

## Referee 2

This work studied CI-NH<sub>4</sub>-Orbitrap as a powerful tool for characterizing oxygenated organic molecules (OOMs) from atmospheric oxidation of VOCs. The manuscript compares the performance of CI-NH<sub>4</sub>-Orbitrap with a few other chemical ionization based mass spectrometers with a range of ionization methods and resolving power. The comparison showed that CI-NH<sub>4</sub>-Orbitrap is a promising instrument to more comprehensively characterize and even quantify a near-complete range of OOMs from oxidation. The work is solid and well written. It will likely deserve publication at AMT. But some sections of the manuscript need to be better clarified and some in-depth discussion is needed.

-We thank the reviewer for his/her careful consideration of our article. We attached a revised version of the manuscript in which we considered all the comments raised by the reviewer. Below, you will find our point-by-point reply.

Detailed comments:

1. Line 39 in Abstract. Change “highly oxidized volatile organic compounds (HOM)” to “highly oxidized molecules (HOM)”.

-Revised to “highly oxidized organic molecules” based on Bianchi et al., 2019.

2. Line 56-58. OOMs can also be generated through bimolecular RO<sub>2</sub> pathways not involving autoxidation. Autoxidation is important, but review OOM formation more compressively, other pathways should also be mentioned here.

-We revised the statement as follows:

*Line 58-60: OOMs can be generated through the bimolecular peroxy radicals (RO<sub>2</sub>) pathway or by the autoxidation of RO<sub>2</sub> followed by the termination pathways (Bianchi et al., 2019; Mohr et al., 2019)*

3. Line 76-87. In the negative ion-based MS, it would be helpful to also mention iodide-CIMS, as it is compared later in the text. One sentence to set up the context would be a good idea, also because iodide-CIMS measures a wide range of OOMs.

-We add a sentence to describe iodide-CIMS in the main text:

*Line 75-78: For example, negative ion-based chemistry, including nitrate (NO<sub>3</sub><sup>-</sup>), can optimally detect HOMs, which only constitute a small subset of the OOMs (Lee et al., 2014; Berndt et al., 2018; Riva et al., 2019b); iodide (I<sup>-</sup>) can efficiently detect various OOMs with 3-5 oxygen atoms (Riva et al., 2019b; Lee et al., 2014).*

4. Line 150. Change the sentence to “The NH<sub>4</sub><sup>+</sup> reagent ion cannot be directly detected due to...”

-Revised.

5. Line 156. In prior studies using the same NH<sub>4</sub><sup>+</sup> ionization but with a ToFwerk LTOF, is there evidence regarding the ratio of the sum of these “surrogates” over the reagent ion abundant? If this data is available, it would be useful to mention here.

-A direct comparison of the cluster and the presence of amines is not possible. First, the Orbitrap cannot detect masses lower than 50 Th preventing the detection of the reagent ions. Secondly, in Tofwerk LTOF (i.e., Vocus-NH<sub>4</sub><sup>+</sup>) the distribution of the reagent ions, i.e., cluster distribution is highly dependent on the user settings (i.e., pressure, NH<sub>3</sub> flow, Vocus RF and voltage settings) and the ion transmission related to the instruments. Finally, no Vocus-NH<sub>4</sub><sup>+</sup> instrument was deployed during the Cloud campaign. As a result, it is not possible to perform such kind of comparison.

6. Line 159-166. The uncertainties regarding this semi-quantification method needs to be discussed somewhere. For example, this method assumes that the C<sub>10</sub>H<sub>14</sub>,<sub>16</sub>O<sub>x</sub> formulas measured by the three instruments are the same species without artifacts? Do dimers in PTR3 decompose to monomers? How can you obtain the calibration factor from correlation analysis alone (cps vs. cps between different instruments)? Do you need response factors (e.g., ppt/cps) from either the PTR3 or NO<sub>3</sub>-LTOF to get concentration results for Orbitrap?

By the way, NO<sub>3</sub>-LTOF is termed in this paragraph, but termed “CI-NO<sub>3</sub>-LTOF” or “CI-NO<sub>3</sub>-APi-LTOF” in other places. The terminology needs to be consistent throughout the manuscript.

-Decomposition of peroxide can be expected as it has been shown for the Vocus PTR, however as discussed by Li et al., (2022) protonation of peroxides (i.e., ROOR and ROOH) can partly lead to the decomposition of the analytes. Determining to which extent the ionization process within the PTR3 fragments peroxide is beyond the scope of this study as it is by itself a dedicated work (e.g., Li et al., 2022). While fragmentation of dimeric compounds can contribute to the overall signal of the monomers as mentioned by Li et al., 2022, the concentration of such species remains minor (as shown in many previous studies and within this work). As a result, we do not expect large enhancement of the monomers signal intensity.

A sentence has been added to mention this potential artifact:

*Lines 154-156: No direct calibration has been performed for the NH<sub>4</sub><sup>+</sup>-Orbitrap, but a semi-quantitative method was used to estimate the concentrations of OOMs measured by NH<sub>4</sub><sup>+</sup>-Orbitrap based on the correlation with NO<sub>3</sub><sup>-</sup>-LTOF or PTR3-TOF.*

*Lines 166-171: However, decomposition of peroxides (i.e., ROOR and ROOH) can be expected within the PTR3-TOF. While fragmentation of dimeric compounds can contribute to the overall signal of the monomers, the concentration of such species remains minor (Li et al., 2022). As a result, we do not expect large enhancement of the monomers signal intensity. Finally, a temperature-dependent sampling-line loss correction factor was applied (Simon et al., 2020)*

We also uniformed the terms of NH<sub>4</sub><sup>+</sup>-Orbitrap, NO<sub>3</sub><sup>-</sup>-LTOF, PTR3-TOF and I-CIMS throughout the manuscript.

7. Line 258-267. The dm threshold is also dependent on the level of knowledge of the possible chemical formulas at the normal m/z. In case the chemical formulas are known at high confidence (in the example of known VOC precursors), the threshold may be smaller. But in real cases where more than two peaks are present, the threshold can be larger. This is a very complex issue. The simplified illustration here is certainly useful, but some more in-depth discussion is warranted in real cases.

-We revised this part as follows:

Lines 301-305: *It should be noted that the NH<sub>4</sub><sup>+</sup>-Orbitrap has shown its strength in separating neighboring peaks in controlled experiments, in which the knowledge of the chemical compositions for OOMs is relatively abundant. The advantages of higher mass resolving power should be further stressed in ambient observations, where the knowledge about OOM species can be limited with a larger number of detectable peaks.*

8. Figure 1. The last plot was not described in the caption.

-We moved Figure 1 to SI considering it is a concept of peak identification and mass resolution. The description of the last plot was added in the caption as follows:

**Figure S3** *Simulated TOF spectra of overlapping peaks of different intensities near m/z 200 (a, b, c), and the ratio of dm to FWHM as a function of peak height ratio (d). Assuming a TOF mass analyzer with a mass resolving power of 8,000, somewhere between a Tofwerk HTOF (“high-resolution time-of-flight”) and LTOF (“long high-resolution time-of-flight”) mass spectrometers. FWHM was the full width at half maximum and dm was the distance between two overlapping peaks. Peak height ratio represented the signal intensity ratio of overlapping peaks and peak distance referred to the ratio of dm to FWHM. The overlapping area represented a greater proportion of the peak area of the less intense peak. The noise wasn’t added to the data.*

9. Line 280. In the comparison between CI-NH<sub>4</sub>-Orbitrap and I-FIGAERO-CIMS, it is unclear that the large difference in number is mainly due to the less selectivity of NH<sub>4</sub><sup>+</sup> ionization or the higher resolving power of the Orbitrap. Some clarification is needed. The range of oxygen number seems comparable based on previous studies of iodide-CIMS (from nO=2 to HOMs). The detection limit issue mentioned in Line 289 seems to suggest that this difference is largely due to instrument sensitivity tuning issue for iodide-CIMS? If this is the case, the comparison does not really speak for the advantages of CI-NH<sub>4</sub>-Orbitrap in ionization method and resolving power.

-No, we did not mean to mention that the I<sup>-</sup>-CIMS equipped with a FIGAERO inlet has a higher detection limit for OOMs. Iodide showed a higher selectivity to OOMs, which detected sufficiently the semi-volatility OOMs with 3-5 oxygen atoms but less the most oxidized OOMs which might arise from losses within the sampling line and the inlet as the instrument was optimized to collect/analyse aerosol particles. We revised the statements as follows:

Line 318-320: *Due to the selectivity and potential losses within the sampling line/inlet of the I<sup>-</sup>-CIMS equipped with a FIGAERO inlet fewer monomers of C<sub>8-10</sub> and dimers of C<sub>19-20</sub> were observed, with an average O:C of 0.5 ± 0.2.*

10. Line 284. How was the O/C ratio estimated? 0.4±/− 0.2 seems to be a very large uncertainty. Is this due to the variation between the two experiments? Or uncertainties in the semi-quantification method? With the accurate formula detection, I would expect smaller uncertainties in O/C ratios.

-The ratio of O to C was calculated based on the assigned formula by each mass spectrometer. Only Run 2211 was used to plot the mass defect figure and the marker size was scaled to signal intensities for NH<sub>4</sub><sup>+</sup>-Orbitrap. 0.2 indicated the variation of O/C, not the uncertainty of the molecular formula identified by the NH<sub>4</sub><sup>+</sup>-Orbitrap. The NH<sub>4</sub><sup>+</sup>-Orbitrap identified ~460 OOMs and the O/C varied from 0.06 to 1.1, the corresponding formulae were C<sub>10</sub>H<sub>10</sub>O and C<sub>8</sub>H<sub>14</sub>O<sub>9</sub>.

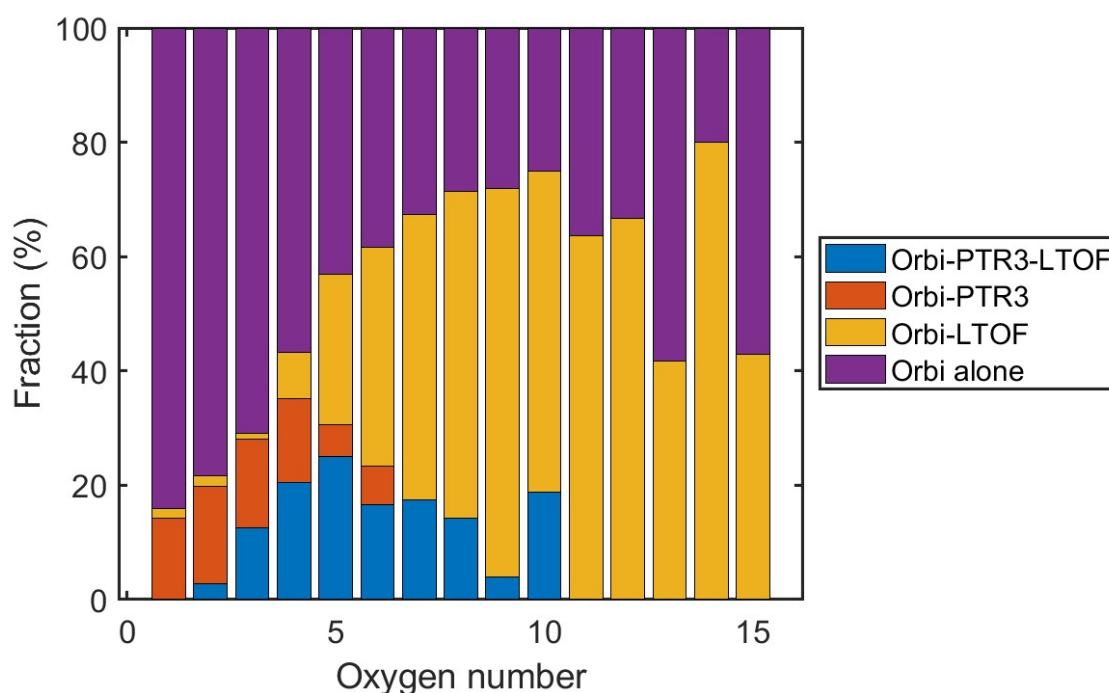
11. Line 294. This number suggests a large fraction of the chemical formulas detected by CI-NH<sub>4</sub>-Orbitrap are not seen by any of the other three instruments. What are the characteristics (e.g., number of C, H, O, O/C, etc.) of the chemical formulas co-detected vs. only detected by CI-NH<sub>4</sub>-Orbitrap? Combining PTR3-TOF, Iodide-CIMS, and NO<sub>3</sub>-LTOF, it appears to me that the overall selectivity is comparable to CI-NH<sub>4</sub>-Orbitrap. If the difference boils down to the discrepancies regarding sensitivity (e.g., Orbitrap much better than the others and most of the formulas only detected by CI-NH<sub>4</sub>-Orbitrap are relatively small peaks) and resolving power (e.g., CI-NH<sub>4</sub>-Orbitrap detects formulas at high confidence, but the other instruments do not), I think it is worth discussing this difference to highlight the superior performance of CI-NH<sub>4</sub>-Orbitrap.

-After we re-checked the dataset, we found a mistake. The actual number is ~42%. Generally, OOMs co-detected by the different chemical ionization techniques show clear characteristics in oxygen number: OOMs with an oxygen number greater than 4 are co-detected by the NO<sub>3</sub><sup>-</sup>-LTOF and the NH<sub>4</sub><sup>+</sup>-Orbitrap, while those co-detected by the PTR3-TOF and NH<sub>4</sub><sup>+</sup>-Orbitrap have an oxygen number < 7 (Figure R4).

For the overall selectivity, we must argue that although there are molecules only detected by the NH<sub>4</sub><sup>+</sup>-Orbitrap, there are still other molecules (e.g., C<sub>18</sub>H<sub>30</sub>O<sub>10</sub> in NO<sub>3</sub><sup>-</sup>-LTOF, C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> in the PTR3-TOF) that could only be detected by the NO<sub>3</sub><sup>-</sup>-LTOF or the PTR3-TOF. Considering that the PTR3-TOF has been optimized for measuring ammonia and amines in this study and is not in the best state for measuring a wider range of OOMs, we cannot conclude that the NH<sub>4</sub><sup>+</sup>-Orbitrap is better than other mass spectrometers in measuring all the OOMs. It should be stressed out that the NH<sub>4</sub><sup>+</sup>-Orbitrap can measure the widest range of oxygen numbers, as shown in Figure R4.

Lines:322-324: *Due to differences in selectivity and sensitivity of the analytical methods toward OOMs, ~42% of the identified species by NH<sub>4</sub><sup>+</sup>-Orbitrap are simultaneously detected by other mass spectrometers.*

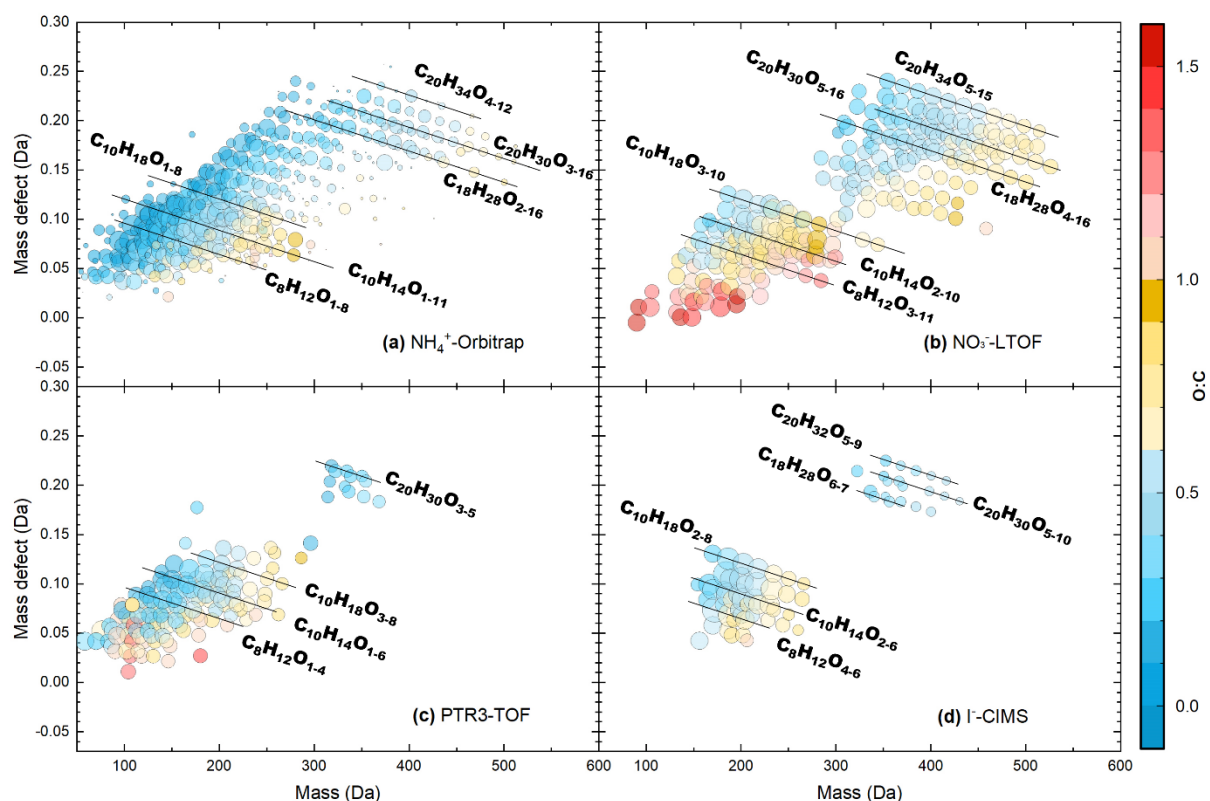
We add Figure R4 to SI as Figure S4.



**Figure S4** The fractions of co-detected OOMs with other instruments among those detected by  $\text{NH}_4^+$ -Orbitrap with the variation of oxygen number. Purple areas represent the OOMs only detected by  $\text{NH}_4^+$ -Orbitrap, which account for approximately 42%; yellow areas were OOMs co-detected by  $\text{NH}_4^+$ -Orbitrap and  $\text{NO}_3^-$ -LTOF; red areas were OOMs co-detected by  $\text{NH}_4^+$ -Orbitrap and PTR3-TOF; and blue areas were OOMs co-detected by the three mass spectrometers.

12. Figure 3. It would be helpful to draw a few lines indicating the major chemical formula series detected by the different instruments in the KMD plots.

-We changed the mass defect with a few lines indicating the major families of OOMs as follows:



**Figure 2:** Mass defect plots for organic compounds measured by (a)  $\text{NH}_4^+$ -Orbitrap, (b)  $\text{NO}_3^-$ -LTOF, (c) PTR3-TOF and (d) I-CIMS in run 2211. The x-axis represents the mass-to-charge ratio of the neutral analyte and the y-axis represents the corresponding mass defect, which is the difference between their exact mass and nominal mass (Schobesberger et al., 2013). Markers were all sized by the logarithm of their corresponding signals and colored by the O:C value. Some major OOMs measured by different instruments were indicated by the black lines.

13. Section 3.3. It is useful to describe a few major chemical formulas which have the worst correlations. Although it is not a chemistry paper, but providing such information can help others think about the chemical reasons behind these correlations.

- There are no clear elemental characteristics among the worst correlated species, as shown in Table R1. When checking the time series of the worst correlated OOMs, we found there were complex reasons why the correlations were lower. For  $\text{C}_{18}\text{H}_{32}\text{O}_3$  detected by the  $\text{NH}_4^+$ -Orbitrap and the PTR3-TOF or  $\text{C}_{18}\text{H}_{30}\text{O}_7$  detected by the  $\text{NH}_4^+$ -Orbitrap and the  $\text{NO}_3^-$ -LTOF, although

the variation trend was similar during part of the experiment, there were clear differences during other periods. This might be because given species were too close to the LoD of one instrument yielding larger uncertainties (Figure R5 and R6). We cannot also rule out that different experimental conditions would have led to the formation of isomers having different sensitivities toward the reagent ions used in this study.

Table R1. The element composition of 20 worst correlation OOMs co-detected by  $\text{NH}_4^+$ -Orbitrap and other instruments

Item	$\text{NH}_4^+$ -Orbitrap & PTR3-TOF				$\text{NH}_4^+$ -Orbitrap & $\text{NO}_3^-$ -LTOF			
	C	H	N	O	C	H	N	O
1	18	32	0	3	12	16	0	6
2	10	12	0	4	15	24	0	15
3	8	12	0	6	20	32	0	20
4	3	6	0	1	20	31	1	7
5	10	16	0	7	6	12	0	5
6	10	14	0	8	18	30	0	7
7	9	14	0	6	8	11	1	6
8	6	11	1	1	9	13	1	4
9	10	20	0	2	12	18	0	8
10	7	13	1	1	12	22	0	5
11	10	16	0	8	12	20	0	9
12	10	18	0	7	19	29	1	6
13	10	17	0	4	19	30	0	10
14	8	14	0	7	7	10	0	7
15	4	6	0	2	7	11	1	5
16	6	9	1	2	8	12	0	7
17	10	14	0	6	4	6	0	2
18	4	6	0	1	18	26	0	5
19	10	20	0	3	5	10	0	3
20	4	6	0	3	8	13	0	8

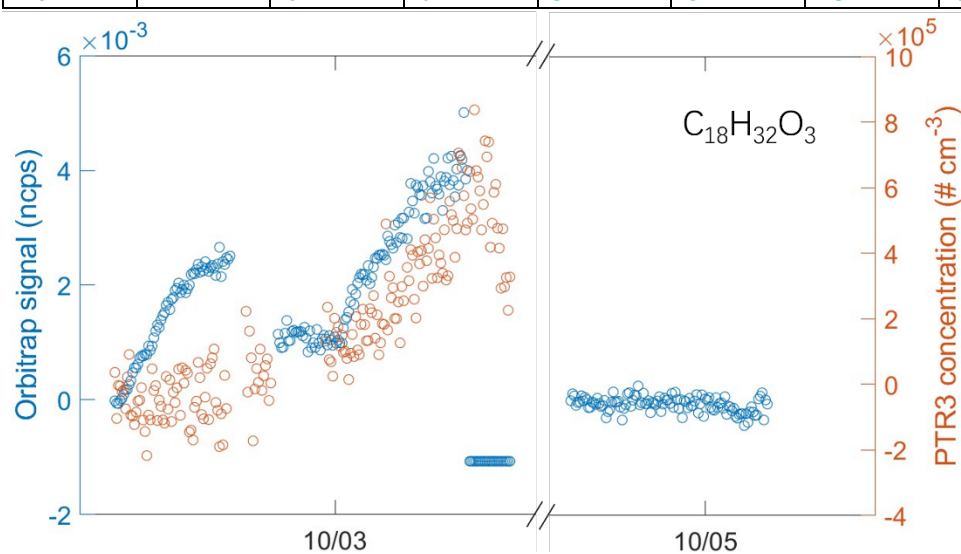


Figure R5. The timeseries of  $\text{C}_{18}\text{H}_{32}\text{O}_3$  measured by  $\text{NH}_4^+$ -Orbitrap and PTR3-TOF.

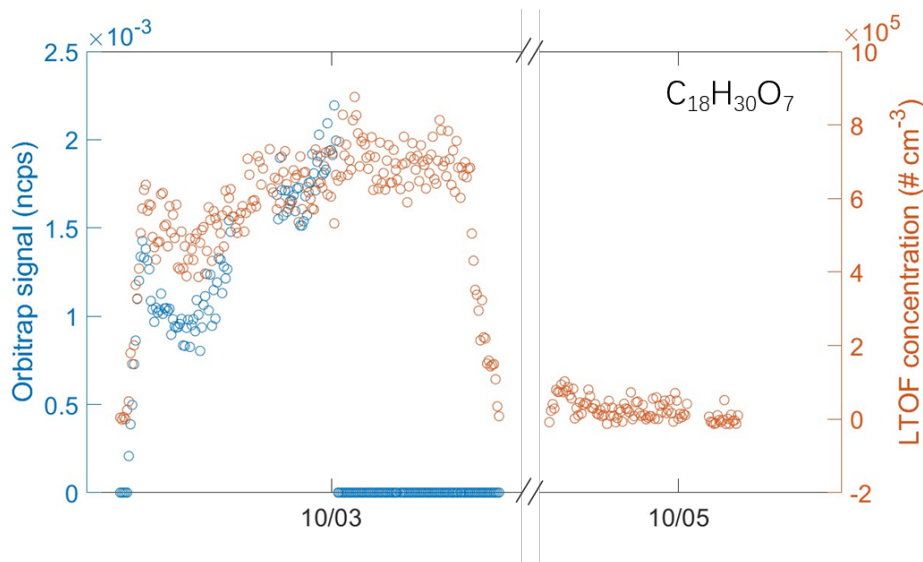


Figure R6. The timeseries of  $C_{18}H_{30}O_7$  measured by the  $NH_4^+$ -Orbitrap and the  $NO_3^-$ -LTOF.

14. Figure 5. The figure legend needs to be explained in figure caption. LTOF means  $NO_3^-$ -LTOF? Orbitrap-LTOF means Orbitrap-derived concentrations using  $NO_3^-$ -LTOF calibration factors? Does the  $NO_3^-$ -LTOF actually measure oxygen number down to 2? Do the concentrations in Orbitrap depend on quantification by PTR3 (proton transfer kinetics) or  $NO_3^-$ -LTOF ( $H_2SO_4$  as the sole standard)? If so, they need to be mentioned. I believe that much of the unclarity stems from Eq. (3), as mentioned in my above comment #6. What are the units of  $c$  and  $[X]$ ? If  $c$  is unitless (i.e., cps/cps from correlation analysis), and  $[X]$  is in concentration (ppt or molecules  $cm^{-3}$ ), the equation does not make sense because the second term in the right side of the equation is unitless.

-The answers should be “Yes” for the first four questions. We agree some descriptions should be added to clarify the meaning of Figure 5. The unit of [OOM] is cps (signals detected by  $NH_4^+$ -Orbitrap) and that of  $C$  is molecules  $cm^{-3}$ , which is the slope of the correlation analysis between the measured concentrations (molecules  $cm^{-3}$ ) from reference instruments and the normalized signal (unitless). We add more description regarding Figure 4, the quantification of the  $NH_4^+$ -Orbitrap, and the units in Eq. (3-5) in Section 2.2 as follows:

**Figure 4:** Estimated concentrations of the main  $C_{10}$  oxidation products (a)  $C_{10}H_{14}O_n$  and (b)  $C_{10}H_{16}O_n$  as a function of oxygen numbers observed in run 2211. Orbitrap-LTOF and Orbitrap-PTR3 represented the estimated concentration of monomers measured by the  $NH_4^+$ -Orbitrap using the calibration factors from correlation analysis with the  $NO_3^-$ -LTOF and the PTR3-TOF, respectively.

Lines 153-171:

$$[OOM]_{nor} = \frac{[(OOM)-NH_4^+] + [(OOM)-H]^+}{\Sigma[Amine]} \quad (3)$$

No direct calibration has been performed for the  $NH_4^+$ -Orbitrap, but a semi-quantitative method was used to estimate the concentrations of OOMs based on the correlation with the  $NO_3^-$ -LTOF or the PTR3-TOF. The values of the Pearson correlation coefficients ( $R^2$ ) were determined between the  $NH_4^+$ -Orbitrap and two other instruments using the timeseries during two runs (run 2211 and 2213). This includes AP injection, steady state stage,  $NO_x$  or CO

injections, and RH variation. As a result, for one compound, 755 data points were recorded and used for the correlation analysis. For each instrument (referred to as REF), OOMs with  $R^2$  greater than 0.9 (i.e.,  $A$ ) between REF and the  $\text{NH}_4^+$ -Orbitrap, were used to determine a calibration factor ( $c_{\text{Orbi-REF}}$ , molecules  $\text{cm}^{-3}$ ) and retrieve the concentrations of OOMs measured by the  $\text{NH}_4^+$ -Orbitrap according to the following equations 4-5:

$$c_{\text{Orbi-REF}} = \frac{[A]_{\text{REF}}}{[A]_{\text{nor}}} \quad (4)$$

$$[\text{OOM}]_{\text{Orbi-REF}} = c_{\text{Orbi-REF}} \times [\text{OOM}]_{\text{nor}} \quad (5)$$

The calibration factor between the  $\text{NH}_4^+$ -Orbitrap and REF ( $\sim 2.62 \times 10^8$  for  $\text{NO}_3^-$ -LTOF and  $4.83 \times 10^8$  for PTR3) was assumed to be constant for all the OOMs. However, decomposition of peroxides (i.e., ROOR and ROOH) can be expected within the PTR3-TOF. While fragmentation of dimeric compounds can contribute to the overall signal of the monomers, the concentration of such species remains minor (Li et al., 2022). As a result, we do not expect large enhancement of the monomers signal intensity. Finally, a temperature-dependent sampling-line loss correction factor was applied (Simon et al., 2020).

15. Line 327 and Figure 6. What are the fractions of the reacted carbon measured by these instruments? Table S1 does not show the steady-state  $\alpha$ -pinene concentrations, so it is not possible to estimate these fractions by audience. It is also unclear how the remaining formulas only detected by Orbitrap is treated here. Are they also quantified by the same calibration factors?

-We agree that if the “fractions of reacted carbon” was presented as a parameter, it would be better to quantify the true value of the fractions. However, as the carbon closure is not a key point in this research, we revised the paragraph and focused the discussions on the lower selectivity of the  $\text{NH}_4^+$ -Orbitrap, compared to the  $\text{NO}_3^-$ -LTOF and the I-CIMS. We clarified the steady-state concentration of  $\alpha$ -pinene in Table S1 and the time series of the precursors are shown in Figure S5 for both experiments. We revised the paragraph as follows:

Lines 363-368: *The concentrations of OOMs measured by the  $\text{NH}_4^+$ -Orbitrap were higher than both the  $\text{NO}_3^-$ -LTOF and the PTR3-TOF which was optimized for measuring ammonia and amines. This indicates that the  $\text{NH}_4^+$ -Orbitrap can provide a better constraint on the concentrations of the primary products. As an example, pinonaldehyde (i.e.,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ ), as one of the most abundant oxidation products, was not efficiently detected by  $\text{NO}_3^-$ -LTOF, which is consistent with the higher selectivity of the  $\text{NO}_3^-$  reagent ion.*

16. Line 372-376. Should this be due to increased partitioning of water-soluble compounds to the aerosol liquid water? If increased RH leads to partitioning of SVOCs, why did  $\text{nO}<5$  signals increase? Presumably these  $\text{C}_8\text{H}_{12}\text{O}<5$  species are SVOC and with the enhanced partitioning, their signals in the gas phase should decrease. The explanation is in contrary to the observation. The changing ionization efficiency and multiphase chemistry described in the following paragraph could be the main reasons. I suggest revising this section. The way it is written is confusing.

-The analysis of the RH effect on SOA component partitioning has been discussed in our collaborative study (Surdu et al., 2023). However, in this study, we do not want to speculate on the evolution of the  $\text{C}_8$  compounds and other compounds with shorter carbon skeletons. Such species are suspected to be formed from heterogeneous/wall reactions of  $\text{C}_9$ - $\text{C}_{10}$  compounds,



so RH influences not only their partitioning but also potentially their formation and sinks. In addition, the scope of the paper is to investigate  $\text{NH}_4^+$  ion-based chemistry not to investigate the RH effect of chemical ionization at medium and atmospheric pressure. We do agree with the reviewer that a dedicated study should focus on the RH effect to measure OOMs in the atmosphere using different ion chemistry. We also agree that the previous version might lead to confusion for the readers, so we rearrange the logic in section 3.6 as follows:

Line 406-449: *The sensitivity of the reagent-adduct ionization has been reported to be affected by the presence of water vapor for a variety of reagent ions (Lee et al., 2014; Breitenlechner et al., 2017). The impact of RH on the detection of OOMs by the  $\text{NH}_4^+$ -Orbitrap was also studied. While the concentrations of gas phase precursor and oxidant remained constant, the RH was raised from 10% to 80%. During this increase the signal of organic vapor behaved inconsistently under an otherwise constant gas-phase production rate (Surdu et al., 2023) and an increase in the condensation sink (Fig. S5). As shown in Fig. 9, the  $\text{NH}_4^+$ -Orbitrap demonstrated an RH dependence. For instance, the signal of less oxygenated molecules (i.e.,  $n_{\text{O}} < 5$ ) increased with increasing RH, especially compounds with  $n_{\text{C}} = 8$ ; while the signal of highly oxygenated molecules (i.e.,  $n_{\text{O}} > 10$ ) decreased as a function of RH. The average behavior of all  $\text{C}_{8-10}$  monomers and  $\text{C}_{18-20}$  dimers was summarized and compared between four instruments (Fig. S6). The other three mass spectrometers also showed obvious RH dependence. Similar to  $\text{NH}_4^+$ -Orbitrap, OOMs with  $n_{\text{O}} < 5$  measured by  $\text{NO}_3^-$ -LTOF and PTR3-TOF increased at high RH, and a reverse tendency for HOMs with  $n_{\text{O}} > 11$ , while OOMs with  $n_{\text{O}} = 8\sim 11$  seemed to be independent to RH. The large variations of OOMs intensity at different RH measured by  $\text{NH}_4^+$ -Orbitrap may be due to the widest range of oxygen atoms. The causes why OOMs with different oxygen numbers measured by four instruments changed with RH was not clear. Here, multiple possible reasons were provided to explain the signal evolution of the ions with changing RH, such as water affecting the ionization efficiency or altering the physicochemical processes of the gas phase chemistry.*

*First, the efficiency of a particular compound partly relied on whether water vapor competes with the ammonium ion, lowering the sensitivity, or whether it acted as a third body to stabilize the ammonium-organic analyte cluster by removing extra energy from the collision, raising the sensitivity (Lee et al., 2014).  $\text{NH}_4^+$  primary ions can cluster with water molecules when humidity increased, thereby reducing the clustering of the  $\text{NH}_4^+$  with organic analytes (Breitenlechner et al., 2017). However, the formed  $\text{NH}_4^+\text{X}_n$  (X being  $\text{NH}_3$  or  $\text{H}_2\text{O}$ ;  $n = 1,2$ ) clusters might also act as reagent ions and ionize OOMs through ligand switching reactions, which were expected to be fast and thus improve the charging efficiency (Hansel et al., 2018). Compared to previous  $\text{NH}_4^+$ -CIMS, the  $\text{NH}_4^+\text{X}_n$  reagent ions were expected to be larger due to the absence of the field in the ion-molecular-reaction zone in Orbitrap, resulting in greater ligand exchanging and increasing the sensitivity for the less oxygenated species (Canaval et al., 2019).*

*For RH-independent compounds, this may be due to the existence of very stable complexes with  $\text{NH}_4^+$  reagent ion, or sufficient internal vibrational modes to disperse extra energy from the collision (Lee et al., 2014). The highly oxygenated dimers in the category of ULVOCs and ELVOCs which largely partition to the particle phase regardless of the presence of water might indicate that water may also affect the physicochemical processes (i.e., multiphase chemistry, partitioning, etc.), in this case possibly leading to an increase in the driving force of gas-particle partitioning of highly oxygenated species (Surdu et al., 2023), and/or causing the decomposition of highly oxygenated molecules in the particle phase to create less and moderately oxygenated products, e.g.,  $\text{C}_8\text{H}_{12}\text{O}_{1-5}$  (up to a 30-fold increase in the gas phase) (Pospisilova et al., 2020), although which in the range of SVOCs (e.g.,  $\text{C}_8\text{H}_{12}\text{O}_{4,5}$ ) was also*

*thought to partition more to the particle phase at higher RH (Surdu et al., 2023). Finally, while water vapor could affect the gas-phase chemistry through water reactions with the Criegee intermediates (CIs), HO<sub>2</sub> chemistry, OH radical concentration, no clear evidence has been identified as earlier discussed by Surdu et al (2023). However, the accurate reasons needs to be further verified in target control experiments like changing the RH in IMR of CI inlet.*