General comments to the referees

First of all, thank you very much to the anonymous referees for this interactive discussion and their productive comments, corrections and suggestions that ensued. Here we have carefully replied to all comments and the paper has been improved following the recommendations of reviewers.

(A) Comments from Referees

Ref1. C1. On line 370 the purities of the synthetized keto-nitrates by FTIR should be given? Were these comparable to the commercially purchased alkyl nitrates? If not what were the major impurities and what are the likely effects on the results presented

Ref2. C1. The authors mentioned the synthesis of few organic nitrates performed during these investigations. However, the purity of the synthesized compounds is verified only by FTIR as the authors stated in line 370. Please consider to add in Supporting information section the IR gas phase spectra of the synthesized compounds. Additionally, please consider that FTIR analysis is a less appropriate method for checking purity of the new compounds when the impurities may have similar functional groups as the synthesized compound. Did you perform NMR analysis of the synthesized compounds? If you compared the synthesized compounds with existing IR reference spectra please specify the reference of the database used. Additionally, please add information of the infrared gas phase cross section values for the organic nitrates obtained in this study as you mentioned to calculate them (line 339-351).

(B) Author's response

Once the functionalized compounds have been synthesized, a recurrent head-space purification step was performed in order to extract the lower volatility byproducts of the synthesis (line 367). The reactor injections were subsequently performed using a vacuum line allowing the quantification of a known volume of analyte before injection. The procedure allows the graduate "distillation" of the bulk synthesis and the injection of the useful fraction in the simulation chamber. Complementary analysis showed that subsequent injected analyte by subsequent headspace sample are gradually increasing the purity level of the injected analyte by subsequent headspace samplings. Therefore is difficult for us to estimate the bulk purity of the synthesis. In addition, it was checked by GC-MS that the reactant used for the synthesis of the organic nitrates (eg. an hydroxy-ketone for the synthesis of a keto-nitrate) was fully consumed preventing any interference in mass spectra.

The remaining main by-product present in the same distillation fraction as the organic nitrate is HNO₃ representing up to 5% of the injected volume. Other impurities can be observed such as the HCOOH, NO₂ or the HONO in the recorded IRTF spectra, representing less than 1% of the injected volume. All these impurities are readily identified and subtracted from the IRTF spectra in order to correctly quantify the organic nitrate absorbance. The impurities may however add supplementary signals in the PTRMS mass spectra. These signals are systematically at lower masses than the ones regarding the main ionization processes of the organic nitrates and therefore won't interfere. However we cannot exclude that some of the PTRMS signals assigned as organic nitrate fragments could have a more or less important contribution from these impurities. Efforts have been made in order to quantify and identify the mass spectrum double peaks into the same mass unit which can be due of this kind of interference.

The FTIR gas-phase spectra of the synthesized organic nitrates were added in supplementary information section and compared with a commercially available alkyl nitrate spectrum. The NMR analysis was not available during the project.

The infrared cross sections for the organic nitrates obtained in this study are mentioned (line 343-348) for the absorption band centered at 820 cm⁻¹ as being the less subject to interferences.

(C) Author's changes in manuscript.

Line 369 added: In addition, it was checked by GC-MS that the organic reactant used for the synthesis, here the hydroxyl-ketone, was fully consumed preventing any interference in IR and mass spectra.

Line 377 added: The total consumption of the bromo-alcohol was checked by GC-MS.

Paragraph to be added in the Chemicals and gases:

The presence of impurities (mainly HNO_3 and HCOOH) as synthesis by-products may add supplementary signals in the PTRMS mass spectra. These signals are however systematically at lower masses than the ones regarding the main ionization processes of the organic nitrates and therefore won't interfere in the main frame of the discussion.

Figure to be added in SI



Figure S1. The FTIR gas phase absorbance spectra of the synthesized organic nitrates (KnC3, KnC5, 10H3C3) compared with a commercially available alkyl nitrate spectra (AlkC3).

Ref1. C2. On line 444 it is mentioned that the abundance of the water clusters were higher than typical during this study. Is there a reason for this?

(B) Author's response

As stated in lines 395-402, and depicted in Figure 1, using a PTRMS instrument at atypical E/N ratios, inferior to 100Td, will rather favor the water clusters formation than the hydronium ions. This condition seems more favorable to the organic nitrate ionization without complete fragmentation.

(C) Author's changes in manuscript.

Line 443 reword "..." to read "At higher abundances of the water clusters, expected to occur in our study due to the usage of low E/N ratios, the R5 mechanism is considered..."

Ref1. C3. In my opinion there are too many figures and the way they are shown prevents a more straightforward comparison of the different ionization schemes. The paper would be greatly improves if the results for each of the different types of organic nitrates were presented in a similar way to Figure 1 were operational differences can be clearly seen and compared.

(B) Author's response

Indeed the suggested changes will significantly improve the appearance of the paper and summerize the obtained results. As you already noticed the top right quadrant of the diagram will not be plotted since the lack of signals in this operational condition forced us to abandon the recordings. The data isn't available for these conditions.

(C) Author's changes in manuscript.

Figures 2,3 and supplementary data are condensed and displayed in the new plot regarding alkyl nitrate ionization modes



Figure 2. The E/N ratio influence over the AlkC3 identification for several representative signals in both ionization modes (H_3O^+ - left; NO⁺ - right) as recorded in absence (up) / presence (down) of a RF funnel. The common signal at m/z=43 is equally plotted as a fragmentation mark (right axis). When the RF mode is on, E/N* ratio were calculated taking into account only the contribution of the dc electric field while the additional input of the ac electric field remains difficult to estimate.





Figure 4. The E/N ratio influence over the 1OH3C3 identification for several representative signals in both ionization modes (H_3O^+ - left; NO⁺ - right) as recorded in absence (up) / presence (down) of a RF funnel. The common signal at m/z=43 is equally plotted as a fragmentation mark (right axis).

Figures 10, 12 and supplementary data are condensed and displayed in the new plot regarding ketonitrates ionization modes:



Figure 6. The E/N ratio influence over the KnC3 identification for several representative signals in both ionization modes (H_3O^+ - left; NO⁺ - right) as recorded in absence (up) / presence (down) of a RF funnel. The common signal at m/z=43 is equally plotted as a fragmentation mark (right axis).



Figure 1. Recorded mass spectrum of AlkC3 (black bars) at the lowest extent of fragmentation of the molecular ion at m/z=106 (E/N=78 Td) in the H_3O^+ ionization mode in absence of the RF (a) and in the NO⁺ ionization mode at m/z=135 in presence of the RF ($E/N^* = 34$ Td) (b). The green thin line represents the expected molecular ion of the analyte. The intense signals depicted by the red thin bars represent the ionizing and matrix analytes at m/z = 30 (NO⁺) and 46 (NO₂⁺) and their isotopic abundance signals at m/z = 31 and 47, 48 respectively. The signals corresponding to the water clusters ($H_3O^+(H_2O)_n$ at m/z 37 and 55 are systematically erased for simplification.



Figure 2. Recorded mass spectrum of 1OH3C3 (black bars) at the lowest extent of fragmentation of the molecular ion (E/N = 62 Td) in the H_3O^+ ionization mode in absence of the RF device (a) and in the NO⁺ ionization mode in presence of the RF ($E/N^* = 45$ Td) (b). The green thin line represents the expected molecular ion of the analyte. The intense signals depicted by the red thin bars represent the ionizing and matrix analytes at m/z = 30 (NO⁺) and 46 (NO₂⁺) and their isotopic abundance signals at m/z = 31 and 47, 48 respectively. The signals corresponding to the water clusters ($H_3O^+(H_2O)_n$ at m/z 37 and 55 are systematically erased for simplification.



Figure 3. Recorded mass spectrum of protonated KnC3 (black bars) for E/N = 75 Td, corresponding to the highest sensibility for the protonated analyte signal detection (m/z 120) in absence of the RF device (a) and in the NO⁺ ionization mode in presence of the RF (E/N* = 40 Td) (b). The green thin line represents the expected molecular ion of the analyte. The intense signals depicted by the red thin bars represent the ionizing and matrix analytes at m/z = 30 (NO⁺) and 46 (NO₂⁺) and their isotopic abundance signals at m/z = 31 and 47, 48 respectively. The signals corresponding to the water clusters (H₃O⁺(H₂O)_n at m/z 37 and 55 are systematically erased for simplification.



Figure S2. Recorded mass spectrum of protonated Alk*i*C4 (black bars) for E/N = 70 Td, corresponding to the highest sensibility for the protonated analyte signal detection (m/z 120) in absence of the RF device (a) and in the NO⁺ ionization mode in presence of the RF (E/N* = 34 Td) (b). The green thin line represents the expected molecular ion of the analyte. The intense signals depicted by the red thin bars represent the ionizing and matrix analytes at m/z = 30 (NO⁺) and 46 (NO₂⁺) and their isotopic abundance signals at m/z = 31 and 47, 48 respectively. The signals corresponding to the water clusters (H₃O⁺(H₂O)_n at m/z 37 and 55 are systematically erased for simplification.



Figure S3. Recorded mass spectrum of protonated KnC5 (black bars) for E/N = 75 Td, corresponding to the highest sensibility for the protonated analyte signal detection (m/z 148) in absence of the RF device (a) and in the NO⁺ ionization mode in presence of the RF ($E/N^* = 36$ Td) (b). The green thin line represents the expected molecular ion of the analyte. The intense signals depicted by the red thin bars represent the ionizing and matrix analytes at m/z = 30 (NO⁺) and 46 (NO₂⁺) and their isotopic abundance signals at m/z = 31 and 47, 48 respectively. The signals corresponding to the water clusters ($H_3O^+(H_2O)_n$ at m/z 37 and 55 are systematically erased for simplification.

Ref1. C4. The optimized conditions appear to be slightly different for each class of organic nitrates and this limits clearly this technique in terms of which compounds can be observed simultaneously...

(B) Author's response

Although slight variations appears for each type of compound and the switch between the two operational modes is not straightforward, two experimental conditions seem to correspond for the widest range of organic nitrates.

- The first one is the NO⁺ adduct formation in presence of RF (since the abundance of ionizing species is higher) around an E/N ratio of 45Td. These experimental condition overlays the area characterized by the highest NO⁺/NO₂⁺ ratio.
- The second one is the protonation mode in absence of the RF, for an E/N ratio around 70Td. In these experimental conditions the $H_3O^{+}(H_2O)$ is the most abundant ionizing species, enhancing probably the organic nitrate soft ionization.

We can easily notice in the E/N dependence plots that a few units shift of the E/N ratios doesn't significantly affect the analytical sensitivity of the method.

(C) Author's changes in manuscript.

Conclusions rephrased... to read:

This study has shown that two complementary ionization modes can be used for the detection of organic nitrates:

- The NO⁺ ionization mode in presence of RF mode with an E/N ratio around 45Td. This mode favors the M-NO⁺ adduct formation and has been shown to be more efficient for the detection of all types of organic nitrates except PANs (i.e. alkyl, hydroxy- and carbonyl-nitrates), as it minimizes fragmentation, favoring the identification of molecular composition. In addition, this mode is much more sensitive for the detection of hydroxy- and ketonitrates than the protonation one. So clearly, we recommend the use of this mode for alkyl and multifunctional organic nitrates.
- The protonation mode in absence of the RF mode, for an E/N ratio around 70Td which is recommended for the detection of PAN type compounds. This ionization mode can also be used for other types of organic nitrates but with lower sensitivity than the NO⁺ mode.

Although slight variations appear in the optimization of the operational conditions for each type of compounds, it has been observed that a few units shift of the E/N ratios doesn't significantly affect the analytical sensitivity of the method.

Ref1. C5. In the introduction there is discussion of the limited measurements of speciated organic nitrate and thus some of the motivation for developing this approach is to provide a method to measure these compounds in the atmosphere. However, data is only presented from a smog chamber containing the specific target compounds and not a more complex mixture that would present an analytical challenge....

Ref2. C2. There is stated in the Abstract and Introduction sections that was performed optimization of the PTR-ToF-MS instrument for the measurements of organic nitrates in the atmosphere but the studies presented in the manuscript are exclusively recorded in a simulation chamber using dry air conditions. My concern related to the measurements into the atmosphere is mainly due to the interference species (gas and particles) and humidity. Did you perform any test for humidity effect? May you comment how these interference could affect the results (decomposition, clustering, partition, hydrolysis, etc.)?

(B) Author's response

Indeed, the motivation of this study is twofold: i) being able to measure individual organic nitrates during simulation chamber experiments for mechanisms development and ii) being able to measure organic nitrates in ambient atmosphere to better assess the role of organic nitrates on photooxidants budgets, in particular on the long range transport on NOx. This study which is focused on laboratory experiments allows fully reaching the first objective. From this study, we now better understand how to run PTR-MS to allow the detection of individual organic nitrates during lab studies and this will be very useful for a number of research groups working on mechanisms studies which are equipped with this instrument. In particular, the operational mode of the instrument has been optimized for the detection of different types of organic nitrates and the ionization pattern (fragmentation/adduct formation/charge transfer/...) of these species is much better understood now.

These results will be also very useful for ambient air measurements, as a first step. In a second step, this method will be tested in real atmosphere in order to identify potential interferences with other species and to test the sensitivity dependence with relative humidity. It is indeed well known that relative humidity affects the signals and thus the quantification of analytes by PTR-MS, and this strongly depends on the class of analytes. The most common approach to overcome this problem is to perform calibration measurements for a wide range of RH% in order to provide humidity dependent calibration curves. However, these additional tests are part of a full study in its own right.

For technical reasons, the instrument is not available at the moment and this work could not be performed here. In particular, we could not perform the preliminary tests in ambient air requested by both referees. But as soon as it will be repaired, it is plan to 1) test the detection of the organic nitrates in ambient air and 2) perform calibrations for a wide range of relative humidity.

Concerning the possible interference with other species, we agree that the molecular ions and especially the mass fragments are certainly not unique (and is equally the case for a wide range of others, more common and more abundant, VOCs present in the atmosphere). Worth noticing however that an N containing molecule exhibits the particularity of odd masses signals in the protonated mode (unlike a major part of the VOCs, containing only C, H and O atoms). Another

useful tool in the analysis of mono-nitrogen containing analyte was depicted by Inomata et all. 2013 (line 769) using the isotopic abundance ratios of adjacent ion signals at odd and even masses. The access to the high mass resolution is equally improving the correct assignment of the spectral signals.

Fragments of organic nitrates which do not contain N any more could indeed interfere with common atmospheric species such as acetone in the given example. But, to limit the risk of interference with another molecule, the identification of organic nitrates is mainly based on molecular and adduct signals rather than fragment ones. Two signals (as a minimum) are used for the identification of the organic nitrate: in NO⁺ ionization mode, for example, AlkC3 is detected from the molecular signal at m/z 105 but also from M-NO⁺ signal at m/z 135. It is the same for hydroxy- and keto-nitrates.

For measurement in ambient air or in any mixture containing aerosols, it is strongly recommended to use a filter in the sampling line in order to prevent any interference with chemical species in the aerosol phase, but also from dirtying of the PTR-MS inlet. Any atmospheric loss process of organic nitrates (decomposition, hydrolysis in aerosol phase ...) will affect the atmospheric lifetime and concentration of these species but won't affect the results of the measurement here.

(C) Author's changes in manuscript.

Conclusions rephrased:

"This high sensitivity is suitable for the detection of organic nitrates in lab studies, in particular in simulation chamber experiments. It also suggests that this method is very promising for the detection of these compounds in ambient air. "

"From this study, we now better understand how to run PTR-MS to allow the detection of individual organic nitrates during lab studies and this will be very useful for a number of research groups working on mechanisms studies which are equipped with this instrument. In particular, the operational mode of the instrument has been optimized for the detection of different types of organic nitrates and the ionization pattern (fragmentation/adduct formation/charge transfer/...) of these species is much better understood now."

"A perspective of this work will be to test the detection of organic nitrates in ambient air with this method. From the detection limits observed in this study, we can expect that accumulations over longer periods will be necessary to below the detection limits."

Ref1. C6. The data presented only refers to unit mass resolution, was the high accuracy mass data also used? I could imagine that it might be useful in distinguishing the organic nitrates from other atmospheric compounds that are also ionized by PTRMS

(B) Author's response

The instrumental setup allowed the recording of high accuracy mass spectra data (line 170, >5000M/dM mass resolution). Mass calibration of the recorded spectra was systematically performed. The procedure allowed to precisely assign the mass spectra peaks at the exact mass. The identification of an N containing molecule is quite straightforward procedure, in the protonation mode, since it generates a signal at an odd mass, in contrast with the large majority of the others VOCs. During the present study no multiple peak (at the same unit mass) was recorded for the assembly of the main ionization processes regarding the organic nitrates molecules (protonation, water adduct and NO⁺ adduct formation). This kind of multiple peaks would have been easily identified since at higher masses the "hydrogen mass default" is usually more consistent.

At lower masses, double peaks are noticed infrequently, and for the large majority of the cases one of the peak is present in the background spectra of the simulation chamber (minor peaks) while the other is related with the injection of the analyte. Of course that the background signals are substracted from the data processing. The lack of multiple peaks is mainly related to the absence of reactivity of the studied systems, reducing the chemical complexity.

(C) Author's changes in manuscript.

Line 170 added:

Mass calibration of the recorded spectra was systematically performed. The procedure allowed to accurately assign the mass spectra peaks.

Rephrasing in line 439:

The presence of the m/z 43 (AlkC3) and respectively 57 (AlkiC4) signal was clearly identified as the alkyl fragment (R^+) of nitrate by the means of high resolution mass spectrometer allowing to differentiate between oxygen containing analytes and alkyl fragments.

Ref1. C7. PAN type compounds are sensitive to thermal decomposition. With the inlet at 40deg C one might expect some thermal decomposition of PANs (inlet residence time dependent) ? Can the authors comment on this and whether this may be a reason for the high detection limits observed for these compounds with this method.

(B) Author's response

We considered the 40°C heating as a compromise between the thermo-lability of the organic nitrates and the risk of condensation in the sampling line. However, the total residence in the sampling line and the instrument inlet is very short, around 3s. At 40°C, the lifetime of PAN (due to thermal decomposition) is around 300 s (ref IUPAC). So decomposition of PANs is expected to be negligible here.

(C) Author's changes in manuscript.

Line 783 added.

The thermo-lability of the PANs was equally considered for the weak response factors of the instrumental setup in both ionization modes, since the sampling is requiring slightly heated inlet lines. We considered the 40°C heating as a compromise between the thermo-lability of the organic nitrates and the risk of condensation in the sampling line. However, the total residence in the sampling line and the instrument inlet is very short, around 3s. At 40°C, the lifetime of PAN (due to thermal decomposition) is around 300 s. So decomposition of PANs is expected to be negligible here.

Ref2. C3. As there is a FTIR instrument available for in situ measurements in the chamber, it will be worth comparing FTIR vs PTR-MS concentration-time dependency for each class of organic nitrates at the most effective PTR-MS conditions during the organic nitrate accommodation into the chamber. These comparisons may add important information for quantitative analysis of organic nitrates using PTR-MS. Such test may also check for possible response delay in the PTR measurements due to the nitrates deposition on the sampling line for example.

(B) Author's response

First, it should be noticed that the FTIR and the PTR-MS do not measure exactly the same thing: the FTIR, which is coupled to an in situ multireflexion cell provides an integrated (in the whole length) measurement of the mixture whereas the PTR-MS samples the mixture at one end of the reactor.

Then, for practical reasons, the injection line and the sampling line of the PTR-MS are located in the opposite ends of the cylindrical, 6m long, simulation chamber. The injection of analytes is made via a multiple nozzle line spanning $\frac{3}{4}$ of the length of the reactor and the time to reach a full mixing of the gas is around 5 min. Hence, quantitative measurements with PTR-MS cannot be performed during this mixing period. So inter-comparisons of PTR-MS and FTIR signals were always performed 10 min after the injection to ensure that the two instruments measure the same mixture. Highly volatile compounds (eg. NO₂) exhibit similar behavior, confirming that this mixing time is mainly due to volumetric homogenization delay of the reactor and less due to the nitrates deposition on the sampling line.

As stated in lines 346-350 repetitive injections of known amounts of analyte and controlled dilutions of the reactor have been systematically performed in order to certify the linearity of the response in between the FTIR and PTRMS analysis.

(C) Author's changes in manuscript.

Ref2. C4. In the Conclusion section, authors conclude that NO+ adduct ionization mode is "suitable for measurement of organic nitrates during lab studies but also in ambient air". There are tests performed in the ambient air?

(B) Author's response

The conclusion referred here to the very good performances of the NO⁺ ionization mode (low fragmentation, low detection limits compatible with ambient concentrations) but we agree that we cannot yet conclude that this method is suitable for measurement in ambient air, as additional tests are absolutely necessary. So the conclusion has been rewritten and we only mention now that the high sensitivity of this method makes it promising for ambient air measurements.

(C) Author's changes in manuscript.

Line 800 rephrased: This high sensitivity is suitable for organic nitrates analysis during lab studies but also in future ambient air measurements, subject to further validations regarding the humidity effect over the analytical setup.

All the specific and technical corrections have been taken into account.