LABORATORY KINETIC STUDIES ON BINARY AND TERNARY HOMOGENOUS NUCLEATION UNDER LOWER TROPOSPHERIC CONDITIONS

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DEDICATION

I dedicate this in loving memory to my late brother SSG Michael Robert Benson (1973-2010). A braver and more thoughtful soldier I could have never known. Although you are gone you will never be forgotten.
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CHAPTER 1

Introduction

Aerosols are ubiquitous in our atmosphere. They can affect human health\textsuperscript{3, 4}, air quality, global radiation budget\textsuperscript{5, 6}, and cloud formation\textsuperscript{7-9}. Aerosols are formed through a gas to particle conversion process known as nucleation. Much is still unknown about the nucleation process. Numerous studies including theoretical models, field observations or laboratory experiments have tried to solve the problem of exactly how nucleation occurs and what are the main chemical species involved. Several possible nucleation mechanisms that have been proposed include ion-induced nucleation, binary homogenous nucleation involving sulfuric acid and water and ternary nucleation involving sulfuric acid and water and a ternary species. While studies (theoretical, field or experimental) have been extensively conducted on these mechanisms, there is still much uncertainty associated with them which will require future analysis of each one.

1.1 Overview of Nucleation

The process of nucleation is shown in Seinfeld and Pandis (2006)\textsuperscript{10}. It occurs mainly through the supersaturation of the vapor phase via different processes (isothermal compression, isobaric cooling and adiabatic expansion). In order to evaluate the nucleation process, it is necessary to consider what happens when an aerosol droplet forms. For the formation of a droplet from the pure vapor\textsuperscript{10}, there is always a certain free energy change, $\Delta G$, associated:
\[ \Delta G = -\frac{4\pi}{3} R_p^3 \frac{kT}{v} \ln S + 4\pi R_p^2 \sigma \]  

(1)

where \( R_p \) is the droplet radius, \( v \) is the volume occupied by a molecule in the aerosol phase, \( S \) is the saturation ratio and \( \sigma \) is the surface tension. A plot of \( \Delta G \) vs \( R_p \) is shown in Figure 1.1. As the figure shows, in a supersaturated environment (\( S>1 \)), when the radius of the aerosol becomes large enough (\( R_p^\ast \)), growth of the droplet will occur spontaneously. This critical radius is found to be \(^{10} \):

\[ R_p^\ast = \frac{2v\sigma}{kT \ln S} \]  

(2)

and the number of molecules in the critical cluster, \( i^\ast \), is found to be \(^{10} \):

\[ i^\ast = \frac{32\pi}{3} \left( \frac{\nu^2 \sigma^3}{(kT)^3 (\ln S)^3} \right) \]  

(3)

\( R_p^\ast \) can be used to find the free energy barrier height, \( \Delta G^\ast \). Once this value is determined the nucleation rate can then be calculated \(^{10} \):

\[ J = C \exp\left(-\frac{\Delta G^\ast}{kT}\right) \]  

(4)
Figure 1.1. The Gibbs free energy change for the formation of an aerosol droplet of radius $R_p$. Adopted from (Seinfeld and Pandis., 2006)$^{10}$.

Experiments show (Viisanen and Strey, 1994)$^{11}$ the nucleation rate is a steep function of $S$ and the critical saturation ratio decreases as $T$ increases (for a constant nucleation rate) and $J$ increases as $T$ increases (for constant $S$) (Figure 1.2). As the figure shows, the homogenous theory often underestimates the experimental results (whereas THN overestimates), while keeping the temperature trend intact.
Figure 1.2. Nucleation rates measured in supersaturated n-butanol vapor as a function of saturation ratio for various temperatures. The symbols indicate experimental values while the lines represent classical nucleation theory (CNT). Adopted from (Viisanen and Strey, 1994)\(^{11}\).

1.2 Binary Homogenous Nucleation (BHN)

One nucleation mechanism that considerable attention has been paid to is binary homogenous nucleation. For binary homogenous nucleation (as well as THN) to occur, the species involved must be supersaturated with respect to a liquid solution droplet\(^{10}\). The thermodynamics characterizing BHN are similar to that of the general nucleation process mentioned in the previous sections. For BHN the free energy of formation of the cluster is given as\(^{12}\):

\[
\Delta G_{\text{unhyd}} = -n_u kT \ln \left( \frac{p_a}{p_{a,s}} \right) - n_u kT \ln \left( \frac{p_w}{p_{w,s}} \right) + 4\pi R_p^2 \sigma
\]  

\hspace{1cm} (5)
where $\Delta G_{\text{unhyd}}$ is the formation free energy of free (unhydrated) clusters, which depends on the number of molecules of species i ($n_i$), the ambient partial pressure of species i ($p_i$), the equilibrium vapor pressure of species i above the surface of a flat solution ($p_{i,s}$), and the other terms as mentioned above. The subscripts $w$ and $a$ denote water and acid, respectively. In BHN, the formation of hydrates must also be taken into account. With the corrections for hydrate formation taken into account $^{12-14}$ the free energy takes the form:

$$
\Delta G_{\text{hyd}} = \Delta G_{\text{unhyd}} - kT \ln C_h
$$

(6)

where $C_h$ is the correction factor for hydrate formation. Field studies$^{15, 16}$ have shown BHN theories work in regions of high RH, such as the outflow regions of clouds, even at lower altitudes when $[\text{H}_2\text{SO}_4]$ is low.

### 1.3 BHN Experiments

There have been a variety of laboratory experiments involving the H$_2$SO$_4$-H$_2$O mechanism. These previous experiments also have utilized different methods to produce sulfuric acid, using vaporized sulfuric acid from a liquid reservoir$^{17-21}$ and using the oxidation of SO$_2$ $^{22, 23}$ or both$^{24}$. These experiments have also chosen different methods to measure the sulfuric acid including mass balance calculations$^{17, 25}$, organic titration reactions together with kinetic model calculations$^{22, 23}$, and direct measurements with a chemical ionization mass spectrometer$^{18, 19, 24}$ (more in depth discussion of this later). The H$_2$SO$_4$ measurements were either initial $[\text{H}_2\text{SO}_4]$ $^{17, 18, 24, 25}$ (measured/calculated at the beginning of the flow tube at the onset of nucleation) and/or residual $[\text{H}_2\text{SO}_4]$ $^{17, 18, 22-24}$ (measured at the end of the flow reactor, more in depth discussion of this later).
Because of the differences in the way sulfuric acid is produced and measured it is hard to make intercomparisons among several different lab experiments. Therefore a more in depth analysis of the nucleation region is needed to make more reliable comparisons between these different methods.

1.4 Overview of Ternary Homogenous Nucleation (THN)

The theory behind ternary homogenous nucleation involving sulfuric acid, ammonia, and water is similar to that of BHN. The nucleation rate will still take the form of equation 4, albeit the value of $\Delta G^*$ and $C$ will be different. $\Delta G$ for THN takes the form:

$$\Delta G = -n_a kT \ln \left( \frac{p_a}{p_{a,s}} \right) - n_w kT \ln \left( \frac{p_w}{p_{w,s}} \right) - n_b kT \ln \left( \frac{p_b}{p_{b,s}} \right) + 4\pi R_p^2 \sigma$$  \hspace{1cm} (7)

where terms for ammonia (subscript $b$) have been added. The composition of the critical cluster can be found by solving the following set of equations\textsuperscript{26}:

$$\nu_{H_2SO_4} \ln \left( \frac{p_{H_2SO_4}}{p_{H_2SO_4,s}} \right) - \nu_{H_2O} \ln \left( \frac{p_{H_2O}}{p_{H_2O,s}} \right) = 0$$

$$\nu_{SO_3} \ln \left( \frac{p_{SO_3}}{p_{SO_3,s}} \right) - \nu_{H_2O} \ln \left( \frac{p_{H_2O}}{p_{H_2O,s}} \right) = 0$$  \hspace{1cm} (8)

where $\nu_i$ is the partial molar volume of species $i$, $p_i$ is the ambient partial pressure of species $i$, and $p_{s,i}$ is the equilibrium vapor pressure of species $i$ above a flat solution surface. Once the composition is known, the radius of the critical cluster can be solved for\textsuperscript{26}:

$$r^* = \frac{2 \sigma \nu_i}{kT \ln \left( \frac{p_i}{p_{s,i}} \right)}$$  \hspace{1cm} (9)
where i refers to either H$_2$SO$_4$, NH$_3$ or H$_2$O.

1.5 THN Experiments

A limited number of laboratory experiments involving ammonia in ternary nucleation are present$^{18, 27-29}$. Two of these involve the NH$_3$-H$_2$SO$_4$-H$_2$O system $^{18, 27}$ and two of these involve applying irradiation to an SO$_2$-NH$_3$-H$_2$O system $^{28, 29}$. The main scientific findings from these experiments are:

1. The presence of NH$_3$ can enhance nucleation$^{18, 28, 29}$ (up to three or four orders of magnitude), but only up to certain levels (0.7 ppm) of NH$_3$ $^{28, 29}$.

2. The possible production of ammonium sulfate which could serve as condensation nuclei$^{28, 29}$

3. In the presence of ammonia, the power dependence of the nucleation rate, $J$, on the [H$_2$SO$_4$] is much smaller than without it$^{18}$ (for example, for an RH value of 15%, the power dependence of $J$ on [H$_2$SO$_4$] is 8.2 without ammonia and 5.2 with it; see Figure 1.3), suggesting less molecules of sulfuric acid in the critical clusters in the presence of ammonia ternary species. The critical cluster may contain as little as two sulfuric acid molecules when ammonia is present$^{27}$. Also, the cluster contains as little as one ammonia molecule$^{27}$.

4. Depending on the chemical species present, different nucleation mechanisms may be occurring$^{29}$. In the H$_2$O/Air mixture and NH$_3$/H$_2$O/Air mixture it is mainly ion-induced nucleation which is favored over neutral homogenous nucleation. In the SO$_2$/H$_2$O/Air mixture there is competition between IIN and homogenous
nucleation (either binary or ternary) but ion-induced nucleation acts quicker. In the NH$_3$/SO$_2$/H$_2$O/Air mixture both mechanisms are also present, but homogenous nucleation is induced by (NH$_4$)$_2$SO$_4$ and/or NH$_3$SO$_3$, whereas for ion-induced nucleation it is NH$_3$SO$_3$ and/or H$_2$SO$_4$ that is responsible.

**Figure 1.3.** Nucleation rates measured as a function of CIMS measured [H$_2$SO$_4$] for two different RH values (indicated in the figure) with and without the presence of ammonia. For each curve, the power dependence ($J = \text{Constant} \times [\text{H}_2\text{SO}_4]^n$) of $J$ on [H$_2$SO$_4$] is indicated. Adopted from (Ball et al., 1999)$^{18}$.

### 1.6 THN Theory vs. Experiments

Theories and parameterized models of THN have been compared to the available laboratory experiments. Overall, the theories agree quite well with the experiments with the exception of what the exact nucleation enhancement should be$^{18,26,30-34}$ (Ball et al., 1999; Napari et al., 2002; Coffman et al., 1995; Yu, 2006; Korhonen et al., 1999; Antilla et al., 2005; Merikanto et al., 2007) and THN will not work for lower [NH$_3$] (less than 1 ppt), close to the binary limit$^{35}$. One theoretical study$^{31}$ examined the effect NH$_3$ would have in the marine boundary layer. This study showed enhancements of ternary
nucleation over binary nucleation as high as $10^{20}$. This is similar to what classical THN theory showed\textsuperscript{30} which showed as much as 30 orders of magnitude enhancement. However, laboratory experiments\textsuperscript{18} have shown only modest enhancements (only about three orders of magnitude). The discrepancy between the experiments and theory could be due to the uncertainties in the thermodynamic data used (the thermodynamic data for the THN system is not available from experiments) and the fact that THN data are highly sensitive to this data\textsuperscript{32}. Also these theories use thermodynamic properties of bulk solution to determine certain properties (surface tension, solution density and equilibrium vapor pressures) which are different from those for smaller clusters.\textsuperscript{26} Other studies\textsuperscript{32-34,\textsuperscript{36}} (Yu, 2006; Antilla et al., 2005; Merikanto et al., 2007), however, have predicted nucleation rates much lower and in better agreement with laboratory studies, by taking into account $(\text{NH}_4)\text{HSO}_4$ formation and including an ammonia stabilizing factor.

1.7 THN Theory vs. Observations

There is debate on whether THN involving $\text{NH}_3$ is responsible for atmospheric observations of new particle formation or not. The calculations from one density functional theory study (DFT)\textsuperscript{37} indicate that $\text{NH}_3$ will not play a major role in new particle formation in the atmosphere. On the other hand, another DFT study\textsuperscript{38} showed that $\text{NH}_3$ can in fact lower the formation free energy of sulfuric acid-water clusters and strengthen the binding of a second sulfuric acid molecule to the existing cluster. Under real atmospheric conditions, however, the amount of $\text{NH}_3$ containing clusters is most likely negligible\textsuperscript{38}, due to the required temperature (245 K) and $[\text{NH}_3]$ (140 ppt) for ammonia containing clusters to dominate. This implies that ternary homogenous
nucleation will not be important in our atmosphere. THN with ammonia has been shown to explain nucleation at coastal sites\textsuperscript{39}, however, but the growth to observable sizes cannot be explained by the low $[\text{H}_2\text{SO}_4]$ present and other vapors must be responsible for this\textsuperscript{39}. Also, thermodynamic nucleation theory has shown that most of the sulfuric acid in the lower atmosphere is bound to stabilized (NH\textsubscript{4})\textsubscript{HSO\textsubscript{4}} clusters\textsuperscript{40}, which would limit sulfuric acids participation in the growth of CCN. However, there are some studies that show THN can be important. Several different nucleation theories/parameterizations tested versus observations from Pittsburgh Air Quality Study (PAQS) showed that the ternary theory matched best with the available data\textsuperscript{41}. Other modeling of in situ particle formation events based on PAQS showed a strong correlation of ammonia with nucleation events, especially for the month of July (possible due to the insensitivity of the data on the [OH] for this month), as well as an accurate prediction of the timing of the events (within 1 hour)\textsuperscript{42}. Data from the PARFORCE coastal field campaign also showed that ternary nucleation is a likely mechanism to explain particle formation events occurring at coastal sites\textsuperscript{39}. Observations from Hyytiala, Finland were compared with a model assuming ternary nucleation and there was good agreement with the theory, assuming that an extra source of condensable vapor is present to grow the particles to detectable sizes\textsuperscript{43}. Measurements made at Macquarie Island, Australia close to penguin colonies (likely a significant source of NH\textsubscript{3}) also suggest the presence of NH\textsubscript{3} in regions of enhanced particle concentrations\textsuperscript{44}. Another study\textsuperscript{16} showed while the binary theory may work at higher altitudes with lower temperatures, participation of ammonia may explain nucleation at lower altitudes where the temperature is higher and the $[\text{H}_2\text{SO}_4]$ is
too low for nucleation to occur via BHN and therefore, in this region, THN may be important. Much more data from field studies will have to be collected to definitively prove that THN can be important in our atmosphere.
CHAPTER 2

The Effects of Airmass History on New Particle Formation in the Free Troposphere: Case Studies

This chapter describes a detailed analysis of aircraft studies showing that new particle formation (NPF) is very active in the free troposphere. Results are presented from NPF studies during the National Science Foundation (NSF) and National Center for Atmospheric Research (NCAR) NSF/NCAR GV Progressive Science Missions. The GV is also known as HIAPER, the High-performance Instrumented Airborne Platform for Environmental Research. The Progressive Science Mission was the first science mission onboard the GV and there were seven days of research flights (Young et al., 2007). There is the Part I paper by Young et al. (2007) that used two days of measurements in the midlatitude tropopause region (on December 1 and 7, 2005) from this mission to show how stratosphere and troposphere air mixing enhances NPF. The present study is the Part II paper (Benson et al., 2008), and we want to investigate when no-/weak- NPF takes place. There is also a third manuscript (Lee et al., 2008) that discusses nighttime ultrafine particles observed from GV.

Here, case studies are provided to show how different meteorological parameters affect NPF in the upper troposphere, using the aerosol size distributions measured at latitudes from 18 °N - 52 °N and altitudes up to 14 km during the NSF/NCAR GV Progressive Science Missions. About 95% of the total samples showed the NPF feature with median number concentrations of particles with diameters from 4 to 9 nm ($N_{4-9}$), 288
± 199 cm⁻³, and the total particle number concentrations with diameters from 4 to 2000 nm ($N_{4-2000}$), 500 ± 259 cm⁻³. Surface areas were in general very low in the free troposphere, 1.58 ± 0.87 μm² cm⁻³, which in part explains the high frequency of NPF measured in this region, but there was no distinctive difference in surface area for the NPF and non-NPF cases. These case studies show that rather airmass history is more important for nucleation in this region. Weak- or non-events did not display uplifting of airmasses. On the other hand, strong NPF events were usually associated with uplifting of airmasses, although there were also NPF cases in which uplift did not occur, consistent with the previous observations (Young et al., 2007). NPF tends to easily occur in the free troposphere because of low surface areas and low temperatures (Carslaw and Kärcher, 2006), but because of the low aerosol precursors in this region, vertical motion (that can bring higher concentrations of aerosol precursors from low altitude source regions to higher altitudes) can play a critical role. Latitude dependence of new particles also shows higher particle concentrations in the midlatitude and subtropics tropopause region than in the tropics, consistent with Hermann et al. (2003).

2.1 NPF Studies

Recent aircraft studies showed new particle formation (NPF) in the free troposphere and lower stratosphere (de Reus et al., 1998, 1999; Nyeki et al., 1999; Twohy et al., 2002; Lee et al., 2003; Young et al., 2007) with high frequencies (up to 86 - 100%) (Young et al., 2007) and strong magnitudes (up to 45,000 cm⁻³) (Twohy et al., 2002). Hermann et al. (2003) have provided so far the most comprehensive statistical analysis of NPF in the northern hemisphere tropopause region from three-year aircraft
measurements; elevated particle number concentrations of 1,500 - 8,000 cm\(^{-3}\) were frequently observed in a wide range of latitudes (5 °N - 50 °N). Twohy et al. (2002)\(^{53}\) showed especially high number concentrations of new particles up to 45,000 cm\(^{-3}\) in the midlatitudes, associated with deep convection. Minikin et al. (2003)'s\(^{55}\) aircraft studies showed relatively high concentrations of Aitken mode particles (up to 1,000 cm\(^{-3}\)) even in the southern hemisphere, where the anthropogenic emission of SO\(_2\) is much lower than in the northern hemisphere; their comparison of particle number concentrations in the northern and southern hemisphere indicated that new particles were directly related to aerosol precursor sources. NPF events take place near or in orographic clouds (Wiedensohler et al., 1997; Mertes et al., 2005)\(^{56, 57}\) and stratus clouds (Hegg et al., 1992)\(^{58}\) during the nighttime, and even in cirrus clouds (Lee et al., 2004)\(^{59}\). As NPF was observed in a wide range of the free troposphere and lower stratosphere (Ström et al., 1999; Twohy et al., 2002; Hermann et al., 2003; Minikin et al., 2003; Lee et al., 2003, 2004; Young et al., 2007)\(^{45, 49, 53-55, 59, 60}\), it is also important to understand when NPF does not occur or when weak NPF occurs.

### 2.2 NSF/NCAR GV Progressive Science Missions

The NSF/NCAR GV Progressive Science Mission NPF studies took place from November 21 to December 19 in 2005 in Broomfield, Colorado. The flights covered the western half of the United States, and parts of Canada and Mexico in latitude from 18 °N to 62 °N and in longitude from 92 °W to 130 °W. There were three days of nighttime NPF experiments (December 2, 12 and 19, 2005) in order to investigate the effects of sun
exposure and the latitude and altitude dependence of new particles (Lee et al., 2008). Nighttime studies in this region are rare.

Aerosol sizes and concentrations were measured with the University of Denver nuclei mode aerosol size spectrometer (NMASS) and focused cavity aerosol spectrometer (FCAS). These instruments are described in detail elsewhere (Jonsson et al., 1995; Brock et al., 2000; Lee et al., 2003, 2004; Young et al., 2007) and have been used for NPF studies in the upper troposphere and lower stratosphere previously (Lee et al., 2003, 2004; Young et al., 2007). Briefly, NMASS has five condensation nucleus counters that measure cumulative number concentrations of aerosols larger than 4, 8, 15, 30 and 60 nm, respectively. FCAS is a light scattering instrument and sizes aerosols from 90 to 2000 nm. Using an inversion algorithm, size distributions from 4 to 2000 nm are obtained. The inversion also includes sampling efficiency, anisokinetic inlet effects, and diffusion loss etc.

The criteria for NPF are (i) $N_{4-9} > 1 \text{ cm}^{-3}$, (ii) more than 1/15 of $N_{4-2000}$ are $N_{4-9}$, and (iii) particles from 4 to 6 nm ($N_{4-6}$) are higher than those from 6 to 9 nm ($N_{6-9}$) (Young et al., 2007). A non-NPF event is defined when at least one of these three criteria is not satisfied. Non-events tended to have size distributions without a peak in the size range < 10 nm, a clear indication of more aged aerosols than for NPF cases (Figure 2.3c). Each NPF event is further classified as a strong or weak event by comparing with “background” concentrations, which are referred to as the median concentration values from all events shown in Table 2.1. Strong events are for the cases when $N_{4-9} > 500 \text{ cm}^{-3}$ [which is approximately the same value as that one median absolute deviation value
higher than the median $N_{4.9}$ for all events, $(275 + 198)$ cm$^{-3}$ in this case; similarly to Young et al., (2007)$^{45}$; weak events are defined when $N_{4.9} < 100$ cm$^{-3}$ (one median absolute deviation value lower than the median $N_{4.9}$ for all events, which is $(275 - 198)$ cm$^{-3}$, and we took 100 cm$^{-3}$ here for simplicity). As shown in Figure 2.1, weak- and non-NPF cases show a similar upper level of $N_{4.9}$, indicating that even though these two cases may have different size distributions (e.g., $N_{4.6}$ vs $N_{6.9}$), they both have low $N_{4.9}$.

Previous NPF studies in the free troposphere made by other investigators have used the criterion that the measured total CN concentrations are higher than the background CN concentrations to identify NPF cases (Twohy et al., 2002)$^{53}$ and numerous references cited therein), for example. In comparison, our criteria for NPF are more quantitative, yet consistent with these cited studies. For example, our non-NPF samples had much lower $N_{4.9}$ and $N_{4.2000}$ than the median concentrations from all days of experiments (Table 2.1) (that is, background concentrations) so they will also be non-NPF cases even with the NPF criterion used in these cited studies.

There were only less than 2% of the measurement data from this mission showed RH values greater than 100%. All case studies presented here were taken from cloud free sections of the flight (e.g., RH < 60%) so new particles were not affected by clouds. Our previous studies also have shown that shattering of clouds in the inlet of the NMASS and FCAS instruments has little effects on the measured aerosol number concentrations (while there are some effects on mass concentrations) (Lee et al., 2004)$^{59}$, so the measured new particles were unlikely affected by cloud processing.
Table 2.1. The measured median values of the particle concentration from 4 - 9 nm ($N_{4-9}$), the particle concentration from 4 - 2000 nm ($N_{4-2000}$), and other key meteorological parameters during the entire NSF/NCAR GV Progressive Science Missions. All 7 research flights are included here. The median absolute deviation values are also included. NPF indicates NPF. In total, 5181 data points of 30 second average data are included here.

<table>
<thead>
<tr>
<th></th>
<th>All Days</th>
<th>NPF</th>
<th>Non-NPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{4-9}$ (cm$^{-3}$)</td>
<td>275 ± 198</td>
<td>288 ± 199</td>
<td>4.93 ± 4.88</td>
</tr>
<tr>
<td>$N_{4-2000}$ (cm$^{-3}$)</td>
<td>457 ± 273</td>
<td>500 ± 259</td>
<td>60.8 ± 42.3</td>
</tr>
<tr>
<td>Surface Area (µm$^2$cm$^{-3}$)</td>
<td>1.58 ± 0.87</td>
<td>1.52 ± 0.84</td>
<td>2.32 ± 1.49</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>228 ± 11</td>
<td>227 ± 8</td>
<td>244 ± 29</td>
</tr>
<tr>
<td>Relative Humidity Over Ice (%)</td>
<td>13.3 ± 11.0</td>
<td>11.4 ± 8.8</td>
<td>24.9 ± 24.0</td>
</tr>
<tr>
<td>Potential Temperature (K)</td>
<td>325 ± 14</td>
<td>327 ± 12</td>
<td>310 ± 26</td>
</tr>
<tr>
<td>H$_2$O Mixing Ratio (ppmv)</td>
<td>115 ± 75</td>
<td>102 ± 58</td>
<td>423 ± 398</td>
</tr>
<tr>
<td>Altitude (km)</td>
<td>9.52 ± 2.31</td>
<td>9.87 ± 1.94</td>
<td>5.67 ± 4.72</td>
</tr>
<tr>
<td>Fraction of samples (%)</td>
<td>100</td>
<td>95</td>
<td>5</td>
</tr>
</tbody>
</table>
2.3 Results

2.3.1 Overall

Table 2.1 summarizes the measured particle concentrations and meteorological conditions during this mission, including the measured $N_{4.9}$, $N_{4-2000}$, surface area density of preexisting aerosols, temperature, relative humidity over ice (RHI), the potential temperature, water mixing ratio, and altitude, along with the fraction of samples that satisfy (thus NPF), or do not satisfy (non-NPF), the NPF criteria. Overall, there were 95% of NPF and 5% of non-NPF cases during the entire Progressive Science Missions (Table 2.1). Furthermore, 30% of NPF cases were strong-NPF and 25% were weak-NPF. For NPF events, the median $N_{4.9}$ value was $288 \pm 199$ cm$^{-3}$ and the median $N_{4-2000}$ was $500 \pm 259$ cm$^{-3}$. On the other hand, non-NPF events had a median $N_{4.9}$ of $4.93 \pm 4.88$ cm$^{-3}$ and a median $N_{4-2000}$ of $60.8 \pm 42.3$ cm$^{-3}$, both much lower than the overall $N_{4.9}$ of $275 \pm 198$ cm$^{-3}$ and $N_{4-2000}$ of $457 \pm 273$ cm$^{-3}$; the important feature here is, however, that a small fraction of measurements (5%), the non-NPF cases, showed an obvious and large deviation from the $N_{4.9}$ median. Surface area concentrations were very low in this region, $1.58 \pm 0.87$ μm$^2$ cm$^{-3}$. For NPF events surface areas were $1.52 \pm 0.84$ μm$^2$ cm$^{-3}$, and for non-events $2.32 \pm 1.49$ μm$^2$ cm$^{-3}$; however, the ranges of surface area were in fact the same for NPF and non-NPF events (Figure 2.1). Our low surface areas are consistent with other studies [4 – 6 μm$^2$ cm$^{-3}$ on average (Young et al., 2007)$^{45}$, $3.4 \pm 1.7$ μm$^2$ cm$^{-3}$ (Lee et al., 2003)$^{54}$ and less than 10 μm$^2$ cm$^{-3}$ (Twohy et al., 2002; Carslaw and Karcher, 2006)$^{48,53}$] and these low surface areas in general also explain the high frequency of NPF observed in this region. The higher median surface area for non-NPF is probably related
to the fact that most of the non-NPF events were measured in the lower altitudes (Figure 2.1b and 2.1c and Table 2.1). For example, for the non-event samples, the median temperature was ~ 244 K, higher than that for NPF cases (~ 228 K) (Table 2.1).

Figure 2.1. The measured $N_{4,9}$ as a function of surface area (a), temperature (b) and RHI (c) during the entire NSF/NCAR GV Progressive Science Mission. All 7 research flights are included here. The data are split into two categories, NPF (red circles) and non-NPF (blue crosses), as discussed in the text. The horizontal bars indicate the level of the
strong- ($N_{4.9} > 500 \text{ cm}^{-3}$) (green) and weak-NPF ($N_{4.9} < 75 \text{ cm}^{-3}$) (brown); note that the weak event line also is nearly the same as that the upper limit of the non-NPF $N_{4.9}$, indicating that both non- and weak-events have sufficiently low $N_{4.9}$.

Our case studies discussed below will show weak- or non-NPF events did not show uplifting of the airmass, whereas strong NPF cases were closely associated with uplifting. In the present study, uplifting of the airmass is defined based on the NOAA HYSPLIT backward trajectory outputs (e.g., airmass altitude dependence with time) (Draxler and Rolph, 2010). Uplifting is referred to as the cases when the airmass was uplifted from a lower altitude, usually less than 2 km above ground level, to higher altitudes at an uplift rate greater than 3 km per day and the airmass was exposed to these low altitude source regions for at least 2 days before the vertical motion. On the other hand, if this rate was less than 3 km per day or if the airmass spent less than two days at an altitude of 2 km or less, we considered such a case as a non-uplifting event. It is noted that this “uplifting” process is slightly different from the conventional “convection”, which is usually defined as a small scale process on the order of kilometers or less in size (the model output from NOAA HYSPLIT calculations only has a grid resolution of 1 degree and cannot truly resolve convective systems).

HYSPLIT trajectories were run for a large number of cases other than those presented in two case studies in Sections 2.3.2 and 2.3.3. However, because of the tremendous amount of data points we did not calculate for each individual data point. Also, when calculating HYSPLIT trajectories, one can only input the UTC time in hours
for the starting time and our measurements were in 1 second and the data presented here were averaged in 30 seconds. Regardless, for NPF events (Table 2.1), in general it seemed that the majority of the time (> 50%) the events displayed some degree of uplift. On the other hand, all non-NPF events found in the free troposphere region did not experience uplifting of airmasses (Section 2.3.2).

2.3.2 Case Study I (December 19, 2005): Strong-, Weak-, and Non-NPF Events

To understand how different meteorological parameters affect NPF, a variety of types of NPF events must be analyzed including strong-, weak- and non-events. However, because there were only 186 data points (5%) that showed absolute non-NPF events (Table 2.2) and some of these data points were also rather sporadically distributed, we provide here only one case study including a non-NPF event. Figure 2.2 shows strong- (a) weak- (b), and non-NPF (c) event cases, for the measured $N_{4-2000}$, $N_{4-9}$, fraction of $N_{4-9}$ in $N_{4-2000}$ ($N_{Frac}$), ratio of the particle number concentration in the size range from 4 to 6 nm ($N_{4-6}$) over that from 6 to 9 nm ($N_{6-9}$) ($N_{4-6}/N_{6-9}$), surface area, temperature and RHI as a function of universal time for December 19, 2005’s flight. On this day, the GV flew north to latitude 62° N before sunrise and returned to Colorado after sunrise, returning along a similar track. This flight was made in the upper troposphere region (altitudes 8 to 14 km) for most of the time and had a ~ 4 hours of daytime and another ~ 4 hours of nighttime measurements. The case studies shown here are taken from the daytime measurement. The strong event occurred at 57 °N, 116 °W, and 7.6 km, the weak event occurred at 50 °N, 112 °W, and 7.6 km, and the non-event was found in a similar geographical region, 52 °N, 113 °W, and 8.0 km (and thus all three events took
place at similar temperatures < 240 K). Figure 2.3 shows the average aerosol size distributions taken for the periods corresponding to these three events (Figure 2.2).

**Table 2.2.** The derived meteorological parameters derived from the five day NOAA HYSPLIT trajectory calculations for the case studies used in the present study. Median, maximum, and minimum values of the altitude, temperature, RHI, cumulative precipitation and cumulative solar flux intensity are shown.

<table>
<thead>
<tr>
<th>Event</th>
<th>Altitude (km)</th>
<th>Temperature (K)</th>
<th>RHI (%)</th>
<th>Prec. (mm)</th>
<th>Solar Flux (kW m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non</td>
<td>7.5</td>
<td>6.9</td>
<td>9.0</td>
<td>242</td>
<td>220</td>
</tr>
<tr>
<td>Weak</td>
<td>6.4</td>
<td>2.2</td>
<td>9.2</td>
<td>251</td>
<td>219</td>
</tr>
<tr>
<td>Strong</td>
<td>2.2</td>
<td>0.8</td>
<td>9.0</td>
<td>276</td>
<td>216</td>
</tr>
</tbody>
</table>

There are substantial differences in the number concentration and size distribution between all three of these events. The strong event had \(N_{4,9}\) of 1,500 cm\(^{-3}\) and \(N_{4,2000}\) of 2,000 cm\(^{-3}\), the weak event had \(N_{4,9}\) of 20 cm\(^{-3}\) and \(N_{4,2000}\) of 60 cm\(^{-3}\), and the non event had \(N_{4,9}\) of 5 cm\(^{-3}\) and \(N_{4,2000}\) of 100 cm\(^{-3}\) [failing to satisfy one of the NPF criteria, the ratio of \(N_{4,9}\) over \(N_{4,2000}\) \((N_{\text{Frac}}) > 6\%\)]. The strong event shows clearly fresh new particles in the size range < 10 nm as does the weak event, but the strong event has a much higher particle concentrations for the smaller particles and the weak event has peaks at 20 nm and 70 nm. The non-event shows almost no particles in the < 10 nm
range and shows more aged aerosols with the highest aerosol mode at around 70 nm. RHI was actually highest (20%) for the non-event compared to the weak event (15%) and strong event (8%) case. The surface area was comparable (~1 \mu m^2 \text{cm}^{-3}) for all three events. The surface areas measured at event times are often related to altitudes, with higher surface areas at lower altitudes (Young et al., 2007).^45

Differences among the three events can also be seen in the back trajectory data from HYSPLIT. The strong event had a higher amount of cumulative precipitation (12.4 mm) compared to the weak event (10.2 mm) and non event (1.8 mm) as is shown in Table 2.2. The solar flux was also slightly higher for the strong event (22.6 kW m\(^{-2}\)) than the weak- (19.3 kW m\(^{-2}\)) and non-event (17.2 kW m\(^{-2}\)). However, the distinctive difference between the three events is the airmass history from the previous five days (Fig. 2.4). These trajectories show two main differences. The first difference is the altitude that the airmasses come from. For the strong NPF event, the airmass originated from a much lower altitude (1 km) three days prior to the event, whereas the airmass for the weak event originated from about 2 km and the airmass for the non event was in the upper troposphere (7 km) for the past 5 proceeding days. Furthermore, for the strong event, the airmass was uplifted over 6 km in the span of a day, whereas the airmass for the weak event rose 6 km in three days. Such differences suggest that the airmass from the strong NPF event underwent a significant extent of vertical motion and rapidly brought higher concentrations of the expected aerosol precursors (e.g., H\(_2\)SO\(_4\), NH\(_3\), organic compounds and water vapor, as well as OH and sulfur compounds that can be oxidized to form H\(_2\)SO\(_4\), including SO\(_2\)) from lower altitudes to aid in NPF at higher
altitudes with lower temperatures. It is also possible that air mixing might occur when the humid and warm air was rapidly uplifted to higher altitudes and mixed with the cold and dry air at the higher altitudes and this case, a steep gradient of temperature and RH took place to enhance nucleation rates, because nucleation is a non-linear process as discussed in Nilsson and Kulmala (1998)\textsuperscript{64}. For the non-event, there was no uplifting present at all. It is noted that it was consistent that other non-event cases all did not have vertical motion, clearly underlying the importance of large scale vertical motion for nucleation in this high altitude region.
**Figure 2.2.** Plots of the measured total particle number concentration ($N_{4-2000}$), ultrafine particle concentration ($N_{4-9}$), fraction of $N_{4-9}$ in $N_{4-2000}$ ($N_{Frac}$), ratio of the particle number concentration in the size range from 4 to 6 nm ($N_{4-6}$) over that from 6 to 9 nm ($N_{6-9}$), surface area, temperature and relative humidity over ice (RHI) as a function of universal time for several different events that were observed on December 19, 2005. (a) A strong NPF event observed during the day which occurred at 57 °N, 116 °W, 7.6 km and temperatures around 238 K. (b) A weak NPF event observed during the day which occurred at 50 °N, 112 °W, 8.0 km and temperatures around 235 K. (c) A non NPF event observed during the day which occurred at 52 °N, 113 °W, 8.0 km and temperatures around 237 K.
Figure 2.3. The measured, average particle size distribution for the events shown in Figure 2.2. The letters here correspond to those from Figure 2.2 and each distribution is for the time period shown for the corresponding event from Figure 2.2. The dip at ~100 nm in the size distribution comes from the inversion program when combining the NMASS and the FCAS data together and may not be representative of the actual aerosols sizes. The same is true for Figure 2.6. The size mode at 20 nm or 70 nm (b and c) is representative of more aged particles that grew from newly formed fresh particles.
Figure 2.4. NOAA HYSPLIT back trajectories for the airmasses for the strong- (upper left panels) (corresponding to Figures 2.2a and 2.3a), weak- (upper right panels) (Figures 2.2b and 2.3b), and non-event (bottom left panels) (Figures 2.2c and 2.3c) on December 19, 2005. The star indicates where the event occurred. Altitude variations as a function of the number of days prior to the event are also shown (12 hours of interval).

2.3.3 Case Study II (December 12, 2005): Strong- and Weak-Events

Figures 2.5 and 2.6 show graphs for a strong and weak NPF event occurring on December 12, 2005. On December 12, 2005, the GV flew from Colorado (40º N latitude) south to latitude 18º N before sunrise and returned along the same track to Colorado after sunrise by flying through similar longitudes, latitudes, and altitudes. The strong event occurred before sunrise (nighttime) at 36 ºN, 115 ºW, and 10 km while the weak event
occurred after sunrise during the day at 37 °N, 111 °W, and 9 km. Both events occurred at temperatures below 240 K.

Similarly to the previous case study, there were substantial differences in number concentration and size distribution between the strong- and the weak-events. The strong event had $N_{4.9}$ of 700 cm$^{-3}$ and $N_{4.2000}$ of 800 cm$^{-3}$, whereas the weak event had $N_{4.9}$ of 90 cm$^{-3}$ and $N_{4.2000}$ of 280 cm$^{-3}$. The strong event also shows many more particles in the size range < 10 nm, whereas the weak event shows similar amounts of smaller and larger particles. RHI was higher (40%) for the strong event compared to the weak event (12%). The surface area was also comparable (~ 2 μm$^2$cm$^{-3}$) for both events.

Once again the HYSPLIT trajectory shows differences between the two events. The strong event had a higher amount of cumulative precipitation (44 mm) compared to the weak event (8 mm) as is shown in Table 2.2. The solar flux, however, was comparable for both cases (~ 55 kW m$^{-2}$). The distinctive difference between the strong and weak events is the back trajectory from the previous five days (Fig. 2.7). These trajectories show the same differences as the previous case study. For the strong NPF event, the airmass originated from a much lower altitude (ground level) three days prior to the event, whereas the airmass for the weak event was only exposed to altitudes as low as 7 km a day prior to the event and was actually at higher altitudes (~ 9 km) 2 to 3 days prior to the event. The strong event experienced rapid vertical motion (10 km in the period of 2 days), whereas the weak event experienced far less an extent of vertical motion (only 2 km in a day). As in the previous case study, this could be a reason why
the strong event had such high levels of new particle concentration compared to the weak event.
Figure 2.5. The same as Figure 2.2 except for a strong (a) and weak (b) NPF event occurring on December 12, 2005. The strong event occurred before sunrise (nighttime) at 36 °N, 115 °W, and 10 km. The weak event occurred during the day at 37 °N, 111 °W, and 9 km.
Figure 2.6. The measured, average particle size distribution for the events from Figure 2.5. The letters here correspond to those from Figure 2.5 and each distribution is for the time period shown for the corresponding event from Figure 2.5.
Figure 2.7. The same as Figure 2.4, except for the strong (left) (corresponding to Figures 2.5a and 2.6a) and weak (right) (Figures 2.5b and 2.6b) NPF events occurring on December 12, 2005.

2.3.4 Latitude Dependence of New Particles

Figure 2.8 shows the latitude dependence of ultrafine particles for all 7 science flights measured at for three different temperature and altitude regions: temperature > 250 K (altitude < 6 km), 230 K < temperature < 250 K (6 km < altitude < 9 km), and 200 K < temperature < 230 K (9 km < altitude < 14 km). These results show that at altitudes from
9 to 14 km, particle concentrations are higher in the subtropics and midlatitudes than in
the tropics, consistent with the Hermann et al. (2003) trend; both the present study and
Hermann et al. (2003) were mostly conducted near the tropopause region in the
midlatitudes at similar latitude ranges. It has been shown that air mixing induced by
convection and the stratosphere and troposphere exchange is strong in the midlatitude
(Pan et al., 2007) and these air mixing processes can enhance NPF; for example, very
high frequency (86 - 100 %) and high magnitude (~ 700 – 3,960 cm$^{-3}$ $N_{4.9}$ and ~ 1,000 –
3,990 cm$^{-3}$ $N_{4.2000}$) of NPF were observed in the mid-latitude tropopause region due to air
mixing (Young et al., 2007). On the other hand, this trend is different from the previous
report by Lee et al. (2003) which showed higher concentrations of ultrafine particles in
the lower latitudes. Because a majority of the data in Lee et al. (2003) were taken in the
subtropics and polar regions, rather than in the midlatitudes, while the present study was
made mostly in the midlatitude region, a direct comparison between Lee et al. (2003) and this study is difficult.
Figure 2.8. The measured $N_{4.9}$ as a function of latitude for different temperatures (and hence different altitudes) during the NSF/NCAR GV Progressive Science Mission. All 7 research flights are included here. Temperatures $> 250$ K (Altitudes $< 6$ km); $230$ K $<$ Temperatures $< 250$ K (6 km $< $ Altitudes $< 9$ km); Temperatures $< 230$ K (Altitudes $> 9$ km).
2.4 Discussions and Conclusion

Because surface area is the sink of new particles, an anti-correlation of $N_{4.9}$ with surface area might be expected. However, our analysis shows little correlation between these two parameters, although the median value of surface areas was higher for non-NPF events than NPF events. This is probably because that the majority of the samples (95%) were NPF cases and the measurements were made in a wide range of the free troposphere region (altitudes up to 14 km and latitudes from 18 °N – 62 °N). This feature in fact is also consistent with Ström et al. (1999) which showed that ultrafine particles are not always anti-correlated to surface areas in the free troposphere. The high frequency and magnitude of NPF observed in this region (Twohy et al., 2002; Young et al., 2007; Hermann et al., 2003; Lee et al., 2003; Benson et al., 2008) are thus due to such low surface areas measured in this region in general [4 – 6 μm$^2$cm$^{-3}$ on average (Young et al., 2007); 3.4 ± 1.7 μm$^2$cm$^{-3}$ (Lee et al., 2003); < 10 μm$^2$cm$^{-3}$ (Twohy et al., 2002; Carslaw and Kärcher, 2006); 1.58 ± 0.87 μm$^2$cm$^{-3}$ from the present study] and in addition to low temperatures (Carslaw and Kärcher, 2006).

Our case studies shown in this study indicate that airmass history is important for nucleation in this region. All non-/weak-NPF cases identified here did not have large scale vertical motion, indicating that airmasses originated from relatively high altitudes, possibly with low concentrations of expected aerosol precursors. On the other hand, strong events usually had uplifting. Large scale uplifting brings higher concentrations of aerosol precursors (including SO$_2$ and water vapor) to higher altitudes where temperature and surface areas are lower. With these factors together, uplifting can create an ideal
condition for aerosol NPF: higher aerosol precursors, lower surface areas, low
temperatures, and air mixing. It is noted that the SO$_2$ photochemical lifetime in the
atmosphere is around 10 - 14 days under the typical free tropospheric conditions. Even
with this relatively long photochemical lifetime, however, the measured [SO$_2$] in the free
troposphere showed a clear vertical profile, with much lower concentrations at higher
altitudes than in the ground level (Thornton et al., 1999)$^{67}$. In this case, uplifting can play
a very important role for bringing higher [SO$_2$] from the source regions to higher altitudes
in a short time. In addition, it is possible that rapid uplifting can also bring insoluble
organic trace gases to higher altitudes to produce new particles (Kulmala et al., 2006)$^{68}$.
Abrupt air mixing can also take place during rapid uplifting. As shown in previous
theoretical predictions (Nilsson and Kulmala., 1998)$^{64}$, because nucleation is a non-linear
process, when two airmasses mix with each other with different RHI, temperatures, and
aerosol precursors, nucleation rates can be much higher than without mixing.

While the role of uplifting of an airmass on NPF is much clear, it is less clear how
other meteorological parameters from the airmass history can also play a role in
determining if nucleation occurs and the extent to which it occurs (Table 2.2). The solar
flux from the previous five days was similar for the strong- and weak- NPF events for
both case studies and if the sun exposure fraction (that is the average ratio of the sun
exposure hours in a day during the five preceding days) also did not vary much day to
day (approximately 0.5 to 0.6), so the average [OH] in airmasses would be similar.
While the RHI was higher for the strong event than the weak event on December 12, the
values were comparable for both events on December 19 (Table 2.2). Precipitation may
have affected the strength of the event as in both cases the strong event experienced more cumulative precipitation (Table 2.2). Precipitation is believed to lower the surface area density because of scavenging, but since for all these events the surface areas were in fact very low in this region, the precipitation effects can be less important under such a condition. For these specific case studies, however, the altitude rather seems to be a dominating factor in determining the strength of the NPF event. Both strong events had a median altitude of less than 2.5 km during the previous five days and had minimum altitudes very close to the ground level (< 1 km), whereas for the weak events the median altitudes were both above 6 km and the air never fell below 2 km (Table 2.2). And, this may again point to the significance of airmass history in determining the extent of NPF.

It was consistent that weak- or non-events did not experience large scale uplifting during the Progressive Science Missions. Because of low surface areas and low temperatures, nucleation can easily take place, but with the limited supply of aerosol precursors in this region, nucleation becomes sensitive to the extent of vertical motion. Our observations are in line with numerous observations (de Reus et al., 1998; Nyeki et al., 1999; Ström et al., 1999; Twohy et al., 2002; Lee et al., 2003; Minikin et al., 2003; Hermann et al., 2003; Carslaw and Kärcher, 2006)\(^{48, 50, 52-55, 60, 65}\) in which NPF was often attributed to air mixing and convection. However, there were also some NPF cases where vertical motion clearly did not occur (< 50\% of the NPF cases), similarly to Young et al. (2007)\(^{45}\), suggesting that airmass history is an important but not the only governing factor for aerosol nucleation in this region.
CHAPTER 3

A Chemical Ionization Mass Spectrometer (CIMS) used for Measurements of Ammonia

This section describes a CIMS instrument for in-situ NH$_3$ detection. It focuses on addressing technical issues including the instrument background, calibration and time response. Also included is the seasonal variation of NH$_3$ in Kent, Ohio (a relatively less polluted U.S. Midwestern town) to demonstrate the instrument capability for atmospheric observations. The purpose of measuring NH$_3$ at this site is to understand the NH$_3$ effects on aerosol nucleation, but the influence of NH$_3$ and sulfuric acid (H$_2$SO$_4$) on aerosol abundance is discussed elsewhere$^{69}$. In an additional paper (V. Kanawade et al., Observations of ultrafine particle sizes, sulfuric acid, and ammonia in the Michigan Forest during the PROPHET 2009 CABINEX mission, in preparation; hereinafter referred to as Kanawade et al., in preparation), inter-comparison results of NH$_3$ instruments in the Michigan forest are shown, with a large number of gas phase species and aerosol measurements together.

3.1 Overview

Ammonia (NH$_3$) is prevalent in the atmosphere and serves as the principal basic gas phase species. NH$_3$ can control the acidity of atmospheric aerosols and in turn, change the chemical composition, reactivity, hygroscopicity, and optical properties of aerosol particles. Atmospheric observations$^{44, 70}$ and aerosol microphysical modeling
simulations\textsuperscript{71-74} have suggested that NH\textsubscript{3} can be important for atmospheric nucleation on the global and regional scale. Chemical analysis of aerosol composition also showed that newly formed atmospheric aerosol particles indeed contain ammonium (NH\textsubscript{4}\textsuperscript{+}) and sulfate (SO\textsubscript{4}\textsuperscript{2-}) along with other components\textsuperscript{75}. Laboratory nucleation observations\textsuperscript{18, 76} further demonstrated that NH\textsubscript{3} can enhance sulfuric acid and water homogenous nucleation\textsuperscript{2}.

Sources of NH\textsubscript{3} stem mostly from anthropogenic emissions such as livestock excrement, biomass burning, fertilizer application, and automobile emissions\textsuperscript{77-82}. Tropospheric NH\textsubscript{3} mixing ratios ([NH\textsubscript{3}]) range from several pptv up to several hundreds ppbv and sometimes even up to several hundreds ppmv levels\textsuperscript{83-87}, depending on the proximity to emission sources, altitude, and acidity of aerosol particles present in the atmosphere. Since even sub ppbv levels of [NH\textsubscript{3}] may be responsible for nucleation events observed in certain atmospheric conditions\textsuperscript{73, 74} and because nucleation occurs rapidly, it is important to develop a technique capable of measuring low [NH\textsubscript{3}] with a fast time response, so that we can identify the role of NH\textsubscript{3} in aerosol nucleation from in-situ real-time observations.

Reliable measurements of NH\textsubscript{3} are difficult, because of different forms present in the atmosphere, for example, gaseous NH\textsubscript{3}, particulate NH\textsubscript{4}\textsuperscript{+} (found in compounds such as (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, NH\textsubscript{4}HSO\textsubscript{4}, and NH\textsubscript{4}NO\textsubscript{3}), and liquid NH\textsubscript{4}OH. NH\textsubscript{3} is also a very sticky molecule, so when even extremely clean air is introduced into the sampling inlet, there is always substantial NH\textsubscript{3} signals (background signals) due to adsorption and desorption of NH\textsubscript{3} on various surfaces; and, the instrument detection limit is ultimately dependent on
the background signals. The instrument time response is also affected by adsorption and desorption of NH$_3$ on the inlet and instrument surfaces. Uncertainties in the background and calibration measurements also need to be addressed for the accurate detection of NH$_3$.

Different measurement techniques have been developed, including citric acid denuder/ion chromatography$^{88, 89}$, molybdenum-oxide converter-difference$^{90}$, tungsten oxide denuder$^{91}$, photofragmentation/laser induced fluorescence$^{92}$, and filterpack/colorimetry$^{93}$. The citric acid denuder/ion chromatography technique is the most commonly used method, as this technique has a high accuracy (within 10%), a simple system, a low cost as well as a low detection limit for the chromatographic system (as low as 25 pptv) (Fehsenfeld et al., 2002)$^{89}$. For these reasons, it has also served as the standard method to which the other techniques are judged, but the time resolution is poor (e.g., 2 hours sampling period). (Schwab et al., 2007)$^{94}$ have also discussed several different methods of NH$_3$ measurements, such as ion mobility spectrometer, tunable diode laser absorption spectrometer, long path absorption photometer, wet effluent diffusion denuder and chemiluminescence analyzer. While most of these instruments have a low detection limit ($< 200$ pptv) with 1 minute integration time, some of the instruments also have a slow response time. More recent methods include Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer or QC-TILDAS$^{95}$, Gradient of Aerosol and Gases Online Registrar or GRAEGOR$^{96}$ and Infrared Atmospheric Sounding Interferometer Spectrometer or IASI Spectrometer$^{82}$. 
Recently, chemical ionization mass spectrometers (CIMS) have been used for fast time resolution detection for NH$_3$$^{87, 97-99}$. These instruments were used in both ground-based$^{97-99}$ and aircraft studies$^{87}$. A summary of NH$_3$-CIMS from these pre-existing techniques is given in Table 3.1 and will be discussed in detail in Section 5 in comparison with our CIMS. The major advantage of CIMS, compared to other techniques, is fast time response (< 1 minute). On the other hand, the lowest reported background in CIMS is only about a few hundred pptv and the stability of the background can be poor$^{97}$.

3.2 Instrument

The NH$_3$-CIMS consists of the following three parts: (i) a sampling inlet used to perform ambient, background and calibration measurements, (ii) the CIMS flow reactor where ion-molecule reactions take place, and (iii) the vacuum region of the mass spectrometer including a collision dissociation chamber (CDC), an octopole ion guide, a quadrupole mass filter and a channeltron detector (Figure 3.1). The third part of the CIMS (vacuum region) is similar to that of the Georgia Tech NH$_3$-CIMS$^{87, 97}$ and of the H$_2$SO$_4$-CIMS described elsewhere$^{100-103}$. The CDC and octopole ion guide dramatically improve the cleanliness of ion mass spectra and the instrument sensitivity (Figure 3.1a) (Section 3.2.3). This is one of the major advantages of our CIMS, along with some NH$_3$-CIMS instruments (Nowak et al., 2006, 2007)$^{87, 97}$, compared to a number of other CIMS instruments currently used for atmospheric observations of various trace gas species. Below, we only describe the inlet and the ion-molecule reaction region (Sections 3.2.2 and 3.2.3).
Figure 3.1. The NH$_3$-CIMS system consists of the following three parts: (i) a sampling inlet used for ambient, background and calibration measurements, (ii) the CIMS flow reactor where ion-molecule reactions occur, and (iii) the vacuum regions of the mass spectrometer including a collision dissociation chamber (CDC), an octopole ion guide, a quadrupole mass filter and a channeltron detector.

We also note that our CIMS is designed to measure gas phase NH$_3$, as opposed to NH$_4^+$ present in solid or liquid aerosol phases. This is because CIMS techniques in principle are based on gas phase ion-molecule reactions (e.g., Reaction 1 in Section 3.2.3). To detect aerosol phase NH$_4^+$, typically, aerosol particles must be first deposited for a substantial period to collect a sufficient volume of aerosol phase NH$_4^+$, which are then vaporized into the gas phase by thermal desorption or laser ablation for further
ionization. But this is not the case for our CIMS which ionizes only gas phase NH₃ molecules using protonated ethanol ions (Section 3.2.3).

There is also the possibility that volatilization of ammonium nitrate (NH₄NO₃) from various surfaces of the instrument can contribute to the measured NH₃ ion signals, but the volatilization is usually negligible for temperatures under 50 °C and residence times (in the inlet) less than 0.05 s (Neuman et al., 2003)¹⁰⁴. Because our temperature (35 °C) was lower than this and inlet residence time (0.068 s) was comparable, there should not be any bias in the signal due to volatile NH₄⁺ aerosol. Another study⁸⁹ also confirmed that NH₄⁺ volatilization in mass spectrometer systems is limited for time scales less than one second. As will be discussed in Sections 3.3.2 and 3.3.3, we also did not see any temperature dependences of the instrument background and sensitivity, and this proves that NH₃ artifacts from vaporization of NH₄⁺ decomposition from the aerosol phases were not significant. We made frequent background measurements (Section 3.3.2) to effectively reduce the effects of these artifacts NH₃ signals.

3.2.1 Measurement Site

The ambient measurements were performed from the top floor of Williams Hall (15 m above the ground level) at Kent State University in Kent, Ohio (41.15° N, 81.36° W), for several weeks covering three seasons starting from winter of 2008 to fall of 2009. Kent is a small college town with a population of about 30,000 located in Northeastern Ohio. Kent is relatively rural itself, but is also surrounded by three urban cities, about 60 km southeast of Cleveland, about 30 km east of Akron, and about 100 km west from Youngstown. The weather in Ohio is especially humid in summer. Northeastern Ohio is
also known for its haze and gray colored sky in winter due to high emission of SO$_2$ from coal burning power plants in this region (http://www.epa.gov/cgi-bin/broker?_service=airdata&_program=progs.webprogs.emisumry.scl&_debug=2&geotype=st&geocode=OH&geoname=Ohio&epolmin=.&epolmax=.&epol=SO2&sic=&netyr=2002&geofeat=&mapsize=zsc&reqtype=getmap). Ohio is also one of the states that currently suffer from air pollution problems, failing to attain the U.S. National Air Quality Standards (NAAQS) for ozone and PM$_{2.5}$ (particulate matter smaller than 2.5 μm) (http://www.epa.gov/air/airtrends/pm.html).

### 3.2.2 Inlet: Background, Ambient and Calibration Mode

Our inlet system was based on the Georgia Tech NH$_3$ inlet$^{97}$, with some differences discussed below. Figure 3.2 illustrates the inlet system used during the fall 2009 measurements. The outer portion of the inlet consisted of a 65 cm, 0.635 cm O.D. fluorinated ethylene propylene (FEP) tube (the depth of the wall of Williams Hall is 50 cm) that stuck out a 1.27 cm hole in our laboratory wall. This tube was connected to a perfluoroalkoxy (PFA) tee. One leg of the tee was connected to the first port of a 3-way PFA valve (ambient mode) and the other leg was connected to the NH$_3$ scrubber housing (stainless steel, 3.5 cm I.D., 15 cm long) (background mode). For the ambient measurement mode, the sampling air traveled through this tee and the first port of the 3-way valve. The ambient mode flow is shown by an orange arrow in Figure 3.2. For the background mode, the sampling air traveled through this same PFA tee and the scrubber housing and the second port of the 3-way valve. The scrubber housing contained silicon phosphates (Perma Pure Inc.), which form phosphoric acid when they are exposed to
ambient RH levels and subsequently remove NH$_3$ from the ambient air (to produce “zero” gases). There was another PFA tee between the scrubber housing and the 3-way valve, which was attached to a pump to constantly suck out 100 – 200 sccm over the scrubber, to prevent the ambient air from stagnating inside the scrubber. The background mode flows are illustrated in blue arrows in Figure 3.2. In either the background or the measurement mode, the sample air exited through the common port of the 3-way valve and through a second PFA tee to flow into the CIMS inlet (0.635 cm I.D.). The flow through the inlet was as high as 15 slpm and the typical residence time in the ambient mode was 68 ms. Of this total flow, 5.2 slpm entered into the CIMS flow reactor and the rest of the flow was vented out via a mass flow controller through a diaphragm pump. The purpose of making (frequent) background measurements is to take into account the artifact NH$_3$ signals that arise from the adsorption/desorption of NH$_3$ on the surfaces of the CIMS inlet.

The sensitivity of the CIMS instrument was measured from a calibration using a known concentration of standard NH$_3$ gases. The standard gases supplied from a source cylinder (Linde, mixing ratio 4.5 ppmv, ± 5%) were added to the system with the flow between 1–10 sccm via a mass flow controller (MKS, ± 0.6%), which was regularly calibrated with a DryCal (Bios). The NH$_3$ gases were then added to a PFA tee to mix with an additional flow of N$_2$ gases (50-100 sccm) from a liquid nitrogen Dewar (Linde). These additional N$_2$ gases were needed so that the calibration was carried out with a high flow to ensure a fast time response (Section 3.3.1). This mixture was then introduced into another PFA tee, with one port connected to the solenoid valve and another port to
another PFA tee, located at the downstream of the 3-way valve on the inlet tubing (Figure 3.2). When performing calibration measurements, the solenoid valve was closed and the calibrations gases entered directly into the inlet tubing (green arrow in Figure 3.2). During the ambient/background measurements, the solenoid valve was open and the calibration gases were rapidly removed through the solenoid valve (50 – 200 sccm) (red arrow in Figure 3.2), to minimize the perturbation of the flow and pressure in the calibration line.

During the fall season, all tubing as well as all tees and valves were also maintained at a constant temperature of 35 °C (±1.5 °C). This was done by wrapping all the tubing and valves, in aluminum foil which was heated using heating tapes. Keeping the inlet at a constant temperature is important for reducing the uncertainties in the background signals (Section 3.3.2). We have also used only PFA and FEP Teflon materials in the entire inlet system, since stainless steel or other metal materials can easily uptake NH$_3$ on their surfaces$^{87, 97, 105}$. 
Figure 3.2. A schematic diagram of the inlet of KSU NH$_3$-CIMS used in the fall 2009 measurements. The air entered through an inlet port (11 slpm) and traveled through a PFA tee. The air flowed either directly through a 3-way PFA valve (measurement mode, orange arrow) or through an NH$_3$ scrubber and into the PFA valve (background mode, blue arrows). Calibration gases were introduced to the CIMS inlet system at the downstream of the 3-way valve. An additional flow (100 sccm) of N$_2$ gases was also brought to the calibration system to mix with the standard NH$_3$ gases, to increase the time response with a high flow. This time response was affected by both the flow rate of gases and the dead volume (shown in the grey shaded area; estimated to be 0.4 cm$^3$) in the tubing. When taking ambient or background measurements, the added calibration gases were removed by the suck back flow through a solenoid valve (red arrow), to reduce perturbation of flow. During the calibration, this solenoid valve was closed, so that calibration gases were introduced into the CIMS inlet system (green arrow).
3.2.3 Ion Molecule Reaction Region

The ion molecule reaction cell of the CIMS was maintained at a low pressure between 20–25 torr (1 torr = 133.3 Pascal). The total flow into the reactor was between 6.7–7.7 slpm, which consisted of the ambient air flow (5.2 slpm) through a 0.8 mm hole in an Al sampling cone and the reagent gas flow (1.5–2.5 slpm) perpendicular to the ambient flow. The reagent gas flow consisted of N\textsubscript{2} gases and a small percentage (2–3%) of ethanol vapor, which was brought by flowing 50 sccm of N\textsubscript{2} through a small glass bottle containing 95% ethanol solution at room temperature. The reaction time in the flow reactor was estimated to be ~40 ms.

The ion source flow was passed over a \textsuperscript{210}Po radioactive source emitting \( \alpha \) particles that led to the production of protonated ethanol ions \((\text{C}_2\text{H}_5\text{OH})\text{H}^+\) and their cluster ions \((\text{C}_2\text{H}_5\text{OH})_n\text{H}^+\), where \( n = 1, 2, 3, \text{etc.} \). These reagent ions reacted with NH\textsubscript{3} under the following pathway\textsuperscript{97}:

\[
(\text{C}_2\text{H}_5\text{OH})_n\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_3(\text{C}_2\text{H}_5\text{OH})_{n-2}\text{H}^+ + y(\text{C}_2\text{H}_5\text{OH})
\]  

(1)

where \( y \) is an integer less than \( n \). A typical mass spectrum taken from the ambient air is shown in Figure 3.3. Primary reagent ions seen in CIMS spectra, in the order of decreasing ion intensity, were protonated ethanol dimer \((\text{C}_2\text{H}_5\text{OH})_2\text{H}^+\) (93 amu), trimer \((\text{C}_2\text{H}_5\text{OH})_3\text{H}^+\), (139 amu) and monomer \((\text{C}_2\text{H}_5\text{OH})\text{H}^+\) (47 amu). Primary product ions were \((\text{C}_2\text{H}_5\text{OH})\text{NH}_4^+\) (64 amu), \( \text{NH}_4^+\) (18 amu) and \((\text{C}_2\text{H}_5\text{OH})_2\text{NH}_4^+\) (110 amu). Only the product ion signal at 64 amu was used for \([\text{NH}_3]\) calculations, since this was the most prominent ion peak (Figure 3.3) and gave the best sensitivity. To account for the possible variations in reagent ion signals which were caused by the fluctuation of pressure in the
ion-molecule reaction region (<10%), we also monitored these primary reagent ions and normalized them when calculating [NH₃]. Reaction rates of these proton transfer ion molecule reactions are very similar to each other, because these are collision limited reactions; this also simplifies normalization of these different reagent ion signals.

The CIMS sensitivity was determined by taking the difference in normalized product ion signals between the calibration and ambient mode, with the amount of the added calibration gases. For the same day, the sensitivity was nearly constant, although there were some day to day variations, likely due to pressure fluctuations in the ionization region. Although the sensitivity varied, this did not affect the ambient measurement results (Figure 3.6), as will be discussed in Section 3.3.3.

Mass scans (Figure 3.3) were performed every several hours to ensure the instrument was running properly. During the normal operation, eight ion peaks including the major reagent and product ions were measured over time. From these measurements, a sequence of the measured data was constructed, including the calibration, background and ambient measurement mode, as shown with ion signals vs. time (Figure 3.5a). With the use of the sensitivity and the measured background signals, plots could then be constructed as [NH₃] vs. time (Figures 3.6 and 3.7). Although the CIMS data were collected at 1 Hz, the median values of [NH₃] calculated over a minute were used for data analysis.
**Figure 3.3.** Typical mass spectra taken for the background (red), ambient (blue dotted), and ambient plus calibration mode (green dashed). The main reagent ion signals were $(\text{C}_2\text{H}_5\text{OH})\text{H}^+$ (47 amu), $(\text{C}_2\text{H}_5\text{OH})_2\text{H}^+$ (93 amu), and $(\text{C}_2\text{H}_5\text{OH})_3\text{H}^+$ (139 amu), and the main product ion signals were $\text{NH}_4^+$ (18 amu), $(\text{C}_2\text{H}_5\text{OH})\text{NH}_4^+$ (64 amu) and $(\text{C}_2\text{H}_5\text{OH})_3\text{NH}_4^+$ (110 amu). To calculate $[\text{NH}_3]$, we used the main product peak at 64 amu and normalized this with the sum of these three reagent ion signals. Larger clusters as well as weakly bound water clusters $\text{H}_2\text{O}(\text{C}_2\text{H}_5\text{OH})_n\text{H}^+$ may also exist, but the use of a collision dissociation chamber (CDC) effectively destroyed these weakly bounded larger ions; ion intensities for peaks at $>150$ amu were insignificant.
3.3 Evaluation of NH$_3$-CIMS

3.3.1 Time Response

The time response of the instrument was determined in the following manner. By measuring the signal decay from removal of a standard addition calibration, the data was fit by an exponential function and the time response was determined from the $1/e^2$ decay mark. For example, for the decay shown in Figure 3.4a (sensitivity of 25 Hz/pptv), the fit was:

$$\% \text{ Steady State } [\text{NH}_3] = 3 + 14e^{-0.018t} + 88e^{-0.524t} \quad (\text{Eq. 1})$$

The preexponential terms represent the percentages of the steady state calibration level and $t$ is the time in seconds after removal of the calibration gases. The time required for the signal to reach $1/e^2$ (13.5%) of the initial signal (before calibration termination) was less than 30 s. Another fitting was made for a different sensitivity (37 Hz/pptv, not shown). The pre-factors were within 12% between the different fittings (the first pre-factor was identical within standard deviation) and the second time constant was within 50% (the first was identical within standard deviation).

The instrument time response was also tested by using different calibration flow configurations: with only 1 sccm of the calibration gas, a mixture of 1 sccm of the calibration gas and an additional 50 sccm of N$_2$, and a mixture of 1 sccm of the calibration gas and an additional 100 sccm of N$_2$ (Figure 3.4b). As shown in Figure 3.4b, the signal rise was much faster with the additional N$_2$ flow. Without the additional N$_2$ gases, it took 5 minutes to reach the steady state, whereas with the additional flow of 100 sccm of N$_2$, the signal reached the steady state in less than a minute. The net increase in
the product ion signal taken with 400 pptv NH₃ calibration gases (added via a Pyrex flow tube; ΔHz ~ 10000 Hz) was also approximately half of that with 800 pptv NH₃ added directly to the CIMS inlet (Figure 3.4b) (ΔHz ~ 20000 Hz). Calibration gases were added directly to CIMS inlet for calibration measurements (C1 – C3 in Figure 3.4b) and also to our flow tube with the CIMS inlet attached (the flow tube was attached to the very beginning of the inlet) (C4 in Figure 3.4b). The response to this addition (C4) shows that there were negligible losses when compared with the other measurements (C1-C3), indicating the effects of the losses in the inlet before the PFA tee 1 on the derived [NH₃] were also minimal (Figure 3.2).
Figure 3.4. (a) Signal decay after removal of calibration. One data set was used to calculate the time response of the CIMS instrument. The data set was for a sensitivity of 24.5 Hz/pptv (maximum signal was 25,000 Hz). The black dotted line represents double exponential fits for the data set and the black solid horizontal line $1/e^2$ decay. (b) A measurement sequence, showing four different calibration measurements. Raw ion signals taken with a 1 s time resolution are shown here. (C$_2$H$_5$OH)$_2$H$^+$, 93 amu (brown); (C$_2$H$_5$OH)NH$_4^+$, 64 amu (light blue dashed). C1 indicates the calibration measurements made using only 1 sccm of 0.8 ppbv NH$_3$ calibration gases, C2 using 1 sccm of 0.8 ppbv NH$_3$ calibration gases and an additional 50 sccm of N$_2$, C3 using 1 sccm of 0.8 ppbv NH$_3$ and an additional 100 sccm of N$_2$, and C4 using 0.4 ppbv NH$_3$ and an additional 100 sccm of N$_2$ through the flow tube.
3.3.2 Background and Uncertainty

Figure 3.5a shows a typical measurement sequence including background, calibration and ambient measurements. Background measurements were performed for 5 minutes every 30 minutes and calibration was performed for 5 minutes every 3 hours. For example, for the case shown in this figure, the background mass spectra signals were ~7000 Hz and the ambient signals are ~9000 Hz. Since the instrument sensitivity was ~15 pptv/Hz for this specific measurement, we can estimate the background [NH₃] as \( \frac{7000 \text{ Hz}}{15 \text{ pptv/Hz}} \approx 0.46 \text{ ppbv} \) and the ambient [NH₃] as \( \frac{9000 \text{ Hz} - 7000 \text{ Hz}}{15 \text{ pptv/Hz}} \approx 0.13 \text{ ppbv} \). This example explains how the background NH₃ signals are taken into account for the calculation of ambient [NH₃].

Background measurements were performed for 5 minutes every 30 minutes (Figure 3.5a). The background [NH₃] values were determined with two methods. The first method uses the average [NH₃] value during a background period (Background 1), and the second method the minimum value (Background 2). The fall and winter data had the best correlation between the two methods, indicating low uncertainties of the signals within the same background period. For the spring data, there was a small difference (13%) between the two methods and this difference was due to a longer time response for background measurements to reach the steady state. In this study, we used Background 1. The estimated instrument background was usually < 1 ppbv and was ~ 300 pptv at lowest. The background [NH₃] varied with the ambient [NH₃] variation, but there were no clear RH and temperature dependences for the background [NH₃].
Uncertainties in the background [NH$_3$] were estimated by combining one standard deviation (1σ) of [NH$_3$] in each background period and the variation in [NH$_3$] between two consecutive background measurements$^{87}$. For the winter and fall measurements, uncertainties from these two sources together were very low (30 pptv); for the spring, the 1σ within the same background period was $\sim$ 100 pptv and the average difference between two consecutive backgrounds was $\sim$ 200 pptv. Since the fall measurements were made using a heated inlet system, these results show the importance of heating at constant temperature.
Figure 3.5. (a) A typical ambient measurement sequence including the ambient (A), background (B), and calibration mode (C) measurements. Raw ion signals taken with a 1 s time resolution are shown here. (b) A calibration curve for the CIMS instrument. The air going into the CIMS was from flow tube air (a mixture of nitrogen gas and water vapor with RH 12 %) and entered the CIMS at 5 slpm. The solid line indicates the linear fitting of the measurement data and the slope is the same as the sensitivity.

3.3.3 Sensitivity and Uncertainty

Figure 3.5b shows a calibration curve. Flows of 1–4 sccm of the 5 ppmv standard NH₃ gases were used to produce calibration concentrations of 1–4 ppbv, along with an additional 100 sccm of N₂ gases. These calibration gases were introduced into PFA tee 1
right before the CIMS (Figure 3.2). The air entering the CIMS (5.2 slpm) was from flow tube air (a mixture of nitrogen gas and water vapor with RH 12%). As the curve shows, the CIMS instrument shows a good linear response ($R^2 = 0.977$) when different amounts of NH$_3$ (1 – 4 ppbv) are added. For this set of calibration measurements, the sensitivity was 4.7 Hz/pptv.

Calibrations were usually made over 5 minutes every 3 hours. The instrument sensitivity was estimated from calibration measurements with two different methods. For Sensitivity 1, we used the rise between the initial calibration value and the final in a calibration period. Sensitivity 2 was taken by fitting the signal rise during the calibration period and using the maximum value from the fitting. These two methods usually produced similar values (within < 10%), signifying that the steady state in the calibration signal was readily achieved within 5 minutes. In this study, Sensitivity 2 was used. The measured instrument sensitivities varied from 4–25 Hz/pptv. At present, we don’t understand which factors affect the stability of sensitivity; but the accuracy was unaffected, because changes in sensitivity were measured and accounted for. For example, the calculated [NH$_3$] during the fall were always in the sub-ppbv level, regardless of the variation of sensitivity over time (Figure 3.6). No clear RH and temperature dependence was observed for the sensitivity.

The uncertainties associated with sensitivity measurements came from several sources, including uncertainties in the mass flow controllers and the NH$_3$ standard gases, as well as the variability in calibration signals. The uncertainty from the mass flow controllers (< 1%) and the NH$_3$ source cylinder (~ 5%) were much less than the
variability in calibration signals, which varied by season and was found highest for the fall (~30%). Thus, the overall uncertainty in the sensitivity was ~30%.

3.4 Ambient Measurements

Figure 3.6 shows the ambient measurements taken during an 8 day period for fall 2009, including the measured raw ion signals (64 amu, the main product ion; 93 amu, the main reagent ion), background, sensitivity, and the ambient [NH₃]. The reagent ion signals ranged between 600,000-700,000 Hz, depending on the pressure in the ion molecule reaction region. The product ion signals varied from 7,000-30,000 Hz, with the same trend as the reagent ion signals. The background and ambient [NH₃] during this time period was between 300–800 pptv and between 60–400 pptv, respectively. Again, the background [NH₃] varied with the same trend as the ambient [NH₃], similarly to¹⁸⁷, but was often higher than the ambient [NH₃].

The ambient measurements taken for the fall, spring and winter of 2009 are shown in Figure 3.7. Overall the median [NH₃] (±1σ) was 60±75 pptv for winter, 200±120 pptv for spring, and 150±80 pptv for fall. There was no distinctive diurnal variation for the ambient [NH₃], although there were some rapid hourly variations. There was also a positive dependence of the ambient [NH₃] on temperature for all seasons, especially for the winter and spring. The spring had the highest temperatures amongst all seasons studied, which may explain the slightly higher [NH₃] seen during this season. The RH dependence for the ambient [NH₃] was unclear: positive for the winter and negative for the spring and fall.
We have performed backward trajectory calculations using the NOAA HYSPLIT program\textsuperscript{63} and derived the wind direction and speed information from Weather Underground (www.wunderground.com), to see how the air mass history affected the local $[\text{NH}_3]$ level. Trajectories calculations were made for each hour. Our data analysis shows that air masses in Kent often originated from northwest in spring and fall and from west/northwest in winter. From the EPA $\text{NH}_3$ emission data in this region (http://www.epa.gov/cgibin/broker?_service=airdata&_program=progs.webprogs.emisdist.t.scl&_debug=2&geotype=st&geocode=OH&geoname=Ohio&empol=NH3&emyear=2002&emtype=&emtier=&emval=a&mapsize=zsc&reqtype=viewmap), although the latest data posted are only for 2002, one can expect that air masses traveling from northwest would contain higher $[\text{NH}_3]$. This could also explain why $[\text{NH}_3]$ were higher in spring and fall, but more current emission data are needed to address the transport effects on the local $[\text{NH}_3]$. 
Figure 3.6. Ambient measurements taken during the fall of 2009 over an 8 day span. Included are the main product (64 amu, blue dashed line) and reagent ion mass signals (93 amu, brown solid line), Background 1 (green crosses) and Sensitivity 2 (purple closed circles), and the ambient [NH₃] (red solid line).
Figure 3.7. The ambient $[\text{NH}_3]$ measured in Kent, Ohio, during the winter over an 8 day span (a), during the spring for 12 days (b), and during the fall for 6 days (c).

3.5 Discussion

There have been four different CIMS instruments used for NH$_3$ detection, reported in the literature$^{87, 97-99}$. Table 3.1 summarizes these NH$_3$-CIMS including the present study, with respect to the sampling inlet and CIMS configuration. While our CIMS was largely based on (Nowak et al., 2006, 2007)$^{87, 97}$, in comparison, our CIMS showed lower background signals than the (Nowak et al., 2006)’s$^{97}$ low pressure version and higher sensitivities than the (Nowak et al., 2007)$^{87}$ version.

When developing a proper inlet for ambient NH$_3$ measurements, there are several key technical issues including the inlet configuration, residence time, and heating.
Keeping a straight flow path from the inlet tip to the CIMS can reduce possible NH\textsubscript{3} losses on tubing surfaces at the curves. Our inlet configuration was not straight due to the commercial 3-way valve used in this study (Figure 3.2); we have recently built a custom made 3-way valve from PFA Teflon based on\textsuperscript{87,97,107} to allow ambient air to flow straight through to the CIMS. It is also important to keep the inlet short and have a high flow, so that the residence time inside the inlet is minimized. Heating the entire inlet system at a constant temperature is also important for the inlet, since this prevents temperature fluctuations, which may lead to adsorption/desorption of NH\textsubscript{3} on the inlet walls and affect the instrument background and stability\textsuperscript{87}. As long as the inlet temperature is above ambient temperature, adsorption (due to being close to the dew point) of NH\textsubscript{3} should not occur. Higher temperatures may be used, but temperatures that are too high could result in volatilization of NH\textsubscript{4}NO\textsubscript{3}. Inlet configurations can also affect signals, as condensation in the tubing can lead to NH\textsubscript{3} losses\textsuperscript{108}. The sampling line effects, such as RH and [NH\textsubscript{3}], can also play a role in background measurements\textsuperscript{95}, although in our case the background signals did not have a clear dependence on RH, but varied with the sampled NH\textsubscript{3} level.

The reagent ions used in these CIMS were protonated ethanol (CH\textsubscript{3}CH\textsubscript{2}OH\textbullet H\textsuperscript{+}), protonated acetone (both CH\textsubscript{3}COCH\textsubscript{3}\textbullet H\textsuperscript{+} and H\textsuperscript{+}(C\textsubscript{3}H\textsubscript{6}O)\textsubscript{2}, and positive oxygen (O\textsubscript{2}\textsuperscript{+}) (Table 3.1). The main difference amongst them was that in the first two cases, the product ions consisted of NH\textsubscript{4}\textsuperscript{+} and its protonated cluster ions (NH\textsubscript{3}(C\textsubscript{2}H\textsubscript{5}OH)\textsubscript{n}H\textsuperscript{+}, for example), whereas the third method employed electron transfer to produce NH\textsubscript{3}\textsuperscript{+}. One reason for choosing the O\textsubscript{2}\textsuperscript{+} method was that the use of O\textsubscript{2}\textsuperscript{+} can possibly limit the amount...
of background signals produced in the ion source region. For the NH₄⁺/proton cluster methods, the residence time was in the 20–160 ms range, whereas for the O₂⁺ method, a much shorter residence time (0.1 – 0.15 ms) was used to minimize the secondary reactions involving NH₃⁺. The sensitivity and background were also different between these two techniques. For the NH₄⁺/proton cluster method, the instrument sensitivity (1–40 Hz/pptv) and the background [NH₃] (up to 2 ppbv) both were higher than those in the electron transfer scheme (0.04 Hz/pptv sensitivity and up to 0.47 ppbv background). While the protonated ethanol ions (CH₃CH₂OH•H⁺) can give higher sensitivity, the protonated acetone ions (CH₃COCH₃•H⁺) can be less prone to NH₃ contamination.

In the present study, we have used the protonated ethanol and obtained moderate sensitivities as well as relatively low background signals. Most of these CIMS instruments utilized a low pressure (< 25 torr) in the reaction region (Table 3.1), although there are also advantages with atmospheric pressure chemical ionization which provides an enhanced sensitivity.

There were certain degrees of variations both in background signals and sensitivity in our CIMS. Background signals usually had the same trends as ambient NH₃ levels, indicating that there were some effects of adsorption and desorption of NH₃ on surfaces inside the inlet, but such effects were taken into account by using background measurements to effectively minimize such artifact effects. Sensitivity also varied day to day, but the measured [NH₃] levels did not vary over time as sensitivity did, indicating that the varying sensitivity indeed did not affect the ambient [NH₃] values. In the present study, we did not make intercomparison tests with other NH₃ instruments. The
intercomparison made during the summer of 2009 in the Michigan forest using our CIMS technique and a wet scrubbing method coupled with long-path absorbance photometry (employed by Dr. Xianliang Zhou from State University of New York - Albany) further showed that this CIMS technique provides reliable NH$_3$ measurements. For example, the [NH$_3$] measured over an 8 day period showed similar results with these two independent methods within experimental uncertainties. A detailed description of these intercomparison results is discussed in (Kanawade et al., in preparation).

The [NH$_3$] measured in Kent was usually below 1 ppbv for all seasons (Figure 3.7). By comparing with other studies cited here, Kent seems to fall into the range of a typical rural region, with regard to the ambient [NH$_3$] level. For example, [NH$_3$] in the remote marine atmosphere were 86 pptv on average$^{78}$ and as low as 20 pptv in some remote areas$^{77}$. Rural regions in the eastern United States have shown [NH$_3$] of 100 – 500 pptv$^{77}$ with a mean [NH$_3$] of 300 pptv (Langford et al., 1992). Global NH$_3$ emission data taken with infrared satellite observations show that [NH$_3$] in the eastern United States are low and no significant hotspots exist in this region$^{82}$. On the other hand, polluted areas have shown [NH$_3$] as high as 30 ppbv$^{77}$ and [NH$_3$] up to 430 ppbv have been seen in strong point source locations$^{78}$. Emission measurements made in different automobile tunnels have shown [NH$_3$] of 50 – 400 ppbv$^{79-81}$. [NH$_3$] of 20 – 70 ppbv have also been reported from smoke$^{110, 111}$, as well as 100-200 ppbv in biomass burning plumes$^{83, 112, 113}$.

A possible reason for the low levels of NH$_3$ is uptake by sulfuric acid aerosols. If high acidity of aerosols was present, this would act as a condensational sink for NH$_3$. A
precursor for sulfuric acid is SO₂. One study¹¹⁴ made during the ICARTT experiments, showed that when flying over the Cleveland area SO₂ emitted from power plant plumes was as high as 70 ppbv and that the ammonium-to-sulfate ratio indicated insufficient amounts of NH₃ present so the high levels of sulfuric acid present would not be neutralized. SO₂ emissions in Ohio generally ranks amongst the top in the nation (http://www.epa.gov/air/sulfurdioxide/) because of the strong SO₂ emission from large size coal-burning power plants in this region (http://www.epa.gov/cgi-bin/broker?_service=airdata&_program=progs.webprogs.emisumry.scl&_debug=2&geotype=st&geocode=OH&geoname=Ohio&epolmin=.&epolmax=.&epol=SO2&sic=&nyr=2002&geofeat=&mapsize=zsc&reqtype=getmap); typically, the reported [SO₂] were nearly at the ppbv or tens of ppbv range all year in Akron and Cleveland in recent years. Data taken from the Ozone Monitoring Instrument on the NASA EOS Aura platform¹¹⁵ showed the average [SO₂] (±1σ) as 0.7 ± 1.3 Dobson units (DU; 1 DU ≈ 1 ppbv) for the winter, 0.3 ± 0.13 DU for the spring, and 0.5 ± 0.52 DU for the fall in the planetary boundary layer in Kent, Ohio. These values were anti-correlated with the median [NH₃] (±1σ) values (60±75 pptv for winter, 200±120 pptv for spring, and 150±80 pptv for fall), showing that when [SO₂] is higher [NH₃] is lower. This could be explained by removal of NH₃ through uptake by acidic aerosols (typically sulfuric acid in this region) via neutralization.

NH₃ has been used to theoretically explain new particle formation in the eastern U. S.⁷¹-⁷⁴. But these nucleation theories include the [NH₃] range only between 0 – 100 pptv in their parameterizations²,¹⁸. Our atmospheric observations, together with other
studies discussed above, suggest that these theories should be revised to include the proper range of [NH₃] to represent all atmospheric conditions. As discussed in⁶⁹, we also have made ternary homogenous nucleation simulations using²'s H₂SO₄-NH₃-H₂O ternary homogenous nucleation parameterizations and using the measured H₂SO₄ and [NH₃] taken in Kent, but the model could not reproduce the atmospherically measured nucleation rates. These results suggest that these nucleation parameterizations need to be constrained by observations.
Table 3.1. A summary of NH$_3$-CIMS instruments found in the literature, with regard to sampling inlet and CIMS detection conditions. Included here are the configuration of the 3-way valve used to switch between the ambient and calibration mode; temperature, flow rate, total length and inner diameter of the sampling inlet; residence time for ambient measurements through the inlet; pressure and residence time in the CIMS flow tube reactor; the reagent ion used for analysis; sensitivity, background, and time response of the CIMS instrument.

<table>
<thead>
<tr>
<th>Reference</th>
<th>3-way valve Configuration$^g$</th>
<th>Inlet Temperature (°C)</th>
<th>Inlet Flow Rate (slpm)</th>
<th>Inlet Length (cm)</th>
<th>Inlet I.D. (cm)</th>
<th>Inlet Residence Time (ms)$^j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nowak et al., (2006)$^a$</td>
<td>Straight</td>
<td>50</td>
<td>4</td>
<td>45</td>
<td>0.4, 0.64</td>
<td>200</td>
</tr>
<tr>
<td>Nowak et al., (2006)$^b$</td>
<td>Straight</td>
<td>40</td>
<td>13.6</td>
<td>40</td>
<td>0.65</td>
<td>50</td>
</tr>
<tr>
<td>Nowak et al., (2007)$^c$</td>
<td>Straight</td>
<td>30</td>
<td>8</td>
<td>55</td>
<td>0.4, 0.8</td>
<td>190</td>
</tr>
<tr>
<td>Norman et al., NA (2007)$^d$</td>
<td>NA</td>
<td>NA</td>
<td>15</td>
<td>1700</td>
<td>1.27</td>
<td>NA</td>
</tr>
<tr>
<td>von Bobrutzki et al., NA (2010)$^e$</td>
<td>NA</td>
<td>40</td>
<td>19.5</td>
<td>10</td>
<td>0.95</td>
<td>NA</td>
</tr>
<tr>
<td>This study$^f$</td>
<td>Bent</td>
<td>35$^h$</td>
<td>5.2 – 15</td>
<td>100$^i$</td>
<td>0.4</td>
<td>68$^k$</td>
</tr>
</tbody>
</table>
Table 3.1. Continued.

<table>
<thead>
<tr>
<th>Reference</th>
<th>CIMS Flow Tube Pressure (torr)</th>
<th>CIMS Flow Tube Residence Time (ms)</th>
<th>Reagent</th>
<th>Sensitivity (Hz/pptv)</th>
<th>Background (ppbv)</th>
<th>CIMS Time Response to Calibration Gases (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nowak et al., 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2006)(^a)</td>
<td>NA</td>
<td>20</td>
<td>CH(_3)CH(_2)OH(\cdot)H(^+)</td>
<td>40</td>
<td>0.1 – 1</td>
<td>10</td>
</tr>
<tr>
<td>Nowak et al., 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2006)(^b)</td>
<td>20</td>
<td>20</td>
<td>CH(_3)CH(_2)OH(\cdot)H(^+)</td>
<td>40</td>
<td>1 – 2</td>
<td>45</td>
</tr>
<tr>
<td>Nowak et al., 18 – 22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2007)(^c)</td>
<td>95 – 160</td>
<td>0.100 – 0.15</td>
<td>O(_2)(^+)</td>
<td>0.04</td>
<td>0.07 – 0.47</td>
<td>30</td>
</tr>
<tr>
<td>Norman et al., 1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2007)(^d)</td>
<td>NA</td>
<td>0.100 – 0.15</td>
<td>O(_2)(^+)</td>
<td>0.04</td>
<td>0.07 – 0.47</td>
<td>30</td>
</tr>
<tr>
<td>Von Bobrutzki et</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>al., (2010)(^e)</td>
<td>NA</td>
<td>NA</td>
<td>H(^+)(C(_3)H(_6)O(_2))</td>
<td>2.5</td>
<td>0.045</td>
<td>NA</td>
</tr>
<tr>
<td>This Study(^f)</td>
<td>20 – 25</td>
<td>25 – 40</td>
<td>CH(_3)CH(_2)OH(\cdot)H(^+)</td>
<td>4 – 25</td>
<td>0.3 – 1</td>
<td>40</td>
</tr>
</tbody>
</table>
This early version of NOAA-CIMS was used in Atlanta, GA during August 2002 for the Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE). Measurements were performed at an urban site 2 meters above the ground level.

The Georgia Tech-CIMS was also used for the ANARChE and intercomparison with the early version of NOAA-CIMS was made.

This upgraded NOAA-CIMS for aircraft measurements was used in the New England Air Quality Study–Intercontinental Transport and Chemical Transformation (NEAQS-ITCT) mission.

The CIMS instrument was used at 1.2 meters above a grass field treated with fertilizer in Oensingen, Switzerland.

This CIMS instrument was used in an intensively managed grassland area in southern Scotland during the intercomparison experiments with a large number of NH₃ instruments.

The KSU-CIMS was used in ambient NH₃ measurements in Kent, Ohio (this study) and in Northern Michigan forests (Kanawade et al., in preparation).

Straight sampling occurred when the flow path from the tip of the inlet (where ambient air enters) through the 3-way valve and to the CIMS was all straight and no bending occurred. Bent sampling occurred when the ambient air enters the 3-way valve perpendicular to the flow that went into the CIMS as shown in Figure 1b.

Heating was only performed for the fall measurements.

100 cm was the total length when taking ambient measurements (including the depth of the wall, 50 cm).
This time was estimated based on the flow rate through the inlet and the inlet tubing dimensions (inner diameter and length).

Residence time for the ambient measurement mode.

This time was estimated based on the flow rate through the CIMS flow tube and the CIMS inlet dimensions (inner diameter and length).

3.6 Conclusion

The instrumental performance of our new NH$_3$-CIMS has been characterized. The CIMS sensitivity ranged from 4 – 25 Hz/pptv with an uncertainty of 30% for > 1 MHz reagent ion signals. The background [NH$_3$] was in the range from 0.3–1 ppbv with an uncertainty of 30 pptv under optimized measurement conditions. The detection limit of the instrument was estimated to be about 60 pptv (1 minute integration time and 3 sigma deviation) and the instrument time response was < 30 s. This new NH$_3$-CIMS has been used for ambient observations in Kent, Ohio during several weeks crossing three seasons. [NH$_3$] was higher during the spring (200±120 pptv) than in winter (60±75 pptv) and fall (150±80 pptv). It should be noted that some degree of bias may also exist due to variations of the inlet setup from season to season so cautions should be taken when looking at seasonal variations. While the CIMS demonstrated sensitivity sufficient for ambient measurements, there is large room for improvement. For example, the inlet residence time can be further reduced by shortening the tubing length. The heating system can also be improved to help minimize temperature fluctuations in the inlet
CHAPTER 4

Preliminary Experiments: Binary Homogenous Nucleation (BHN) from Sulfuric Acid – Water

In this section, laboratory studies of the binary H$_2$SO$_4$/H$_2$O system at the residual [H$_2$SO$_4$] (measured by CIMS at the end of the nucleation reactor) ranging from $4 \times 10^6$ – $3 \times 10^9$ cm$^{-3}$ and RH from 10 – 55 % are presented. H$_2$SO$_4$ vapor was produced *in-situ* by gas phase reactions of SO$_2$, OH, O$_2$ and H$_2$O as occurring in the atmosphere and similarly to Berndt et al. [2005, 2006]$^{22}$. Wall loss factors (WLFs) of H$_2$SO$_4$ were calculated by assuming that wall loss is diffusion limited (supplement material). We report the laboratory-measured aerosol sizes, growth rates, $J$, and threshold [H$_2$SO$_4$] (corrected by WLF), and compare them with previous laboratory studies and atmospheric measurements.

4.1 Overview

Atmospheric observations show that nucleation takes place in a wide range of atmospheric conditions at the typical [H$_2$SO$_4$] of $10^6$ - $10^7$ cm$^{-3}$ [Kulmala et al., 2004, and references therein]$^{117}$. Aerosol nucleation has been studied intensively by modeling simulations [Vekhamaki, 2002; Yu, 2006; Lucas and Akimoto, 2006]$^1.72,118$, but these calculations contain high uncertainties, because they are not fully tested by experiments. The H$_2$SO$_4$-H$_2$O binary homogenous nucleation (BHN) system is the most important
atmospheric nucleation system, but there are only a limited number of experimental studies on this system [Wyslouzil et al., 1991a; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005, 2006]^{17-19, 22, 116, 119}, because of the technical difficulties associated with laboratory nucleation studies including difficulties of measuring low [H\(_2\)SO\(_4\)] at atmospherically relevant conditions and wall loss of H\(_2\)SO\(_4\). These previous H\(_2\)SO\(_4\)-H\(_2\)O nucleation studies were made at [H\(_2\)SO\(_4\)] from 10\(^6\) - 10\(^{11}\) cm\(^{-3}\), RH from 1 - 60% and room temperature, and showed nucleation rates (J) ranging from 10\(^{-3}\) – 10\(^5\) cm\(^{-3}\)s\(^{-1}\) [Wyslouzil et al., 1991a; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005, 2006]^{17-19, 22, 116, 119}. Most of these studies have also used vaporized H\(_2\)SO\(_4\) gases from H\(_2\)SO\(_4\) liquid samples at the residual [H\(_2\)SO\(_4\)] ≥ 10\(^9\) cm\(^{-3}\) [Wyslouzil et al., 1991a; Ball et al., 1999; Zhang et al., 2004]^{18, 19, 119}, and these studies could not reproduce the atmospherically observed J under atmospherically relevant conditions. Berndt et al. [2005, 2006]^{22, 116} used the SO\(_2\) + OH → HSO\(_3\) reaction (R1) to produce H\(_2\)SO\(_4\) and for the first time, produced a unit nucleation rate (1 cm\(^{-3}\)s\(^{-1}\)) at atmospherically relevant conditions (e.g., 6 × 10\(^7\) cm\(^{-3}\)). However, in Berndt et al. [2005, 2006]^{22,116}, [H\(_2\)SO\(_4\)] was not directly measured and instead was calculated from OH titration reactions by introducing various hydrocarbon compounds in a system that also contains high concentrations of O\(_3\), H\(_2\)O, OH, and UV light (in such a condition, highly oxidized low volatility organic compounds can also be produced).

Wall loss of H\(_2\)SO\(_4\) is one of the major challenges in nucleation experiments. Most previous studies [Wyslouzil et al., 1991a; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005, 2006]^{17-19, 22, 116, 119} have provided the residual
[H₂SO₄] measured or estimated at the end of the nucleation reactor, whereas some have also calculated the initial [H₂SO₄] based on their conditions [Wyslouzil et al., 1991a; Viisanen et al., 1997; Ball et al., 1999]¹⁷, ¹⁸, ¹¹⁹. Viisanen et al. (1997)¹⁷ and Ball et al. (1999)¹⁸ have characterized the wall loss. Laboratory studies of H₂SO₄-H₂O BHN have often investigated how J depends on [H₂SO₄] and RH [Wyslouzil et al., 1991a; Viisanen et al., 1997; Ball et al., 1999]¹⁷, ¹⁸, ¹¹⁹, since such information can be directly used for testing theoretical models. While nucleation rate dependence on [H₂SO₄] has been investigated previously [Wyslouzil et al., 1991a; Viisanen et al., 1997; Ball et al., 1999; Berndt et al., 2006]¹⁷, ¹⁸, ¹¹⁶, ¹¹⁹, the J dependence on RH is not well established [Wyslouzil et al., 1991a; Ball et al., 1999]¹⁸, ¹¹⁹. Also, it is important to understand how these newly formed particles grow to become cloud condensation nuclei, but aerosol growth rates have not been measured in laboratory studies.

4.2 Experimental Setup

Our H₂SO₄-H₂O BHN kinetics experimental setup consists of four main components: (i) an OH generator with water vapor UV absorption, (ii) a fast flow reactor in which nucleation occurs, (iii) a CIMS which measures equilibrium vapor [H₂SO₄], and (iv) a TSI scanning mobility particle sizer (SMPS) (TSI 3936N76) (Figure 4.1). The water photolysis region is made of a Purasil quartz tube where OH radicals form from water UV absorption (wavelengths < 185 nm) with a mercury lamp (Pen-Ray Model 11SC-1) housed in a temperature-controlled box. The photon flux emitted from the lamp is stabilized with a constant N₂ flow and is measured with a CsI phototube (Hamamatsu Model R5764), which is calibrated against a NIST-certified Si photodiode (40599S).
When $[\text{SO}_2] \gg [\text{OH}]$, all OH radicals are rapidly converted to $\text{H}_2\text{SO}_4$ and the produced $[\text{H}_2\text{SO}_4]$ are the same as $[\text{OH}]$.

**Figure 4.1** The Kent State University experimental setup for $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ binary homogenous nucleation kinetics. This setup consists of an OH generator, a fast-flow nucleation reactor, an atmospheric pressure chemical ionization mass spectrometer (CIMS), a nanoparticle differential mobility analyzer (nano-DMA) and a water condensation particle counter (WCPC).

The actual nucleation region ($L=82 \text{ cm, ID}=5.08 \text{ cm}$) is encompassed in a jacketed region through which a circulating bath is run to maintain a constant temperature. Only high purity standard gases (oxygen and SO₂) (Linde Gas and Airgas Inc.), nitrogen gases blown off from a liquid nitrogen tank, and the water vapor evaporated from deionized water are introduced in the nucleation region to reduce possible ammonia impurities. Ammonia contamination from liquid nitrogen gases is minimal ($< 20 \text{ pptv}$) [Nowak et al., 2007]. We have used the silicon phosphates ammonia scrubber (Perma Pure Inc.) to test the effects of possible ammonia impurities in
our system on the H$_2$SO$_4$-H$_2$O BHN experiments, and those effects were found negligible. The nucleation reactor’s pressure is also kept slightly higher than the air pressure to prevent a leak of the indoor air into the nucleation system.

The SMPS is composed of an ultrafine water-based condensation particle counter (CPC) (TSI Model 3786) and a nano-particle differential mobility analyzer (DMA) (TSI Model 308500) and measures aerosol sizes and concentrations in the diameter range from 3 to 102 nm. We assume that nucleation takes place in the entire region of the flow tube. The measured particle sizes and number concentrations increased with increasing nucleation time and these results confirm that this assumption is correct. Our results are however different from Ball et al. (1999)$^{18}$ where nucleation takes place only in a portion of their nucleation reactor and this difference is probably related to the different methods used to produce H$_2$SO$_4$ vapor in these two studies.

The CIMS uses the NO$_3^-$ + H$_2$SO$_4$ → HSO$_4^-$ + HNO$_3$ ion molecule reaction scheme to detect H$_2$SO$_4$ based on Eisele and Tanner [1993]$^{100}$. The detection limit of our CIMS is as low as $1 \times 10^5$ cm$^{-3}$ at the atmospheric pressure. [H$_2$SO$_4$] was measured at the end of the nucleation reactor and hence is the equilibrium or residual concentration rather than the initial aerosol precursor concentration. Wall loss factors (WLFs) of H$_2$SO$_4$ are estimated by assuming that wall loss of H$_2$SO$_4$ is diffusion-limited based on Hanson and Eisele (2000)$^{120}$ (supplement material). Table 4.1 shows the detailed experimental conditions used in this study and the calculated WLFs. Figure 4.2 shows the time evolution of the aerosol precursors in the nucleation reactor as a function of time.
Table 4.1. Experimental conditions used in the present study and the wall loss factors (WLFs) calculated by assuming that wall loss is diffusion-limited. All experiments were made at the absolute temperature of 288 K, total flow of 1.3 - 5.0 l min\(^{-1}\), and at atmospheric pressure. The initial \([H_2SO_4]\) were estimated from the WLFs, the CIMS-measured \([H_2SO_4]\) and the measured \([H_2SO_4]\) in the particle phase (Figure 4.2).

<table>
<thead>
<tr>
<th>Data Used</th>
<th>Particle Measurement Mode</th>
<th>RH, %</th>
<th>Initial [SO(_2)] (x10^{13}) cm(^{-3})</th>
<th>([H_2SO_4]_0) Calculated From WLF(^{b}) (x10^{1\text{b}}) cm(^{-3})</th>
<th>CIMS-Measured ([H_2SO_4]) (x10^{1\text{c}}) cm(^{-3})</th>
<th>([H_2SO_4])-Particle(^{b}) (x10^{1\text{d}}) cm(^{-3})</th>
<th>J(^{b}) cm(^{-3}) s(^{-1})</th>
<th>WLF(^{b})</th>
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<tr>
<td>Figure 1a</td>
<td>CPC</td>
<td>20</td>
<td>11-14</td>
<td>4.8-12</td>
<td>12.9-32.4</td>
<td>4.6-12.5</td>
<td>0.025-0.41</td>
<td>0.33-0.54</td>
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<td>Figure 1a</td>
<td>CPC</td>
<td>54</td>
<td>22</td>
<td>1.6-13</td>
<td>3.86</td>
<td>0.32</td>
<td>3.1</td>
<td>15.31</td>
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<td>Figures 1a and 2</td>
<td>SMPS/CPC(^{e})</td>
<td>38</td>
<td>22-30</td>
<td>4.5-23</td>
<td>22.6-38.7</td>
<td>3.9-4.83</td>
<td>94.6-1800</td>
<td>270-2900</td>
</tr>
<tr>
<td>Figures 1a and 2</td>
<td>SMPS/CPC(^{e})</td>
<td>66 or 60</td>
<td>26-38</td>
<td>12-40</td>
<td>1.6-54.1</td>
<td>0.058-0.078</td>
<td>5.6-80.4(^{d})</td>
<td>38-4500</td>
</tr>
<tr>
<td>Figure 1b</td>
<td>CPC</td>
<td>77</td>
<td>25-55</td>
<td>0.07-.84</td>
<td>6.0-21.6</td>
<td>0.2-0.7</td>
<td>1.2-46.26</td>
<td>2.2-81</td>
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<tr>
<td>Figure 3</td>
<td>SMPS/CPC(^{e})</td>
<td>33</td>
<td>28-57</td>
<td>1.7-6.7</td>
<td>33.9-54.8</td>
<td>7.6-11.0</td>
<td>450-3080</td>
<td>970-3940</td>
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<tr>
<td>Figure 3</td>
<td>SMPS/CPC(^{e})</td>
<td>50</td>
<td>16-55</td>
<td>2.5-10</td>
<td>46.0-360</td>
<td>0.4-0.6</td>
<td>4500-38600(^{d})</td>
<td>4700-19000</td>
</tr>
</tbody>
</table>

\(^{b}\)For these parameters, the ranges are the median value ranges
\(^{c}\)Note, some data were taken by the CPC alone and some by the SMPS; the measured particle number concentrations were up to at least a factor of 10 higher with the CPC mode than with the SMPS mode under the same experimental conditions

\(^{d}\)In these cases, \([H_2SO_4]\) in the particle phases were larger than those measured by the CIMS and therefore, when estimating \([H_2SO_4]_0\), \([H_2SO_4]\) in the particle phase becomes important
Concentration of molecules

Time in the Reactor

Figure 4.2. Simulation of the aerosol precursor concentrations as a function of reaction time for the nucleation time of 54 s. WLFs are calculated by assuming that wall loss is diffusion-limited. $[\text{H}_2\text{SO}_4]_p$, $[\text{H}_2\text{SO}_4]_{\text{cims}}$, $[\text{H}_2\text{SO}_4]_w$, and $[\text{H}_2\text{SO}_4]_0$ indicate the $[\text{H}_2\text{SO}_4]$ in the particle-phase, that measured by CIMS, that taken by the wall, and the initial concentrations in the nucleation reactor, respectively. $[\text{H}_2\text{SO}_4]_p$ is calculated from the measured aerosol sizes and number concentrations. $[\text{H}_2\text{SO}_4]_0 = \text{WLF} \times ([\text{H}_2\text{SO}_4]_{\text{cims}} + [\text{H}_2\text{SO}_4]_p)$. $[\text{H}_2\text{SO}_4]_w = (\text{WLF} - 1) \times ([\text{H}_2\text{SO}_4]_{\text{cims}} + [\text{H}_2\text{SO}_4]_p)$. For most of the experimental conditions, $[\text{H}_2\text{SO}_4]_{\text{cims}} \gg [\text{H}_2\text{SO}_4]_p$. 86% of the OH radicals generated from water UV photolysis remain after the $\text{CO} + \text{OH} (+ \text{O}_2) \rightarrow \text{CO}_2 + \text{HO}_2$ reaction for 100 ppbv $[\text{CO}]$ impurities (originating from the nitrogen gases blown from liquid nitrogen) and a reaction time of 1 s (representing the distance of 9 cm from the photolysis region to the point where $\text{SO}_2$ and $\text{O}_2$ are introduced; i.d. = 5.08 cm). Thus, the produced
\([\text{OH}] = [\text{H}_2\text{SO}_4]_0 / 0.86\). Total flow is 2.5 l min\(^{-1}\) at the typical condition. Nitrogen gages introduced to produce water vapor at the uppermost stream are the main flow in the system and hence the further dilution by \(\text{SO}_2\) and \(\text{O}_2\) gases is negligible. The \(\text{OH}\) photolysis time is 0.24 s. The reaction time of \(\text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3\) is very short (< 1 ms at [\(\text{SO}_2\) (ppmv) >> 1000 × [OH]). Nucleation starts from the time when \(\text{H}_2\text{SO}_4\) is formed. Note that the times and concentrations shown in here represent the true values, but they are shown not at the actual scales.

4.3 Results

Figure 4.3 shows the measured \(J\) as a function of [\(\text{H}_2\text{SO}_4\)] at different RH and nucleation times. Overall, \(J\) varied from \(10^{-1} - 10^4\) cm\(^{-3}\) s\(^{-1}\), at nucleation times from 20 - 66 s, RH from 11 - 38% and with residual [\(\text{H}_2\text{SO}_4\)] (measured by CIMS) from \(4 \times 10^6 - 3 \times 10^9\) cm\(^{-3}\). The CIMS-measured [\(\text{H}_2\text{SO}_4\)] that is needed to produce the unit \(J\) ranged from \(10^7 - 10^8\) cm\(^{-3}\), and when wall loss is taken into account, the threshold [\(\text{H}_2\text{SO}_4\)] ranged from \(10^8 - 10^9\) cm\(^{-3}\). The numbers of \(\text{H}_2\text{SO}_4\) molecules in the critical clusters, \(n_{\text{H}_2\text{SO}_4}\), were derived from the slopes of curves for \(J\) vs [\(\text{H}_2\text{SO}_4\)] based on Kashchiev [1982]\(^{121}\). The derived \(n_{\text{H}_2\text{SO}_4}\) ranged from 2 - 10 with larger values as RH decreases, a trend consistent with other studies [Ball et al., 1999; Zhang et al., 2004; Berndt et al., 2005, 2006]\(^{18,19,22,116}\). At the CIMS-measured [\(\text{H}_2\text{SO}_4\)] from \(1 \times 10^7 - 1 \times 10^8\) cm\(^{-3}\) (the corresponding [\(\text{H}_2\text{SO}_4\)] in the nucleation reactor from \(3 \times 10^8 - 5 \times 10^9\) cm\(^{-3}\) with wall loss taken into account) (Table 4.1), RH of 22 - 55% and a nucleation time of 77 s, the number of water molecules in the critical clusters (\(n_{\text{H}_2\text{O}}\)) ranged from 11 – 15 (Figure 4.4). These \(n_{\text{H}_2\text{O}}\) values also decreased with increasing [\(\text{H}_2\text{SO}_4\)], consistent with the
predictions from the homogenous nucleation theories. The $n_{H_2O}$ values calculated from this study are higher than Ball et al. [1999] (\(n_{H_2O} = 4 - 6\)) and Wyslouzil et al. [1991] (\(n_{H_2O} = 9\)), likely because of lower [H$_2$SO$_4$] used in this study.

The measured aerosol sizes ($D_p$) were between 3 - 10 nm at the CIMS-measured [H$_2$SO$_4$] from $2 \times 10^8 - 5 \times 10^8$ cm$^{-3}$ (corresponding to [H$_2$SO$_4$] in the nucleation region from $1.3 \times 10^9 - 1.3 \times 10^{10}$ cm$^{-3}$ with a WLF of 8), RH from 22 – 30% and a nucleation time of 38 seconds (Figure 4.5). The $D_p$ increased with increasing [H$_2$SO$_4$], RH and nucleation time. At larger aerosol number concentrations and at larger $D_p$, condensation loss of H$_2$SO$_4$ became noticeable. For example, the CIMS-measured [H$_2$SO$_4$] were lower for largest aerosol sizes than those for smaller sizes (Figures 4.5 and 4.6). We also found that the measured $D_p$ was linearly proportional to log RH, showing a weak RH dependence of aerosol growth (Figure 4.7). However the slopes of $D_p$ vs log RH curves were steeper at higher [H$_2$SO$_4$], indicating that the RH effects on the aerosol growth are more pronounced at higher [H$_2$SO$_4$] conditions.
Figure 4.3. The laboratory-measured nucleation rates $J$ as a function of $[\text{H}_2\text{SO}_4]$. The $[\text{H}_2\text{SO}_4]$ shown here with symbols are those measured by CIMS; horizontal bars show the calculated WLF values for each experimental condition. NT indicates the nucleation time. The solid lines represent linear fitting for log $J$ vs log $\text{H}_2\text{SO}_4$ curves. Also included are experimental results from Ball et al. [1999] (black dashed) and Zhang et al. [2004] (black dot) for similar temperature and RH conditions. For both these cited data, CIMS-measured $[\text{H}_2\text{SO}_4]$ are shown without wall loss corrections; WLF of 22 was provided by Ball et al. (1999), and no WLF was provided in Zhang et al. (2004). Not shown here are the Berndt et al. [2005 and 2006] data because the $[\text{H}_2\text{SO}_4]$ is much lower ($10^6 \text{ - } 10^7 \text{ cm}^{-3}$).
but their value for $n_{H_2SO_4}$ is also 5. The experimental conditions and WLFs for the data sets used in this figure are shown in Table 1 (the same for other figures).

Figure 4.4. The laboratory-measured $J$ as a function of RH. The $[H_2SO_4]$ shown here are the CIMS-measured $[H_2SO_4]$; for a nucleation time (NT) of 77 s, WLF is 29.9 (Table 1). The initial $[SO_2]$ are also shown here. The lines represent linear fitting for log $J$ vs log RH curves.
Figure 4.5. The measured aerosol size distributions at 288 K, 38 s nucleation time and RH of (a) 22%, (b) 26%, and (c) 30% under different CIMS-measured $[\text{H}_2\text{SO}_4]$ conditions (along with the initial $[\text{SO}_2]$). WLF = 8 (Table 1). These datasets are also used in Figure 4.3. At the largest aerosol size (6 - 8 nm) at 26% and 30% RH, the CIMS-measured $[\text{H}_2\text{SO}_4]$ was lower than that with the next smaller size particles, even though the SO$_2$ flow is higher in the case of largest size particles; this is because of the H$_2$SO$_4$
condensation loss at larger particles and with higher particle concentrations (see also Figure 4.6).

**Figure 4.6.** The CIMS-measured $[\text{H}_2\text{SO}_4]$ as a function of the particle number concentration for the same dataset shown in Figure 4.5 (for experimental conditions, see Table 1). At larger particle concentrations (50,000 cm$^{-3}$), the CIMS-measured $[\text{H}_2\text{SO}_4]$ start to level off and eventually decrease at very high concentrations (200,000 cm$^{-3}$), even though the initial [SO$_2$] and the CIMS-measured [H$_2$SO$_4$] are increasing, because of the H$_2$SO$_4$ condensation losses for high particle concentrations.
Figure 4.7. The measures aerosol sizes ($D_p$) as a function of RH for different [$\text{H}_2\text{SO}_4$] and nucleation times (NT). The [$\text{H}_2\text{SO}_4$] shown here are the CIMS-measured [$\text{H}_2\text{SO}_4$]. For NT of 33 s, WLF is 4; for NT of 50 s, WLF is 9 (Table 1). $G_{RH}$ values indicate the slopes of linear fitting for $D_p$ vs log RH curves. The initial [$\text{SO}_2$] are also shown here.

4.4 Discussion

An evident trend found from the present study is that $n_{\text{H}_2\text{SO}_4}$ decreases with increasing RH and $n_{\text{H}_2\text{O}}$ decreases with increasing [$\text{H}_2\text{SO}_4$] (Figure 4.3 and 4.4), consistent with classical nucleation theories [Seinfeld and Pandis, 2006] and with the trend found in previous laboratory works [Wyslouzil et al., 1991; Viisanen et al., 1997;
Ball et al., 1999; Berndt et al., 2006\textsuperscript{17, 18, 116, 119}. One objective of this kind of kinetic study is to provide experimental data to compare with nucleation predictions to test the theories. Recently, Yu [2007]\textsuperscript{123} provided the improved quasi-unary nucleation modeling calculation of H$_2$SO$_4$-H$_2$O BHN. The model predicted $n_{H2SO4}$ ranged from 5 - 12 at [H$_2$SO$_4$] of $1 \times 10^{11}$ cm$^{-3}$, 30 \% RH, and 298 K [Yu, 2007]\textsuperscript{123}, consistent with those found in the present and other laboratory studies [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Berndt et al., 2006]\textsuperscript{17, 18, 116, 119} which showed $n_{H2SO4}$ values of 2 – 10 overall.

The measured $D_p$ was linearly proportional to log RH (Figure 4.7), showing a weak RH dependence. However, those RH effects were more pronounced at higher [H$_2$SO$_4$], indicating that RH is more important for aerosol growth in a polluted atmosphere, an important atmospheric implication. The measured aerosol size $D_p$ increased with increasing [H$_2$SO$_4$], RH and nucleation time (Figure 4.5 and 4.7). From the $D_p$ dependence on [H$_2$SO$_4$], RH and nucleation time, one can expect that aerosol growth rates must also be dependent on the above factors in a similar fashion and our results confirmed this trend. The growth rates estimated in our study from the aerosol growth from different nucleation times are roughly from 160 - 490 nm hr$^{-1}$. The growth rates increased with increasing [H$_2$SO$_4$], consistent with atmospheric observations [Kulmala et al., 2004]\textsuperscript{117} which showed a positive correlation between the growth rate and non-volatile vapor concentration. Our growth rates are however much higher than those found in the atmosphere (usually between 1 - 20 nm hr$^{-1}$) [Kulmala et al., 2004]\textsuperscript{117};
this is because of the higher [H$_2$SO$_4$] range used in this study than the atmospheric conditions.

There has been a debate on the threshold [H$_2$SO$_4$] required to produce the unit $J$. Atmospheric observations often show that unit nucleation rates can be achieved even at [H$_2$SO$_4$] of 10$^6$ cm$^{-3}$ [Weber et al., 1999; Birmili et al., 2000]$^{16,14}$, whereas BHN theories cannot reproduce the unit $J$ at this low [H$_2$SO$_4$] [Kulmala et al., 1998; Vehkamäki et al. 2002]$^{1,125}$. Our study shows that the threshold [H$_2$SO$_4$] is on the order of 10$^8$ – 10$^9$ cm$^{-3}$ (with wall loss taken into account) (Figure 4.3). This threshold is lower than those found in the liquid H$_2$SO$_4$ sample experiments [Ball et al., 1999; Zhang et al., 2004]$^{18,19}$ (Figure 4.3), but is still higher than those in Berndt et al. [2005, 2006]$^{22,116}$ which also used R1 to produce H$_2$SO$_4$ and higher than the atmospheric conditions. Furthermore, the laboratory-produced $J$ are usually proportional to [H$_2$SO$_4$] with the second to thirtieth powers [Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Berndt et al., 2005, 2006; Benson et al., 2008]$^{17,18,22,103,116,119}$, whereas the atmospherically-observed $J$ are often linearly proportional to [H$_2$SO$_4$] [e.g., McMurry and Eisele, 2005]$^{126}$. These higher threshold of [H$_2$SO$_4$] and the larger number of H$_2$SO$_4$ in the critical clusters observed in the laboratory BHN studies compared to those measured in the atmosphere suggest that ternary species other than sulfuric acid and water can be important for atmospheric aerosol nucleation and growth.
CHAPTER 5

Laboratory-Measured H$_2$SO$_4$-H$_2$O-NH$_3$ Ternary Homogenous Nucleation Rates:

Initial Observations

In this section data is presented from laboratory observations of NH$_3$-THN rates as a function of aerosol precursor concentrations (NH$_3$, H$_2$SO$_4$ and RH), using a similar approach by simultaneously measuring nucleation precursors. The numbers of H$_2$SO$_4$, NH$_3$, and H$_2$O molecules in the critical clusters are also derived from these observations. Nucleation enhancement factors ($EF$) induced by NH$_3$ are investigated, by comparing with BHN rates measured under similar experimental conditions. The present study provides a direct comparison with our previous binary studies$^{101,103}$.

5.1 Overview

Nucleation is a gas-to-particle conversion process$^{122}$ and is a source of new aerosol particles. These newly formed particles have a high potential to grow to cloud condensation nuclei and hence have an important impact on the regional and global climate. The current nucleation parameterizations are hampered by high uncertainties because they are not vigorously tested by experiments. Recent aerosol modeling$^{72}$ and field studies$^{44,71}$ show that ammonia (NH$_3$) can be important for aerosol nucleation on the
global and regional scale. Chemical analysis of atmospheric aerosols also demonstrates that these newly formed particles often contain ammonium sulfate, along with various oxygenated organic compounds. While sulfuric acid-water-ammonia (H$_2$SO$_4$-H$_2$O-NH$_3$) ternary homogenous nucleation (THN) is considered as the most important ternary nucleation system in the atmosphere, there is a large “hole” in the literature of laboratory studies for this NH$_3$-ternary nucleation system.

There are also large discrepancies amongst model predicted, laboratory measured, and atmospherically observed nucleation rates of the NH$_3$-ternary system. The classical binary homogenous nucleation (BHN) theories predict much lower nucleation rates compared to atmospheric observations. Inclusion of NH$_3$ can enhance nucleation rates, but the THN theories with NH$_3$ also often over-predict the nucleation rates (e.g., even over ten orders of magnitude higher than those from BHN), with some exceptions. On the other hand, laboratory measured THN rates are only one to three orders of magnitude higher than the BHN rates. Whereas the laboratory studies show that THN rates increase with RH, the THN theories predict that nucleation rates are independent of RH or even anti-correlated with RH. Density functional calculations also give contradictory predictions on whether or not NH$_3$ can stabilize small clusters of H$_2$SO$_4$ and H$_2$O molecules. While THN can enhance nucleation rates, aerosol modeling studies show that the amount of NH$_3$ included in the THN calculations are not sufficient to explain atmospheric observations and other condensable organic species are also required in THN calculations. In fact, THN parameterizations include NH$_3$ only in the range from 0-100 pptv and for NH$_3$ higher than 100 pptv, the NH$_3$ effects in the THN.
models become “saturated”\(^2\). However, atmospheric \([\text{NH}_3]\) in the troposphere are typically at the sub-ppbv or ppbv level\(^87\). There are high uncertainties on exactly how much \(\text{NH}_3\) is needed to effectively enhance BHN rates; this is in part because \([\text{NH}_3]\) have not been directly measured in laboratory experiments\(^{18, 19, 29}\).

5.2 Experimental

The experimental setup used to study THN with \(\text{NH}_3\) is shown in Figure 5.1. This setup is based on the previous experimental design used for \(\text{H}_2\text{SO}_4-\text{H}_2\text{O}\) BHN studies in our lab\(^{101, 103}\), with the addition of a second CIMS to measure \([\text{NH}_3]\). The system consists of five main regions: (i) a photolysis region where \(\text{OH}\) radicals are produced from the photodissociation of \(\text{H}_2\text{O}\) vapor using a UV lamp \((\lambda < 185\ \text{nm})\), (ii) a mixing region, where \(\text{SO}_2\), \(\text{O}_2\) and \(\text{NH}_3\) gases are introduced and where \(\text{H}_2\text{SO}_4\) vapor forms from the \(\text{SO}_2 + \text{OH}\) reaction, (iii) a temperature-regulated nucleation region (fast flow reactor), (iv) an \(\text{H}_2\text{O}\)-based ultrafine condensation particle counter (UW CPC, TSI 3786) as well as a butanol-based ultrafine condensation particle counter (UCPC, TSI 3776), and (v) two chemical ionization mass spectrometers (CIMSs) to simultaneously measure pre-nucleation \([\text{H}_2\text{SO}_4]\) and \([\text{NH}_3]\). Figure 5.2 also shows the detailed configuration and dimension of the flow reactor with regard to production of aerosol precursors (OH and \(\text{H}_2\text{SO}_4\)) and mixing. Experimental conditions used in this study are summarized in Table 5.1, in detail.
Figure 5.1. A schematic diagram showing the experimental setup used for the THN experiments of H$_2$SO$_4$-H$_2$O-NH$_3$. Figure 5.2 shows a detailed configuration of the photolysis and mixing region.
We produce $\text{H}_2\text{SO}_4$ vapor from the $\text{SO}_2 + \text{OH} \rightarrow \text{HSO}_3$ reaction, as it occurs in the atmosphere and similarly to previous nucleation studies\textsuperscript{22, 101, 103}. $\text{OH}$ is produced from water UV absorption and the typical $[\text{OH}]$ are in the $10^9$-$10^{10}$ cm$^{-3}$ range\textsuperscript{101}. This $\text{H}_2\text{SO}_4$-CIMS has been described elsewhere\textsuperscript{100, 101, 103}. Briefly, to detect $\text{H}_2\text{SO}_4$, $\text{NO}_3^-$ ions are used as reagents. Our current CIMS detection limit for $\text{H}_2\text{SO}_4$ ranges from $2 \times 10^5$ – $6 \times 10^5$ cm$^{-3}$. In the present study, we provide the initial $[\text{H}_2\text{SO}_4]$ measured by CIMS at the beginning of the nucleation reactor, as opposed to the residual $[\text{H}_2\text{SO}_4]$ at the end of the nucleation reactor we previously reported\textsuperscript{101, 103}; wall loss factors are described below in this section.

The $\text{NH}_3$-CIMS is based on (Nowak et a., 2007)\textsuperscript{87}. This $\text{NH}_3$-CIMS instrument is identical to the $\text{H}_2\text{SO}_4$-CIMS mentioned above, except with a different ion-molecule reaction in a low pressure ionization region (~ 20 Torr). Protonated clusters of ethanol are used as ion reagents for $\text{NH}_3$ detection\textsuperscript{87}. Whereas the $\text{H}_2\text{SO}_4$-CIMS detection limit depends on the CIMS sensitivity, the $\text{NH}_3$-CIMS detection limit ultimately depends on its background signals, which are extremely sensitive to the sampled $[\text{NH}_3]$. Air from the nucleation reactor is brought in through one of two ports. One port is used for measurements of $\text{NH}_3$ from the nucleation reactor while the second port is used to deliver air through an $\text{NH}_3$ scrubber (Perma Pure Inc.) containing phosphoric acid that removes $\text{NH}_3$ from the sampled air to determine the instrumental background. A three way valve is actuated pneumatically to rotate and switch the sampled airflow between the two ports. We use an $\text{NH}_3$ standard gas, after dilution with pure nitrogen blown from liquid nitrogen (these nitrogen gases contain much lower impurity of $\text{NH}_3$ than the
Figure 5.2. A detailed configuration of the photolysis and mixing regions with dimensions indicated. Main flow of the system is nitrogen gases used in water bath in the upstream of the reactor, which is around 10 liters per minute.

bottled standard nitrogen gases), to calibrate \([\text{NH}_3]\). For ambient \text{NH}_3 measurements, our CIMS background signals typically range from 0.5-1 ppbv and the sensitivity of \text{NH}_3 detection is approximately 3 Hz/pptv; under these conditions, we can measure \text{NH}_3 down to 50 pptv from ambient air. For the flow tube studies, the background \text{NH}_3 signals
(likely generated from deionized water) range from 0 – 1.3 ppbv for RH ranging from 0 - 50 %. NH₃ effects on nucleation are significant only after [NH₃] > 4 ppbv.

We have previously characterized the nucleation zone with a simple nucleation model based on the measured H₂SO₄ and aerosol size distributions¹⁰¹; these simulations show that nucleation takes place in the first half of the nucleation reactor. Nucleation rates shown here have taken into account the nucleation zone as well as particle stability, as shown in¹⁰¹. That is, the reported nucleation rates in the present study are 2.5 times lower than the ratios of particle number concentrations over the residences time in the nucleation reactor. We also have determined the wall loss of H₂SO₄ using numerical calculations from H₂SO₄ diffusion coefficients¹²⁰ and also by measuring the initial and residual H₂SO₄ with two CIMSs simultaneously¹⁰¹. Wall loss factor of H₂SO₄ is about 1.7, under the typical experimental conditions used in this study. NH₃ wall loss is considered to be negligible compared to H₂SO₄, based on our atmospheric observations of NH₃ and H₂SO₄ with CIMSs.

**Table 5.1.** Summary of the experimental conditions and results. Initial [H₂SO₄] and [NH₃] are measured at the beginning of nucleation reactor by two CIMSs simultaneously. Particle numbers are measured with butanol- or water-CPC at the end of the nucleation reactor. EF, enhancement factor by NH₃ in the nucleation reactor, is the ratio of nucleation or NH₃-THN over that of BHN under the same experimental conditions. 

$n_{H2SO4}$, $n_{H2O}$, $n_{NH3}$ are numbers of H₂SO₄, H₂O, and NH₃ molecules in critical clusters.
derived from Figure 5.3; shown here are the values for THN studies. Total flow rate is 10 liters per minute (corresponding to residence time of 10 s).

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<th>Initial [NH$_3$] (ppb)</th>
<th>Particle number (10$^3$ cm$^{-3}$)</th>
<th>$J$ (cm$^{-3}$ s$^{-1}$)</th>
<th>EF</th>
<th>$n_{H_2SO_4}$</th>
<th>$n_{H_2O}$</th>
<th>$n_{NH_3}$</th>
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<td>1.5–6.3</td>
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<td>0.002–79.8</td>
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<td>6–7.8</td>
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<td>10–54</td>
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<td>0.02–14,020</td>
<td>1.4–994</td>
<td>4–7.8</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

### 5.3 Results

The measured nucleation rates, $J$, as a function of aerosol precursor concentrations ([H$_2$SO$_4$] and RH) in the absence or presence of NH$_3$ are shown in Figures 5.3. The total flow in the reactor is maintained at 10 liters per minute corresponding to residence time of 10 seconds. $J$ values range from $2 \times 10^{-2} – 1.4 \times 10^4$ cm$^{-3}$ s$^{-1}$ depending on RH (4–42%) and the initial [H$_2$SO$_4$] (in the 10$^8$ – 10$^9$ cm$^{-3}$ range), with higher $J$ values in the presence of NH$_3$ than in the absence of NH$_3$.

For the binary system, the numbers of H$_2$SO$_4$ molecules in the critical clusters ($n_{H_2SO_4}$) are obtained from slopes of linear fits of Log $J$ vs. Log [H$_2$SO$_4$], based on$^{121, 132}$;
Figure 5.3 The measured nucleation rates for H$_2$SO$_4$-H$_2$O-NH$_3$ THN at 288K as a function of (a) the initial [H$_2$SO$_4$], and (b) RH. The initial [NH$_3$] = 20 ppbv (4.6×10$^{10}$ cm$^{-3}$) for the THN experiments shown; the measured nucleation rates for H$_2$SO$_4$-H$_2$O BHN are also included in (a) and (b) in comparison with the THN results. Background
$[\text{NH}_3] < 0.1 \text{ ppbv}$ in the nucleation reactor with low RH, and NH$_3$ effects on nucleation are significant only after $[\text{NH}_3] > 1 \text{ ppbv}$ under the typical experimental conditions used. Solid lines are fits to the experimental data. Detailed experimental conditions are shown in Table 5.1.

$n_{\text{H}_2\text{SO}_4}$ range from 9 – 10, increasing as RH decreases. The numbers of H$_2$O molecules in the critical clusters ($n_{\text{H}_2\text{O}}$), obtained in a similar manner, range from 6 – 15. These results are consistent with our previous BHN studies$^{101, 103}$. For the THN results shown in Figures 5.3a and 5.3b, 20 ppb of $[\text{NH}_3]$ is used to result in a significant increase in particle number concentration, compared to the binary system.

Similarly to the BHN case, in the NH$_3$-THN case, the $n_{\text{H}_2\text{SO}_4}$ values (6-8) are smaller at higher RH and $n_{\text{H}_2\text{O}}$ (4-10) are also smaller at higher [SO$_2$] (and therefore higher [H$_2$SO$_4$]). In the presence of NH$_3$, however, both $n_{\text{H}_2\text{SO}_4}$ and $n_{\text{H}_2\text{O}}$ become smaller than in the case without NH$_3$, indicating that NH$_3$ indeed reduces nucleation barriers for H$_2$SO$_4$ and H$_2$O. This trend is consistent with the (Ball et al., 1999)$^{18}$ and (Kim et al., 1998)$^{29}$ studies. The numbers of NH$_3$ molecules in the critical clusters ($n_{\text{NH}_3}$) are also estimated to be about 0 – 2, with values increasing as RH or [H$_2$SO$_4$] decreases.

Enhancement factor (EF) is defined as the ratios of the measured CPC particle number concentration in NH$_3$-THN vs. that in BHN under similar experimental conditions. Figure 5.4 shows the measured EF values as a function of H$_2$SO$_4$ and RH. EF ranges from 2-1000 depending on the RH (4-33%) and [H$_2$SO$_4$] (in the $10^8$ – $10^9$ cm$^{-3}$ range). The solid lines in Figures 5.4a and 5.4b represent an exponential fit to the EF
Figure 5.4. Measured enhancement factors (EF) of nucleation by NH$_3$ in THN as compared to BHN as a function of (a) initial [H$_2$SO$_4$] and (b) RH. For the THN studies (5.4a and 5.4b), [NH$_3$] = 20 ppbv. Detailed experimental conditions are shown in Table 1.
values and this shows that $EF$ increases exponentially with decreasing RH and $[\text{H}_2\text{SO}_4]$. Laboratory observations by (Ball et al., 1999)$^{18}$ and (Kim et al., 1998)$^{29}$ and THN parameterizations by (Napari et al., 2002)$^{35}$ have also indicated higher enhancement factors at lower RH and lower $[\text{H}_2\text{SO}_4]$. The measured $EF$ values also increase linearly with $[\text{NH}_3]$ (not shown).

5.4 Discussions and Conclusion

The main conclusion of our laboratory observations is that $\text{H}_2\text{SO}_4$ plays important roles in atmospheric nucleation even in the presence of $\text{NH}_3$. Our observations also show that $\text{NH}_3$ enhances nucleation rates of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ exponentially as a function of $\text{H}_2\text{SO}_4$ and RH, at the initial $[\text{H}_2\text{SO}_4]$ $10^8 - 10^9$ cm$^{-3}$ range and RH from 4 – 42% and for $[\text{NH}_3]$ at the ppbv or tenth ppbv level. Under these experimental conditions, $EF$ reaches up to $\sim$1,000 at lower $[\text{H}_2\text{SO}_4]$ and RH; but no significant $\text{NH}_3$ effects are observed in our experiments for $[\text{NH}_3] < 4$ ppbv. This result is different from (Ball et al., 1999)$^{18}$ who have made $\text{NH}_3$-THN laboratory observations at 295 K and $[\text{H}_2\text{SO}_4]$ in the $10^{10} - 10^{11}$ cm$^{-3}$ range and RH 5% and 15%. Their observations showed $\text{NH}_3$ enhancement of nucleation rate up to 3 orders of magnitude for even a low $[\text{NH}_3]$ of 0.08 ppbv and 0.17 ppbv. There are three main differences in the experimental methods used in our study and in (Ball et al., 1999)$^{18}$. First, we produce $\text{H}_2\text{SO}_4$ vapor from the $\text{SO}_2 + \text{OH}$ reaction, whereas (Ball et al., 1999)$^{18}$ have used liquid $\text{H}_2\text{SO}_4$ solutions. Also, the nucleation zone $[\text{H}_2\text{SO}_4]$ was about $10^{10}$ to $10^{11}$ cm$^{-3}$ in the Ball et al. study, which is 2 to 3 orders of magnitude higher than the initial $[\text{H}_2\text{SO}_4]$ measured in this study. In addition, we
measure [NH₃] directly with CIMS, whereas the (Ball et al., 1999)¹⁸ study did not measure NH₃ and noted large uncertainties in estimation of NH₃. It is unclear at present, however, what causes this difference in the minimum [NH₃] needed to have the NH₃ ternary effect (EF > 1) between these two studies. On the other hand, new particle formation from NH₃/SO₂/H₂O/air mixture by ionizing irradiation showed that with [SO₂] and [NH₃] at the ppmv level, a moderate EF (2-4) of nucleation rate was seen in the presence of NH₃²⁹, more similarly to our results, although the precursor concentrations used in (Kim et al., 1998)²⁹ were much higher than ours in general.

Another important finding of our observations is that THN rates are a sensitive function of RH and this result has an important atmospheric implication, as nucleation events have been often seen under high RH conditions with some exceptions¹⁶. Our observations show that n_H₂SO₄ and n_H₂O values in THN (and BHN) are smaller at higher RH and higher H₂SO₄, as expected from nucleation theories. However, these THN parameterizations also often show that n_H₂O is close to zero²,³⁵,¹³³ (that is, THN rates are insensitive to RH); this is inconsistent with our experiments where n_H₂O ranges from 4-10, indicating THN rates are sensitive to RH. In addition, our studies show that EF is also highly dependent on RH (and [H₂SO₄]).

Although our observations show that n_H₂SO₄ and n_H₂O are reduced in the presence of NH₃, the n_H₂SO₄ (6-8) values in THN measured from our laboratory studies are still much larger than 1-2, reported from the most of atmospheric observations¹¹⁷. Our observations are also different from molecular cluster studies with CIMS by (Hanson and Eisele, 2002)¹²⁹, which showed that THN critical clusters contain only two H₂SO₄ (and
one NH₃ molecule). Further experiments are needed to fully investigate these differences.

One of the purposes of laboratory studies is to provide experimental data to test and constrain nucleation theories. Our laboratory-measured EF values are not as significant as those reported from previous THN parameterizations which showed significant EF (up to ten orders of magnitude) in NH₃-THN than in BHN; it is noted that [NH₃] used in these models also ranged from 0-100 pptv, much lower than those used in our experiments (ppbv). Later parameterizations by (Antilla et al., 2005) and (Merikanto et al., 2007) have reduced this huge EF for [NH₃] from 0-1,000 pptv, by including formation of ammonium bisulfate clusters. And, these newer THN parameterizations showed that in order to produce a nucleation rate of 1 cm⁻³ s⁻¹ for an [H₂SO₄] of less than 10⁹ cm⁻³, RH of 50%, and temperature of 288 K the required [NH₃] is at least 1 ppbv.

The H₂SO₄-H₂O-NH₃ THN is one of the most important atmospheric nucleation systems, but laboratory observations on this system are critically lacking at present. Our studies provide an important initial understanding of atmospheric ternary nucleation involving NH₃ from the experimental viewpoint, by providing nucleation rates together with constrained aerosol precursor concentrations. But many important aerosol nucleation questions remain, including EF by NH₃ at lower [H₂SO₄] (e.g., 10⁵-10⁷ cm⁻³) and temperature effects on NH₃-THN. Also, it is still open if NH₃ can explain atmospheric nucleation and what is the role of NH₃ with regard to organic compounds for
aerosol nucleation\textsuperscript{127}. Future studies are required to experimentally examine these critical atmospheric science questions.
CHAPTER 6

Laboratory-Measured Binary and Ternary Homogenous Nucleation Rates involving
\( \text{H}_2\text{SO}_4-\text{H}_2\text{O}-\text{NH}_3 \) at Atmospherically Relevant Conditions

This section presents laboratory studies of homogenous nucleation involving, \( \text{H}_2\text{SO}_4 \), \( \text{NH}_3 \), and \( \text{H}_2\text{O} \). Particles are produced at the atmospherically relevant [\( \text{H}_2\text{SO}_4 \)] (\( 10^6-10^7 \text{ cm}^{-3} \)), RH of 6 – 40 %, temperature of 288 K and \( \text{NH}_3 \) of 0.08 – 2.6 ppbv (except only one occasion where 20 ppbv \( \text{NH}_3 \) was used) in a temperature- and RH-controlled fast flow nucleation reactor. Experiments were made with chemical ionization mass spectrometers (CIMS) and CPC (TSI 3786); these instruments have been widely used in field measurements\(^{69,117} \). Our \( \text{H}_2\text{SO}_4 \) source was also a local source generated only at the beginning of the nucleation reactor as used in previous studies\(^{101,134} \), but the nucleation reactor had a larger diameter to substantially reduce the wall loss of aerosol precursors and residence times (60 – 240 s) were longer than previously (5 – 77 s). We also employed two CIMSs to simultaneously measure the initial and residual [\( \text{H}_2\text{SO}_4 \)] in the nucleation reactor\(^{101} \), in order to provide well-constrained aerosol precursor concentrations that are responsible for aerosol nucleation, as nucleation is a non-linear process and extremely sensitive to [\( \text{H}_2\text{SO}_4 \)]\(^{54} \).
6.1 Overview

Aerosol nucleation is an important step in the chain reactions that lead to cloud formation but the nucleation processes are poorly understood. There are also large discrepancies amongst laboratory studies, field observations and theoretical predictions. These discrepancies include the different values of the threshold of H$_2$SO$_4$ needed to produce the unit nucleation rate ($J = 1 \text{ cm}^{-3}\text{ s}^{-1}$) and the slope of $J$ vs. H$_2$SO$_4$, measured from field and laboratory observations. Field studies show the threshold is $10^6 \text{ cm}^{-3}$ and the slope is between 1 and 2$^{117}$. On the other hand, previous laboratory studies of the binary nucleation show the threshold is between $10^6$-$10^{10} \text{ cm}^{-3}$ and the slope is between 2 – 20$^{18, 22, 101, 119, 134}$. Atmospheric observations$^{69, 70, 117}$ and laboratory studies$^{22, 24, 101, 116, 134}$ have shown that sulfuric acid (H$_2$SO$_4$) is the main nucleation precursor, but the role of other ternary species such as ammonia (NH$_3$) and organic compounds is unclear.

A recent study$^{135}$ reproduced atmospherically observed nucleation threshold of $10^6 \text{ cm}^{-3}$ and the slope of $J$ vs. H$_2$SO$_4$ of 2, from laboratory studies of H$_2$SO$_4$-H$_2$O BHN. By comparing with previous laboratory observations$^{18, 22, 101, 119, 134}$, they concluded that this new finding is due to the following factors: (a) a new, unique particle counter, particle counter 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) (measures down to 3 nm) used in atmospheric observations$^{117}$ and previous laboratory studies (the main reason), (b) a longer residence time (~ 60 – 240 s), and (c) a continuous source of H$_2$SO$_4$ production in the entire nucleation reactor, as opposed to a local source used some studies$^{101, 134}$. Compared to (Berndt et al., 2005)$^{22}$, however,
(Sipila et al., 2010) also used the very similar experimental approach, with the only difference in the type of particle counters used. So this raises an important question: is it possible to reproduce atmospheric observations in the laboratory using exactly the same instruments used in field studies to detect particles?

Chemical composition analysis of nanometer size particles made at various locations has shown these newly formed particles contain sulfate, ammonium and various organic compounds including amines. Global atmospheric aerosol model calculations also suggested that in a wide range of the troposphere and the lower stratosphere, nucleation rates can be predicted by the ternary homogenous nucleation (THN) of $\text{H}_2\text{SO}_4$, $\text{NH}_3$, and $\text{H}_2\text{O}$. Especially in the Eastern U.S., new particle formation has been explained by THN for many years. The above mentioned modeling predictions were based on (Napari et al., 2002)'s THN parameterization, which also over-predicts nucleation rates of THN over binary homogenous nucleation (BHN) of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$. This THN parameterization includes the $\text{NH}_3$ range from 0 – 100 pptv and for $\text{NH}_3$ greater than 100 pptv, it assumes that there is no effect on the nucleation rate except for $\text{H}_2\text{SO}_4$ less than $10^6$ cm$^{-3}$, while atmospherically observed $\text{NH}_3$ are typically at the sub-ppbv and ppbv level. Later THN parameterizations included the effects of stable ammonium bisulfate ($\text{NH}_4\text{HSO}_4$) formation to match the available laboratory THN observations in the $\text{NH}_3$ range from 0 – 170 pptv.

At present, the exact amount of $\text{NH}_3$ needed to enhance nucleation rates over BHN and the magnitude of enhancement in nucleation due to $\text{NH}_3$ are both uncertain, mostly because there are only a very limited number of laboratory studies of $\text{NH}_3$-THN
To produce particles, these experiments also used $H_2SO_4 > 10^8 \text{ cm}^{-3}$, two to three orders of magnitude higher than typical atmospheric concentrations. These limited observations have shown that at such high $[H_2SO_4]$, $[NH_3]$ of ppbv or sub-ppbv can increase nucleation rates up to 3 orders of magnitude, although often the enhancement factors (EF; defined as the ratio of nucleation rates in THN vs. in BHN) due to $NH_3$ are around one order of magnitude.

6.2 Experimental

Our nucleation experimental setup was described in detail in previous studies$^{101,134,138}$. Briefly, the system consists of five main sections: (i) a photolysis region where OH radicals are produced from the photodissociation of $H_2O$ vapor with a UV lamp ($\lambda < 185 \text{ nm}$), (ii) a mixing region where the trace gases ($SO_2$, $O_2$, and $N_2$) are introduced into the flow tube and where $H_2SO_4$ is also produced from the $SO_2 + OH \rightarrow HSO_3$ reaction (R1, $2.0 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$) at a local source (as opposed to continuously form in the nucleation reactor), (iii) a double jacket, fast flow nucleation reactor (RH- and temperature-controlled), (iv) two chemical ionization mass spectrometers (CIMSs) to measure $H_2SO_4$ and $NH_3$ at the beginning of the nucleation reactor, and (v) a CPC (TSI 3786), which is connected to the end of the nucleation reactor, to measure particle number concentrations for $> 3 \text{ nm}$ particles.

The main characteristic of our setup is the design allows us to perform measurements at very clean, well-controlled experimental conditions. $H_2SO_4$ was always
measured for all experiments. We have also measured radical [OH] simultaneously with H$_2$SO$_4$\textsuperscript{101, 134}; OH measurements can be used as a calibration tool for [H$_2$SO$_4$] and the measured OH and H$_2$SO$_4$ were in the same order. To minimize impurity contaminations from the room air, the pressure of the nucleation reactor is slightly higher than atmospheric pressure to prevent NH$_3$ and organic compounds from entering the system. To minimize adsorption and desorption of NH$_3$, the entire mixing region was built exclusively by fluorinated ethylene propylene (FEP) or perfluoroalkoxy (PFA) Teflon, without any metal materials, since NH$_3$ can adsorb on metal material most effectively\textsuperscript{87}. We also used nitrogen gases vaporized from liquid nitrogen, which has the lowest level of NH$_3$ impurities, < 20 pptv\textsuperscript{87}. The impurity NH$_3$ gases in the system, mostly likely originated from deionized water, were also systematically determined with an NH$_3$-CIMS\textsuperscript{138, 139}; under our typical experimental conditions, these impurities are approximately 95 pptv on average.

There are also several improvements in the current nucleation setup (Figure 6.1). We have designed a new nucleation reactor with larger size diameters (13 cm now vs. 2.54 or 5.08 cm previously) based on another study\textsuperscript{140} to significantly reduce wall loss factors (WLF) of H$_2$SO$_4$ (1.5 – 4 now vs. 2 – 360 previously), by using large size inner diameters and by introducing trace species from the center of the flow reactor under high flow. [H$_2$SO$_4$] are changed by changing OH with an iris beam splitter to control the UV beam; previously, H$_2$SO$_4$ was changed by changing SO$_2$\textsuperscript{101, 103, 134, 138}. In addition, RH values are changed by adding water vapor at the downstream end after the production of
$\text{H}_2\text{SO}_4$, to allow independent changes in RH in the nucleation reactor and [OH] (thus $[\text{H}_2\text{SO}_4]$).

**Figure 6.1.** New flow reactor used in KSU aerosol nucleation setup. This new design allows for significantly less wall of H$_2$SO$_4$ in the nucleation reactor.

The initial H$_2$SO$_4$ measured by CIMS ranged from $10^6$-$10^7$ cm$^{-3}$, within the actual atmospheric conditions$^{69}$ and also one or three orders of magnitude lower than our previous experimental conditions$^{101, 134, 138}$. H$_2$SO$_4$ vapor was produced as a local source as before. The H$_2$SO$_4$ was changed by changing the OH level, which was changed by the UV light intensities (Figure 6.1); a moveable iris beam splitter was placed between the box containing the UV lamp and the flow tube in which photolysis took place. Also, RH values in the nucleation reactor were changed by changing water vapor which was additionally introduced after H$_2$SO$_4$ production (Figure 6.1); this also allows for independent changes in OH and RH. This approach provides an advantage over previous
experiments where [OH] were also changed with the changing RH values, since there was only one water tank at the upstream of the experimental setup\textsuperscript{101, 134, 138}.

The detection scheme for the H\textsubscript{2}SO\textsubscript{4} -CIMS is based on NO\textsubscript{3}\textsuperscript{-} + H\textsubscript{2}SO\textsubscript{4} → HNO\textsubscript{3} + HSO\textsubscript{4}\textsuperscript{-} \textsubscript{(R2, 2.3×10\textsuperscript{-9} cm\textsuperscript{3}s\textsuperscript{-1})} at atmospheric pressure\textsuperscript{69, 100, 101, 134, 138}. NH\textsubscript{3} is detected in another CIMS using protonated ethanol ions as reagent based on NH\textsubscript{3} + CH\textsubscript{3}CH\textsubscript{2}OH\textsuperscript{•H\textsuperscript{+}} → NH\textsubscript{4}\textsuperscript{+} + CH\textsubscript{3}CH\textsubscript{2}OH \textsubscript{(R3, 2.0×10\textsuperscript{-9} cm\textsuperscript{3}s\textsuperscript{-1})} at a lower pressure (20 torr)\textsuperscript{69, 97, 101, 134, 138, 139}. One issue that must be taken into account in the nucleation experiments is the amount of NH\textsubscript{3} that comes from the flow tube system, which was most likely originated from water vapor\textsuperscript{97}. This background NH\textsubscript{3}, measured with CIMS, increased linearly with RH in the flow tube, but for RH from 6 – 40 %, the NH\textsubscript{3} from water vapor in the flow tube was \textasciitilde20 – 100 pptv.

6.3 Results

Figure 6.2 shows changes in the measured H\textsubscript{2}SO\textsubscript{4} and nucleation rates when SO\textsubscript{2} and UV were introduced. Initially, without SO\textsubscript{2} and UV, there were no measurable signals in H\textsubscript{2}SO\textsubscript{4} and particle concentrations. When only SO\textsubscript{2} (2.25 ppm) was introduced, there were some low but still recognizable H\textsubscript{2}SO\textsubscript{4} and particle concentrations, likely due to dark H\textsubscript{2}SO\textsubscript{4} formation on wet surfaces on the flow tubes via heterogeneous oxidation processes\textsuperscript{101}. But rapid increases in H\textsubscript{2}SO\textsubscript{4} \textsubscript{(2.4 × 10\textsuperscript{7} cm\textsuperscript{-3})} and particles \textsubscript{(J \approx 500 cm\textsuperscript{3})} appeared, when UV was introduced. The time difference between H\textsubscript{2}SO\textsubscript{4} and particles were approximately 5 minutes, suggesting a growth rate of 1nm minute\textsuperscript{-1}. Similar orders of rapid growth rates, with respect to low [H\textsubscript{2}SO\textsubscript{4}] \textsubscript{(10\textsuperscript{7} cm\textsuperscript{3})}, were also seen in other H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O BHN flow tube experiments\textsuperscript{22, 116}. 
Figure 6.2. The measured nucleation rates and \([\text{H}_2\text{SO}_4]\) when \(\text{SO}_2\) and UV were introduced to the reactor. The residence time was 190 sec, total flow 11.1 lpm, RH at the end of the flow tube 22%, and \(\text{SO}_2\) flow 0.25 lpm (corresponding to 2.25 ppm – after diluting).

The wall loss factors (WLFs) were found to be dependent on the initial \(\text{H}_2\text{SO}_4\) and increased with increasing the initial \(\text{H}_2\text{SO}_4\) (Figure 6.3); these wall losses measured by two CIMS located at the beginning and end of the nucleation reactor and these two CIMS measurements are consistent within <3% differences (Figure 6.4). Therefore, it is possible that the slopes of \(\log J\) vs. \(\log [\text{H}_2\text{SO}_4]\) may actually represent the lower limit and the true slopes can be even higher, if nucleation and wall loss are competitive processes; often only a small fraction of \(\text{H}_2\text{SO}_4\) participate in nucleation\textsuperscript{101, 103}, compare
to those lost on the wall. Therefore, our low wall loss factors also indicate that even though the H$_2$SO$_4$ source is a local source, this fact does not make a difference for nucleation rates compared to continuous H$_2$SO$_4$ sources.

**Figure 6.3** The measured wall loss factor (WLF) with two CIMSs located at the beginning (initial H$_2$SO$_4$) and end of the nucleation reactor (residual H$_2$SO$_4$) as a function of initial [H$_2$SO$_4$]. WLF is defined as the ratio of initial H$_2$SO$_4$ over residual H$_2$SO$_4$. WLF is the ratio of initial to residual [H$_2$SO$_4$]. RH = 20%. Total flows of 7 (squares), 10.5 (circles) and 14 lpm (triangles) correspond to residence time of 135, 85, and 59 s.
Figure 6.4. [H$_2$SO$_4$] measured by two CIMS at the beginning of the nucleation reactor. RH = 14%, total flow was 7.1 (rectangles) and 8.3 lpm (circles). Dashed line is 1:1 line. Average difference between the CIMS was < 3%.

Figure 6.5 shows the measured Log J vs. Log [H$_2$SO$_4$], for the initial [H$_2$SO$_4$] at different RH (9%, 13% and 16%) and residence times (60, 133, and 240 s). $J$ varied from $3 \times 10^{-3} - 2 \times 10^2$ cm$^{-3}$ s$^{-1}$ for the initial [H$_2$SO$_4$] from $2 \times 10^6 - 2 \times 10^7$ cm$^{-3}$ and RH from 6 – 16%. The slope of Log J vs. Log [H$_2$SO$_4$] was 4 – 6 for most of time. In Figure 6.5 also included is data from$^{135}$ which utilized the newly developed, unique CPC which measures particles down to 1.5 nm. Both these two studies show nucleation threshold of
$10^6$ cm$^{-3}$ H$_2$SO$_4$, but the slopes are drastically different, which is one of the main conclusions of the present study.

**Figure 6.5** The measured Log J vs. Log [H$_2$SO$_4$] for H$_2$SO$_4$-H$_2$O BHN at different RH (9%, 13% and 16%) and residence times (60, 133, and 240 s). The slope is shown as $n_{H_2SO_4}$ values inset. The horizontal and vertical bars indicate one standard deviation of H$_2$SO$_4$ and particle number concentrations. In comparison, we also included data from$^{24}$ for residence times of 115 and 379 s and RH 22%.
Figure 6.6 shows the measured nucleation rate \((J)\) as a function of initial \([\text{H}_2\text{SO}_4]\) for different RH values with and without NH\(_3\). The total flow through the reactor was 10.3 lpm (2.8 lpm through the nucleation region and 7.5 lpm to the two CIMSs), corresponding to a residence time through the nucleation region of 240 s. \(J\) values varied from \(3\times10^{-3} - 2\times10^2\ \text{cm}^{-3}\ \text{s}^{-1}\) for RH values 9 – 16% and initial \([\text{H}_2\text{SO}_4]\) from \(2\times10^6 - 2\times10^7\ \text{cm}^{-3}\) and in general, was higher in the presence of NH\(_3\) (1.2 ppbv) than in the absence of it. However, in both BHN and THN cases, the \(\text{H}_2\text{SO}_4\) threshold to produce the unit \(J\) (1 cm\(^{-3}\)s\(^{-1}\)) was at the \(10^6\ \text{cm}^{-3}\) range, the same as the previous graph (Figure 6.5).

From a plot of \(\log J\) vs. \(\log [\text{H}_2\text{SO}_4]\), one can obtain the number of \(\text{H}_2\text{SO}_4\) molecules in the critical cluster \((n_{\text{H}_2\text{SO}_4})\) if saturation ratios of other components are constant, based on the first nucleation theorem\(^{121, 132}\). The derived \(n_{\text{H}_2\text{SO}_4}\) was 3 – 5 for both BHN and THN cases. Unlike the previous study\(^{138}\) in which \(n_{\text{H}_2\text{SO}_4}\) increased with decreasing RH, there was no clear trend in \(n_{\text{H}_2\text{SO}_4}\) as a function of RH. The \(n_{\text{H}_2\text{SO}_4}\) values only slightly decreased (reduced by 0.04 to 0.4 molecules) for THN compared to BHN for the same RH.

Figure 6.7 shows the measured \(\log J\) vs. \(\log \text{RH}\) for BHN and THN with NH\(_3\) (20 ppbv). \(J\) varied from \(3\times10^{-3} - 3\times10^1\ \text{cm}^{-3}\ \text{s}^{-1}\) for RH values 6 – 40%, initial \([\text{H}_2\text{SO}_4]\) in the range of \(3\times10^6 - 7\times10^6\ \text{cm}^{-3}\) and at a residence time of 120 s, and was usually higher in the presence of NH\(_3\) than without it. In both the BHN and THN cases, the \(\text{H}_2\text{SO}_4\) threshold to produce the unit \(J\) was again at the \(10^6\ \text{cm}^{-3}\) range. The slope ranged from 1-4, consistent with those provided by the liquid-drop model\(^{141}\). The slope
Figure 6.6 The measured Log $J$ vs. Log $[\text{H}_2\text{SO}_4]$ for binary (filled symbols) and ammonia-ternary nucleation (open symbols) at RH = 9% (squares), 13% (triangles), 16% (circles). Solid and dashed lines show the linear fitting curve of the data. These data are for a 240 s residence time. $\text{NH}_3 = 1.20$ ppbv for THN. The horizontal and vertical bars indicate one standard deviation of $[\text{H}_2\text{SO}_4]$ and nucleation rate.

of $J$ vs. RH also reduced at higher $[\text{H}_2\text{SO}_4]$, similarly to \textsuperscript{138} and consistent with nucleation thermodynamics; the slope also decreased with increasing residence time. The slope was in general much lower than those measured previously (6-15)\textsuperscript{101,134,138}; this is because in
previous experiments when we changed RH in the nucleation reactor, OH was (and hence 
H$_2$SO$_4$) also changed accordingly. The slope of J vs. RH was only slightly reduced in the 
presence of NH$_3$. Thus, under these experimental conditions, there was also no change in 
the composition of H$_2$SO$_4$ and H$_2$O molecules in critical clusters in the presence and 
absence of NH$_3$.

Figure 6.7  Graph of Log J vs. Log RH. The number of water molecules in the critical 
cluster is 1 – 4. This number is slightly reduced in the presence of ammonia (20 ppbv). 
The total flow through the reactor is 13.1 lpm (5.6 lpm through the nucleation region and 
7.5 lpm to the two CIMSs), corresponding to a residence time through the nucleation
region of 120 s. $J$ varies from $3 \times 10^{-3} - 3 \times 10^{1} \text{ cm}^{-3} \text{ s}^{-1}$ for RH values 6 – 40 % and initial $[\text{H}_2\text{SO}_4]$ in the range of $3 \times 10^{6} – 7 \times 10^{6} \text{ cm}^{-3}$ and is usually higher in the presence of NH$_3$ than without it. In both the BHN and THN cases, the H$_2$SO$_4$ threshold to produce the unit $J (1 \text{ cm}^{-3} \text{ s}^{-1})$ is at the $10^{6} \text{ cm}^{-3}$ range.

Figure 6.8 shows the measured $J$ vs. NH$_3$ at H$_2$SO$_4$ of $8.2 \times 10^{6} \text{ cm}^{-3}$, NH$_3$ from 0.08 – 0.80 ppbv, RH of 8 %, and a residence time of 170 s. At NH$_3$ from 0.08 – 1 ppbv, $J$ varied from 0.2 – 2 cm$^{-3}$ s$^{-1}$. The slope of Log $J$ vs. Log NH$_3$ was nearly one, indicating that there is only one molecule of NH$_3$ present in the critical clusters, consistent with the above result that $n_{\text{H}_2\text{SO}_4}$ and $n_{\text{H}_2\text{O}}$ values did not change in BHN and THN (Figures 6.6 and 6.7).

By comparing the measured nucleation rates in THN vs. BHN taken under similar experimental conditions, enhancement factors (EF) were derived. EF values were usually lower than 10 for H$_2$SO$_4$ from $2 \times 10^{6} – 2 \times 10^{7} \text{ cm}^{-3}$, NH$_3$ from 1.22 – 2.6 ppbv, RH from 6 – 16 % and residence times of 60 – 240 s (Figure 6.9). Similarly to a previous study$^{138}$, EF was in general higher for lower H$_2$SO$_4$ (Figure 6.9) and lower RH (Figure 6.10) and higher at higher NH$_3$ (Figure 6.11).
Figure 6.8 The measured Log $J$ vs Log [NH$_3$] for THN experiments. RH = 8%. H$_2$SO$_4$ = 8.2×10$^6$ cm$^{-3}$. Residence time = 170 s. The solid line shows the liner fitting curve of the data.
Figure 6.9  The measured nucleation enhancement factor (EF) as a function of $[\text{H}_2\text{SO}_4]$. EF is defined as the ratio of nucleation rates in the NH$_3$ ternary homogenous nucleation vs. rates in the binary homogenous nucleation. RH = 6 – 16 %. [NH$_3$] = 1.22 – 2.6 ppbv. Residence time = 60 – 240 s.
Figure 6.10 The measured nucleation enhancement factor (EF) as a function of RH. $[\text{H}_2\text{SO}_4] = 5 \times 10^6 - 7 \times 10^6 \text{ cm}^{-3}$. RH = 7 – 39 %. $[\text{NH}_3] = 20 \text{ ppbv}$. Residence time = 80 – 240 s.
The measured nucleation enhancement factor (EF) as a function of NH$_3$ mixing ratio. RH = 8%. [H$_2$SO$_4$] = 8.2×10$^6$ cm$^{-3}$. Residence time = 170 s.

6.4 Discussion

Our observations show that the onset H$_2$SO$_4$ for nucleation to occur ($J = 1$ cm$^{-3}$s$^{-1}$) is on the order of 10$^6$ cm$^{-3}$ with or without NH$_3$. Atmospheric observations$^{16, 69, 70, 117, 124}$ have shown that nucleation occurs at H$_2$SO$_4$ of 10$^6$ – 10$^8$ cm$^{-3}$. On the other hand, BHN parameterizations typically require H$_2$SO$_4$ of 10$^9$ cm$^{-3}$ or higher$^1$. Recent laboratory studies$^{22, 135, 142, 143}$ have shown that nucleation can occur at [H$_2$SO$_4$] as low as 10$^6$ cm$^{-3}$. 

Figure 6.11 The measured nucleation enhancement factor (EF) as a function of NH$_3$ mixing ratio. RH = 8%. [H$_2$SO$_4$] = 8.2×10$^6$ cm$^{-3}$. Residence time = 170 s.
However, only two studies so far have shown the power dependence of $J$ on $[\text{H}_2\text{SO}_4]$ of one$^{143}$ or two$^{135}$, as found from atmospheric observations. (Sipila et al., 2010)$^{135}$ used a newly developed particle detector that measures particles down to 1.5 nm and also incorporated a longer residence time in the nucleation reactor and a continuous source of H$_2$SO$_4$ production in the nucleation reactor. (Metzger et al., 2010)$^{143}$ added organic compounds (i.e. trimethylbenzene) in the H$_2$SO$_4$ aerosol nucleation, but used a regular TSI CPC 3025 to detect particles.

Our slopes taken from laboratory studies are higher than those found from the atmospheric observations$^{69,117}$. The reason behind the different slopes seen from our laboratory experiments and atmospheric observations can be explained by the technical difference in the methods used to make these slopes in the laboratory studies and field observations. The atmospherically derived slopes use ensemble observation data obtained at various RH and saturation ratios of possible ternary precursors (which are unknown currently) by simply making correlations between $J$ vs. H$_2$SO$_4$, whereas laboratory values are derived from the data taken under the constant RH and constant [NH$_3$]. This difference has been neglected, but should be taken into account when comparing the slopes derived from field and laboratory studies. A more rigorous approach applying the first nucleation theorem is needed to be developed to solve this problem.

In the present study, we found the threshold of $10^6 \text{ cm}^{-3}$ H$_2$SO$_4$ and the slope of $J$ vs. H$_2$SO$_4$ between 3 – 5 for both BHN and NH$_3$-THN cases, using the same instrument used in field studies to measure particles (TSI CPC 3876). While we used a longer
residence time (60 – 240 s) in the nucleation region, H$_2$SO$_4$ was also produced in a local source. The slopes (3 – 5, as compared to 1 – 2) found in BHN are, however, thermodynamically consistent with quantum chemical calculations which show that a monomer or dimer of H$_2$SO$_4$ would spontaneously evaporate and is difficult to form critical clusters by themselves$^{132,141,144,145}$.

One of the main principles of THN is that it could explain nucleation occurring at lower [H$_2$SO$_4$] where BHN would fail$^{144}$. As shown by the present study and others$^{18,138}$, the threshold H$_2$SO$_4$ for nucleation was similar for BHN and THN. It was usually on the same order of magnitude and at most only about half of the value found in BHN, implying that while THN can occur at lower H$_2$SO$_4$, any enhancement with NH$_3$ would not be large enough to shift the threshold value. Most EF values were largest at three orders of magnitude for H$_2$SO$_4$ from $10^8$ – $10^{10}$ cm$^{-3}$ $^{18,138}$. As shown in the present study, when H$_2$SO$_4$ ($10^6$ – $10^7$ cm$^{-3}$) and NH$_3$ (0.08 – 2.6 ppbv) were one or three orders of magnitude lower than in these cited studies, the EF values were mostly < 10 (Figure 6.9 – 6.11). These observation results may be consistent with density functional calculations which show that NH$_3$ can lower the Gibbs free energy of H$_2$SO$_4$-H$_2$O clusters under actual atmospheric conditions, but the amount of such clusters would be also negligible due to the required temperatures and NH$_3$$^{38}$.

These results show that the $n_{H_2SO_4}$ and $n_{H_2O}$ values were reduced under THN than in BHN, but $n_{H_2SO_4}$ and $n_{H_2O}$ both were also very similar in BHN and THN cases. For example, the $n_{H_2SO_4}$ value was reduced only by a fraction of a molecule (0.04 to 0.4 molecules). Thus, while the nucleation rate was enhanced, an addition of NH$_3$ did not
drastically change the H$_2$SO$_4$ and H$_2$O composition of the critical clusters under atmospheric conditions. These results are different from previous studies$^{18,138}$ which showed that the critical cluster contains 2 – 3 less molecules of H$_2$SO$_4$ in the presence of NH$_3$. This difference may be due to much longer nucleation times used in this study (60 – 240 s) or much lower [H$_2$SO$_4$] used here (10$^6$ – 10$^7$ cm$^{-3}$). The estimated $n_{\text{NH}_3}$ was only one, which is consistent with cluster measurements$^{129}$ and this unit value also explains the small reduction in $n_{\text{H}_2\text{SO}_4}$ and $n_{\text{H}_2\text{O}}$ in THN than in BHN. This low $n_{\text{NH}_3}$ value may also imply that NH$_3$ actually acts rather as a catalysis agent and is less physically incorporated into the cluster formation itself during the THN process. It is also possible that there is an energy reduction due to the exothermic heat released from the acid-base neutralization reaction between H$_2$SO$_4$ and NH$_3$, so that even only one molecule of NH$_3$ is sufficient to reduce the Gibbs free energy for critical cluster formation.

Field studies of new particle formation made in Atlanta, Georgia in the summer 2002 showed that H$_2$SO$_4$, NH$_3$ and particle concentrations are approximately 10$^6$ – 10$^8$ cm$^{-3}$, 1 – 10 ppbv, and 10$^3$ – 10$^5$ cm$^{-3}$, respectively$^{70}$. And, the present experimental conditions fall within this observation results. One study$^{70}$ also showed the slope of particle concentration vs. NH$_3$ is nearly one$^{70}$, similar to the present study showing that $n_{\text{NH}_3}$ is only one. Another study made in Kent, Ohio crossing four different seasons showed the threshold of H$_2$SO$_4$ is around 10$^6$ cm$^{-3}$, even when NH$_3$ was at the sub-ppbv level$^{69}$. While our laboratory observations also fall within the observation results taken in Kent, the Kent measurements had a nearly constant NH$_3$ level (sub-ppbv) over different
seasons, so it was difficult to use these data to quantitatively test the $J$ vs. $NH_3$ relationship.

Our laboratory observations show the threshold of $H_2SO_4$ for the unit $J$ is $10^6$ cm$^{-3}$, with $NH_3$ from 0.08 – 2.6 ppbv at 288 K. In comparison, the threshold in the THN parameterization is, for example, $[H_2SO_4]$ of $10^9$ cm$^{-3}$ for $NH_3$ of 1 ppbv at 273 K$^2$ (Figure 6.12). A similar $[H_2SO_4]$ threshold is also required in the BHN parameterization$^1$(Vekhamaki et al., 2002) (Figure 6.12). We also used our typical experimental conditions of $H_2SO_4$, $NH_3$, RH and temperature used in the present study, but the THN parameterization$^2$ did not produce particles. As discussed elsewhere$^{69}$, this THN parameterization also did not reproduce atmospheric observations made in Kent.

6.5 Conclusions

Our laboratory observations show that both the BHN and THN thresholds are $10^6$ cm$^{-3}$ $H_2SO_4$ and the slope of $J$ vs. $H_2SO_4$ (that is, $n_{H_2SO_4}$) is 3 – 5, $n_{H_2O}$ is 1 – 4, using the same instruments (CIMS and TSI CPC 3876) used in field studies. The slope of nucleation rate vs. $H_2SO_4$ is 4-6; these values are physically sound, considering that monomers and dimers of $H_2SO_4$ can easily evaporate and are difficult to become critical clusters. The slope of $J$ vs. $NH_3$ ($n_{NH_3}$) was only one for THN. Nucleation enhancement factors by $NH_3$ varied depending on $H_2SO_4$, RH and residence times, but was for most time <10. These results imply that nucleation can be enhanced by $NH_3$, but $H_2SO_4$ is still the main nucleation precursor responsible for new particle formation in the atmosphere. While our laboratory study could reproduce atmospheric observations made in Atlanta$^{70}$.
and Kenl^69^, the current THN parameterization^2, 33^ fails to produce particles under conditions used in our laboratory study and those found in Kent field observations.

**Figure 6.12.** Log $J$ vs. Log $[\text{H}_2\text{SO}_4]$ based on predictions by (Vehkamaki et al., 2002)^1 (BHN) and (Merikanto et al., 2007)^2 (THN). The parameters are a temperature of 288 K, RH of 40 % and $[\text{NH}_3]$ of 100 pptv (for THN only).
CHAPTER 7

Conclusions

This dissertation presented research on laboratory studies of binary and ternary homogenous nucleation. Preliminary studies\textsuperscript{103,138} showed that in order to produce a measureable amount of particles, an $[\text{H}_2\text{SO}_4]$ of at least $10^8$ cm$^{-3}$ was required. Even with ppb and tenth ppb levels of $[\text{NH}_3]$ were present, $[\text{H}_2\text{SO}_4]$ of $10^8$ cm$^{-3}$ was still required although the nucleation rate was enhanced, even up to a factor of 1000. This would imply that $\text{H}_2\text{SO}_4$ is still the main component responsible for nucleation to occur. In the newer studies\textsuperscript{146,147} the $[\text{H}_2\text{SO}_4]$ to produce particles was $10^6 – 10^7$ cm$^{-3}$. Once again, there was enhancement with $\text{NH}_3$, but not enough to produce particles at a lower $[\text{H}_2\text{SO}_4]$. The common theme here was that $\text{NH}_3$ can in fact enhance nucleation, but $\text{H}_2\text{SO}_4$ is the main precursor that controls when nucleation occurs. However, it is hard to predict if it really is only $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ in some cases because even small impurities present (as low as 1 pptv) can cause nucleation enhancements. Also, the time for nucleation to occur can affect the amount of precursor $[\text{H}_2\text{SO}_4]$ required for nucleation. Longer times can make growth to measurable sizes more efficient. However, this can also lead to higher losses (via wall loss) and a greater uncertainty of the exact precursor concentration that participates in nucleation. Future studies should entail a more detailed analysis of the flow dynamics of the system as well as studying growth processes more in depth. Also, further minimization of background $\text{NH}_3$ or other impurities will establish a
better controlled system. This will require instruments that can measure very low (~ 1 ppt) concentration of chemical species.
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