

Atmos. Meas. Tech. Discuss., author comment AC3
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Reply on RC3

Dina Alfaouri et al.

Author comment on "A study on the fragmentation of sulfuric acid and dimethylamine clusters inside an atmospheric pressure interface time-of-flight mass spectrometer" by Dina Alfaouri et al., Atmos. Meas. Tech. Discuss.,
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Thank you very much for your comments and questions. Below are the answers for each question individually.

General comments:

Section 2.1:

The ultrahigh resolution of the planar-DMA is the reason why we choose this device for studying the mobility of the clusters produced in our system, and complex cluster systems in general (especially for ambient measurements). The ultrahigh resolution of the planar-DMA allows for the separation of ions and clusters with electrical mobilities close to each other, which would not be possible with some other DMAs. This paper (<https://doi.org/10.1021/acs.analchem.8b00579>), provides a good comparison of resolving power between different types of DMA in Table 1. We will follow your suggestion and introduce the planar DMA only at the beginning of the experimental section.

Section 3:

We explain how to relate information from Figure 2 to clusters in Figure 3 in the answer of Technical comments Figure 2.

We will add a column in the Table S2 (supporting information) including the DMA voltage for each identified cluster. Figure 3 shows all Sulfuric acid/Dimethylamine clusters produced and detected in our system. The discrepancy between the number of clusters in Figure 2 and 3 comes from the fact that in any system like ours a lot of other clusters (mostly impurities) are produced. Those clusters are not relevant for this fragmentation study so they were not mentioned in the text. But an explanation is now provided in the description of figure 3.

From line 115 'Figure 3 shows a mass defect plot of all the 11 charged dimethylamine and sulfuric acid clusters produced and detected in our system. Other clusters or impurities are not shown in the figure as they are not relevant for this study. The DMA voltages and the m/z values for each detected clusters are reported in Table S3 of the Supporting Information.'

Lines 178-191: We are not sure about the reason for this larger discrepancy for the 2D3S1B cluster. It could be a combined reason of both the experimental and model uncertainty in the evaluation of the survival probability.

As reported in the manuscript there can be several reasons for the discrepancies in the survival probability between the experiments and the model:

▪

For some parent clusters multiple fragmentation pathways can occur simultaneously within the same experiment.

▪

The fragmentation of a multi-charged cluster having the same mobility as a different singly charged cluster can produce the same fragments which leads to an underestimation of the experimental survival probability of the studied singly charged cluster.

▪

Clusters with mobilities very close to each other can have overlapping signals which are difficult to separate.

On one side the trend in the clusters 2D2S1B, 3D3S1B, and 4D4S1B could be explained by the increasing role of anharmonicity with cluster size, while 2D3S1B does not fit to this trend due to different ratio of dimethylamine to sulfuric acid molecules. 2D3S1B has less hydrogen bonds since there are only 2 dimethylamine molecules in the cluster, this corresponds to lower bond network which may lead to a higher uncertainty. In addition to that, as indicated by table S1 in the supporting information, for the cluster 2D3S1B more simultaneous fragmentation pathways were observed experimentally in comparison to all other clusters. This contributes to a higher uncertainty in the experimental survival probability calculation for this cluster.

Technical comments:

line 53: Done.

Line 73-74: Adjusted.

line 76: Yes, and it has been adjusted in the text.

Fig 2: The main advantage of figure 2 is the visualization of the clusters and their fragments over the range of DMA voltages scanned for this experiment. This way of visualizing the data allows us to evaluate the presence of multi-charged compounds, the presence of fragmented clusters and the range of m/z and mobility of the clusters produced in the ESI. The raw data are the mass spectra and the DMA spectra, which we combine (after synchronizing the instruments) through a Matlab script to visualize the data and provide an overview of the results. To identify the clusters (in our case sulfuric acid-dimethylamine clusters) we analyze the MS data using TofTools (a Matlab GUI created in our institute) and for each of the identified cluster we retrieve the DMA mobility data through a Matlab script. Summarizing, the identification of the 11 clusters of sulfuric

acid and dimethylamine in our system is done using the mass spectrum. Following that, the DMA voltage at which each cluster appeared was determined by evaluating the electrical mobility of each of those clusters.

Finally, to quantitatively study the fragmentation, experiments at fixed voltage scans of the DMA are performed. This allowed only clusters of that specific mobility to enter into the APi-TOF MS which allowed us to study the fragmentation and fragmentation pathways of the individual clusters (an example is reported in Figure 4).

We will add the following explanations in the main text to better explain the use of figure 2 and the connection with figure 3:

From line 95 '...colour scale. This type of data visualization allows to evaluate the presence of multi-charged compounds, the presence of fragmented clusters and the range of m/z and mobility of the clusters produced in the ESI. Indeed, this plot...'

From line 115 '...good enough. To identify sulfuric acid-dimethylamine clusters the MS data have been analysed and clusters are reported in Figure 3. In particular, Figure 3 shows...'

Supplement:

Line 20 and 22: Done.

Line 26: Done.

Line 78: Done.

Line 83: It is a type of high resolution DMA that was developed at Yale-University. This article (<https://doi.org/10.1080/02786826.2016.1142065>) talks more about this specific type of DMA. We will add this reference in the text.