

Interactive Comment On “Clustering, Methodology, and Mechanistic Insights Into Acetate Chemical Ionization Using High-Resolution Time-of-Flight Mass Spectrometry”

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We thank the two reviewers for useful and insightful comments. The resulting discussion has led to a more rigorous manuscript with increased clarity. Below, we respond to each reviewer comment, and note the resulting changes in our revised manuscript (submitted separately).

Reviewer #2 General Comments

1. Voltage Switching Implications for real atmospheric data

Reviewer #2 Comment:

“While the comprehensiveness and detail of the analysis are outstanding, I was somewhat missing the stronger and perhaps a little more optimistic visioning relevant for real atmosphere measurements where mixtures of acids, peroxides, esters and other potentially interfering ions could be present. Could approaches like fast switching of optimal configurations favoring clustering or declustering regimes, variable E/N settings at constant API settings alternating with variable API settings at constant E/N settings, or other be an inspiration for readers?”

Authors Response: We thank the reviewer for their comments. The most direct atmospheric implications of this work are with data quality control and methods development in HR-TOF-CIMS. Voltage scanning experiments in the ambient atmosphere can be conducted when using reagent ions that require declustering. This would provide further evidence that ions are being properly identified as individual ions rather than clusters.

There are also significant implications for API-TOF (often called APi-TOF) measurements of ambient ions. Ions and ion-neutral clusters exist up to very large m/z ratios in both the positive and negative modes in the ambient atmosphere and laboratory experiments, such as the CERN CLOUD chamber. Understanding the stability of the clusters is of interest for new particle formation science and the transformation of individual molecules to clusters and eventually nano-particles that act as condensation nuclei. This transitional “phase” of matter is poorly understood and only recently measured by TOF-MS.

2. Thuner moved to main paper

Reviewer #2 Comment:

“Furthermore, such an excellent use of the Thuner capabilities seems particularly valuable to control clustering while optimizing the ion transmission. I find the Thuner application description very interesting. Perhaps it would be even more relevant to make its own section in the main text instead of the SI.”

Authors Response: This is beyond the scope of this paper and will require substantial development which should be pursued. Although the data presented SI Figure 2 is impressive, it lacks many of the constraints that can now be applied with the information presented in this paper. The length of this paper is already quite substantial, and we feel that further increasing the length of the paper will decrease the readability and focus. Thuner is a very Tofwerk-TOF specific piece of software and is aimed at advanced users. We are delighted that reviewer #2 found this section valuable as Thuner was integral in progressing our understanding of the API as it relates to cluster control and transmission.

3. Very simple vs very complex, and use of Thuner

Reviewer #2 Comment:

“In addition, the number of ions used in the Thuner is relatively small and in the low mass range. This observation should not be regarded as criticism as I am simply curious why the authors did not try to optimize the detection of specific ions on a more diverse group of chemicals (e.g. diols, esters, peroxides) across a broader mass range?”

Authors Response: See Authors Response in section titled **Reviewer #2 Specific Comments** item #3.

4. Propose standardization of acetate CIMS

Reviewer #2 Comments

“It could still be instructive for readers if the standardized IMR conditions were proposed which could facilitate the comparisons between different instruments”

Authors Response: This was attempted by emphasizing the importance of the acetate cluster ratio. Unfortunately, it remains nebulous as to how to produce concentrations of acetic anhydride with great reproducibility between systems that often vary drastically with regard to the acetic anhydride reservoir, operating conditions of the reagent system, and transfer line operation (e.g. heated, unheated, dilution, etc). The other major complication is that acetate concentrations are dependent on the radioactivity of the Po-210 source, which changes as a function of time as it decays. At this point, we hope this paper highlights the complexities of this method and the level of care that must be taken when operating these systems in a non-targeted approach.

Reviewer #2 Specific Comments

1. L.229 “TOF duty cycle corrections are made at m/z 59 for all data collected”. It would be useful for some readers to describe explicitly how this was done. Please provide description or reference the approach because there are sometimes inconsistencies in how duty cycle is defined and corrected for.

Authors Response: Line 229, Page 7 Reads:

“TOF duty cycle corrections are made at m/z 59 for all data collected.”

This was changed to read (line 238 page 7) :

“TOF duty cycle corrections are made within Tofware at m/z 59 for all data collected (Drewnick, et al. 2005).”

2. Sect. 2.2 the calibration setup generates single component standards. Did you try making the multicomponent standards as well? For example, could be useful with Thuner optimizations?

Authors Response: All calibrations were made with permeation tubes, which require the preparation of individual standards. The output from the permeation tubes can be mixed, but we did not want to increase the complexity of the observed clusters. This could be used to provide strong signals for Thuner, but Thuner would need further constraints in light of this work because optimization at the deprotonated-declustered mass does not necessarily mean that associated clusters have been eliminated.

3. L 177 I would not expect that the instrument saw many or abundant heavy ions, but I wonder if you can be convinced that the ions larger than m/z 494 did not wrap around the mass scale to appear at the subsequent cycle (at the wrong mass)? For example, in Fig. 3 the ions look somewhat cut-off but they may have been minor anyway. Also have you identified what these high molecular weight ions are (i.e. between 400 and 500 Th)?

Authors Response: Ion wraparound from previous extractions can occur if the TOF is not properly configured. No evidence of this was observed in the mass spectrum. Ions from previous extractions would show up at very strange m/z ratios meaning that if wraparound was occurring then we would observe ions at impossible mass defects. HR analysis did not find these types of ions. Identification of the high m/z ions is extremely difficult due to insufficient resolution at these masses. Additionally, low signal-to-noise and overlapping peaks makes HR analysis in this range highly suspect. We have investigated the composition of these ions previously, but it would be inappropriate to speculate their identity.

4. Table S3 shows ions that were used with Thuner. Depending on which ions were chosen in the sensitivity column 3 it could lead to different optimization results. Would it not make even more sense to include other desired ions from analytical standards in addition to formate ion, spanning the broader m/z range?

Authors Response: Yes it would make sense to include other ions. The issue is that Thuner needs isolated, individual ions with large signal-to-noise because full HR fitting procedures are not conducted online with Thuner experiments. Thus, if multiple overlapping ions exist where one would like to optimize using Thuner, then the resolution and symmetry would be improperly calculated. Moreover, overlapping ions can be complex mixes of clusters and non-clustered ions. This can cause very strange behavior in the observed ion signal intensity (again, partly due to the lack of high resolution fitting). Ultimately, the Thuner experiment fits the experimental data to a model. Understanding the inputs for Thuner ions is essential to prevent unexpected behavior during voltage experiments. These factors caused us to limit the number and types of ions used to optimize and explore the voltage space in the API.

5. Sect. 2.4. Do you know or is it worth discussing how the cleanliness of the skimmers (and perhaps other components) would impact the results (e.g. de-clustering) and if that could be responsible for differences between the newer and older instruments if these components are old and never cleaned?

Authors Response: This is an unknown effect. We know Tofwerk has cleaned the API of some TOF instrument, but we do not know how residues may change instrument performance. Extreme amounts of dust and contamination can lead to charge buildup on ion optics. This should, however, be observed in the voltage monitors.

6. The experiments and calibrations use the concept of relative humidity. Would it not be more relevant to operate in absolute humidity? Was the temperature always the same?

Authors Response: A mixture of relative humidity and absolute water vapor concentrations are discussed. Figure 6, for example, uses the calculated partial pressure of water inside the IMR after dilution with the reagent ion flow. Figure 5 uses relative humidity to highlight that ambient RH changes the distribution of observed ions. During the experiments where RH is presented, the temperature remained constant for the duration of the experiments.

7. The paper contains many useful observations improving understanding of observed ions, for example, [acetate + C₂H₃O₅]⁻ which is indicated as a potential product of autooxidation which can be eliminated by removing O₂ from the reaction chamber. Can oxygen from the ambient sample be an issue for this and similar reactions?

Authors Response: Oxygen from the ambient air absolutely produces the $\text{C}_2\text{H}_3\text{O}_5$ radical, which clusters with acetate. We see this effect by simply sampling laboratory air. The reason this is observed to such an extent is because the precursor radical is produced to the same extent as acetate from the dissociation of acetic anhydride. Radical species are not suspected to be efficiently sampled in the IMR, and if they are, then the reactions would be expected to proceed no faster than in the atmosphere because the oxygen concentration is lower in the IMR due to dilution by the reagent/ N_2 mixture.

Reviewer #2 Technical Comments

1. L183 What was the internal diameter of the 1/8" OD tubing?

Authors Response: Original sentence Line 183, Page 5:

"All connections to and from the reagent reservoir are made with instrument grade 1/8" stainless steel instrument-grade lines (Restek, Inc.) and stainless steel Swagelok fittings and ferrules."

This is changed to read Line 191, Page 6:

"All connections to and from the reagent reservoir are made with instrument grade 1/8" outer diameter, 0.055" inner diameter stainless steel instrument-grade lines (Restek, Inc.) and stainless steel Swagelok fittings and ferrules."

2. L. 207 what materials was the solenoid valve made of? Any other information (orifice, dead volume)?

Authors Response: Original sentence line 207, page 6:

"The gas sample flow is sent to the HR-TOF-CIMS through a 3-way solenoid valve (NResearch, Inc) positioned upstream from the humidified air system."

This was changed to read at line 215, page 6:

"The gas sample flow is sent to the HR-TOF-CIMS through a polychlorotrifluoroethene 3-way solenoid valve with a 3 mm orifice (NResearch, Inc) positioned upstream from the humidified air system."

3. Figure 7. The differences in vertical are difficult to see clearly. Might consider making the figure less stretched-out in horizontal

Authors Response: If this manuscript is accepted for final publication with AMT, we will consider formatting of this figure.

4. Fig S1, - Consider adding flow rates, tube diameters and tube materials, on the diagram if not presented in the text. -Was the RH sensor in the line to the instrument (rather than in the vent)? If so, was it not the source of any detectable impurities?

Authors Response: Flows and tubing details added to figure and/or the caption. The "vent" text in the figure is repositioned for clarity. The RH sensor is not vented. We did not observe any sources of impurity from the RH sensor.

5. Table SI2, Even though it might be obvious, the units should be included (both in the case of voltages and pressures (Primary beam region)).

Authors Response: Unit labels were added to the PB region and voltage header.

6. SI Line 51, change Figure SI1 to Figure SI2

Authors Response: SI line 51 figure SI1 changed to figure SI2

Work Cited

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