**Answers to the 2nd review comments on the manuscript:**

# Multi-scheme chemical ionization inlet (MION) for fast switching of reagent ion chemistry in atmospheric pressure chemical ionization mass spectrometry (CIMS) applications

By: Matti P. Rissanen, Jyri Mikkilä, Siddharth Iyer and Jani Hakala

**Reviewer#1**

*The author has addressed my major comments and questions and the paper has greatly improved upon revision. I would like to recommend the manuscript for publication in AMT, but have one last suggestion:*

*Redo Figure S4 similarly as Figure 4 (mark the numbers of oxygen atoms and several major peaks, which would be essential information for the discussion).*

**Author reply:**

Figure S4 was redone in-line with the reviewer recommendation. Below are the old and new versions of the Figure S4 and their captions.

**New Figure S4 and its caption:**

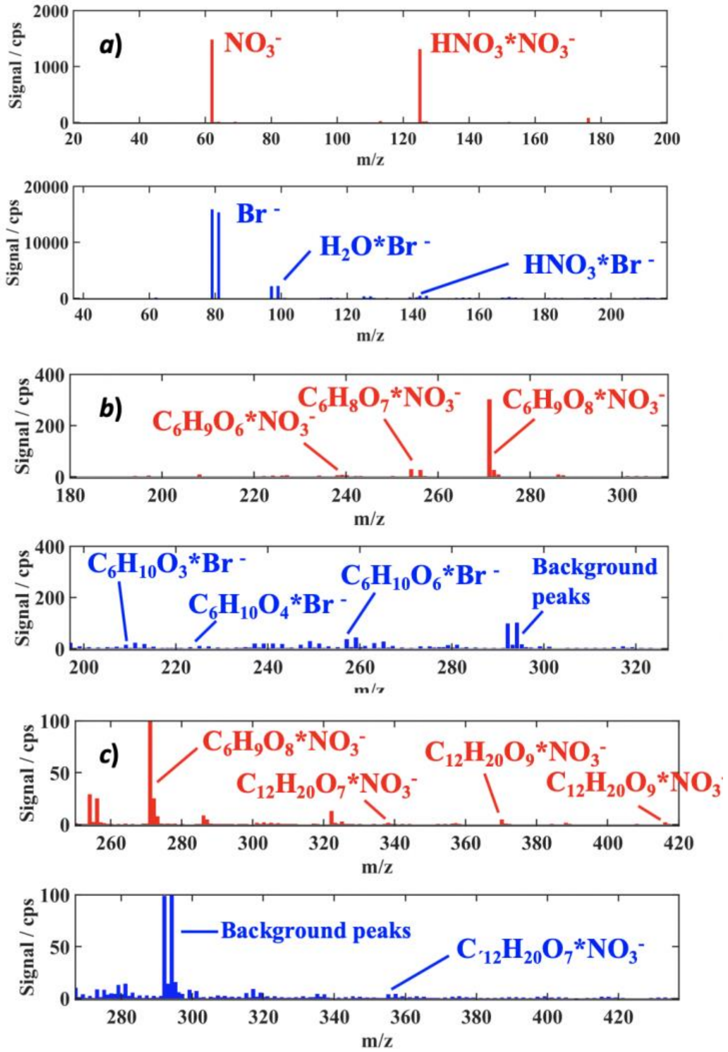

**Figure S4** Example spectra obtained from cyclohexene ozonolysis experiments in both ion modes shown with a common product mass axis, *i.e.*, the $Br^-$ spectrum is displaced by 17 Th (=difference between reagent ion $Br^-$ and $NO_3^-$ masses) to overlap the same composition products horizontally. Upper panels show nitrate spectra (red) and lower panels bromide spectra (blue). ***a)*** Illustrates the reagent ion peaks, ***b)*** the monomer range (*i.e.*, oxidation products which have the same number or less carbon atoms than cyclohexene), and ***c)*** the dimer range (*i.e.*, oxidation products with about two times the carbon number of cyclohexene), respectively. For a few of the most prominent product peaks also the explicit compositions are shown.

## Old Figure S4 and its caption:

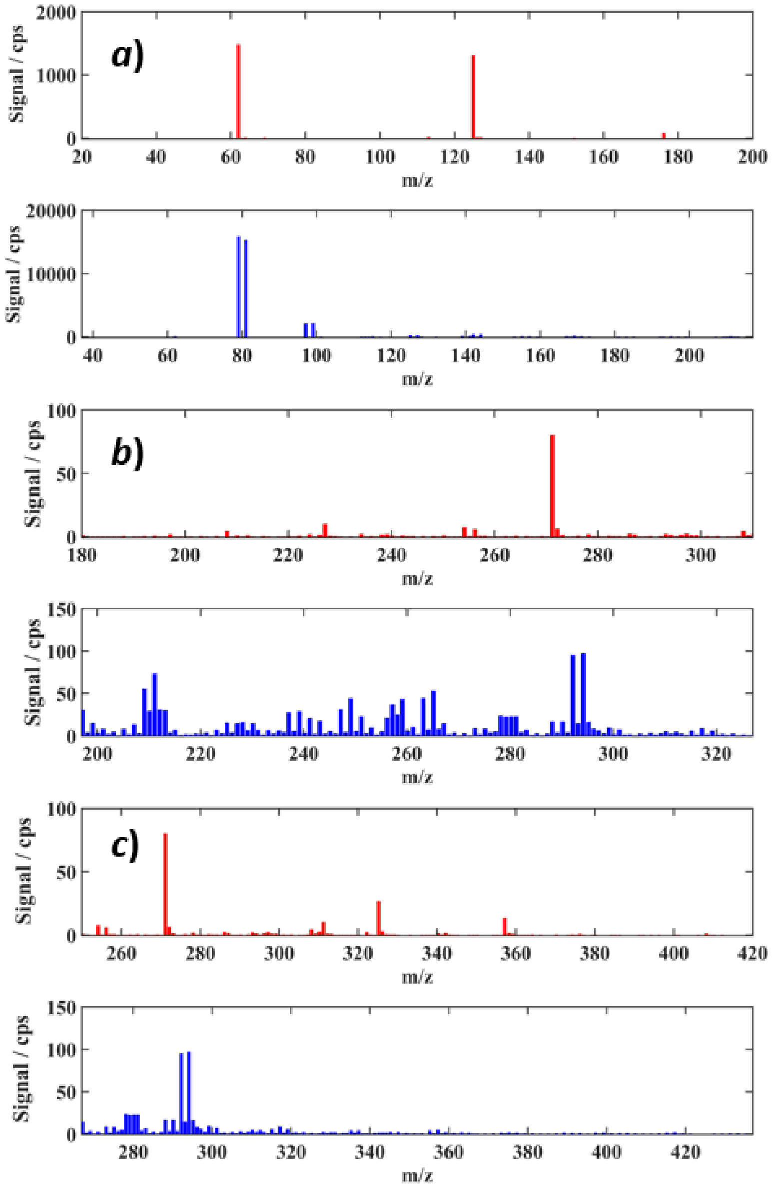

**Figure S4** Example spectra obtained from cyclohexene ozonolysis experiments in both ion modes shown with a common product mass axis, *i.e.*, the $Br^-$ spectrum is displaced by 17 Th (=difference between reagent ion $Br^-$ and $NO_3^-$ masses) to overlap the same composition products horizontally. Upper panels show nitrate spectra (red) and lower panels bromide spectra (blue). ***a)*** Illustrates the reagent ion peaks, ***b)*** the monomer range (*i.e.*, oxidation products which have the same number or less carbon atoms than cyclohexene), and ***c)*** the dimer range (*i.e.*, oxidation products with about two times the carbon number of cyclohexene), respectively.

**Reviewer#2**
*Review of Rissanen et al.*
*I wish to point out that I was not a reviewer of this manuscript in the first round of review.*
*I find it a pleasure to read the updated manuscript. The novel inlet for fast switching of reagent ions is of great interest to the community. I only have minor comments.*

1. *As the main focus of the manuscript is to introduce the inlet design, more details about the inlet should be provided, such as the dimensions of the source blocks. What's the weight of each ionization stage? This may be an issue when multiple ionization stages are deployed.*

**Author reply:** More physical details were added to the main text, based on the reviewer recommendation. In addition, an additional schematic figure of the inlet with marked dimensions was added to the supplementary material.

**Addition to text (page 2, line 103):** "The ion source connecting MION to the mass spectrometer entrance weights about 2.1 kg, with every additional stage weighting roughly 1.5 kg each. The distance of the first ion source to the mass spectrometer inlet orifice is approximately 3 cm, and the length of an additional ionization stage is about 10 cm, with a height of 16 cm. A schematic Figure S1 with marked dimensions can be found in the supplementary material."

**New figure S1:**

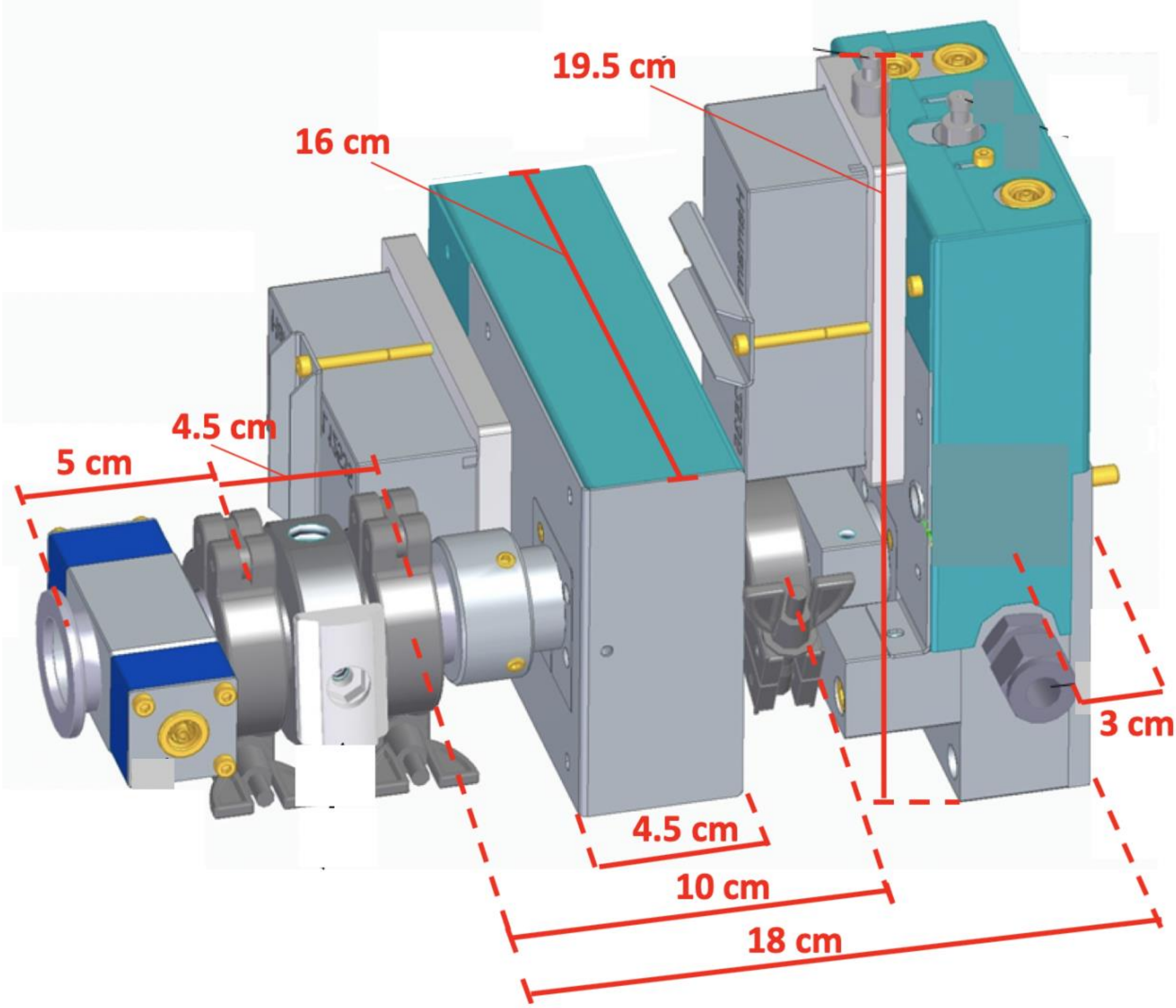

**Figure S1** Schematic of the MION showing the approximate dimensions of the inlet design.

2. *From figure 1a, it looks like that the directions of two ionization stages are 90degree different. Is this for experimental reason or for illustration?*

**Author reply:** This is the schematic of the current design. The ion sources are 90degrees to each other to enable easier usage of the inlet connections. This should not matter to the measurement to any significant extent, as the flow inside the pipe has a circular symmetry.

3. *Figure 2. It would be nice to include an insert figure with shorter time period, to better show the switch between two reagent ions.*

**Author reply:** According to the reviewer recommendation we have added an insert figure to better demonstrate the rapid ion mode switch.

**New figure 2 and its caption:**

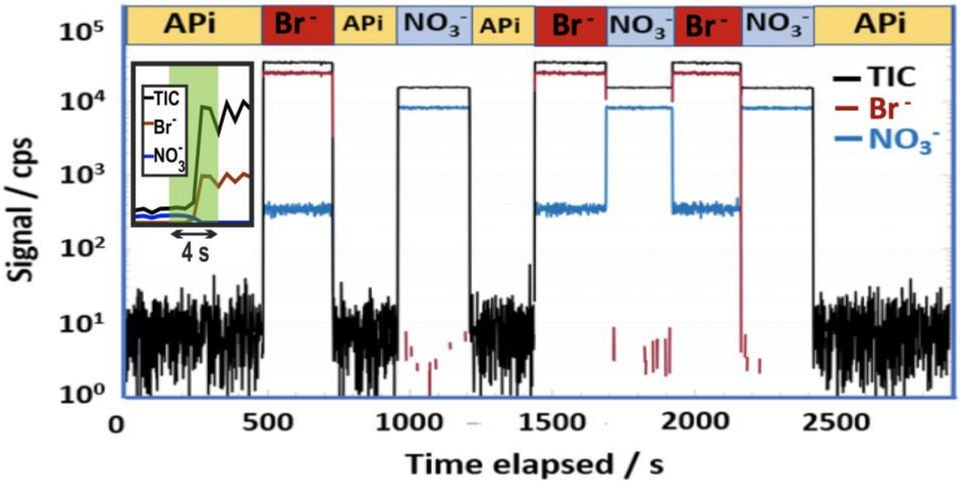

**Figure 2** An example of switching between multiple ion chemistries while sampling laboratory air. The ion modes utilized have been marked with separate colours and are further labelled above the figure with abbreviations: APi for ambient ion mode (no active ionization applied; black trace), $Br^-$ for bromide ion ionization mode (red trace), $NO_3^-$ for nitrate ion ionization mode (blue trace), and TIC is used to indicate total ion count measured (black trace). The insert demonstrates the rapid ion mode switch, shown in a linear scale. All signals shown here were retrieved by high resolution peak fitting.

**Old Figure 2 and its caption:**

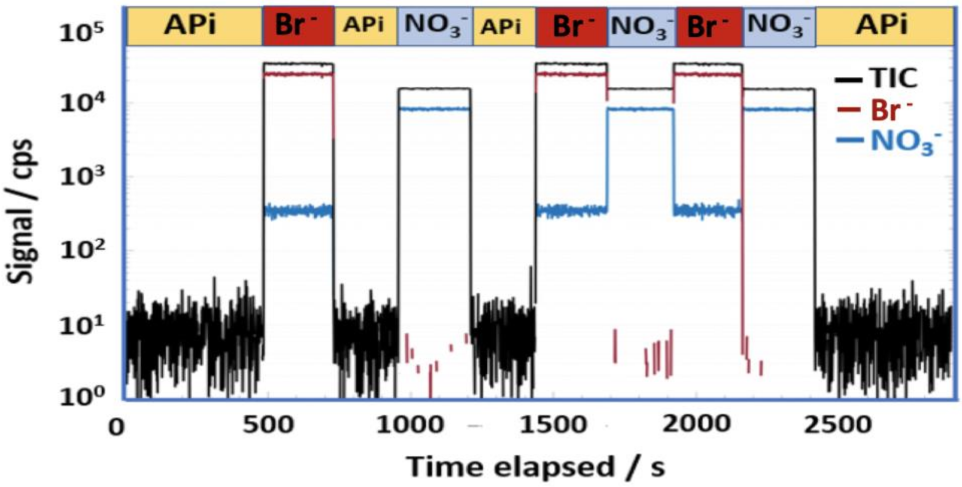

**Figure 2** An example of switching between multiple ion chemistries while sampling laboratory air. The ion modes utilized have been marked with separate colours and are further labelled above the figure with abbreviations: APi for ambient ion mode (no active ionization applied; black trace), $Br^-$ for bromide ion ionization mode (red trace), $NO_{3^-}$ for nitrate ion ionization mode (blue trace), and TIC is used to indicate total ion count measured (black trace). All signals shown here were retrieved by high resolution peak fitting.

*4. The authors hypothesized that the difference in sulfuric acid calibration factors between Br- and NO3- is due to the ion-molecule reaction time. This is an easy hypothesis to test, just by switching the positions of two reagent ions.*

**Author reply:** We do agree with the reviewer that this would be a relatively easy task to do but unfortunately, we do not have the needed instrumentation to repeat the calibration measurement in the near future. We do appreciate the comment and will return to this issue when the needed equipment is again available to us.