

***Interactive comment on “Clustering, Methodology, and Mechanistic Insights Into Acetate Chemical Ionization Using High-Resolution Time-of-Flight Mass Spectrometry” by Patrick Brophy and Delphine K. Farmer***

**Anonymous Referee #1**

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Review of “Clustering, Methodology, and Mechanistic Insights Into Acetate Chemical Ionization Using High-Resolution Time-of-Flight Mass Spectrometry” by Patrick Brophy and Delphine Farmer

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Anonymous Referee Comments

This manuscript presents a thorough analysis of the impact of post-reaction clustering and declustering that occur during the transmission stages during measurement using an acetate ion TOF CIMS. This type of laboratory investigation is crucial to improving

C1

analysis of ambient measurements collected using TOF CIMS methods, particularly considering the speed at which this field is currently growing. The experiments are done in a controlled thoughtful manner and conveyed in a good amount of detail. Overall I find the manuscript to be in good shape, but do have a few comments and edits that should be made prior to publication of this manuscript. This journal is in my opinion the most appropriate forum for the publication of such work and will be extremely informative and useful to its audience. My recommendation is to approve this manuscript for publication after minor corrections.

General comments:

A significant concern of mine is with potential reader misinterpretation that what is being studied here is the ionization mechanisms of the acetate ion chemistry itself. This work probes the effect of ion optics tuning on the creation of declustered or clustered ions in a region that is outside of the ion molecule reactor (IMR). The reactions which ionize neutral analyte gases are occurring in the IMR and the impacts being studied here, while they are indeed helpful and yield insight into the processes occurring in the IMR, do not directly indicate relative sensitivity of the reaction of a single analyte with an acetate ion, an acetate-acetic acid cluster ion, or an acetate-water cluster ion. While there are a few statements throughout the manuscript that indicate that the authors do indeed realize this, the point needs to be made in a more explicit manner to the reader: This work is studying the impacts of altering the  $m/z$  at which a specific ion product is detected by varying the electric field and thus the extent of declustering or fragmentation, not changing the ionization pathway of the fundamental chemical ionization method. This comes down to an issue with vernacular and clarity. What is being studied is not the sensitivity as is classically interpreted and discussed, which is in its most simplistic form a function of the rate of a reaction between an ion (or cluster ion) and a neutral (or neutral cluster). When the authors describe changes in sensitivity due to changes in voltages, what is really being discussed is changes in signals detected in a particular time bin. A quantity of formate ions are created with

C2

a certain sensitivity in the reaction region, based on the tuning in the SSQ and BSQ that ion will either be detected at the cluster or monomer mass. The caveat on that statement are the experiments that are designed to probe the effect of RH. In these experiments the cluster distribution in the IMR is now being fundamentally altered and the ionization reaction pathways are being changed. At a constant voltage setting, if the RH is increased and signal at the formate ion mass increases then in fact the sensitivity to formic acid, as classically defined, did increase as a result of a change in the cluster distribution. Since both processes are studied in this manuscript the language needs to be tightened up to reflect the manner in which sensitivity is commonly used. At a very minimum the authors must make it absolutely clear to the reader what is being discussed, actual changes in the sensitivity driven by changes in the cluster distribution in the IMR, or a change in 'sensitivity' as a result of redistribution of signal onto various masses. I do acknowledge that there are likely reactions that are occurring in the SSQ and BSQ that change the classically defined sensitivity and are affected by these voltage changes, but this is not what the authors are focused on and ultimately indicate that those reactions are not occurring or insignificant.

On a somewhat related note, there are several instances at which results from multiple instruments are being discussed. In particular, there are comparative statements between the results of this study and those of the Veres 2008 work using a quadrupole instrument. These types of comparisons are often very useful but the comparisons can be misleading. The following line of discussion is somewhat confusing so I will do my best to describe the issue here. The IMR is operated at a pressure of 100 mbar (assumed from Brophy 2015) and acetic anhydride is being added in a very specific manner at a specific mixing ratio described in the manuscript. The geometry and field applied to the IMR is also very specific to the TOF CIMS version of the instrument used in this particular project. In comparison, the Veres 2008 flow tube operated at 43 mbar, with an unknown mixing ratio of acetic anhydride in the flow tube, a small bias applied to the flow tube and is physically of a different design leading to reaction times that are presumably quite different than the TOF instrument in this work. The result

C3

is that the the ion-neutral cluster distribution in each instrument is different thus the reactions occurring in the are likely also quite different. Due to the fact that the transfer optics are operated at different pressures and electric field strengths, the resulting mass spectra cannot be directly compared as the detected distribution of signal is not reflective of the distribution within the reaction region. Therefore, the detected acetate to acetate-acetic acid cluster ratios observed are not necessarily reflective of the distribution in the reaction region which is where the absolute sensitivity is determined. It is not possible to compare the observed signal ratios between instrument unless they are operated under identical conditions. This is a very important issue because of statements such as thus: "This is inconsistent with previous quadrupole acetate CIMS experiments that indicate no humidity dependence for formic acid". The fact that the water cluster distributions in that 2008 work and this study may have been very different due to the operating conditions means these results may not be inconsistent rather incomparable.

In the abstract the authors state "We show that the majority, if not all, ion neutral chemistry occurs in the ion molecule reactor where incoming air mixes with the output of the ion source." After reading the manuscript I have failed to see a strong case for such claims. It is likely that there are in fact some degree of reactions occurring in the SSQ and even the BSQ, though they are likely negligible w.r.t the reaction in the IMR. In any case, the evidence for the above claim is relatively weak and more discussion should be included on the topic should the authors decide to keep this as a focal point of the work. My suggestions would be to remove this from the abstract as it is not once of the focal points of the work, and only comment on how some of the results suggest that this is true. Additional work must be done to show that this is the case.

There is a statement made comparing the work that can be performed using a TOF versus a Quadrupole. On page two the authors state "Ideally, quadrupole CI is deployed with the intent of measuring specific species with readily available authentic calibration standards and well-characterized interferences." This can be and should be

C4

also said about TOF CIMS. In this context you make it seem like TOF instruments are not deployed with the target of calibrating gases and understanding interferences or at least that it is not necessary to do so. It is very much a necessary part of using a TOF CIMS to provide accurate high quality quantitative data. Even though these instruments provide higher mass resolution a knowledge of the air matrix is necessary to separate many of the overlapping peaks, as the resolution of this instrument is not quite good enough to unambiguously identify all signal. Furthermore, in the sentence prior to that example, even with the quad systems one can “identify and observe the temporal behavior of compounds that have not previously known to exist or calibrated in a non-targeted approach”. This is done by performing mass scans, the only limitation being the lower duty cycle. You must be more careful in this section discussing the limitations and benefits of the two techniques against each other. This paragraph is in need of some cleaning up so as to not mislead the reader as to the relative advantages.

On page 5, line 163, the authors indicate that this work provides “a detailed investigation of the acetate ionization mechanisms”. However, as my comments above indicate, it is my belief that the authors have studied mechanisms that are not the same as the acetate ionization mechanisms, rather the effects of inducing fragmentation or declustering through ion optic voltage scanning, RH experiments being the exception.

This work is making it quite clear that the procedures of normalization that are typically used likely cannot be applied to all data. Some ions respond positively with RH and other negatively, the same would be said for changes in pressure if one extrapolates from this work. In the data analysis section, the authors describe a normalization procedure, it could be useful to have a discussion either here or later in the manuscript on what the result of this study suggest should be done. Can signals be traditionally normalized? Or is there some other method that can be used? Or are there going to be things that we simply have to calibrate for?

The description and logic of the statements made in section 3.3, page 10, lines 352 – 259 is hard to follow. It is important that this is clear, because the conclusions being

C5

drawn here, as mention in comments above, are rather important.

On page 14, the authors point out “The original development of this method by Veres et al. (2008) overlooks the importance of clustering. . .” While they are correct to identify the work does not go into the details of the importance of clustering, the work was performed using calibration standards for all of the data presented thereby avoiding any issues related to the formation of ion-neutral clusters on the sensitivities. Overlooking the importance of something and identifying but not going into the details are two very different actions. This again is a language issue that is somewhat misleading. The scanning mass range of those quadrupole systems is typically in the 300 – 500 amu range, well within the range necessary to observe and study this aspect. The fact that a quadrupole was used does not limit one from performing a similar study as indicated by the language used here. On page 14, line 495, in talking about the TOF results and discussion here the authors indicate the necessity of effective collisional dissociation. This is consistent with previous work, which the authors themselves have already acknowledged “Although Veres et al. (2008) note that a collisional dissociation chamber is important to “dissociate weakly bound cluster ions such as  $\text{CH}_3\text{C}(\text{O})\text{O}-(\text{H}_2\text{O})_n$ ”. Another indication the 2008 work does not overlook the importance of clustering on the sensitivity of the ion chemistry.

On page 15, line 506, have the authors considered any other explanations for the water dependencies such as the hydration of acids to diols, or another water catalyzed reaction occurring in the IMR? Something that comes to mind is the Maron et al. 2011 Chem. Phys. Lett. work on pyruvic acid hydration to a geminal-diol. Again remember when the RH is changed the reaction in the IMR change fundamentally, and then the effects being studied are the fragmentation and breakup of clusters in the transfer optics.

On page 17, the author makes the statement that the lessons here could apply to the iodide adduct CIMS. However, if one operates in declustered mode as presented in the acetate work nothing would be detected as iodide does not charge transfer or

C6

deprotonate (it could react to form IO as in the case of PAN iodide CIMS).

The last general comment that I have is that all of this work is extremely useful towards understanding how the TOF is detecting products of the ionization reactions. I think the authors should take a short amount of time to discuss calibrations however. All of these features of the declustering can essentially be 'ignored' if one is dedicated to calibrating the instrument. The elucidation of these details is specifically geared at getting the most and best understood amount of data from a uncalibrated bulk data set. There is a big differentiation between those two concepts, and one that I feel needs to be stressed considering the recent rapid growth in the use of newer TOF CIMS instruments. Without this added discussion somewhere in the manuscript the paper is still of sufficient quality to publish, but it is my opinion that such a discussion would be beneficial to the readers and add to the strength of the work.

Specific Comments:

Page 2, line 43, pluralize the word collect

Page 2, line 48, need to add the word "been" into the phrase 'been known'

Page 2, line 57, instead of absence do the authors mean 'presence'

Page 6, as a result of some of the concerns I included above, knowing the operating pressures of the IMR and other vacuum regions would be beneficial.

Page 7, line 228, make "curves" singular

Page 11, line 394, are the authors referring to an acetate-water or RH-water cluster here?

Page 13, line 463, the word 'cluster' needs to be plural.

Page 16, line 559, I believe this should read "dissociation is not a straightforward approach due to"

C7

On page 17, line 603 the word underestimation is used, however, depending on where you are in the dV space, you could be under or overestimating these bulk parameters.

Figure 5, 7, and 9 are really difficult to see the relative changes because of the log scale. Perhaps there might be a better way to show this data.

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C8