

Aerosol Research Letter

First Measurements of Neutral Atmospheric Cluster and 1–2 nm Particle Number Size Distributions During Nucleation Events

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INTRODUCTION

Recent observations throughout the atmosphere have shown that nucleation occurs frequently (Kulmala et al. 2004). Modeling studies and observations have shown that nucleated particles contribute significantly to concentrations of cloud condensation nuclei (Spracklen et al. 2008), thereby affecting climate (IPCC 2007). Size-resolved measurements extending down to molecular dimensions can provide information on processes that lead to nucleation and would enable development and verification of theories for particle nucleation and growth in the atmosphere and other aerosol systems.

This article describes measurements of the complete number size distribution, spanning the size range from vapor molecules and molecular clusters to submicrometer particles, during atmospheric nucleation events. The measurements used two new instruments, the cluster chemical ionization mass spectrometer

(Cluster CIMS) and the DEG SMPS. The Cluster CIMS measures neutral molecular clusters from 50 to 900 amu. The DEG SMPS is a scanning mobility particle spectrometer (SMPS) equipped with a diethylene glycol (DEG)-based condensation particle counter (CPC) capable of 1.1 nm mobility diameter particle detection, and overlapping the sizes detected by the Cluster CIMS (Iida et al. 2009; Jiang et al. 2011). The Cluster CIMS distinguishes neutral clusters from ions formed by ion-induced clustering by varying the reaction time for ions with the sampled air (Zhao et al. 2010). It distinguishes clusters from high molecular weight gases by measuring the incremental signal at a specified mass detected during nucleation events. The clusters that were measured in this study contain sulfuric acid, which is known to participate in atmospheric nucleation (Kuang et al. 2008).

EXPERIMENT DESCRIPTION

The nucleation and cloud condensation nuclei (NCCN) study was carried out in Atlanta, Georgia, during July and August 2009. Estimated nucleation rates (1 to 1000 particles $\text{cm}^{-3}\text{s}^{-1}$) for summertime boundary layer nucleation in locations such as Atlanta greatly exceed ion production rates (2–30 ion pairs $\text{cm}^{-3}\text{s}^{-1}$), indicating that nucleation is dominated by clustering of neutral species (Iida et al. 2006). Therefore, our measurements during NCCN focused on neutral clusters and nanoparticles.

Complete number size distributions were obtained using the Cluster CIMS (50–900 amu), and the DEG SMPS (~1–10 nm), operated alongside a conventional particle size distribution (PSD; ~3–500 nm) system consisting of a pair of aerosol mobility spectrometers (Woo et al. 2001). Measurement setups are described in the Supplemental Information. The Cluster CIMS

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measurements were carried out with a resolution of 1 amu, and signals well above the detection limit were measured at all masses analyzed (up to 900 amu). To convert the Cluster CIMS mass measurements to cluster geometric diameter, a bulk density of sulfuric acid (1.83 g/cm³) was assumed, although the results shown are not very sensitive to this value.

The Cluster CIMS was operated for selected ions at $m/z = 160, 293,$ and 391 and/or in the scanning mode. Mass 160 (size 1) corresponds to $\text{HSO}_4^- \cdot \text{HNO}_3$, which is formed by the chemical ionization of H_2SO_4 by NO_3^- (Eisele and Tanner 1993). This signal is used to determine concentrations of sulfuric acid vapor. The signals at masses 293 and 391 correspond to deprotonated $[\text{H}_2\text{SO}_4]_3$ (size 3) and $[\text{H}_2\text{SO}_4]_4$ (size 4) which are formed by NO_3^- chemical ionization followed by HNO_3 loss. As discussed by Zhao et al. (2010), signals for $[\text{H}_2\text{SO}_4]_2$ (size 2) are also detected, but much of that signal arises from ion-induced clustering in the ion reaction region of the Cluster CIMS inlet. Therefore, data for $[\text{H}_2\text{SO}_4]_2$ are not shown. The approach that was used to obtain distribution functions is discussed in the Supplemental Information.

Although we only detected $[\text{H}_2\text{SO}_4]_3$ and $[\text{H}_2\text{SO}_4]_4$, we are quite certain that stabilizing species, such as ammonia, amines or other organics, must also be present in many clusters. This is because pure sulfuric acid clusters are too volatile to explain the high cluster concentrations that we observe (Hanson and Lovejoy 2006). It is possible that the stabilizing species were not detected because chemical ionization led to their dissociation from the original clusters (Curtius et al. 2001; Hanson and Eisele 2002). It is also possible that small signals from clusters containing those species were hidden in the complex mass spectra, which are dominated by high molecular weight species that are not associated with nucleation (Zhao et al. 2010). In this paper we report what was measured, recognizing that the full story is undoubtedly more complex and requires further study.

The estimated geometric diameter that is calculated from cluster mass differs from mobility diameters. Tammet (1995) discussed the theoretical relationships between these sizes, and Ku and Fernández de la Mora (2009) carried out measurements to empirically determine their relationship. They found that for mass diameters down to 1.3 nm,

$$D_{p \text{ geometric}} = D_{p \text{ mass}} = D_{p \text{ mobility}} - 0.3 \text{ nm} \quad [1]$$

Our data extend down to mass diameters of about 1 nm, and we have extrapolated this relationship down to that size when converting mobility sizes to the geometric (or mass) diameters. This introduces uncertainties that must be kept in mind for our smallest mobility diameters, where the DEG SMPS and Cluster CIMS data overlap.

RESULTS AND DISCUSSION

Figure 1 shows fifteen number distributions measured during nucleation events on August 7 and 23, 2009. On August 7, the

Cluster CIMS measurement protocol involved scanning from 200 to 500 amu followed by selected ion measurements at $m/z = 160, 293,$ and 391 . Only selected ion measurements were done on August 23. On both days, nucleation was caused by sulfur dioxide emissions from upwind coal-fired power plants. When the Cluster CIMS was operated in the scanning mode, signals well above the lower detection limit were always observed at all masses, including at night (e.g., data for August 7 at 7:10 and 18:50). Signals at masses 293 and 391 exceeded those background levels only when nanoparticles were detected with the DEG SMPS (e.g., 10:00 on August 7 and 8:05–16:35 on August 23). We conclude that most of the Cluster CIMS signal is due to the chemical ionization of unknown high molecular weight gas molecules that are not associated with nucleation. For the August 23 measurements, sulfuric acid vapor and size 3 clusters were first detected at 7:15. By 8:05, size 3 and 4 clusters were detected, and the DEG SMPS also detected particles down to ~ 1 nm. Size 3 and 4 clusters and nanoparticles down to 1 nm were detected by both instruments throughout the nucleation event.

The smallest nano CN that were detected by the DEG SMPS are comparable in size to the size 3 and 4 clusters detected by the Cluster CIMS, and the distribution functions measured by the Cluster CIMS and DEG SMPS tend to follow a similar trend with size. At ~ 1 nm, values of the distribution functions measured by these instruments typically agree to within the estimated measurement uncertainty. The DEG SMPS and the PSD also agree well in the overlapping 3 to 10 nm range.

Ion mobility spectrometry, which measures mobility distributions of small ion clusters (Tammet 2006), provides information on charged particle concentrations to sizes below 1 nm, but not for neutrals which are likely much more abundant. The neutral cluster—air ion spectrometer (NAIS) is an ion mobility spectrometer that charges the sampled aerosol prior to measurement (Kulmala et al. 2007). When interpreting NAIS data it is assumed that, as for larger (>3 nm) particles, particle charging rates are determined by ion transport and are unaffected by the chemical properties of the particles or ions. This allows calculations of total (neutral + charged) concentrations. The Cluster CIMS data shown in Figure 1 illustrate the need to distinguish between signal from charged molecules and from clusters when interpreting data from instruments such as the NAIS.

Error bars are shown for the Cluster CIMS and DEG SMPS data measured at 9:35 on August 23. Estimated relative uncertainties for $[\text{H}_2\text{SO}_4]$, $[\text{H}_2\text{SO}_4]_3$, and $[\text{H}_2\text{SO}_4]_4$ are $\sim 1.75, 2.5,$ and $2.5,$ respectively. Relative standard deviations of DEG SMPS data are $\sim 10\%$ at 3 nm and $\sim 50\%$ at 1 nm. In calculating distribution functions from DEG SMPS measurements, it was assumed that charging rates given by Wiedensohler (1988) can be extrapolated down to 1 nm, that sampling losses in the laminar flow inlet can be calculated theoretically (e.g., $\sim 56\%$ at 1 nm and 21% at 3 nm), and that DEG CPC activation efficiencies for ambient nano CN are equal to those for NaCl (Jiang et al. 2011). The DEG activation efficiencies reported by Iida

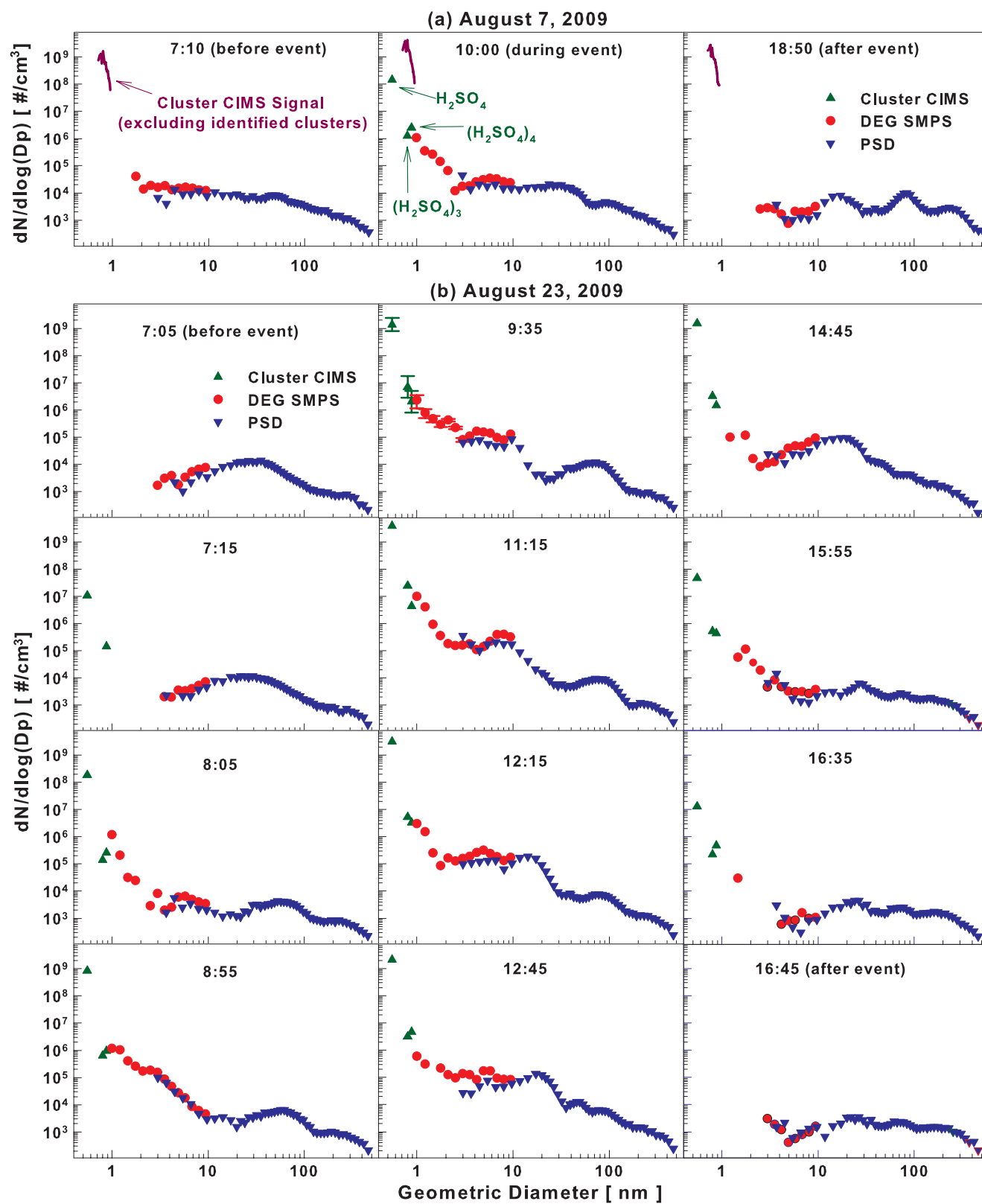


FIG. 1. Aerosol number distribution functions measured with three instruments during nucleation events in Atlanta, GA on August 7 and 23, 2009. On August 7, the Cluster CIMS carried out sequential scans of all masses from 200 to 500 followed by selected ion measurements at 160, 293, and 391. On August 23, only selected ion measurements were done. The estimated uncertainties shown for 9:35 on August 23 apply to all data. Times shown are local standard time.

et al. (2009) for nanoparticles produced by nucleating vapors formed by vaporizing $(\text{NH}_4)_2\text{SO}_4$ are similar to those shown for NaCl in the supplemental information. These assumptions lead to additional uncertainties that are difficult to quantify. Charging efficiencies and activation efficiency for freshly nucleated atmospheric particles would be needed to reduce such uncertainties.

CONCLUSIONS

We report the first complete measurements of neutral aerosol number distributions in a nucleating system, including condensing vapor molecules and neutral molecular clusters. A new aerosol mobility spectrometer, the DEG SMPS, was used to detect nano CN down to sizes comparable to the largest sizes measured by the Cluster CIMS mass spectrometer. The distribution functions measured with the DEG SMPS and the Cluster CIMS are in reasonable agreement and show a consistent trend with size. The DEG SMPS also agrees well with conventional aerosol mobility spectrometers (PSD) in the 3–10 nm size range, where they overlap.

It is not obvious that the Cluster CIMS data should agree so well with the DEG SMPS data. As was discussed by Zhao et al. (2010) and shown in Figure 1, mass spectra measured with the Cluster CIMS include signals from many unknown high molecular weight species that are not associated with nucleation. The total concentration of these species exceeds the concentrations of the size 3 and 4 clusters by at least an order of magnitude. These high mass ions will be efficiently sampled by mobility spectrometers such as the NAIS and the DEG SMPS. Activation efficiencies of the DEG CPC depend on composition, while the electrometers used in instruments such as the NAIS detect all charged particles. The fact that Cluster CIMS number distributions for identified clusters are comparable to number distributions measured by the DEG SMPS suggests that particles that undergo condensational growth in the atmosphere also undergo condensational growth in the DEG CPC. Even at night, however, when nucleation was not occurring and mass at sizes 3 and 4 was not elevated, the Cluster CIMS always detected high concentrations of species having mass as high as 900 amu that were never detected by the DEG CPC even though they were larger than size 4 clusters. Clearly, condensational growth on sub 2 nm particles is sensitive to particle composition. Further work is needed to understand this sensitivity.

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