

Interactive comment on “Furthering information from OH and HO₂ +RO₂ observations using a high resolution time of flight mass spectrometer” by R. L. Mauldin III et al.

Anonymous Referee #2

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This manuscript describes the coupling of previously developed OH, H₂SO₄, HO₂+RO₂, and oxidized organics measurements using a High Resolution Time-of-Flight Mass Spectrometer. The system has the same sensitivity towards OH and HO₂+RO₂ as previous quadrupole CIMS measurements. Some sample data from measurements conducted at the Hyttiälä research station were provided. The authors proposed that the combination of these measurements into one instrument can provide additional insights into the formation mechanisms of organic species.

The manuscript is generally well-written. The authors described the method thoroughly and took great care to obtain appropriate backgrounds and limit the additional cycling of radicals from contributing to the HSO₄⁻ signal. The measurements described are

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very useful on their own, and the practical gains from being able to perform them using a single instrument can be significant.

However, I do not think that the manuscript in its current form suffices as a standalone publication. 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, H₂SO₄, and HO₂+RO₂ measurements have also been conducted together before. In this regard, the “instrumentation” section reads like a summary of previously CIMS literature. 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 NO₃⁻ with HR-ToF-CIMS is not new and has already been the topic of multiple recent publications, which are cited in the manuscript.

The title is also misleading in that no information is presented here which utilizes OH or HO₂+RO₂ measurements, but rather the addition of NO or SO₂. The authors claimed that addition of NO and SO₂ may provide insights into oxidation mechanisms, and pointed out observations of representative masses for the α -pinene system. The SO₂-induced decrease in some of the signals (during the OH mode) is not explained. The effect of NO is due to the titration of oxidized RO₂. The incomplete decrease in RO₂ when adding NO is thought to be due to the formation of an alkoxy radical which can isomerize and aid in the oxidation sequence, but this is speculative. 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 HO₂+RO₂.

Overall, while the coupling of all measurements is new, the descriptions of the various measurement modes are essentially the same as previous CIMS literature, the combined system also has the same sensitivity towards OH and HO₂+RO₂ as previous CIMS measurements. I agree with the authors that the combined system could po-

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tentially provide additional insights into the oxidation mechanisms, however, this is not demonstrated sufficiently in this manuscript. With all this, I do not think this manuscript adds substantially to literature as it stands. It is clear that the authors have already acquired ambient data from Hyytiälä research station with the combined instrument. 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).

Specific/minor comments:

Figure 2: The absolute (HNO₃)NO₃⁻ counts seem low. Is this because of transmission or long reaction time in the inlet? If reaction time is long, are the authors concerned about secondary reactions of HSO₄⁻ with oxidized organics? Does this affect the behavior of the organic signals from perturbations?

Page 2 line 6: “mass spectroscopy” should read “mass spectrometry”

Page 5 line 10: “forming organo-nitrates through reaction 4a”, should refer to 5a.

Page 6 lines 25-27: Breakdown of errors would be useful.

Page 7 line 17-18: “The difference between the OH “signal” and “background” values is the concentration of H₂SO₄ attribute to production from OH”, should change “attribute” to “attributed”.

Page 8, line 15: “(RONO₂; reactions 4 and 4a, respectively” should read 5 and 5a.

Page 8, lines 21-22. “From the plot it can be seen that the mass 309 and 340 peaks are anti-correlated and correlated with the addition of SO₂ respectively.” Mass 309 is correlated and 340 is anti-correlated.

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Figure 1. The 3 in HNO₃ needs reformatting in the diagram.

Figure 3. I suggest using multiple y-axis, log-linear scale can be used if necessary. The log scale makes time series unclear. If this is reformatted, lines pointing out H₂SO₄ concentrations are probably unnecessary.

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