, V.-M., Keskinen, H., Kim, J., Kirkby, J., Kupc, A., Kupiainen-Määttä, O., Laaksonen, A., Lawler, M. J., Leiminger, M., Mathot, S., Olenius, T., Ortega, I. K., Onnela, A., Petäjä, T., Praplan, A., Rissanen, M. P., Ruuskanen, T., Santos, F. D., Schallhart, S., Schnitzhofer, R., Simon, M., Smith, J. N., Tröstl, J., Tsagkogeorgas, G., Tomé, A., Vaattovaara, P., Vehkamäki, H., Vrtala, A. E., Wagner, P. E., Williamson, C., Wimmer, D., Winkler, P. M., Virtanen, A., Donahue, N. M., Carslaw, K. S., Baltensperger, U., Riipinen, I., Curtius, J., Worsnop, D. R., and Kulmala, M.: The effect of acid–base clustering and ions on the growth of atmospheric nano-particles, *Nat. Commun.*, 7, 11594, 10.1038/ncomms11594 <http://www.nature.com/articles/ncomms11594#supplementary-information>, 2016.
- Lehtipalo, K., Yan, C., Dada, L., Bianchi, F., Xiao, M., Wagner, R., Stolzenburg, D., Ahonen, L. R., Amorim, A., Baccarini, A., Bauer, P. S., Baumgartner, B., Bergen, A., Bernhammer, A.-K., Breitenlechner, M., Brilke, S., Buchholz, A., Mazon, S. B., Chen, D., Chen, X., Dias, A., Dommen, J., Draper, D. C., Duplissy, J., Ehn, M., Finkenzeller, H., Fischer, L., Frege, C., Fuchs, C., Garmash, O., Gordon, H., Hakala, J., He, X., Heikkinen, L., Heinritzi, M., Helm, J. C., Hofbauer, V., Hoyle, C. R., Jokinen, T., Kangasluoma, J., Kerminen, V.-M., Kim, C., Kirkby, J., Kontkanen, J., Kürten, A., Lawler, M. J., Mai, H., Mathot, S., Mauldin, R. L., Molteni, U., Nichman, L., Nie, W., Nieminen, T., Ojdanic, A., Onnela, A., Passananti, M., Petäjä, T., Piel, F., Pospisilova, V., Quéléver, L. L. J., Rissanen, M. P., Rose, C., Sarnela, N., Schallhart, S., Schuchmann, S., Sengupta, K.,

- Simon, M., Sipilä, M., Tauber, C., Tomé, A., Tröstl, J., Väisänen, O., Vogel, A. L., Volkamer, R., Wagner, A. C., Wang, M., Weitz, L., Wimmer, D., Ye, P., Ylisirniö, A., Zha, Q., Carslaw, K. S., Curtius, J., Donahue, N. M., Flagan, R. C., Hansel, A., Riipinen, I., Virtanen, A., Winkler, P. M., Baltensperger, U., Kulmala, M., and Worsnop, D. R.: Multicomponent new particle formation from sulfuric acid, ammonia, and biogenic vapors, 4, eaau5363, 10.1126/sciadv.aau5363 %J Science Advances, 5 2018.
- Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulfuric acid and water J. Geophys. Res., 109, Doi: 10.1029/2003JD004460, 10.1029/2003JD004460, 2004.
- Malila, J., McGraw, R., Laaksonen, A., and Lehtinen, K. E. J.: Repairing the First Nucleation Theorem: Precritical Cluster Losses, in: Nucleation and Atmospheric Aerosols, edited by: DeMott, P. J., and Odowd, C. D., AIP Conference Proceedings, 10 Amer Inst Physics, Melville, 31-34, 2013.
- Martin, S. T., Artaxo, P., Machado, L., Manzi, A. O., Souza, R. A. F., Schumacher, C., Wang, J., Biscaro, T., Brito, J., Calheiros, A., Jardine, K., Medeiros, A., Portela, B., de Sá, S. S., Adachi, K., Aiken, A. C., Albrecht, R., Alexander, L., Andreae, M. O., Barbosa, H. M. J., Buseck, P., Chand, D., Comstock, J. M., Day, D. A., Dubey, M., Fan, J., Fast, J., Fisch, G., Fortner, E., Giangrande, S., Gilles, M., Goldstein, A. H., Guenther, A., Hubbe, J., Jensen, M., Jimenez, J. L., Keutsch, F. N., Kim, S., Kuang, C., Laskin, A., McKinney, K., Mei, F., Miller, M., Nascimento, R., Pauliquevis, T., Pekour, M., Peres, J., Petäjä, T., Pöhlker, C., Pöschl, U., Rizzo, L., Schmid, B., Shilling, J. E., Dias, M. A. S., Smith, J. N., Tomlinson, J. M., Tóta, J., and Wendisch, M.: The Green Ocean Amazon Experiment (GoAmazon2014/5) Observes Pollution Affecting Gases, Aerosols, Clouds, and Rainfall over the Rain Forest, Bulletin of the American Meteorological Society, 98, 981-997, 10.1175/BAMS-D-15-00221.1, 2016.
- 15 McGraw, R., and Zhang, R.: Multivariate analysis of homogeneous nucleation rate measurements. Nucleation in the p-toluic acid/sulfuric acid/water system, J. Chem. Phys., 128, Doi: 10.1063/1.2830030, 10.1063/1.2830030, 2008.
- Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of nucleation on global CCN, Atmos. Chem. Phys., 9, 8601-8616, 2009.
- Nieminen, T., Paasonen, P., Manninen, H. E., Sellegri, K., Kerminen, V. M., and Kulmala, M.: Parameterization of ion-induced nucleation rates based on ambient observations, Atmos. Chem. Phys., 11, 3393-3402, 10.5194/acp-11-3393-2011, 2011.
- 25 Petäjä, T., Mauldin III, R. L., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T., and Kulmala, M.: Sulfuric acid on OH concentrations in boreal forest site, Atmos. Chem. Phys., 9, 7435-7448, 2009.
- Raes, F.: Entrainment of free tropospheric aerosols as a regulating mechanism for cloud condensation nuclei in the remote marine boundary layer, 100, 2893-2903, 10.1029/94jd02832, 1995.
- 30 Rizzo, V. L., Roldin, P., Brito, J., Backman, J., Swietlicki, E., Krejci, R., Tunved, P., Petäjä, T., Kulmala, M., and Artaxo, P.: Multi-year statistical and modeling analysis of submicrometer aerosol number size distributions at a rain forest site in Amazonia, Atmos. Chem. Phys., 18, 10255-10274, 10.5194/acp-18-10255-2018, 2018.
- Russell, L. M., Pandis, S. N., and Seinfeld, J. H.: Aerosol production and growth in the marine boundary layer, Journal of Geophysical Research: Atmospheres, 99, 20989-21003, 10.1029/94jd01932, 1994.

- Schobesberger, S., Franchin, A., Bianchi, F., Rondo, L., Duplissy, J., Kürten, A., Ortega, I. K., Metzger, A., Schnitzhofer, R., Almeida, J., Amorim, A., Dommen, J., Dunne, E. M., Ehn, M., Gagné, S., Ickes, L., Junninen, H., Hansel, A., Kerminen, V. M., Kirkby, J., Kupc, A., Laaksonen, A., Lehtipalo, K., Mathot, S., Onnela, A., Petäjä, T., Riccobono, F., Santos, F. D., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Viisanen, Y., Wagner, P. E., Wimmer, D., Curtius, J., Donahue, N. M., Baltensperger, U.,
- 5 Kulmala, M., and Worsnop, D. R.: On the composition of ammonia–sulfuric-acid ion clusters during aerosol particle formation, *Atmos. Chem. Phys.*, 15, 55-78, 10.5194/acp-15-55-2015, 2015.
- Seinfeld, J. H., and Pandis, S. N.: *Atmospheric chemistry and physics: From air pollution to climate change*, John Wiley and Sons, Inc., New Jersey, 2016.
- Skrabalova, L., Brus, D., Anttila, T., Zdimal, V., and Lihavainen, H.: Growth of sulphuric acid nanoparticles under wet and
- 10 dry conditions, *Atmos. Chem. Phys.*, 14, 6461-6475, 10.5194/acp-14-6461-2014, 2014.
- Stangl, C., Krasnomowitz, J., Apsokardu, M., Tiszenkel, L., Ouyang, Q., Lee, S., and V. Johnston, M.: Sulfur Dioxide Modifies Aerosol Particle Formation and Growth by Ozonolysis of Monoterpenes and Isoprene, 2019.
- Stangl, C. M., Krasnomowitz, J. M., Apsokardu, M. J., Tiszenkel, L., Ouyang, Q., Lee, S., and Johnston, M. V.: Sulfur dioxide modifies aerosol particle formation and growth by ozonolysis of monoterpenes and isoprene, *J. Geophys. Res.*, Under review,
- 15 2018.
- Stolzenburg, D., Fischer, L., Vogel, A. L., Heinritzi, M., Schervish, M., Simon, M., Wagner, A. C., Dada, L., Ahonen, L. R., Amorim, A., Baccarini, A., Bauer, P. S., Baumgartner, B., Bergen, A., Bianchi, F., Breitenlechner, M., Brilke, S., Mazon, S. B., Chen, D. X., Dias, A., Draper, D. C., Duplissy, J., Haddad, I., Finkenzeller, H., Frege, C., Fuchs, C., Garmash, O., Gordon, H., He, X., Helm, J., Hofbauer, V., Hoyle, C. R., Kim, C., Kirkby, J., Kontkanen, J., Kuerten, A., Lampilahti, J., Lawler, M.,
- 20 Lehtipalo, K., Leiminger, M., Mai, H., Mathot, S., Mentler, B., Molteni, U., Nie, W., Nieminen, T., Nowak, J. B., Ojdanic, A., Onnela, A., Passananti, M., Petaja, T., Quelever, L. L. J., Rissanen, M. P., Sarnela, N., Schallhart, S., Tauber, C., Tome, A., Wagner, R., Wang, M., Weitz, L., Wimmer, D., Xiao, M., Yan, C., Ye, P., Zha, Q., Baltensperger, U., Curtius, J., Dommen, J., Flagan, R. C., Kulmala, M., Smith, J. N., Worsnop, D. R., Hansel, A., Donahue, N. M., and Winkler, P. M.: Rapid growth of organic aerosol nanoparticles over a wide tropospheric temperature range, *Proc. Natl. Acad. Sci. U. S. A.*, 115, 9122-9127,
- 25 10.1073/pnas.1807604115, 2018.
- Tröstl, J., Chuang, W. K., Gordon, H., Heinritzi, M., Yan, C., Molteni, U., Ahlm, L., Frege, C., Bianchi, F., Wagner, R., Simon, M., Lehtipalo, K., Williamson, C., Craven, J. S., Duplissy, J., Adamov, A., Almeida, J., Bernhammer, A.-K., Breitenlechner, M., Brilke, S., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Gysel, M., Hansel, A., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Keskinen, H., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lawler, M.,
- 30 Leiminger, M., Mathot, S., Möhler, O., Nieminen, T., Onnela, A., Petäjä, T., Piel, F. M., Miettinen, P., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Sengupta, K., Sipilä, M., Smith, J. N., Steiner, G., Tomé, A., Virtanen, A., Wagner, A. C., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Carslaw, K. S., Curtius, J., Dommen, J., Kirkby, J., Kulmala, M., Riipinen, I., Worsnop, D. R., Donahue, N. M., and Baltensperger, U.: The role of low-volatility organic compounds in initial particle growth in the atmosphere, *Nature*, 533, 527-531, 10.1038/nature18271, 2016.

- Vanhanen, J., Mikkilä, J., Lehtipalo, K., Sipilä, M., Manninen, H. E., Siivola, E., Petaja, T., and Kulmala, M.: Particle size magnifier for nano-CN detection, *Aerosol Sci. Technol.*, 45, 533-542, 10.1080/02786826.2010.547889, 2011.
- Vehkamäki, H., McGrath, M. J., Kurtén, T., Julin, J., Lehtinen, K. E. J., and Kulmala, M.: Rethinking the application of the first nucleation theorem to particle formation, *J. Chem. Phys.*, 136, Doi: 10.1063/1061.3689227, 2012.
- 5 Wang, J., Krejci, R., Giangrande, S., Kuang, C., Barbosa, H. M. J., Brito, J., Carbone, S., Chi, X., Comstock, J., Ditas, F., Lavric, J., Manninen, H. E., Mei, F., Moran-Zuloaga, D., Pöhlker, C., Pöhlker, M. L., Saturno, J., Schmid, B., Souza, R. A. F., Springston, S. R., Tomlinson, J. M., Toto, T., Walter, D., Wimmer, D., Smith, J. N., Kulmala, M., Machado, L. A. T., Artaxo, P., Andreae, M. O., Petäjä, T., and Martin, S. T.: Amazon boundary layer aerosol concentration sustained by vertical transport during rainfall, *Nature*, 539, 416-419, 10.1038/nature19819, 2016.
- 10 Wang, M., and Penner, J. E.: Aerosol indirect forcing in a global model with particle nucleation, *Atmos. Chem. Phys.*, 9, 239-260, 2009.
- Yao, L., Garmash, O., Bianchi, F., Zheng, J., Yan, C., Kontkanen, J., Junninen, H., Mazon, S. B., Ehn, M., Paasonen, P., Sipilä, M., Wang, M. Y., Wang, X. K., Xiao, S., Chen, H. F., Lu, Y. Q., Zhang, B. W., Wang, D. F., Fu, Q. Y., Geng, F. H., Li, L., Wang, H. L., Qiao, L. P., Yang, X., Chen, J. M., Kerminen, V. M., Petaja, T., Worsnop, D. R., Kulmala, M., and Wang, L.:
15 Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity, *Science*, 361, 278-+, 10.1126/science.aao4839, 2018.
- You, Y., Kanawade, V. P., de Gouw, J. A., Guenther, A. B., Madronich, S., Sierra-Hernández, M. R., Lawler, M., Smith, J. N., Takahama, S., Ruggeri, G., Koss, A., Olson, K., Baumann, K., Weber, R. J., Nenes, A., Guo, H., Edgerton, E. S., Porcelli, L., Brune, W. H., Goldstein, A. H., and Lee, S. H.: Atmospheric amines and ammonia measured with a Chemical Ionization
20 Mass Spectrometer (CIMS), *Atmos. Chem. Phys.*, 14, 12181-12194, 10.5194/acpd-14-16411-2014, 2014.
- Young, L. H., Benson, D. R., Rifkha, F., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S. H.: Laboratory studies of sulfuric acid and water binary homogeneous nucleation: evaluation of laboratory setup and preliminary results, *Atmos. Chem. Phys.*, 8, 1-20, 2008a.
- Young, L. H., Benson, D. R., Rifkha, F., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S. H.: Laboratory studies of sulfuric
25 acid and water binary homogeneous nucleation: Evaluation of laboratory setup and preliminary results, *Atmos. Chem. Phys.*, 8, 4997-5016, 2008b.
- Yu, F., and Luo, G.: Simulation of particle size distribution with a global aerosol model: contribution of nucleation to aerosol and CCN number concentrations, *Atmos. Chem. Phys.*, 9, 7691-7710, 10.5194/acp-9-7691-2009, 2009.
- Yu, F., Luo, G., Pryor, S. C., Pillai, P. R., Lee, S. H., Ortega, J., Schwab, J. J., Hallar, A. G., Leaitch, W. R., Aneja, V. P.,
30 Smith, J. N., Walker, J. T., Hogrefe, O., and Demerjian, K. L.: Spring and summer contrast in new particle formation over nine forest areas in North America, *Atmos. Chem. Phys.*, 15, 13993-14003, 10.5194/acpd-15-21271-2015, 2015.
- Yu, H., McGraw, R., and Lee, S. H.: Effects of amines on formation of sub-3 nm particles and their subsequent growth, *Geophys. Res. Lett.*, 39, Doi: 10.1029/2011gl050099, 10.1029/2011gl050099, 2012.

- Yu, H., and Lee, S. H.: A chemical ionization mass spectrometer for the detection of atmospheric amines, *Environ. Chem.*, 9, 190-201, 2012
- Yu, H., Dai, L., Zhao, Y., Kanawade, V. P., Tripathi, S. N., Ge, X., Chen, M., and Lee, S.-H.: Laboratory observations of temperature and humidity dependencies of nucleation and growth rates of sub-3 nm particles, *J. Geophys. Res.*, 122, 1919-1929, 10.1002/2016JD025619, 2017a.
- Yu, H., Ren, L., and Kanawade, V. P.: New Particle Formation and Growth Mechanisms in Highly Polluted Environments, *Current Pollution Reports*, 3, 245-253, 10.1007/s40726-017-0067-3, 2017b.
- Zhang, R., Khalizov, A. F., Wang, L., Hu, M., and Xu, W.: Nucleation and growth of nanoparticles in the atmosphere, *Chem. Rev.*, 112, 957-2011, 2012.
- 10 Zollner, J. H., Glasoe, W. A., Panta, B., Carlson, K. K., McMurry, P. H., and Hanson, D. R.: Sulfuric acid nucleation: power dependencies, variation with relative humidity, and effect of bases, *Atmos. Chem. Phys.*, 12, 4399-4411, 10.5194/acpd-12-1117-2012, 2012.

Table 1. Typical experimental conditions used in FT-1 and FT-2. *J* in FT-1 is the nucleation rate for sub-2 nm particles. *J* in FT-2 is the formation rate of total particles in the size range from 3 to 60 nm; the particle mean diameter ranged from 2.7 to 3.4 nm depending on the ozone concentration. *GR* in FT-1 is the growth rate of sub-3 nm particles. *GR* in FT-2 is the growth rate of total particles from 3 to 60 nm. NH₃ and amine measurements are from IOP 2017 under similar conditions.

5

FT-1: Nucleation Region						FT-2: Growth Region	
Temperature (K)	297	288	278	268	258	Temperature (K)	297
RH	20% - 45%	8% - 60%	12% - 80%	23% - 80%	46% - 85%	RH	10%
[H ₂ SO ₄] (cm ⁻³)	1- × 10 ⁷ – 3- × 10 ⁸	7- × 10 ⁶ – 2- × 10 ⁸	2- × 10 ⁶ – 7- × 10 ⁷	2- × 10 ⁶ – 4- × 10 ⁷	4- × 10 ⁶ – 7- × 10 ⁷	SO ₂ (ppbv)	100-5000
RA	4- × 10 ⁻⁵ – 7- × 10 ⁻⁴	7- × 10 ⁻⁵ – 1- × 10 ⁻³	6- × 10 ⁻⁵ – 2- × 10 ⁻³	3- × 10 ⁻⁴ – 5- × 10 ⁻³	3- × 10 ⁻³ – 4- × 10 ⁻²	O ₃ (ppbv)	0 - 248
GR (nm h ⁻¹)	1 - 20	1 - 20	2 - 80	3 - 45	2 – 35	GR (nm h ⁻¹)	14.9 – 23 12.0- 28.1
J (cm ⁻³ s ⁻¹)	10 ¹ – 10 ⁵	10 ² – 10 ⁵	10 ² – 10 ⁵	10 ² – 10 ⁵	10 ² – 10 ⁵	J (cm ⁻³ s ⁻¹)	0 - 189.9
[NH ₃] (pptv)	14.2 ± 6.9						
[NH ₃]/[H ₂ SO ₄]	0.6 – 52.7	0.9 – 75.2	2.6 - 263	4.5 - 263	2.6 – 132		
[C1 amine] (pptv)	4.5 ± 2.60						
[C2 amine] (pptv)	44.8 ± 41.8						
[C3 amine] (pptv)	7.27 ± 2.50						
[C4 amine] (pptv)	21.7 ± 7.5						
[C5 amine] (pptv)	13.9 ± 4.3						
[C6 amine] (pptv)	8.42 ± 1.8						

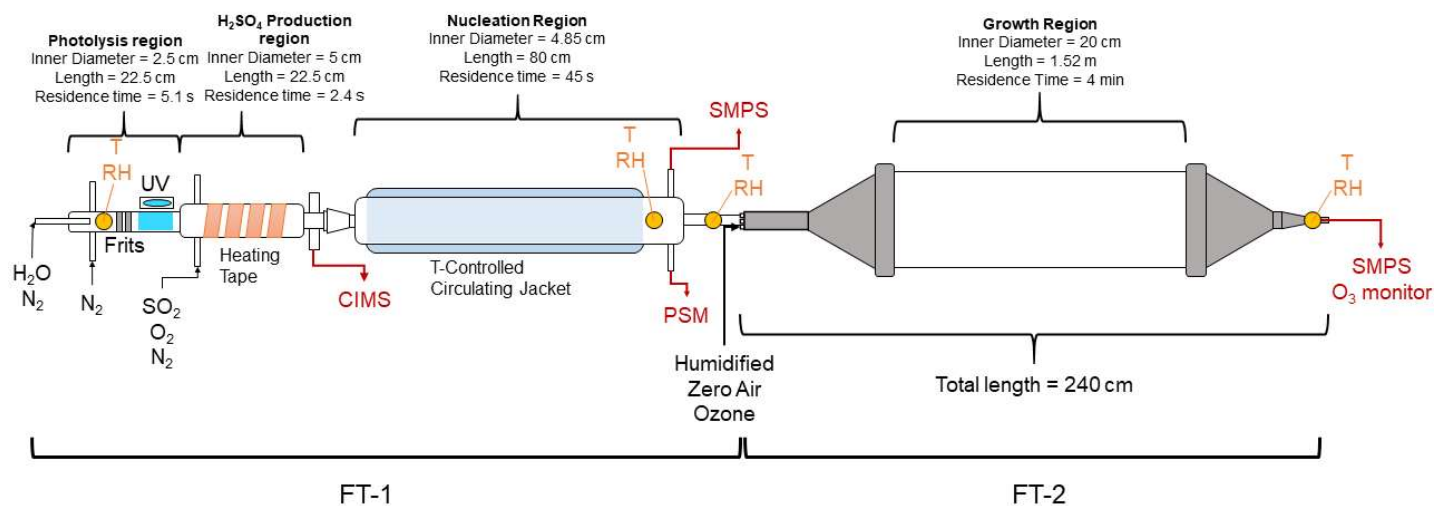
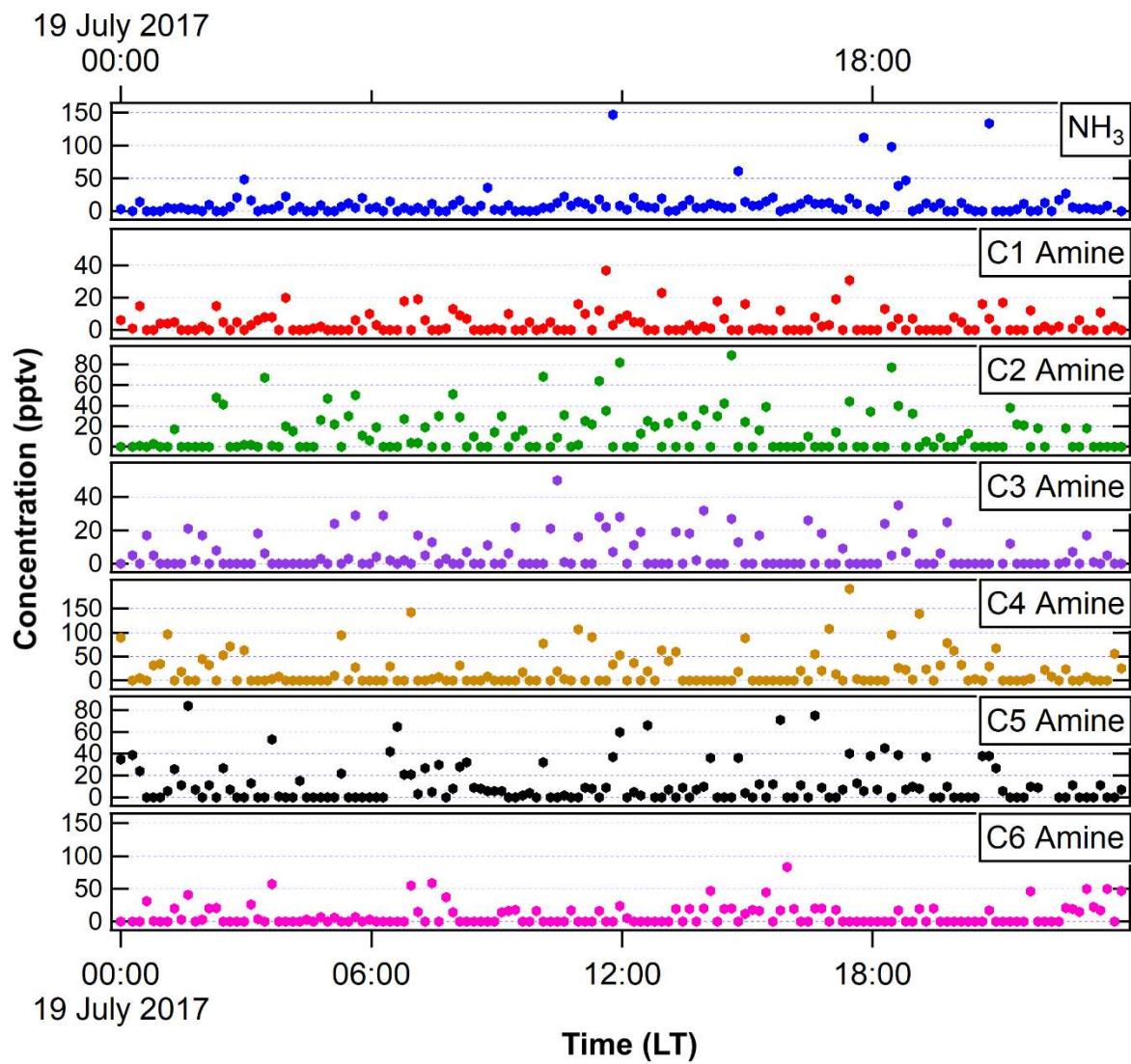


Figure 1. Schematic diagram of the TANGENT experimental setup. This setup consists of two flow tubes (FT). T indicates temperature. FT-1 is used as the nucleation region and FT-2 as the growth region. Table 1 shows the typical experimental conditions used during the 2018 IOP study.



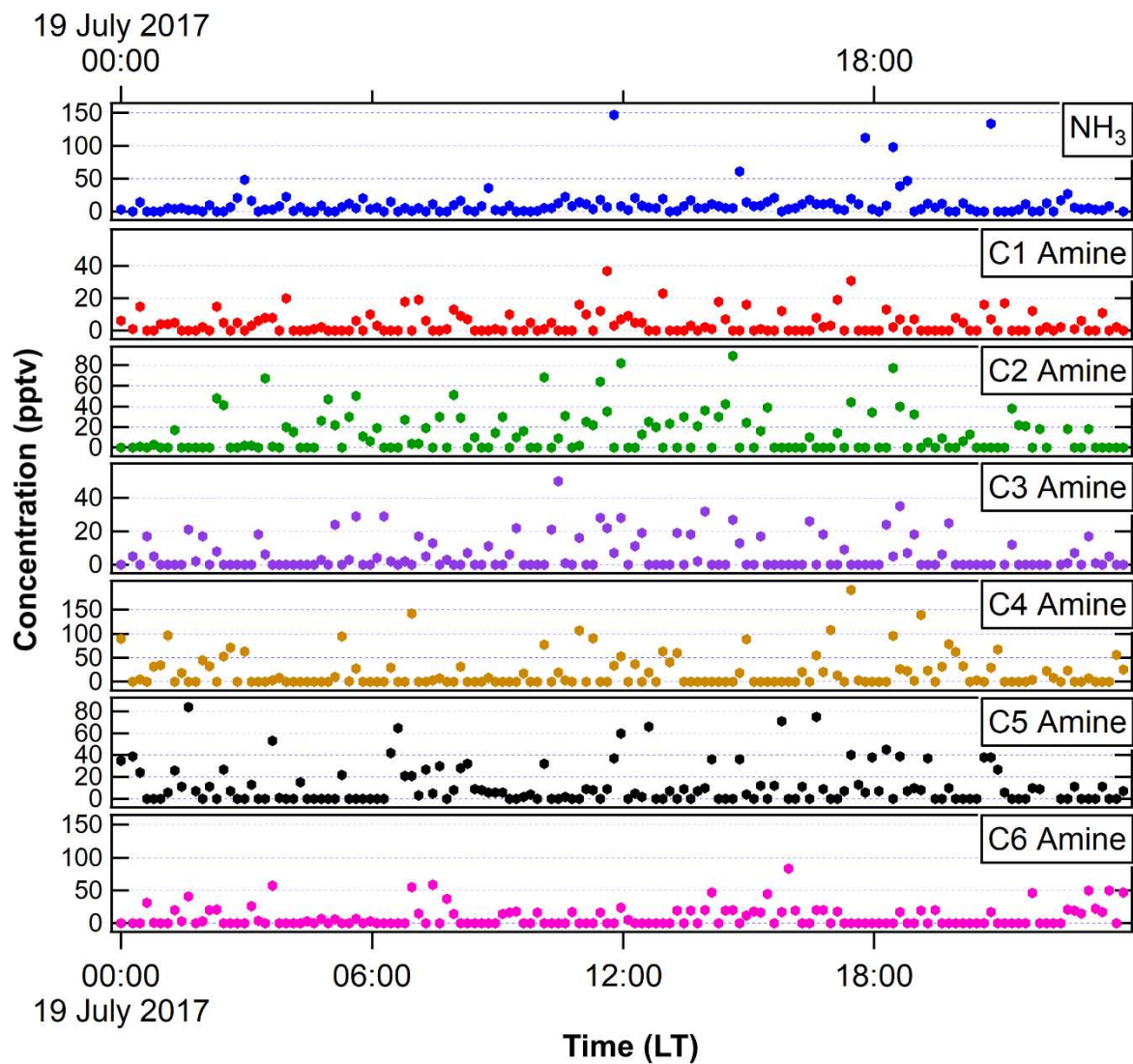


Figure 2. NH₃ and amines measured with the ethanol-CIMS in the FT-1 during the 2017 IOP in a very similar experimental condition as in 2018 IOP. We show here an example of one day measurements (July 19, 2017).

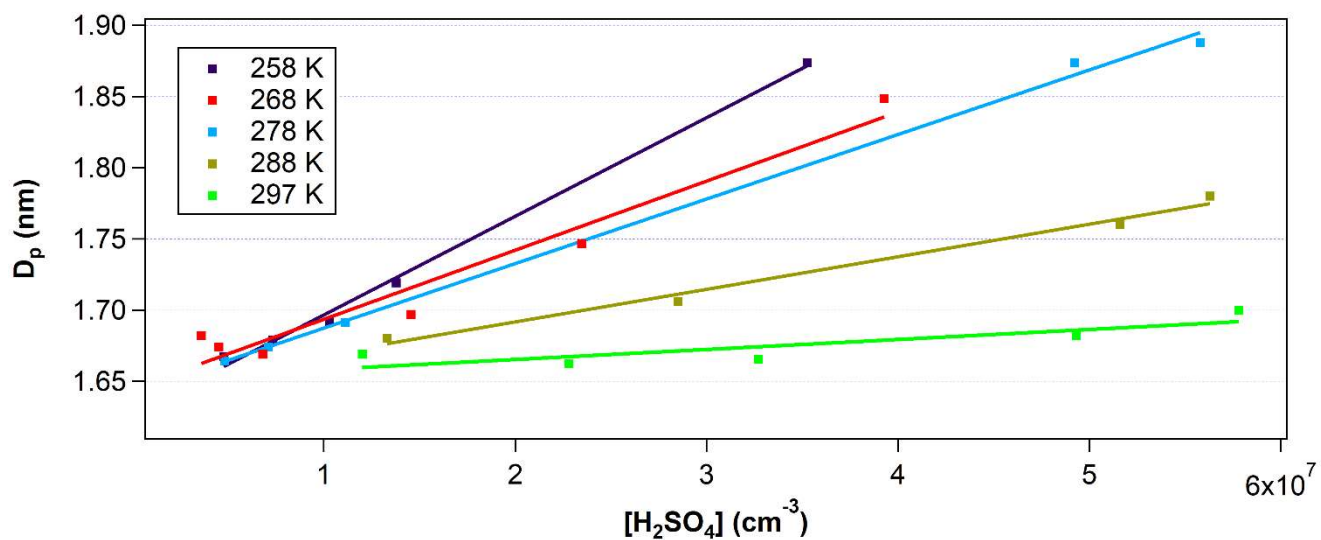


Figure 3. Mean diameter of particles (D_p) inverted from the PSM measurements at the end of the nucleation tube as a function of $[\text{H}_2\text{SO}_4]$ and temperature. Data points were taken at RH between 20% and 30%. Solid lines are linear fittings of the measurement data (coloured squares) under different temperatures. Error in $[\text{H}_2\text{SO}_4]$ is estimated to be $\pm 60\%$. Error in D_p at this size range is estimated to be ± 0.2 nm, or approximately $\pm 12\%$.

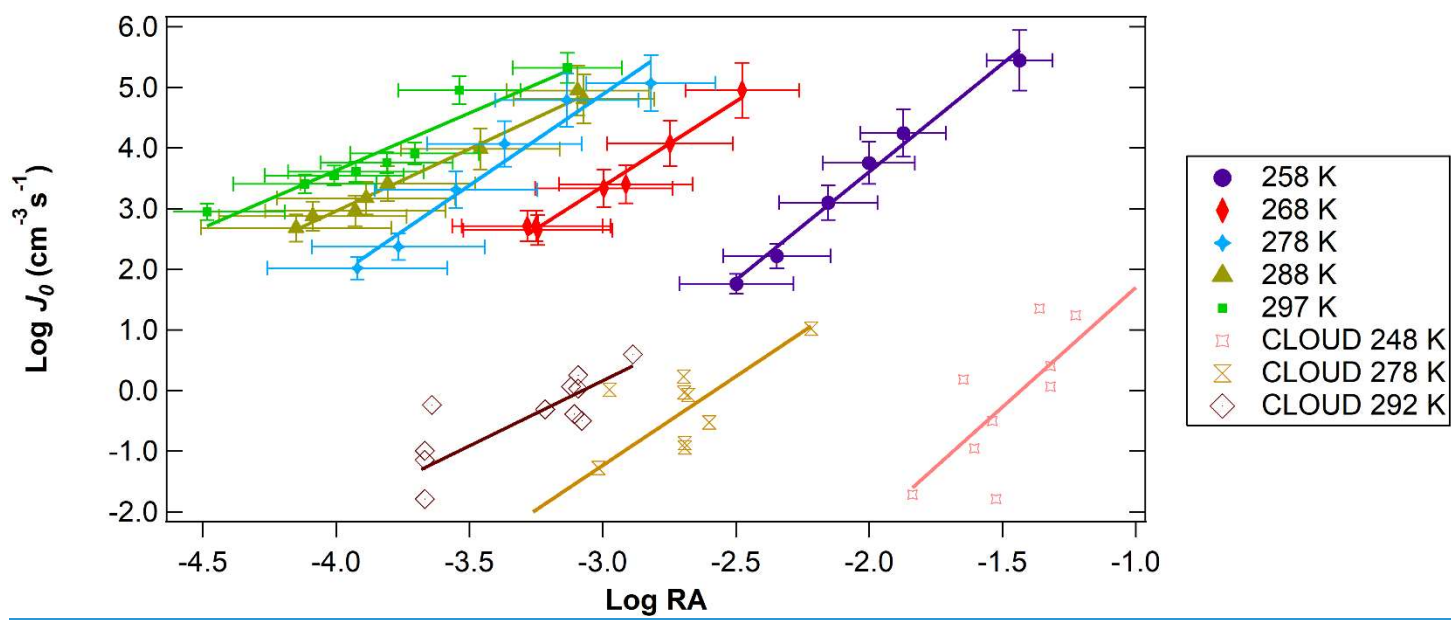
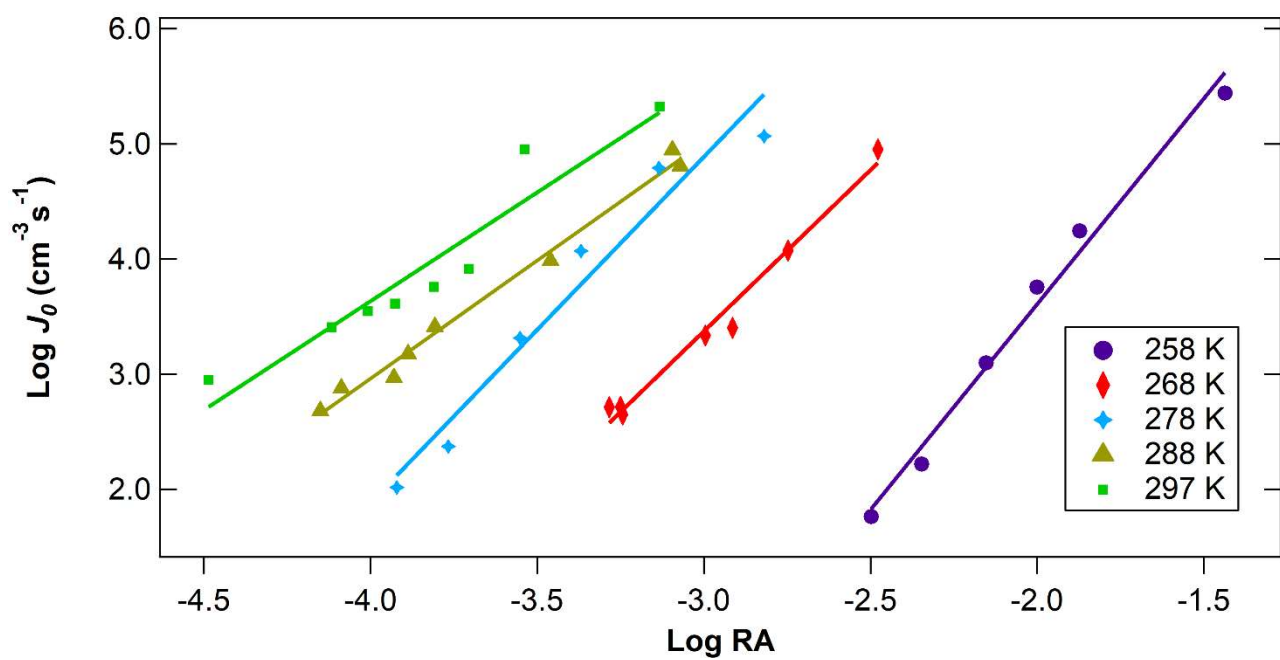
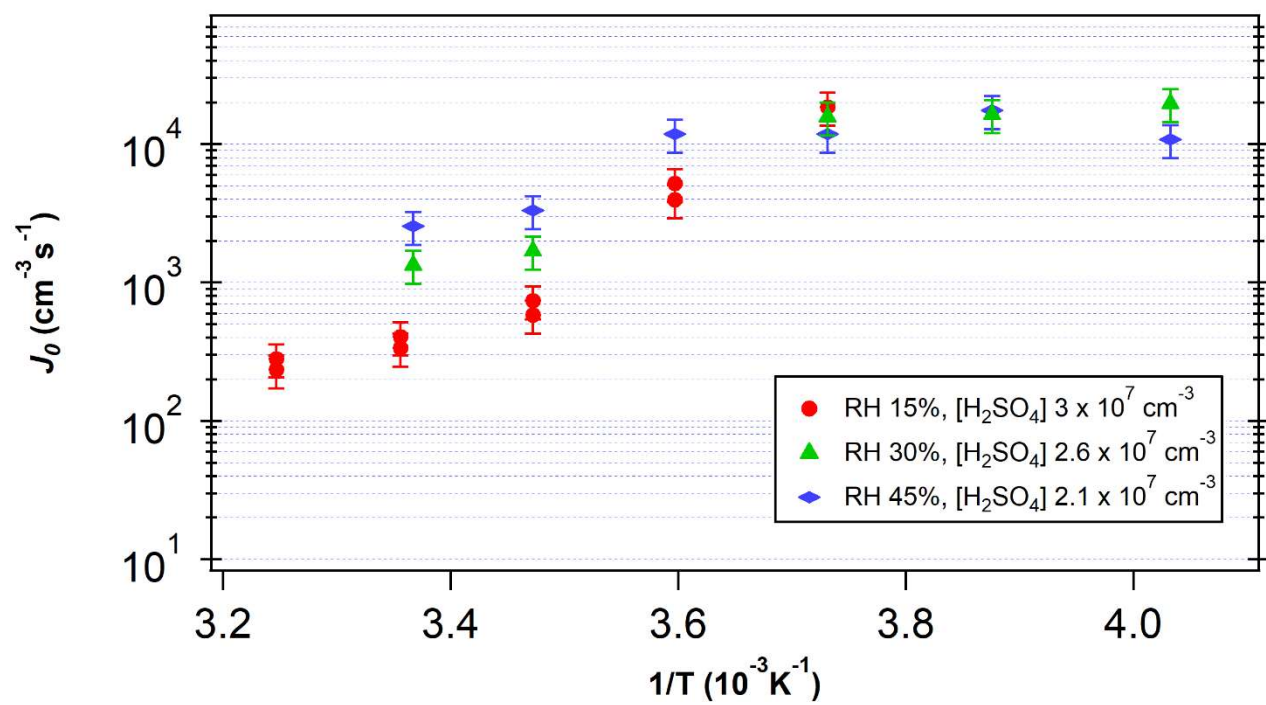


Figure 4. Log J_0 vs. Log RA for different temperatures at a relatively constant RH (41% - 45%). Temperatures ranged from 258 to 297 K. [CLOUD data for similar RA and temperature conditions is shown from \(Dunne et al., 2016\)](#)



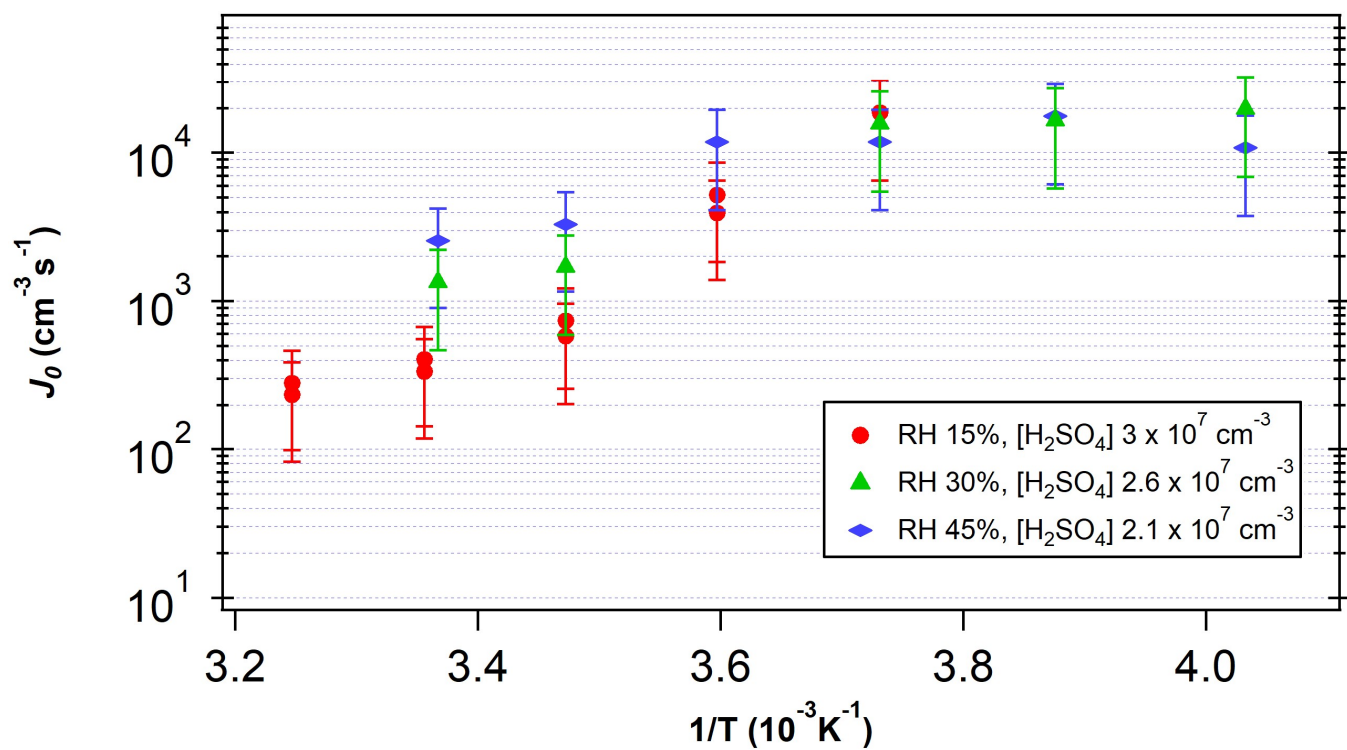
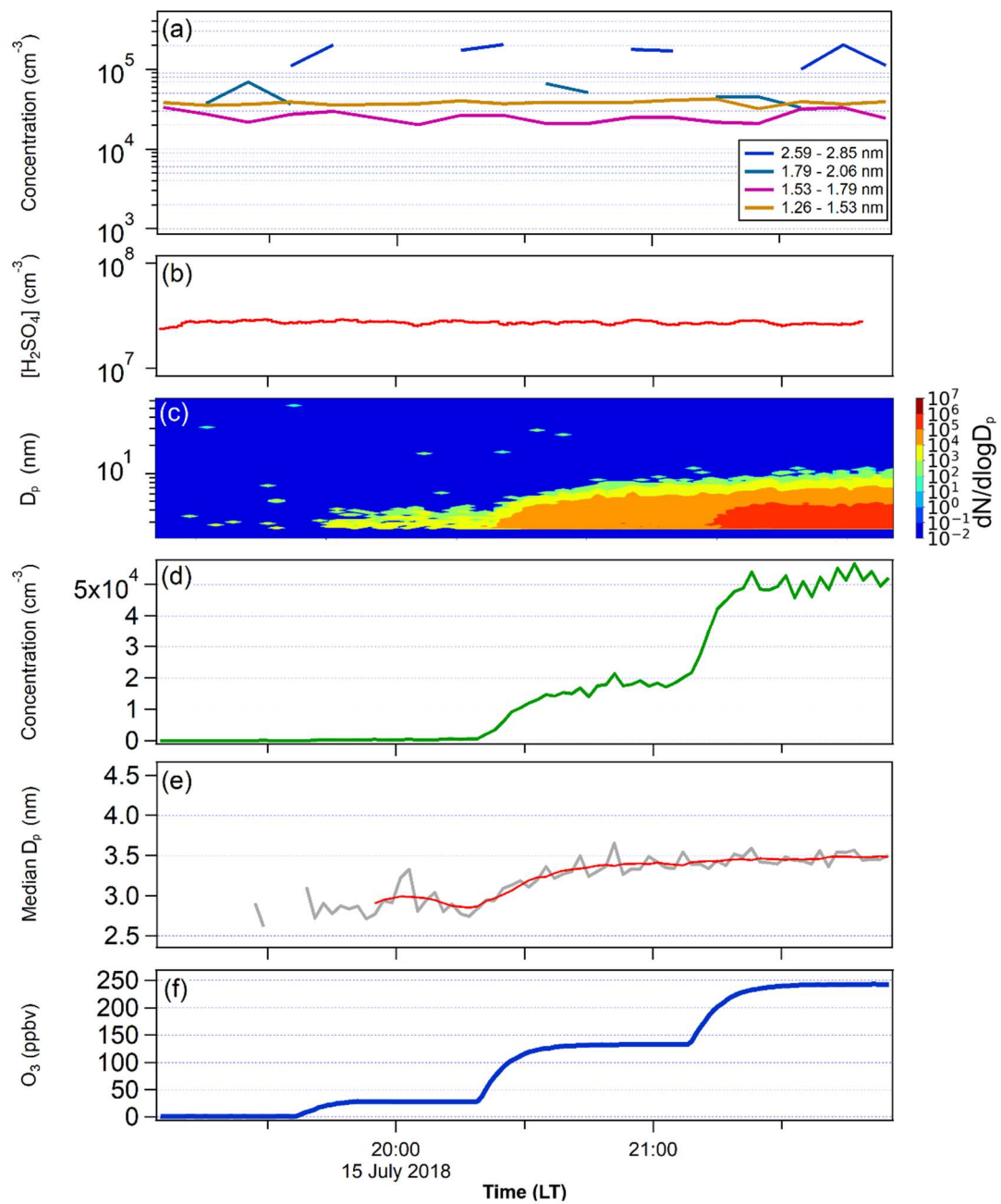


Figure 5. Log J_0 vs. $1/T$ for $[\text{H}_2\text{SO}_4]$ between 2×10^7 and $3 \times 10^7 \text{ cm}^{-3}$. T is the temperature in FT-1. RH ranged from 15% to 45%. Vertical bars indicate one standard deviation of the measured nucleation rates.



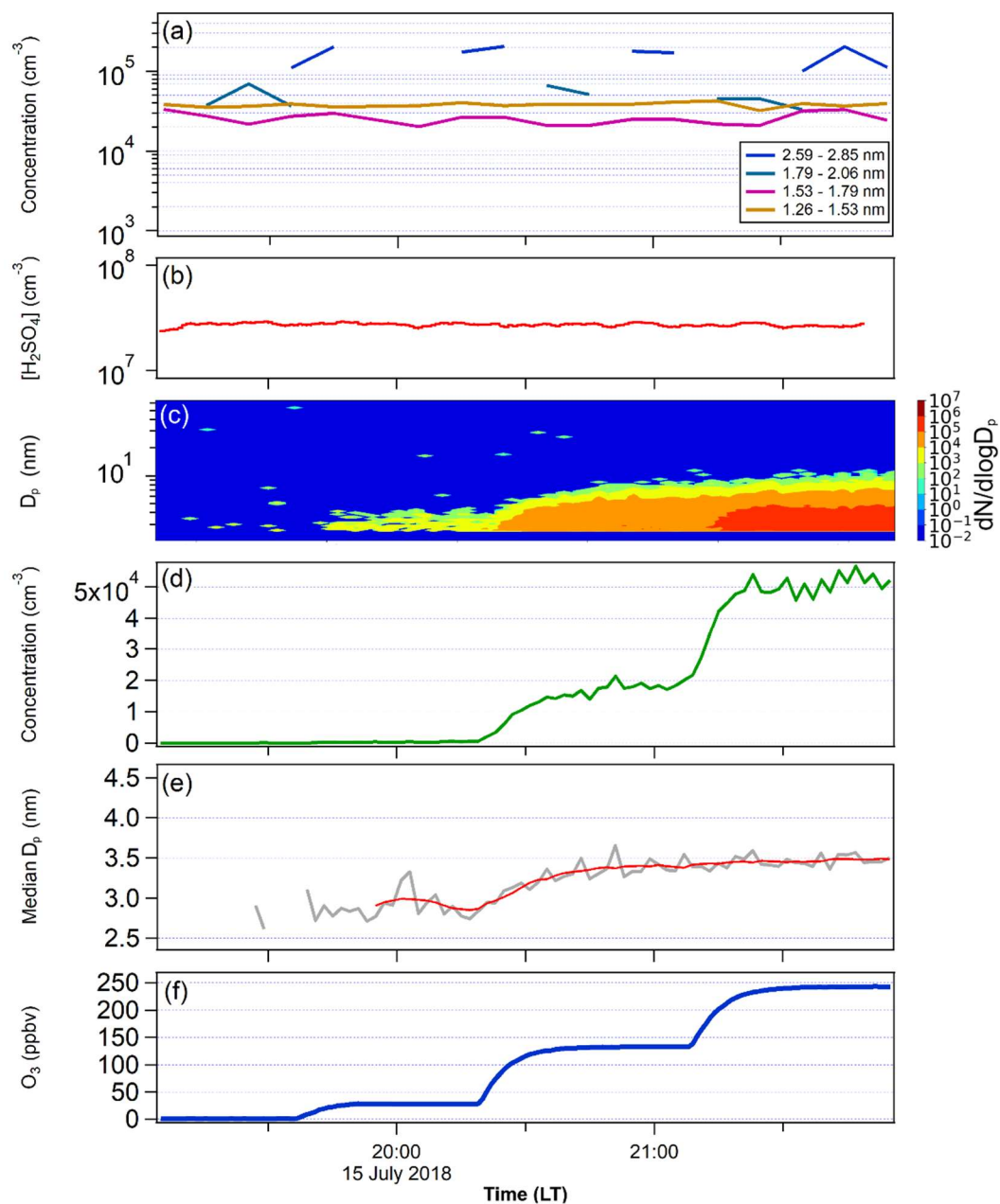


Figure 6. (a) The PSM-inverted size distribution and (b) $[\text{H}_2\text{SO}_4]$ measured in FT-1- during the temperature gradient TANGENT experiment. FT-1 was at 268 K, residence time 45 s. Total concentration at the end of FT-1 was $1.79 \times 10^5 \text{ cm}^{-3}$ with a mean D_p of 1.919 nm. (c) SMPS-measured particle size distribution, (d) total number concentration, (e) the particle median diameter D_p , and (f) O_3 concentrations in FT-2. FT-2 was kept at 297 K, and the residence time was 4 min. The red line in (e) indicates the average values of D_p . SO_2 was 500 and 83 ppbv in FT-1 and FT-2, respectively. H_2SO_4 was not measured at FT-2; however, after considering wall loss in FT-1 and the 1:6 dilution FT-2, $[\text{H}_2\text{SO}_4]$ in FT-2 was estimated to be $1.15 \times 10^6 \text{ cm}^{-3}$.

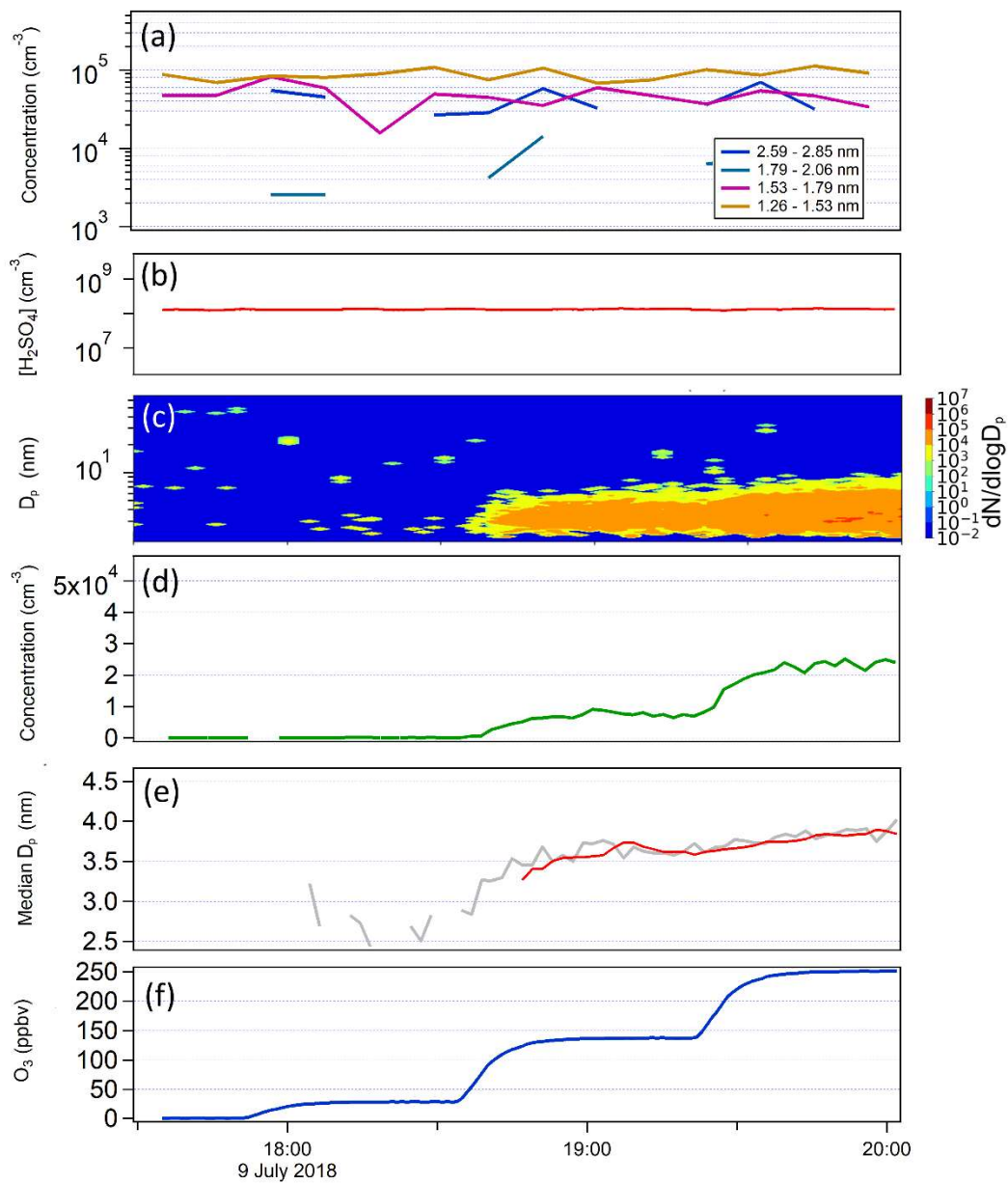


Figure 7. The same as Figure 6, except that FT-1 and FT-2 had a constant temperature in this test. Total particle concentration at the end of FT-1 was $1.7 \times 10^5 \text{ cm}^{-3}$ with a mean D_p of 1.9 nm and $[\text{H}_2\text{SO}_4]$ in the FT-1 was $1.3 \times 10^8 \text{ cm}^{-3}$. In FT-2, the $[\text{H}_2\text{SO}_4]$ was estimated to be $2.5 \times 10^6 \text{ cm}^{-3}$.