

Referee 1

The manuscript proposed by Dandan Li et al. entitled “Ammonium *Cl-Orbitrap: a tool for characterizing the reactivity of oxygenated organic molecules*” presents the application and potential of a new instruments for the characterisation of a large range of gas phase oxygenated organic molecules (OOMs). OOMs are essential compounds involved in SOA formation and new particle formation processes, their characterization being one of the main challenges in atmospheric chemistry. In that sense, the paper is of great interest for the international scientific community. The paper is clear, and well-structured and contains valuable information. The methodologies regarding the experiments and state of art instruments used are well described, even if some precisions could be added to some extent. The interest of the NH_4^+ .Orbitrap is evidenced; but the results could be discussed more. As a consequence, I recommend the publication of the paper after the authors address the following points:

-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.

Main comments

1 155: Figure S1 does not support the stability of amines, as it does vary over ca. 1 order of magnitude during the period the period shown on Figure S1. Also I do not understand why a time series of 15 days is presented on Figure S1 while the paper focuses on 2 experiments. It is clear from figure 1 that humidity and to a lesser extent T are affecting amines signal, and it might be discussed in the section 3.6 about RH dependence. The same time series corresponding to runs 2211 and 2213 would be more appropriated than a 15 days time series to support authors statement.

-Thank you for the referee’s suggestions. Two runs (2211 and 2213) were chosen to study the performance of the NH_4^+ -Orbitrap due to the following reasons, (i) α -pinene (AP) ozonolysis is well known compared to other VOCs oxidation processes that were studied within these two weeks. As it is the first study using the NH_4^+ -Orbitrap coupling, it is more reliable to evaluate the NH_4^+ -Orbitrap for detecting products from AP+O₃ and compare it with previous reports such as Riva et al. (2019). Additionally, NH_4^+ mode was applied from run 2209 to 2221 for 15 days. Of these 13 runs, 4 runs aimed to study the nucleation mechanism of H₂SO₄-NH₃ (runs 2217-2219); 3 runs were for pure isoprene (IP) nucleation (runs 2215-2216) and 2 runs for AP+IP nucleation (runs 2209-2210); and 2 runs with inconstant experiment conditions (runs 2210 and 2221). Therefore, only runs 2211 and 2213 focused AP oxidation under different conditions (RH/NO_x) were used to compare the different instruments.

As suggested by the reviewer, we have modified the time series of the amines to focus on the specific runs used in this study. The average signal was $1.9 \times 10^6 \pm 1.2 \times 10^5$ (cps).

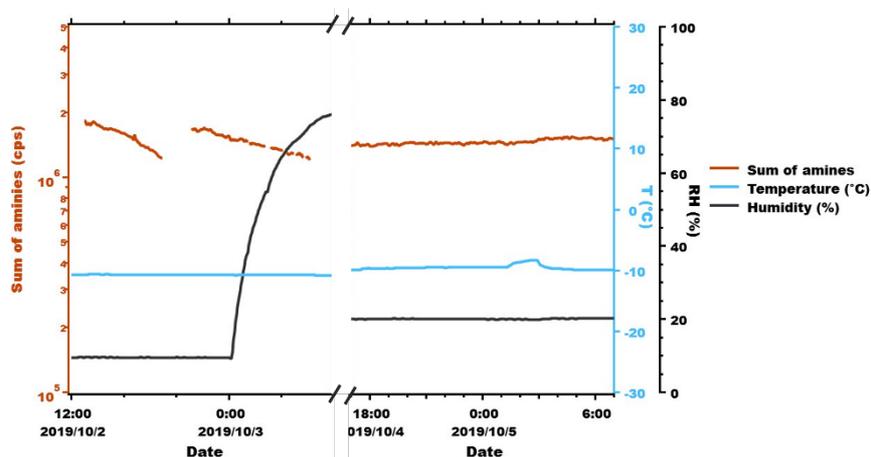


Figure S1 Time evolution of the sum of the 13 amines used to normalize signal intensity in runs 2211 and 2213. Temperature and humidity were also reported throughout the different experiments when the NH_4^+ -Orbitrap was used.

2 Experimental approach and product analysis: A brief comment on how instruments other than NH_4^+ orbitrap have been calibrated or how quantification estimates were performed is necessary. Even if some well-established methodologies exist. This can be part of Supplementary material if the authors do not want to make the manuscript longer.

- We have added more descriptions regarding the calibration of the NO_3^- -LTOF and the PTR3-TOF. The particle phase data of I^- -CIMS were not analyzed in this study and the normalized signals of the gas phase were used to compare the volatility range and correlation analysis with the NH_4^+ -Orbitrap. Hence, the calibration methods were not mentioned in this study.

Lines 185-194: *The NO_3^- -LTOF was directly calibrated using sulfuric acid (H_2SO_4), where the detection efficiency of HOMs was assumed as similar to H_2SO_4 (Kurten et al., 2012). However, OOMs with less oxygen number ($O < 6$) were prone to a lower detection efficiency compared to H_2SO_4 , leading to an underestimation (Stolzenburg et al., 2018a; Ehn et al., 2014). A calibration factor C was determined to be $\sim 4.13 \times 10^{10}$ molecules cm^{-3} during CLOUD14 (Caudillo et al., 2021). The concentration of OOMs was also corrected using a mass dependent transmission efficiency inferred by depleting the reagent ions with several perfluorinated acids. Assuming that OOMs got lost in sampling lines due to diffusion, the losses of OOMs were corrected with a diffusion coefficient scaling with the molecular mass. More information could be found in former studies (Heinritzi et al., 2016; Stolzenburg et al., 2018; Simon et al., 2020; Caudillo et al., 2021).*

Lines 205-219: *A gas standard mixture containing 1 ppm of 3-hexanone, heptanone, and α -pinene in nitrogen was dynamically diluted by a factor of 1000 in VOC-free air to contain 1 ppbv of each compound, and then was used to calibrate the PTR3-TOF. All data were analyzed using TOF-Tracer software running on Julia 0.6 (<https://github.com/lukasfischer83/TOF-Tracer>) and were further corrected for the duty cycle transmission of TOF and temperature dependent sampling line losses (Stolzenburg et al., 2018). On the one hand, duty cycle corrected counts per second dcps , $\text{dcps}_i = \text{cps}_i \times (101/m_i)^{1/2}$, was utilized to account for the mass-dependent transmission of the TOF mass spectrometer (Breitenlechner et al., 2017). The calculated sensitivities of 3-hexanone and heptanone were comparable to the observed ones. Therefore, the concentration of oxygenated products was estimated using the sensitivity of 3-hexanone as lower-limit values due to possible fragmentation (Breitenlechner et al., 2017; Stolzenburg et al., 2018). On the other hand, the detected OOMs having (extremely) low volatility were assumed to be lost by diffusion and adjusted by a temperature dependent loss-*

correction. The sampling line losses considered three loss sections under different temperatures, including losses at the sampling lines within and outside the chamber, and within the PTR3-TOF instrument. Details can be found in previous studies (Breitenlechner et al., 2017; Stolzenburg et al., 2018).

2.3 How do the authors differentiate a peak from the background? In online-MS studied; it is commonly assumed that a peak is detected when its area is 3 times higher than the standard deviation of noise. Is it what has been done using ORBITOOL?

-The background was determined and removed from the average spectra using Orbitool. The raw data were first averaged to 5 mins, reducing the intensities of noise peaks. Then Orbitool took all detected peaks within a mass range between $X+0.5$ to $X+0.8$ Da, where most compounds (i.e., containing C, H, O, S, N) are not located. Signal intensity below a certain percentile is considered as noise, which was set as 70th percentile in this study. Hence, the noise and discriminator levels were calculated as μ and $\mu + 3\sigma$, where μ and σ were the mean and the standard deviation of the noise signal, respectively. Noise signals lower than the discriminator level were removed from the average spectrum. Details can be found in our previous paper (Cai et al., 2021).

Section 3.1: I am not sure this part is necessary, because this is an illustration that an instrument with a high mass resolving power separates more easily isobaric compounds compared to instruments with a lower mass resolution. Any scientist able to understand what a mass resolution of 160 000 compared to 10 000 means is convinced that the first one is far better for separating isobaric compounds (without any demonstration needed). The interest of the paper is not the mass resolution of the orbitrap but its association to NH_4^+ as CI. Finally, if the authors find a justification to keep this section, I recommend them to normalize to 1 the Y scale each plot of figure 2.

-There is no doubt that the high mass resolving power of Orbitrap eases the identification of isobaric compounds and its performance of identifying the overlapping peaks has been compared to CI-TOF in our previous studies (Riva et al., 2019a; Riva et al., 2020). An additional aspect to consider is the selectivity of the reagent ion. For example, the NO_3^- ion chemistry is so selective that the higher mass resolving power of the Orbitrap is not critical to resolving the identity of the OOMs. On the contrary, when using reagent ions with very low selectivity, i.e., NH_4^+ , a greater mass resolving power is necessary to resolve all the ions observed notably those with low signal intensities. Hence, we do believe it is important to highlight the importance of the mass resolving power when using such kinds of reagent ions. Figure 1 is moved to SI considering it is a concept of peak identification and mass resolving power.

Section 3.2 must be improved based on comments below:

L.287 288: Does it make sense to compare NH_4^+ .orbitrap to another instrument (PTR-3) that is not optimised to compare OOMs? The authors showed the NH_4^+ .orbitrap is more suited for OOMs detection, but the comparison is not on an equal foot with the PTR-3. Maybe the latter should be excluded from this study?

-We do not mean to conclude that the NH_4^+ -Orbitrap has a better detection for OOMs compared to the PTR3-TOF. Although the PTR3-TOF was optimized to be sensitive to ammonia, it still

observed many oxygenated species that were used for the correlation analysis and the semi-quantification of the less oxidized OOMs observed by the NH_4^+ -Orbitrap. This section has been revised as follows:

Line 313-318: *The PTR3-TOF mainly detected compounds below m/Q 300 Th with an average O:C of 0.5 ± 0.3 , which was due to the optimization to (i.e., lowering E/N value) measure ammonia and amines sensitively, which ultimately impacted its capability to detect efficiently OOMs. However, many less oxygenated OOMs were still observed by the PTR3-TOF and were used to conduct the correlation analysis of time series with those detected by the NH_4^+ -Orbitrap.*

L.288-289: As mentioned, the quantification limit of the I-CIMS is higher than gas phase OOMs concentration. Giving a detection limit for each compound detected by each instrument is probably unrealistic, but the information about the range of limit of detection/quantification for each instrument would be helpful for a reader not expert with all these instruments.

While we haven't directly measured the LoD for the instruments, we report LoD from the existing literature.

Line 177: *The limit of detection (LoD) for OOMs is 5×10^4 molecules cm^{-3} (Simon et al., 2020).*

Line 201-202: *The LoD of PTR3-TOF for detecting OOMs is 8×10^5 molecules cm^{-3} (Breitenlechner et al., 2017).*

Line 225-226: *The LoD of I-CIMS for OOMs could be lower to $\sim 10^7$ molecules cm^{-3} (Lee et al., 2014).*

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

L.302-303: A $R^2 > 0.5$ alone is not a good criterion for “high correlation”, as it depends on the number of points associated to each sample, etc. In addition, the good correlation with other instruments could be explained by similar biases, for example. Please temper statements, or strengthen the statistical analysis.

-We agree with the referee that a correlation factor greater $R^2 > 0.5$ alone is not enough to conclude that two parameters are highly correlated. In our case, two runs (run 2211 and 2213) were used to analyze the correlation of time series for the compounds measured by the different instruments. 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, providing statistical confidence for the correlation factor. As an example, the time series of $\text{C}_{10}\text{H}_{14}\text{O}_2$ and $\text{C}_{10}\text{H}_{14}\text{O}_{10}$ measured by three instruments in run 2211 are displayed in Figure R1.

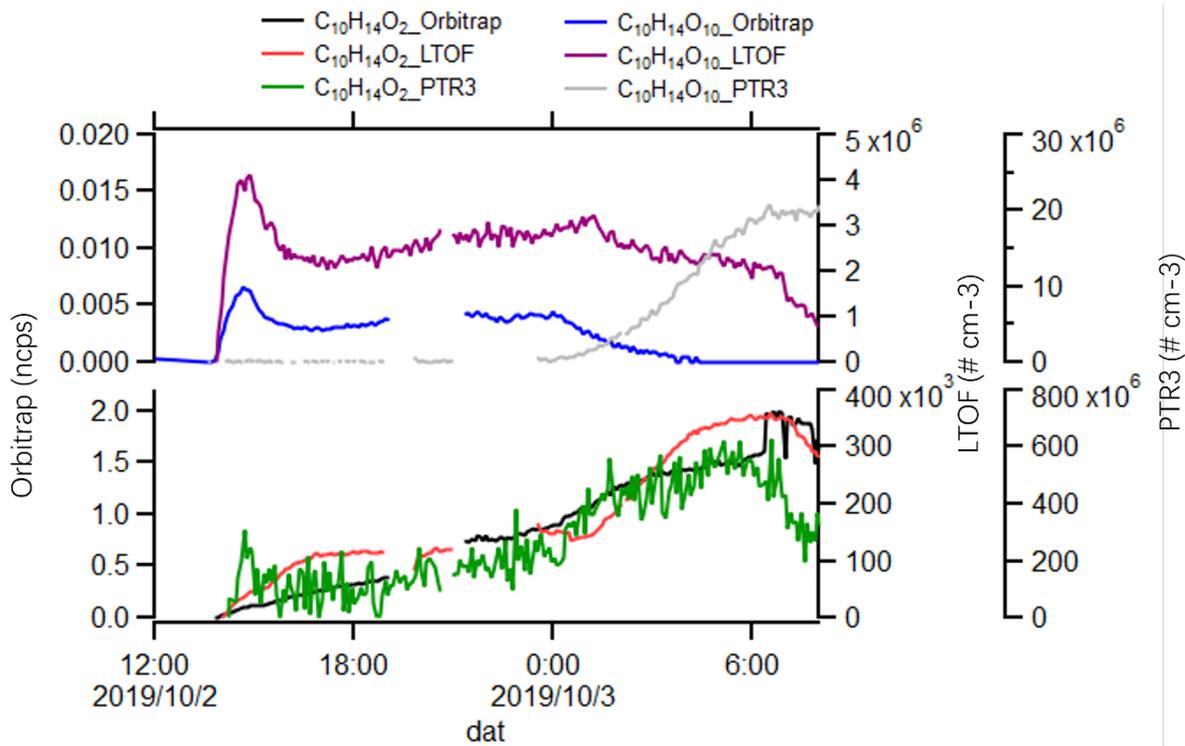


Figure R1. Timeseries of $C_{10}H_{14}O_2$ and $C_{10}H_{14}O_{10}$ measured by the NH_4^+ -Orbitrap (Orbitrap), the NO_3^- -LTOF (LTOF), and the PTR3-TOF (PTR3).

More detailed for the semi-quantification method was added as follows:

Line 154-171: *No direct calibration has been performed for the NH_4^+ -Orbitrap, but a semi-quantitative method was used to estimate the OOMs concentrations based on the correlation analysis using 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 NH_4^+ -Orbitrap, were used to determine a calibration factor ($c_{Orbi-REF}$, molecules cm^{-3}) and retrieve the concentrations of OOMs measured by the NH_4^+ -Orbitrap according to the following equations 4-5:*

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

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

The calibration factor between the NH_4^+ -Orbitrap and REF ($\sim 2.62 \times 10^8$ for NO_3^- -LTOF and $\sim 4.83 \times 10^8$ for PTR3-TOF) 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).

The description of the instrumental comparison was modified as follows:

Line 330-339: *The NH_4^+ -Orbitrap and the NO_3^- -LTOF detected OOMs with the same chemical compositions, covering monomers and dimers, among which 18 OOMs showed $R^2 > 0.9$. Regarding the PTR3-TOF, the NH_4^+ -Orbitrap demonstrated high correlations for most of the monomers and fewer dimers, including 32 species having an $R^2 > 0.9$. Due to potential losses within the FIGAERO inlet, fewer OOMs were detected by the I-CIMS. However, certain families of compounds, including $\text{C}_{10}\text{H}_{15}\text{O}_{5-7}\text{N}$ and $\text{C}_{20}\text{H}_{31}\text{O}_{7,9}\text{N}$ showed high correlations (i.e., $R^2 > 0.9$) between the NH_4^+ -Orbitrap and with the I-CIMS. Finally, the NO_3^- -LTOF was regarded as the reference instrument for HOMs measurements. Only fewer monomers with high oxygen content were detected by the NO_3^- -LTOF and the PTR3-TOF, and only a few dimers between the NO_3^- -LTOF and the I-CIMS with moderate relevance.*

L.353: It is not clear if the raw signal (i.e., counts) or concentrations have been used here? If raw signals are used, can the authors justify their choice? And would Figure 8 be different if the concentrations are used instead of signals?

-Concentrations were used for the NO_3^- -LTOF and the PTR3-TOF, while the signal intensities were used for the NH_4^+ -Orbitrap and the I-CIMS. It is important to point out that using concentration or raw signal will not change the relative volatility distribution for a given reagent ion as concentrations are determined by applying a unique calibration factor (e.g., 4.13×10^{10} molecules cm^{-3} for the NO_3^- -LTOF).

Section 3.4: a simple comparison on couple of common compounds detected by both PTR-3 and NO_3^- -CIMS would be nice to validate their quantification, showing there. Both instruments are used as reference to “calibrate” NH_4^+ .orbitrap, but are PTR-3 and NO_3^- -CIMS consistent when measuring the same compound? In addition, the NH_4^+ .orbitrap falls in a factor 2 comparing with other instruments, which is satisfying and reasonable considering all the uncertainties associated with quantification on online-MS, but cannot be qualified as “good”, which is subjective term.

-There were some species like $\text{C}_8\text{H}_{12}\text{O}_4$ which was consistent between the NO_3^- -LTOF and the PTR3-TOF as depicted in Figure R2.

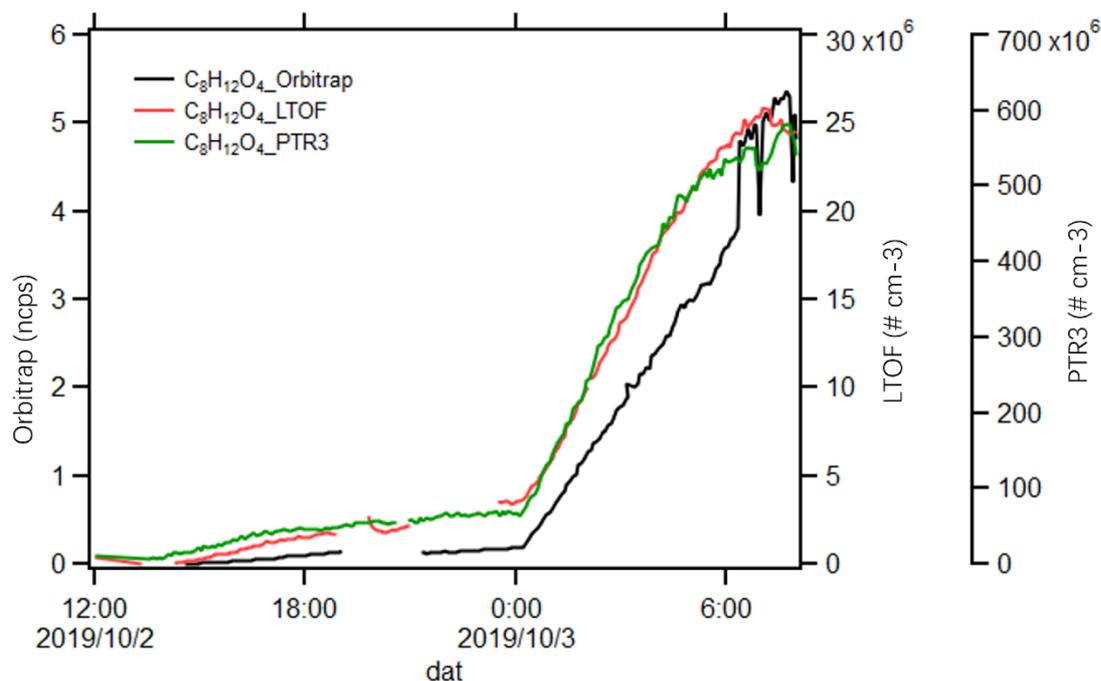


Figure R2. The timeseries of $C_8H_{12}O_4$ measured by the NH_4^+ -Orbitrap (Orbitrap), the NO_3^- -LTOF (LTOF), and the PTR3-TOF (PTR3).

While the two instruments are not necessarily consistent for an extensive range of compounds, such as $C_{10}H_{14}O_2$ or $C_{10}H_{14}O_{10}$ (Figure R1); The NO_3^- -LTOF and the PTR3-TOF cannot be directly compared as they measure different types of OOMs due to the selectivity of the reagent ions. The former was sensitive to HOMs with $n_O > 6$ while the latter detected efficiently OOMs with $n_O = 1\sim 5$. We revised the description of the NH_4^+ correlation results as follows:

Lines 347-353: *The concentrations of C_{10} -monomers measured by the NH_4^+ -Orbitrap based on the two calibration factors vary within a factor of 2, which indicates the consistency between the two correlation analyses. The variation trend of concentrations with the oxygen number of the NH_4^+ -Orbitrap is similar to that of the NO_3^- -LTOF in the range of $n_O > 6$, and it is similar to that of the PTR3-TOF in the range of $n_O = 1\sim 5$. Taking into consideration that such ranges are also the oxygen number ranges with high sensitivities respectively, this proves the robustness of the the NH_4^+ -Orbitrap and the semi-quantification method.*

Section 3.6: the discussion is interesting here, but the results should be more detailed. For example, it is not discussed that intensity of C_8 compounds increased whatever the number of O atoms, while it is more contrasted for other compounds. In addition, this increase can be up to ca. 20 for $C_8H_{12}O_{2-4}$ compounds, while it is limited to 1.6 for C_{10} , C_{19} and C_{20} . Is there an explanation here? In addition, based on Figure S6, it seems the effect of RH is very important at $n_O < 8$, but what about the effect of n_C ? As I just mentioned, the effect of RH seemed to be stronger for C_8 compounds. The increased in polarity or O/C with decreasing C number might be an explanation? This must be investigated. Figure S6 also evidenced that I-FIGAERO-CIMS sensitivity is only decreasing with increasing RH, while it is not the case for other instruments. The authors should comment this result. Finally, as the authors cannot distinguish the effect of increasing RH on chemical and physical processes (based on experiments presented in the present paper), it is evident that RH influences NH_4^+ -Orbitrap sensitivity, that can be different for each OOM, but this specific effect requires more attention and dedicated studies before the NH_4^+ -Orbitrap can be used in field studies (for example, injection of pure or

mixture of standards in atmospheric chamber at varying RH). From what is presented here, the understanding of RH effect on the NH_4^+ -Orbitrap capabilities is too scarce to be able to understand the time series evolution of OOMs that would be obtained in the real atmosphere.

-We do not want to speculate on the evolution of the C_8 compounds and other compounds with shorter carbon skeletons as such species are suspected to be formed from heterogeneous/wall reactions of C_9 - C_{10} compounds produced from the gas phase oxidation of monoterpene. Figure S7 has been reported as a reference to underline the potential bias when measuring oxidation products when changing humidity. Instead, we focused on monomers and dimers that are produced from well-known gas phase reactions. In addition, the scope of the paper is to investigate 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.

Minor comments:

Section 3.1: OVOCs should be replaced by OOMs, as most of detected compounds are not volatiles.

-Revised.

Figure 5: caption should be more explicit.

-We add more description about current Figure 4 as follows:

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

Figure 7: here the PTR-3 is probably limited compared its real potential to OOMs, because it has been tuned for efficient detection of NH_4^+ ...

1. 409: is.

-Revised.

2. 757: concentrations of OOMs

-Revised.