

## ***Interactive comment on “Furthering information from OH and HO<sub>2</sub> +RO<sub>2</sub> observations using a high resolution time of flight mass spectrometer” by R. L. Mauldin III et al.***

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Reply to referees for manuscript amt-2015-398 “Furthering information from OH and HO<sub>2</sub>+RO<sub>2</sub> observations using a high resolution time of flight mass spectrometer” by Mauldin et al. We would like to thank the referees for their time to review the manuscript and their comments. We will respond to them below.

Referee #1 General Comments These comments refer mainly to a need of more description of the operating conditions of the instrument. These comments arise out of a misunderstanding that the HO<sub>x</sub>RO<sub>x</sub> chemical ionization source is different from those used in previous studies. In fact the source used in this study as well as other nitrate CIMS sources used recently for TOF measurements are all based upon the same de-

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sign and dimensions as those used originally by Eisele. Text to this fact has been added to the NO<sub>3</sub><sup>-</sup> Mode section. Specific Comments The term HR-ToF has been replaced with CI-API-ToF as requested Question as to whether we also add HNO through the rear injectors as Sjostedt et al. did. We also do. This maintains the reagent ion (NO<sub>3</sub><sup>-</sup>) cluster distribution which is important for keeping the instrument calibration constant. Text has been added to the OH Mode section to this effect. Question as to whether we use the sum of the signals at 97 Th and 160 Th for the calculation of H<sub>2</sub>SO<sub>4</sub>. Yes, and text has been added to the NO<sub>3</sub><sup>-</sup> Mode section to this effect. Question regarding the stated detection limits. The stated limits are for the entire signal and background measurements. Text clarifying the time has been added. Question as to how using unlabeled SO<sub>2</sub> changes the detection limit. Our feeling is not much. While the background is increased, it only perhaps doubles from that when labeled SO<sub>2</sub> is used. The largest effect are changes in the H<sub>2</sub>SO<sub>4</sub> between signal and background measurements, but this effect goes down as the OH goes down. Labeled is always preferable. We changed the wrongly cited reactions 4 and 4a to 5 and 5a. The final comments were towards making Figures 4 and 5 more readable. We expanded both plots to show less time as suggested.

Referee #2 While the coupling of all measurements is new, all the measurement techniques described in the manuscript are the same as what have been done previously for quadrupole CIMS, and OH, H<sub>2</sub>SO<sub>4</sub>, and HO<sub>2</sub>+RO<sub>2</sub> measurements have also been conducted together before. In this regard, the “instrumentation” section reads like a summary of previously CIMS literature. While all of the techniques have been previously reported we believe the summary given aids the reader, especially in regards to the chemistry of the different modes when discussing the organic species. The addition in this manuscript is the monitoring of oxidized organic species which is made possible by the collection of complete mass spectra on the HR-ToF-CIMS, something that is not possible with a quadrupole. Nevertheless, the use of NO<sub>3</sub><sup>-</sup> with HR-ToF-CIMS is not new and has already been the topic of multiple recent publications, which are cited in the manuscript. Yes, the NO<sub>3</sub><sup>-</sup> has found wide use in VOC oxidation experi-

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ments currently due to its selectivity toward highly-oxidized species detection, but it is the combination of the ability to see these species together with the quantification of their source strengths that is the novelty here. The authors claimed that addition of NO and SO<sub>2</sub> may provide insights into oxidation mechanisms, and pointed out observations of representative masses for the  $\alpha$ -pinene system. The SO<sub>2</sub>-induced decrease in some of the signals (during the OH mode) is not explained. A section has been added to address this comment. The authors noted that the purpose of the current manuscript is not to analyze the changes in the spectra and that this is the topic of future work, but more support should be provided from other masses in the spectra to showcase the usefulness of perturbations, which are limited in NO concentration by the need to measure HO<sub>2</sub>+RO<sub>2</sub>. We have changed the mass spectrum figure to show spectra from two different modes (NO<sub>3</sub><sup>-</sup> and HO<sub>2</sub>+RO<sub>2</sub>) as well as expanded versions showing the behavior of the organic species in these modes. Discussion of this figure and the changes between modes has been added to the text. I do not think that there is a need to separate their work into two papers, one on instrumentation and one on the data analysis, since all the measurement techniques are well-established already. A manuscript with some brief descriptions of the measurement techniques and in-depth data analysis to showcase the potential capability of the combined system in providing further insights into oxidation mechanisms, on the other hand, would have been much stronger and would be of great interest, but will be more suitable for a more general journal (not an instrumentation journal). While we recognize that much of the information gathered on these measurement and chemical conversion techniques have been presented previously, we find it very useful to have it all described in one publication due to, for example, poor availability of the previous papers for wider audience and the scattered nature of the previous reports. So even though we noticed this redundancy, we still thought the gain of this clearly outweighs the potential harm of repetition (it should also be noted that we definitely do want to cite all the relevant papers where progress has been made in these techniques). The quantitative data interpretation from the field with these type of chemical perturbation experiments is

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a very tedious task due to large amount of peaks in the ToF spectra, which origin is currently unclear. This is true especially with this type of technique (NO<sub>3</sub><sup>-</sup> ionization), which only measures selected highly-oxidized end-products of an oxidation chain reaction with large uncertainties still existing in their specific formation mechanisms. The “full interpretation” of the spectra will take much more time and potentially require specific lab experiments to support the identifications. Thereby we feel that the advantage of using these techniques together is significant and merits a separate publication outlining this to a wider audience. As a result we want to keep the discussion of the details of the techniques largely as it is now. Nevertheless, due to the Referee’s comment the discussion was extended and Figure 3 augmented to more clearly illustrate the usefulness of this combination of techniques. Specific Comments Question as to the count rate for the reagent ion seeming low. This value is well within operational values for the measurement and is similar to that seen by other NO<sub>3</sub><sup>-</sup> ToFs in our group. Spectroscopy is now spectrometry. 4a is now 5a in the text A discussion of the error and times has been given Attribute is now attributed 4 and 4a have been changed to 5 and 5a Figure 3 has been changed

Again we would like to thank the referees for their helpful comments and suggestions. They have made the manuscript a better piece of work.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/amt-2015-398/amt-2015-398-AC1-supplement.pdf>

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