Supplemental Information

Towards reconciling measurements of atmospherically relevant clusters by chemical ionization mass spectrometry and mobility classification/vapor condensation

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S1) Experimental setup:

The Cluster CIMS and DEG MPS data were taken in the extraordinarily clean and highly repeatable Augsburg flow reactor. The flow reactor setup and procedure have been described previously (Jen et al. 2014). The nitrogen flow rate in the reactor was 4 (STP) LPM with trace amounts of sulfuric acid, water vapor, and injected basic gases. The base injection point to the Cluster CIMS sampling region results in a ~3 s reaction time between the basic gas and the sulfuric acid vapor and clusters. Since the DEG MPS samples gas 10 cm above the Cluster CIMS sampling region, a higher base injection port was used to preserve the ~3 s reaction time. The basic gas studied here is dimethylamine (DMA) and its concentrations ([DMA]) were measured by the Cluster CIMS in positive ion mode (see Jen et al. (2014)) and calculated *a priori*. The Cluster CIMS separately used nitrate ion (with a ligand, $\text{HNO}_3 \cdot \text{NO}_3^-$) and acetate (with a water ligand, $\text{H}_2\text{O} \cdot \text{CH}_3\text{CO}_2^-$) to chemically ionize sulfuric acid clusters. Acetate was produced by passing nitrogen above a reservoir of acetic anhydride and then over a radioactive charger (Po-210). The cluster signals from the Cluster CIMS were converted to concentrations using a chemical ionization reaction time of 15 ms for nitrate and 18 ms for acetate and following the inversion detailed below and in Jen et al. (2014).

The DEG MPS also used a Po-210 strip to charge clusters and particles before they entered the TSI 3085 mobility classifier. From Jiang et al. (2011), we assume that theoretically predicted bipolar steady-state charging efficiencies can be extrapolated to the 1 nm size range.

Premnath et al. (2011) showed that chemical ionization is important up to a critical size of ~0.5 nm for amino acids and trimethylamine, above which charging is controlled by ion transport. This critical size is dependent on the chemical system involved and must differ from the system studied here as nitrate and acetate clearly chemically ionize different clusters at a much larger size of 1.34 nm. The Po-210 charger used with the DEG MPS produces numerous types of ionizing ions, many of which have not been characterized, that go on to charge the neutral sulfuric acid+DMA clusters. Further refinements in the bipolar charging of the smallest clusters require a better understanding of the chemical system.

The mobility classifier operated in positive polarity (negative ions) with 13.0 ± 0.5 LPM sheath flow rate and a 2.2 ± 0.2 LPM sample flow rate. Operating conditions of the DEG CPC followed that of Jiang et al. (2011), with the saturator and condenser temperatures at 59 and 20°C, respectively. The capillary and condenser flow rates were 0.03 and 0.3 LPM respectively.

S2) Clusters and their mobilities:

Mobilities of various sulfuric acid and DMA ion clusters were calculated using a particle dynamics simulation (Larriba and Hogan 2013a; b). Table S1 lists the ion cluster compositions and their calculated mobilities. Ion structures were taken from the SI of Ortega et al. (2014) and computed via density functional theory. These structures represent the minimum energy at zero K. At room temperature, these clusters can access many lower energy structures and thus could alter the calculated mobility. Furthermore, under ambient conditions, clusters likely include water, and this is probably a larger source of uncertainty in the ion mobilities. The following shorthand notation is used: A_1^- is HSO_4^- , A_2^- is $\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$, etc.

Table S1 Mobilities of sulfuric acid clusters with DMA in N_2 carrier gas

Cluster	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
A_1^-	2.21
A_2^-	1.79
A_3^-	1.39
A_4^-	1.29
$A_2^- \cdot \text{DMA}$	1.53
$A_3^- \cdot \text{DMA}$	1.33
$A_4^- \cdot \text{DMA}$	1.10
$A_2^- \cdot \text{DMA}_2$	1.37
$A_3^- \cdot \text{DMA}_2$	1.24
$A_4^- \cdot \text{DMA}_2$	1.07
$A_4^- \cdot \text{DMA}_3$	1.00
$A_5^- \cdot \text{DMA}_3^*$	0.90
$A_5^- \cdot \text{DMA}_4^*$	0.85

*Extrapolated mobility as no ion coordinates have been published.

S3) Ion-induced clustering (IIC) in sulfuric acid/dimethylamine environment:

IIC has been modeled for the pure sulfuric acid environment where the list of reactions is given in Chen et al. (2012). The amount of IIC produced clusters depends primarily on the chemical ionization (CI) reaction time, t , and $[A_1]$. The relationship between the dimer signal (S_{195} , for nitrate-detected A_2) to monomer signal (S_{160} , $\text{HNO}_3 \cdot \text{HSO}_4^-$, for nitrate-detected A_1) that takes into account direct ionization of A_2 and IIC-produced A_2^- can be obtained by integrating the rate equations with respect to time (see Hanson and Lovejoy (2006) and Chen et al. (2012)) and assuming no change in reagent ion concentration as a function of time.

$$\frac{S_{195}}{S_{160}} = \frac{k_2}{k_1} \frac{[A_2]}{[A_1]} + \frac{1}{2} k_{21} [A_1] t \quad \text{Equation S1}$$

Where

A_1 = neutral monomer

A_2 = neutral dimer

k_i = nitrate ionization rate constant

k_{ij} = IIC rate constant

This relationship implies that as time goes to 0 s, the amount of IIC-produced A_2^- reduces to zero. As a result, applying a linear fit to measurements of S_{195}/S_{160} as a function of t gives a y-intercept that describes the amount of neutral $[A_2]$ compared to $[A_1]$. For nitrate reagent ion, measured k_1 is $1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Viggiano et al. 1997) and k_2 is taken to be the ion-molecule collisional rate constant of $1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Su and Bowers 1973). Therefore, with these values of k_1 and k_2 and assuming negligible background signal, the y-intercept gives the amount of neutral $[A_2]$ for a measured $[A_1]$.

Figure S1 depicts how nitrate measured S_{195}/S_{160} changes with CI reaction time at four different [DMA] and equivalent initial concentrations of A_1 , $[A_1]_0$. The dotted line illustrates the S_{195}/S_{160} at the CI reaction time used in this study of 0.018 s. A linear fit was applied to the data (solid line) and extrapolated to $t=0$ s (dashed line). At [DMA]=0 pptv, the S_{195}/S_{160} at $t=0$ s is significantly different than at $t=0.018$ s (0.004 compared to 0.05 respectively). This signifies that IIC produced dimers account for the vast majority of detected dimer ions and must be subtracted from the apparent $[A_2]$ to obtain true $[A_2]$. However, in the presence of DMA, S_{195}/S_{160} at $t=0$ s closely matches the ratio values at $t=0.018$ s. This suggests that IIC produces a negligible amount of dimer ions at $t=0.018$ s in the sulfuric acid+DMA system for conditions pertinent to this study.

Figure S1 Nitrate measured ratios of S_{195}/S_{160} as a function of CI reaction time at the same $[A_1]_0$ and four [DMA]. Measured $[A_1]$ at each [DMA] is given in the legend. Dashed line extrapolates the linear fit to $t=0$ s, where the y-intercept gives the fraction of neutral $[A_2]$ to the neutral $[A_1]$. The dotted line indicates the CI reaction time used in this study with nitrate of 0.018 s.

S4) Nitrate vs. acetate sulfuric acid/DMA spectra comparison:

Figure S2 compares the mass spectra between nitrate (black) and acetate (red) at $[DMA]=110$ pptv and $[A_1]_0=4 \times 10^9$ cm⁻³. Note that higher cluster concentrations were found with acetate than nitrate. For example, $A_3^- \cdot DMA_2$ measured using acetate is about a factor of 10 higher than with nitrate. Also, acetate allowed more types of cluster to be detected. As the only variation between these experiments is the chemical ionization ion, we infer that the difference in cluster signals is due to the higher proton affinity (gas phase basicity) of acetate relative to nitrate. These results would appear to be at variance with recent results of Kürten et al. (2014), who reported the efficient detection of clusters such as $A_3 \cdot DMA_2$ using nitrate. More work is needed to reconcile these results.

Figure S2 also shows that the nitrate spectrum is very clean with almost no background peaks obscuring the important sulfuric acid peaks. This is to be expected as nitrate is a very selective ion, i.e. it can only chemically ionize very acidic clusters. The acetate spectrum has a high background which can artificially increase the signals at the key masses. The background is due to trace impurities in the acetic anhydride reservoir or their evaporation from surfaces; we believe these impurities get ionized by Po-210 but do not affect the chemical ionization of sulfuric acid clusters by acetate or the formation of neutral clusters in the flow reactor. This assumption is based upon very good agreement for both total $[A_1]$ and $[A_2]$ as measured by either nitrate or acetate. In addition, the acetate spectrum shows a nitrate peak (125 m/z) at ~15% of the value in the nitrate spectrum. Nitrate in the acetate system is probably due to adsorbed nitric acid on the surfaces outside the source holder from when the Cluster CIMS used nitrate as its source ion. We believe that such a small amount of nitrate will not alter the amount of sulfuric acid clusters detected by acetate.

Since there is high background using acetate, we took the signals at low $[A_1]_0 \approx 10^7$ cm⁻³ (DMA=0 pptv) as the background concentration level for all pure sulfuric acid cluster

concentrations (e.g., $[A_2]$ at 195 m/z, $[A_3]$ at 293 m/z, etc.). The backgrounds for the aminated clusters was taken to be the concentration at those specific masses without DMA added but at the equivalent $[A_1]_0$, though changes in $[A_1]_0$ had no effect on these background concentrations.

Figure S2 Mass spectra comparison between nitrate (black) and acetate (red) chemical ionization ions. These spectra were measured at $[DMA]=110$ pptv and $[A_1]_0=4 \times 10^9 \text{ cm}^{-3}$. Key peaks are identified with acetate abbreviated as Ac^- .

S5) Cluster CIMS vs. DEG MPS at 1.34 nm centroid mobility diameter without DMA:

The comparison detailed in the main body of the paper was also done for a pure sulfuric acid environment ($[DMA]=0$ pptv). Figure S3 shows the comparison between predicted DEG MPS concentration and measured concentrations at 1.34 nm centroid mobility diameter. Cluster concentrations measured by acetate and nitrate were nearly equal, thus only measurements using nitrate are shown. While concentrations measured by the DEG MPS are correlated with those predicted from Cluster CIMS measurements, the DEG MPS concentrations are about 100 times higher.

Two possibilities exist: either the Cluster CIMS is under-measuring the cluster concentrations or the DEG MPS is over-measuring. We believe that in the pure sulfuric acid/water environment, the Cluster CIMS accurately measures the cluster concentrations. The chemical ionization of sulfuric acid by nitrate is fairly well understood and occurs at the collision rate. In addition, the formation of A_2^- via IIC from sulfuric acid vapor and bisulfate ion can be modeled accurately and subtracted from the measured $[A_2]$ (see section above). Both processes depend on the chemical ionization reaction time which can be calculated from the electric field and gap distance between the ion source and the Cluster CIMS inlet. Overall, the uncertainties from these processes are estimated to be no greater than 50% and they cannot not account for a factor of 100 difference.

Therefore, we conclude the DEG MPS over measures the cluster concentrations under these conditions. One reason is that IIC can occur after the sample flow is ionized. The residence time of the ionized sample flow is ~ 1 s (from the charger to the point the sample enters the mobility classifier), resulting in the formation of ionic clusters large enough to penetrate the mobility classifier. Unlike the Cluster CIMS, a straightforward method does not exist to take account for IIC in the DEG MPS.

Another possibility is that sulfuric acid vapor or clusters reacts with the diethylene glycol condensation vapors in the DEG CPC. Hanson et al. (2002) showed that sulfuric acid reacts with n-butanol to form particles. Dehydration of ethylene glycol by sulfuric acid is a well-known reaction (McMurry 2008), so it is possible that diethylene glycol may also undergo a similar dehydration reaction. This process could produce particles inside the DEG CPC in a pure sulfuric acid environment or could alter the activation efficiency of the smallest clusters.. In the presence of a base such as DMA, a large fraction of the sulfuric acid vapor is bound to one or two DMA molecules. Sulfuric acid+DMA clusters may not interact with DEG in the same manner as pure sulfuric acid. Regardless, more studies need to be done to understand the activation efficiency of DEG in the presence of atmospherically relevant small clusters.

Figure S3 Comparison between predicted DEG MPS concentration from Cluster CIMS (nitrate) to the measured DEG MPS concentration at a classifying voltage of 4.50 V (1.34 nm centroid mobility diameter) and [DMA]=0pptv. The black line is the 1:1 comparison. Only one type of cluster was detected. The other clusters were below detection limit.

S6) Predicted DEG MPS comparisons at 1.23 and 1.55 nm mobility diameter:

Figure S4 shows the transfer functions of the TSI 3085 mobility classifier at three different voltages: 3.80, 4.50, and 6.00 V. This corresponds to the centroid sizes of 1.23, 1.34, and 1.55 nm mobility diameter and mobilities of 1.47, 1.27, and 0.92 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ respectively. Following the procedure detailed in the main paper, Figure S5 and Figure S6 compare predicted DEG MPS concentrations measured using acetate as the reagent ion with the Cluster CIMS to measured DEG MPS concentration at 1.23 and 1.55 nm. For all three sizes, the predicted concentrations agree well with the measured concentrations to within an average factor of 3. However, we observe two systematic trends: 1) the ratio between predicted concentrations to those measured decrease with increasing [DMA] and 2) the ratio between predicted and measured concentrations increase as the measured concentration (or $[A_1]$) decreases. For the latter at low $[A_1]$, the cluster distribution is primarily composed of dimers. The DEG

MPS calibration curves have not been measured down to this size and could explain the poorer agreement.

The [DMA] dependence indicates a systematic uncertainty with one of the instruments. We believe this may be due to very small clusters/vapors that are unobserved by the Cluster CIMS but still penetrate the mobility classifier. Consider at 1.23 nm where this trend is most pronounced (Figure S5). The transfer function for 1.23 nm displayed on the left of Figure S4 suggests that clusters smaller than the dimer can penetrate through the mobility classifier but are not observed by the Cluster CIMS. For example, $A_1 \bullet \text{DMA}_x$, where $x \geq 1$ and is number of DMA molecules, is not seen by the Cluster CIMS with either nitrate or acetate but would penetrate the mobility classifier and might be measured by the DEG MPS. Also sulfuric acid vapor can pass through the mobility classifier, which could mean that other vapor molecules, such as amines, might also be measured by the DEG CPC. Both possibilities might explain why at high [DMA], the agreement worsens.

However in the presence of DMA, the overall agreement is reasonable (on average a factor of 5 difference) which gives us confidence that our method for comparing the two types of instruments is valid. Also, this agreement supports our conclusions drawn from the IIC study detailed above. If IIC played a role in the sulfuric acid+DMA system, then we would expect the DEG MPS measured number concentration at 1.23 nm to be biased much higher because even in a short reaction time IIC would still produce a considerable amount of A_2^- . These would penetrate the mobility classifier and may be counted by the DEG CPC in the 1.23 nm size bin. Our measurements suggest this does not occur.

Figure S4 Transfer function (lines) of the TSI 3085 mobility classifier at three different voltages (3.80, 4.50, 6.00 V), corresponding to centroid mobility diameters of 1.23, 1.34, and 1.55 nm and centroid geometric (mass) diameters of 0.83, 1.04, and 1.25 nm. The points represent the clusters' mobilities and their transfer function value at each size bin. Red clusters are detected by the Cluster CIMS using nitrate and red+black detected using acetate.

Figure S5 Comparison between predicted DEG MPS concentration from Cluster CIMS measured concentration (using acetate) to the measured DEG MPS concentration at a classifying voltage of 3.80 V (1.23 nm centroid mobility diameter) at four different [DMA]. The different color types in the bar represent the different types of clusters measured by the Cluster CIMS and their contribution to the predicted total number concentration.

Figure S6 Comparison between predicted DEG MPS concentration from Cluster CIMS measured concentration (acetate) to the measured DEG MPS concentration at a classifying voltage of 6.00 V (1.55 nm centroid mobility diameter) at four different [DMA].

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