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Atmospheric homogeneous nucleation of H_2SO_4 and H_2O

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Abstract

We report laboratory observations of H_2SO_4 and H_2O homogeneous nucleation made under atmospherically relevant conditions ([H_2SO_4] of 10^6-10^7 cm^{-3} and 287 K). Our observations show that nucleation takes place at [H_2SO_4] of 10^6-10^7 cm^{-3}, as observed in the atmosphere. The slope of nucleation rate (J) vs. [H_2SO_4] ranges between 4–6, consistent with thermodynamic predictions of neutral H_2SO_4 clusters, but is higher than those observed in the atmosphere. These results indicate that ternary aerosol precursors are needed to reduce the slope to 1–2 in the atmosphere. This study also discusses the effects of experimental parameters on laboratory observation results, in order to properly interpret the experimental data.

1 Introduction

Nucleation is a gas to particle conversion process in which solid or liquid phase particles form from gas phase species (Seinfeld and Pandis, 2006). These newly formed, small size particles can directly affect human health and can grow to climatically sensitive aerosol sizes. At present, however, there are large discrepancies amongst laboratory studies, field observations and theoretical predictions on nucleation involving H_2SO_4, although this is the most important atmospheric nucleation process (Benson et al., 2008, 2009, 2010a; Berndt et al., 2005; Erupe et al., 2010a; Kuang et al., 2008; Kulmala et al., 2004; McMurry et al., 2005; Sipilä et al., 2010; Young et al., 2008). One of the main challenges in the laboratory studies is that the experimental results are often not reproducible between different studies. It is also unclear how different experimental techniques and parameters affect nucleation results. The different experimental parameters include the method to produce H_2SO_4 vapor Reactions (R1–R3) at in-situ or vaporization from liquid H_2SO_4 samples; a point or continuous source in the nucleation reactor], determination of aerosol precursor concentrations (e.g., [H_2SO_4] are measured with mass spectrometry or calculated from the estimated [SO_2] and [OH] in the

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nucleation reactor), estimation of wall loss of aerosol precursors and nucleation time in the nucleation reactor, and particle detection with different lower limit sizes. While particle instruments with different lower size limits can affect the slope of Log J vs. Log $[H_2SO_4]$ (Sipilä et al., 2010), direct detection of gas phase precursors is also critical because nucleation is a non-linear process so the nucleation rates are extremely sensitive to precursor concentrations (Lee et al., 2003). Because different parameters are used in different studies, each study has its own strength and weakness.

There are also several technical limitations in laboratory nucleation studies. For example, in binary homogeneous nucleation (BHN) studies that usually use water vapor to produce different RH values in the nucleation reactor, it is usually assumed that ternary species do not exist in the nucleation system (Ball et al., 1999; Benson et al., 2008; Berndt et al., 2005, 2006; Sipilä et al., 2010; Young et al., 2008), but in fact NH_3 impurities are unavoidable, because even highly purified water contains some amounts of NH_3 as impurities (Benson et al., 2010b; Nowak et al., 2006). Depending on the material used in the nucleation reactor, the effects of such impurity NH_3 can be also different. Experimental tests have shown that whereas adsorption of NH_3 is most effective on stainless steel material, NH_3 adsorption is minimal on fluorinated ethylene propylene (FEP) or perfluoroalkoxy (PFA) Teflon surfaces (Benson et al., 2010b; Nowak et al., 2006; Yokelson et al., 2003). Such impurities are one of the major limitations of nucleation studies, especially considering that NH_3 can increase nucleation of H_2SO_4 aerosols (Ball et al., 1999; Benson et al., 2009, 2010a; Berndt et al., 2010). It is also possible that amines can co-exist with NH_3, as they both have similar sources, and even these amines can also enhance H_2SO_4 aerosol nucleation (Berndt et al., 2010; Kurtén et al., 2008; Smith et al., 2009) and (Erupe et al., 2010b).

(Berndt et al., 2005, 2006) have shown for the first time that binary homogeneous nucleation (BHN) takes place at atmospherically relevant conditions ($[H_2SO_4]$ of $7 \times 10^6\ cm^{-3}$) when H_2SO_4 vapor was produced from the $SO_2 + OH$ reaction, while liquid sample experiments had failed to do so (Ball et al., 1999; Wyslouzil et al., 1991; Zhang et al., 2004). In (Berndt et al., 2005, 2006), however, the $[H_2SO_4]$ was not

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directly measured and instead calculated from [SO_2] and [OH] in the nucleation reactor. The [OH] was also calculated from titration reactions with various hydrocarbon compounds, but it is unclear how these organic compounds and their oxidation products affect the measured J. To explain the unity J ($1\,cm^{-3}\,s^{-1}$) obtained at such a low [H_2SO_4], they suggested a possible formation of HSO_5 from SO_2 and OH in the gas phase (Berndt et al., 2008), but this hypothesis was dismissed by a recent study by (Sipilä et al., 2010). The slope of Log J vs. Log [H_2SO_4] was between 5–7 (Berndt et al., 2005, 2006).

(Sipilä et al., 2010) have reported atmospherically observed nucleation threshold of $10^6\,cm^{-3}$ and the slope of Log J vs. Log [H_2SO_4] to be $1-2.1$, from laboratory studies of H_2SO_4-H_2O BHN. By comparing with previous laboratory observations (Ball et al., 1999; Benson et al., 2008; Berndt et al., 2005; Wyslouzil et al., 1991; Young et al., 2008), they concluded that this new finding is due to the following factors: (a) a new, unique particle counter, particle size magnifier (PSM) which measures small particles down to 1.5 nm, as opposed to the common type of particle condensation counters (CPC; e.g., TSI 3025 and 3786) (measuring down to 3 nm) used in atmospheric observations (Kulmala et al., 2004) and previous laboratory studies, (b) a longer residence time ($\sim 60-240$ s), and (c) a continuous source of H_2SO_4 production in the entire nucleation reactor, as opposed to a local source used in (Benson et al., 2008; Young et al., 2008). Compared to (Berndt et al., 2005, 2006), (Sipilä et al., 2010) also used the same experimental approach, with the only difference in the type of particle counters used. While the BHN study by (Sipilä et al., 2010) successfully reproduced the slope of Log J vs. Log [H_2SO_4] derived from field studies ($1-2$) (Kulmala et al., 2004), it is also difficult to understand how pure H_2SO_4 neutral monomers or dimers can act as critical clusters without a ternary species present, from a thermodynamics viewpoint (Zhang, 2010).

We have made nucleation experiments at atmospherically relevant conditions with [H_2SO_4] ($10^6-10^7\,cm^{-3}$), using chemical ionization mass spectrometers (CIMS) and CPC (TSI 3786). These instruments have been widely used in field measurements

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(Erupe et al., 2010a; Kulmala et al., 2004; McMurry et al., 2005). Our H_2SO_4 source was a local source at the beginning of the nucleation reactor, as in our previous studies (Benson et al., 2008, 2009; Young et al., 2008). In the present study, we have used two different types of nucleation reactors to allow a larger range of residence times (50–240 s). Possible impurities of NH_3 in the nucleation system were also quantitatively examined with CIMS.

2 Experiments

The nucleation experimental setup used in the present study was similar to that used in our previous studies (Benson et al., 2008, 2009; Young et al., 2008). In this section, we make clarifications on some technical issues, in order to properly interpret the experimental data. Recently, we have also made several modifications in our setup (Benson et al., 2010a) and these improvements and their implications are described in detail in this section.

We have designed our nucleation experimental setup to make well-controlled experiments, so that we can provide constrained data of aerosol precursors and nucleation rates. H_2SO_4 vapor was produced from Reaction (R1), and OH radicals were produced from UV dissociation of water vapor; this allows for an ozone-free system and so provides an advantage compared to other studies where OH was produced from ozone photolysis (Berndt et al., 2005, 2006; Sipilä et al., 2010). The [OH] was also directly measured from UV photon flux measurements; this method also allows for a hydrocarbon-free system compared to the OH titration method using hydrocarbons (Berndt et al., 2005, 2006). For all experimental data reported, $[H_2SO_4]$ were measured directly by CIMS. To minimize adsorption and desorption of NH_3, the entire experimental setup was built exclusively by FEP or PFA Teflon, without any metal materials. We have also used nitrogen gases vaporized from liquid nitrogen, which has the minimum NH_3 impurities, <20 pptv (Nowak et al., 2007). The impurity NH_3 gases in the system, mostly likely originated from deionized water, were systematically determined as

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a function of RH in the system with the CIMS (Benson et al., 2010b; Nowak et al., 2006). Under the typical experimental conditions, the mixing ratio of NH_3 existing in the nucleation reactor was estimated to be between 20 – 100 pptv for RH from 6 – 40%. Also, we have estimated the nucleation region using an inversion model, based on the measured $[H_2SO_4]$ and particle size distributions (Young et al., 2008); our calculations show that nucleation usually takes place during the first half of the nucleation reactor, so we have used half of the residence time as the nucleation time. Laminar flow was assumed in the gas mixing region and the nucleation reactor, based on the calculated Reynolds numbers ($Re \approx 60 - 1200$ at the typical experimental conditions). Using these nucleation times and the measured total particle number concentrations measured by CPC (TSI 3786) (>3 nm), we derived J (apparent nucleation rate, in our case).

In (Benson et al., 2008, 2009; Young et al., 2008), we have discussed that the measured $[H_2SO_4]$ varied with both $[SO_2]$ and [OH], even when $[SO_2] \gg [OH]$. $[H_2SO_4]$ should be equal to [OH] independent of $[SO_2]$, if H_2SO_4 vapor is produced only via Reaction (R1) [rate limiting step; rate constant $k1 = 8.8 \times 10^{-13}\,cm^3\,s^{-1}$ (Finlayson-Pitts and Pitts, 2000)] and the following two subsequent reactions:

$$SO_2 + OH \rightarrow HSO_3 \quad (R1)$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \quad (R2)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (R3)$$

In the flow tube in the presence of high $[SO_2]$, however, OH can also be produced from [$k4 = 8.7 \times 10^{-16}\,cm^3\,s^{-1}$ (Finlayson-Pitts and Pitts, 2000)]

$$HO_2 + SO_2 \rightarrow SO_3 + OH \quad (R4)$$

Reaction (R4) is less important in the atmosphere at the moderate $[SO_2]$ (ppbv or less), but in the flow tube when we used high $[SO_2]$ (ppmv or higher), this reaction should be taken into account. Therefore, it is possible that in the flow tube, more than

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one H_2SO_4 molecule is formed from each OH radical due to the recycle (or amplification) between OH and HO_2. Because the OH recycling process depends on $k4$, this explains why [H_2SO_4] were dependent not only on [OH], but also [SO_2]. Additionally, there is also the possibility that some H_2SO_4 vapor can be produced in the absence of OH and UV, via heterogeneous oxidation or dark oxidation processes on surfaces (including on nanopaticles), as discussed in (Lee et al., 2008; Young et al., 2008). H_2SO_4 vapor was produced at a local source at the beginning of the nucleation reactor as opposed to a continuous source in the nucleation reactor, but this fact would not affect the measured J values, because the amount of H_2SO_4 molecules used by nucleation is typically much smaller than those lost on the wall and left in the gas phase (Benson et al., 2008; Young et al., 2008).

[H_2SO_4] were detected with CIMS, using the following ion-molecule reaction:

$$NO_3^- + H_2SO_4 \rightarrow HNO_3 + HSO_4^- \quad \text{(R5)}$$

at atmospheric pressure, using ^{210}Po as the ion source (Benson et al., 2008, 2009; Eisele and Tanner, 1993; Erupe et al., 2010a; Young et al., 2008). The CIMS can detect [H_2SO_4] as low as $10^5\,cm^{-3}$. The rate constant of Reaction (R5) ($k5$) is $2.32 \times 10^{-9}\,cm^3\,s^{-1}$ with a factor of 2 uncertainties (Viggiano et al., 1997); the ion-molecule reaction time was 0.1 s. As discussed in (Erupe et al., 2010a), it is also possible that in the ion molecule reaction region, NO_3^- ions can make clusters, such as $NO_3^-{\cdot}(HNO_3)_m$, where m = 1, 2, 3... etc., and $NO_3^-{\cdot}(H_2O)_n$, and n = 1, 2, 3... etc. Laboratory measurements have showed that these clusters also react with H_2SO_4 to produce corresponding clusters (Viggiano et al., 1997):

$$NO_3^- \cdot (HNO_3)_m + H_2SO_4 \rightarrow HNO_3 + HSO_4^- \cdot (HNO_3)_m \quad \text{(R6)}$$

$$NO_3^- \cdot (H_2O)_n + H_2SO_4 \rightarrow HNO_3(H_2O)_m + HSO_4^- \cdot (H_2O)_{n-m} \quad \text{(R7)}$$

But their reaction rates, $k6$ and $k7$, are approximately $1.8 \times 10^{-9}\,cm^3s^{-1}$, very similar to $k5$ (Viggiano et al., 1997). A collision dissociation chamber (CDC) was also used to

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effectively dissociate these clusters in our CIMS. Therefore, the presence of possible clusters of ion reagents would not affect the CIMS sensitivity. This is the case for the gas phase H_2SO_4 detection, but for the measurements of atmospheric neutral or charged clusters containing H_2SO_4, these ion reagent clusters can affect the mass peak identification and the instrument sensitivity of individual H_2SO_4 clusters sampled from ambient air.

In our previous studies (Benson et al., 2008; Young et al., 2008), we reported the residual [H_2SO_4] (measured at the end of the nucleation reactor) and further used the calculated wall loss factors (WLFs; the ratios of [H_2SO_4] at the beginning vs. at end of the nucleation reactor) to indicate the [H_2SO_4] range in the nucleation reactor. Here, we make a correction that these initial [H_2SO_4] should be a factor of 4.6 lower (due to the 2.3 times lower $k3$ and the 2 times lower ion molecule reaction time) than the reported values, but this error does not affect the main conclusions of these papers, because of the high WLFs (up to 30).

Our previous setup had residence times up to 77 s (Benson et al., 2008, 2009; Young et al., 2008), and recently we have redesigned the nucleation reactor (Fig. 1) to increase the range of residence times (50 – 240 s). In the present study, we report the results taken with both this new and old nucleation reactors, to understand how different residence times affect nucleation rates and processes. The new nucleation reactor was designed to reduce wall loss of aerosol precursors significantly, by using a larger diameter size [ID of 12.8 cm now vs. 2.54 or 5.08 cm previously (Benson et al., 2008, 2009; Young et al., 2008)] and by introducing trace gases from the center of the flow tube with fast flows (Fig. 1), based on (Donahue et al., 1996). The combination of the large diameter and high flows effectively minimizes the chances for gas phase molecules to travel from the center of the flow tube to the wall. The WLFs were measured by two CIMSs. These two CIMS measurements showed a very good consistency within <3% differences when they were located at the same location of the flow reactor (Fig. 2a). The measured WLFs were <4 (Fig. 2b), significantly lower than those in the previous experiments (up to 30) (Benson et al., 2008; Young et al., 2008). We also found that

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the measured WLFs were also dependent on the initial [H_2SO_4] and increased with increasing the initial [H_2SO_4]. These results suggest that at low [H_2SO_4], wall loss of H_2SO_4 may be no longer a diffusion limited process. It is also possible that inhomogeneous air mixing was present in the nucleation reactor which could affect our WLF measurements. In the future, we plan to investigate flow dynamics in the air mixing region and the nucleation reactor, in order to understand how different flow conditions affect nucleation experimental conditions.

The initial [H_2SO_4] measured by CIMS ranged from $10^6 - 10^7$ cm^{-3}, within the actual atmospheric conditions (Erupe et al., 2010a), and were one to three orders of magnitude lower than our previous experimental conditions (Benson et al., 2008, 2009; Young et al., 2008). Also, [H_2SO_4] were changed by changing [OH], which were changed by the UV light intensities (Fig. 1). A moveable iris beam splitter was placed between the box containing the UV lamp (Pen-Ray 11SC-1) and the flow tube in which photolysis took place. RH values in the nucleation reactor were changed by changing water vapor which was additionally introduced after H_2SO_4 production; this also allows for independent changes in OH and RH. This approach provides an advantage over our previous experiments where [OH] (and thus [H_2SO_4]) were also changed with the changing RH (Benson et al., 2008, 2009; Young et al., 2008).

3 Results

Figure 3 shows the changes in the measured [H_2SO_4] and J when SO_2 and UV were introduced. Without SO_2 and UV, there were no measurable signals in [H_2SO_4] and particle concentrations. When only SO_2 (2.25 ppmv) was introduced, there were some low but still recognizable [H_2SO_4] and particle concentrations, likely due to dark H_2SO_4 formation on various surfaces of the flow tube via heterogeneous oxidation processes (Lee et al., 2008; Young et al., 2008). Then rapid increases in [H_2SO_4] (2.4×10^7 cm^{-3}) and particles ($J \approx 1000$ cm^{-3}) appeared, when UV was introduced.

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The time difference between $[H_2SO_4]$ and particles was nearly the same as the residence time (Fig. 3). From this time difference, we derived a *GR* of ~28 nm h^{-1}. This *GR* is obviously much higher than that expected from the H_2SO_4 condensation alone (~1 nm h^{-1}) at $[H_2SO_4]$ of 1.4×10^7 cm^{-3}. Roughly, $[H_2SO_4]$ of 1×10^7 corresponds to *GR* of ~1 nm h^{-1} (Erupe et al., 2010a; Seinfeld and Pandis, 2006). Such a high *GR* indicates the existence of possible NH_3 in the nucleation reactor, as discussed in the above section. A similar order of rapid *GR* (~ 13 nm h^{-1}; particles growing from critical clusters of 1.5 nm to measurable size of 3 nm in 420 s) was also seen at lower $[H_2SO_4]$ of 7×10^6 cm^{-3} from other BHN flow tube experiments (Berndt et al., 2005, 2006). It is possible that these studies also had some low concentrations of NH_3 (lower than the detection limit of 93 pptv of the NH_3 instrument used in their studies).

Figure 4a shows the measured Log *J* vs. Log $[H_2SO_4]$, for the initial $[H_2SO_4]$ at different RH (6–41%) and residence times (50–240 s), using both the old and new nucleation reactors. *J* varied from $6 \times 10^{-3} - 3.6 \times 10^3$ cm^{-3} s^{-1} for the initial $[H_2SO_4]$ from $2 \times 10^6 - 4 \times 10^7$ cm^{-3}. The threshold $[H_2SO_4]$ measured in the nucleation reactor (ID 5.08 cm; residence time of 50 s) was at 10^7 cm^{-3}, consistent with (Benson et al., 2008; Young et al., 2008), and in the new nucleation reactor (ID 12.8 cm; residence time of 133–240 s) at 10^6 cm^{-3}. The slope of Log *J* vs. Log $[H_2SO_4]$ was 4–6 for most of time. In comparison, in Fig. 4a we also included data from (Sipilä et al., 2010). Both these two studies show nucleation threshold of 10^6 cm^{-3} H_2SO_4, but the slopes are drastically different, because (Sipilä et al., 2010) utilized PSM which measures particles down to 1.5 nm.

Figure 4b shows the measured Log *J* vs. Log RH for $[H_2SO_4]$ of 10^6 cm^{-3}. *J* varied from $6 \times 10^{-3} - 4 \times 10^2$ cm^{-3}s^{-1} for RH values 9–16% and initial $[H_2SO_4]$ in the range of $2 \times 10^6 - 2 \times 10^7$ cm^{-3}. The slope ranged from 1–4, consistent with those provided by the liquid-drop model (McGraw and Weber, 1998). The slope also reduced at higher $[H_2SO_4]$, similarly to (Benson et al., 2009) and consistent with nucleation thermodynamics. The slope was in general much lower than those measured previously (6–15)

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(Benson et al., 2008, 2009; Young et al., 2008); this is because in previous experiments when we changed RH in the nucleation reactor, [OH] and [H_2SO_4] also changed.

To understand the effects of residence time on the slope of Log J vs. Log [H_2SO_4], we also compared data taken at different residence times (thus nucleation times) using different diameters of nucleation reactors (Fig. 4a). We found that at shorter residence times the slopes were higher and J values were lower at similar [H_2SO_4] (10^7 cm^{-3}). For low [H_2SO_4], increasing residence time can enhance apparent J, because longer residence times would allow more particles to grow from critical clusters (~1.5 nm) to 3 nm (measurable by CPC). On the other hand, for high [H_2SO_4], increasing residence time would decrease the apparent J, because H_2SO_4 molecules may be lost by the competitive scavenging process on the tube wall and on aerosol surfaces larger than 3 nm. As a result, the slope should be smaller at a long residence time than at a short residence time. That is, depending on different residence times and different levels of [H_2SO_4], either nucleation or scavenging can be dominant, as discussed in (Young et al., 2008), and such competing processes are reflected in different slopes taken at different residence times. The same trend was also observed for n_{H_2O}. The slope also decreased with increasing residence time (Fig. 4c).(Kim et al., 1998) have also suggested that even different mechanisms can occur for different residence times.

4 Discussion

Our laboratory observations also show that, unlike (Sipilä et al., 2010), the slope of Log J vs. Log [H_2SO_4] ranges between 4 – 6 (Fig. 4a). This slope can be considered as the number of H_2SO_4 molecules in critical clusters ($n_{H_2SO_4}$), if the slope is derived at constant saturation ratios of all other aerosol precursors (that is, constant RH and constant precursor concentrations at a constant temperature), based on the first nucleation theorem (Kashchiev, 1982; McGraw and Zhang, 2008). Our slope taken from laboratory studies is higher than those found from the atmospheric observations (1 – 2) (Erupe et al., 2010a; Kulmala et al., 2004). There is a difference in the method used to make

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these slopes in the laboratory studies and field observations. The atmospherically derived slopes are usually from ensemble data obtained at various RH and temperatures and different saturation ratios of possible ternary precursors (which are unknown currently). On the other hand, laboratory values are derived from the data taken under a constant temperature and RH, and presumably in the absence of, or at least in the possibly lowest amount of, ternary species in the binary case. Such a difference has been neglected when comparing the slopes derived from field and laboratory studies. Perhaps, a more rigorous approach directly applying the first nucleation theorem in atmospheric observations is needed to better understand the chemical composition of critical clusters in the atmosphere.

However, our slopes taken from the binary nucleation system (4 – 6) are thermodynamically consistent with quantum chemical calculations which show that neutral H_2SO_4 dimers would spontaneously evaporate (at 287 K), rather than grow further, because of the high Gibbs free energy barrier towards larger size H_2SO_4 clusters (Kurdi and Kochanski, 1989). Therefore, during atmospheric observations, other condensable species including NH_3 and low volatility organic compounds also participate to suppress the Gibbs free energy barrier for nucleation of neutral clusters. So the number of H_2SO_4 molecules in critical clusters is reduced in the presence of ternary species, such as NH_3 and organic compounds (Ball et al., 1999; Benson et al., 2009, 2010a; McGraw and Zhang, 2008; Metzger et al., 2010; Zhao et al., 2009).

Our results, together with [Berndt et al., 2005, 2006; Sipilä et al., 2010], show that $[H_2SO_4]$ threshold for H_2SO_4-H_2O BHN is 10^6 cm^{-3}, as found in the atmosphere (Erupe et al., 2010a; Kulmala et al., 2004). As discussed in the present study, it is likely that all these studies were under the influence of certain levels of impurities of NH_3 at least, which is also easily available in the atmosphere. Since the $[H_2SO_4]$ threshold is well within the typical atmospheric conditions (Erupe et al., 2010a), one would expect that aerosol nucleation should take place instantly under most atmospheric conditions via the binary nucleation process alone. But in the real atmosphere, the frequency of new particle formation event is seasonally dependent and is usually ~30–50% or higher

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during the spring and fall and <20% in summer and winter (Erupe et al., 2010a; Kulmala et al., 2004). And, even at [H_2SO_4] of 10^7 cm^{-3}, nucleation often does not occur with low surface areas of preexisting aerosols (Erupe et al., 2010a). These results open an important atmospheric question which requires future studies to answer: under what atmospheric conditions does new particle formation actually not occur? Future studies are required to answer this important atmospheric science question.

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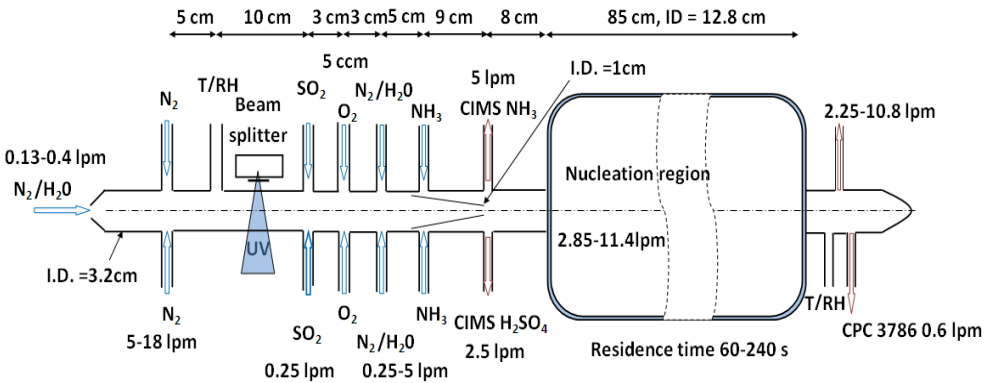

Fig. 1. A flow reactor used in KSU aerosol nucleation setup. This new design allows for significantly less wall loss of H_2SO_4 in the nucleation reactor (see Fig. 2b).

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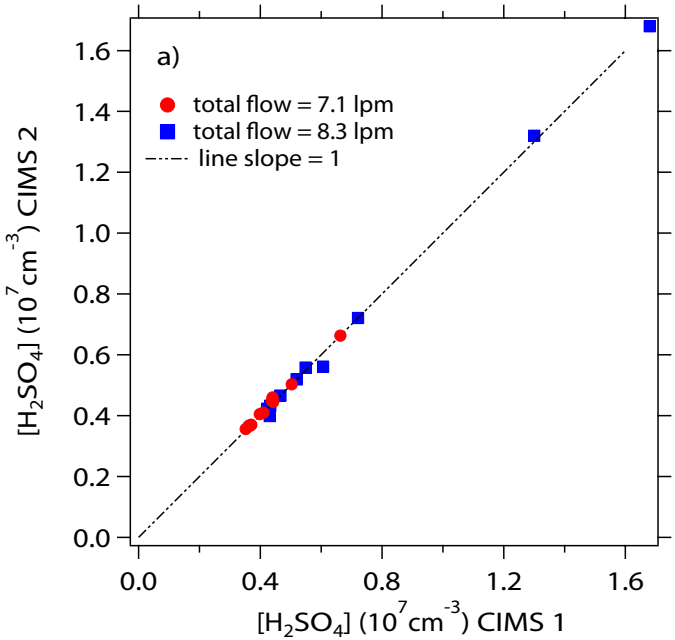

Fig. 2a. $[H_2SO_4]$ measured by two CIMSs at the beginning of the nucleation reactor. RH = 14%. Dashed line shows the linear fitting of the data.

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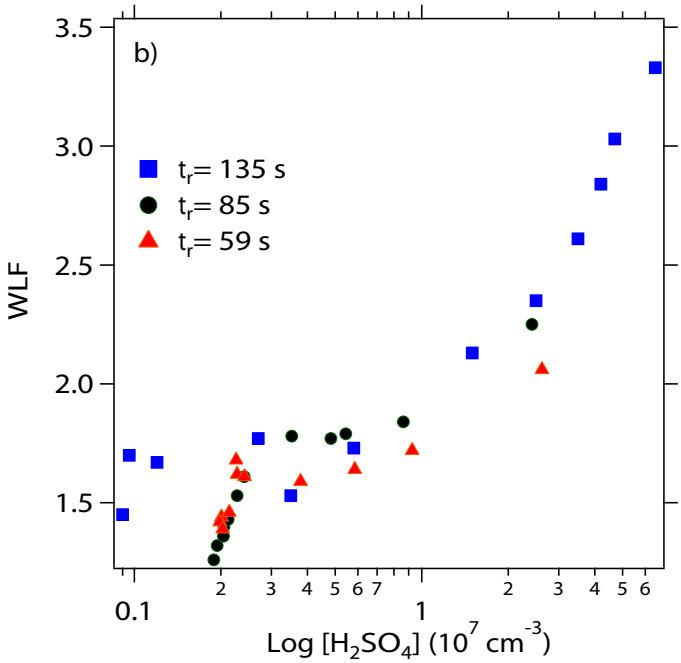

Fig. 2b. The measured WLF with two CIMSs located at the beginning (initial [H_2SO_4]) and end of the nucleation reactor (residual [H_2SO_4]) as a function of initial [H_2SO_4]. WLF is the ratio of initial to residual [H_2SO_4]. RH = 20%.

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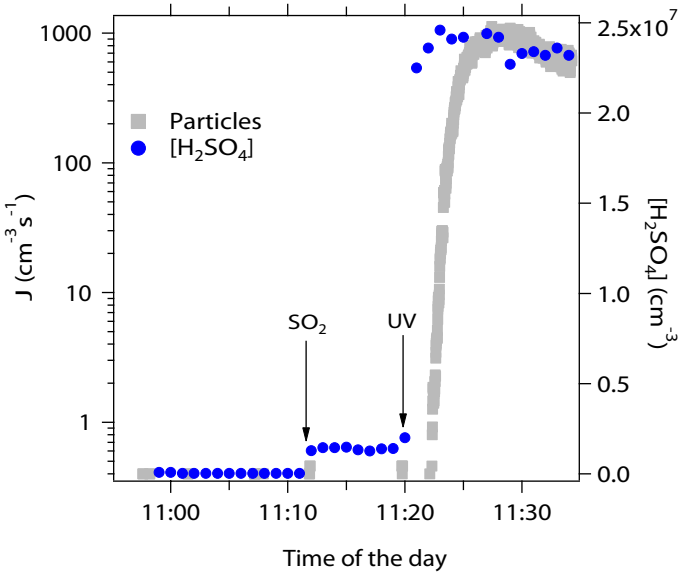

Fig. 3. The measured nucleation rates and [H_2SO_4] when SO_2 and UV were introduced to the reactor. The residence time was 190 s, total flow 11.1 lpm, RH 22%, and [SO_2] 2.25 ppmv.

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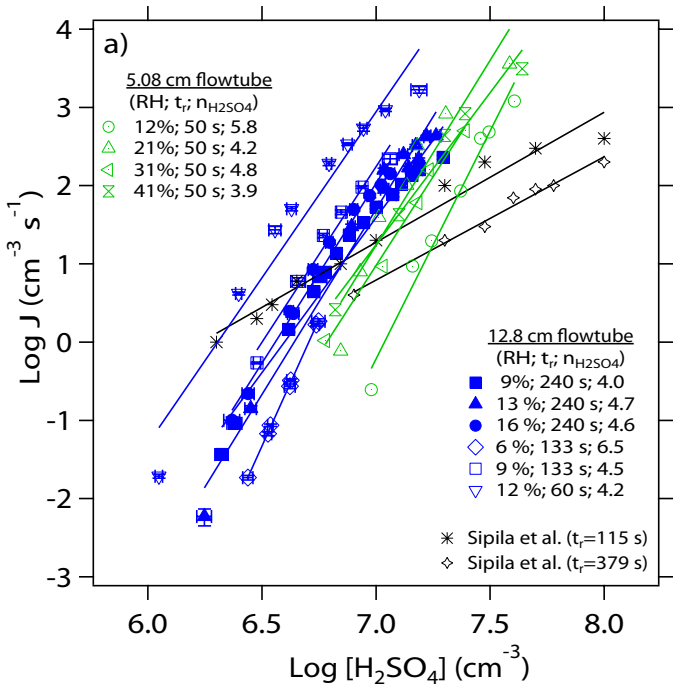

Fig. 4a. The measured Log J vs. Log [H_2SO_4] for H_2SO_4-H_2O BHN at different RH and residence times using two different nucleation reactors (12.8 cm ID 5.08 cm ID). The slope is shown as $n_{H_2SO_4}$. In comparison, we also included data from (Sipilä et al., 2010) for residence times of 115 and 379 s and RH 22%. Horizontal and vertical bars show the one standard deviation of the measured [H_2SO_4] and J.

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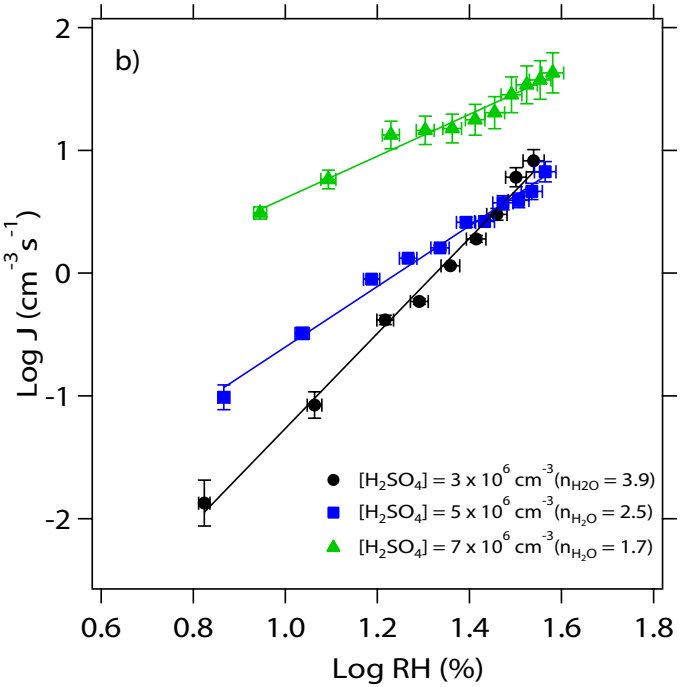

Fig. 4b. The measured Log J vs. Log RH at different [H_2SO_4] ($3 \times 10^6 - 7 \times 10^6$ cm^{-3}). Total flow was 10 lpm and residence time was ~120 s with the 12.8 cm ID nucleation reactor. The horizontal and vertical bars indicate one standard variation in RH and J.

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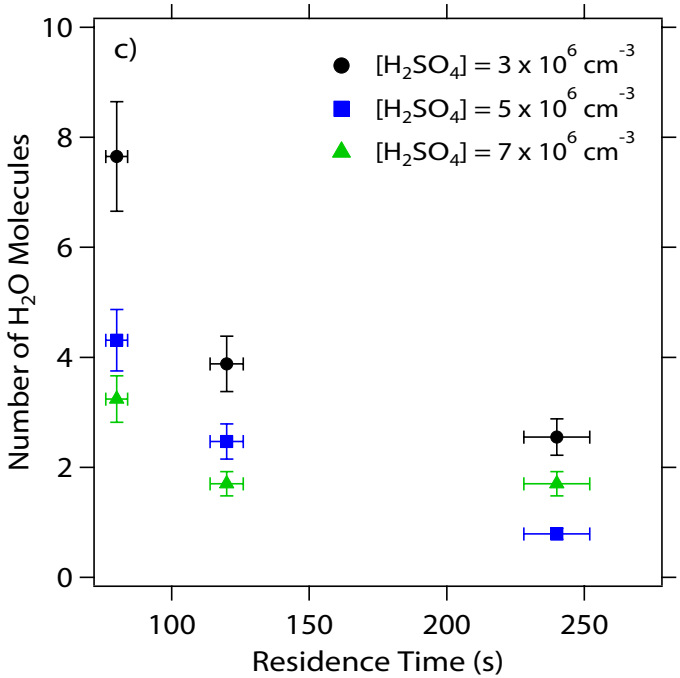

Fig. 4c. The n_{H_2O} values (derived from Log J vs. Log RH) as a function of residence time and $[H_2SO_4]$. Figure 4a shows the same trend for $n_{H_2SO_4}$. The horizontal and vertical bars indicate one standard variation in residence time and n_{H_2O}.

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