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Atmospheric Measurement Techniques Discussions

Measurement of alkyl and multifunctional organic nitrates by Proton Transfer Reaction Mass Spectrometry

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Highlights

- PTR-MS technique is proposed as a reliable measurement tool of individual organic nitrates.
- Different clases of organic nitrates are characterized from the mass spectrometric point of view.
- Different ionization modes and reagent ions are proposed for each type of organic nitrates.

Abstract

A commercial PTR-ToF-MS has been optimized in order to allow the measurement of individual organic nitrates in the atmosphere. This has been accomplished by shifting the distribution between different ionizing analytes, $H_3O^+/H_3O^+(H_2O)_n$ or NO^+/NO_2^+. The proposed approach has been proved to be appropriate for the on-line detection of individual alkyl nitrates and functionalized nitrates. It has been shown that hydroxyl- and keto-nitrates have a high affinity towards NO^+, leading to the formation of an adduct that allows to easily identify the organic nitrate (R) with the $R\text{-}NO^+$ ion signal. The recorded sensitivities for both ionization modes correspond to detection limits of tens of ppt min^{-1} in the case of hydroxy- and keto-nitrates. Alkyl nitrates exhibit a moderate affinity towards NO^+ ionization leading to detection units of few hundreds of ppt and the highest sensitivity in H_3O^+ mode was obtained for the water adducts signals. This method exhibits however lower capabilities for the detection of PANs with detection limits in the ppb range.

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1 Introduction

Organic nitrates are important species of the reactive nitrogen (NOy) budget in the troposphere. They are formed in NOx rich air by the degradation of hydrocarbons initiated by OH (daytime) and NO_3 (nighttime) radicals. Since organic nitrates have lifetimes of several days or weeks (Perring et al., 2013), they can act as reservoirs for reactive nitrogen by undergoing long-range transport in the free troposphere before decomposing and releasing NOx. They play therefore a key role in the ozone formation as they sequester reactive nitrogen in rich NOx regions and release it in regions where production of ozone may be NOx limited. The significant impact of organic nitrates chemistry on ozone budget has been confirmed by recent modelling studies (Curci et al., 2009; Horowitz et al., 2007).

In addition, several field studies have shown that both polluted and remote atmospheres contain a large variety of organic nitrates which significantly affects the NOy budget (for example, 35 - 40 % as reported by Buhr et al. (1990) and up to 70% according to a modeling study performed by Madronich and Calvert (1990)). They are monofunctional alkyl nitrates, PANs but also multifunctional alkyl nitrates (Browne et al., 2013; Fischer et al., 2000; Kastler and Ballschmiter, 1999; Muthuramu et al., 1993; O'Brien et al., 1995). These latter include i) hydroxynitrates which are formed by the oxidation of alkenes initiated by OH radicals and by isomerisation processes of alkoxy radicals (Arey et al., 2001), ii) carbonyl-nitrates which are produced by the NO_3-oxidation of alkenes but are also second-generation oxidation products of hydrocarbons and iii) dinitrates which are also expected to be second-generation oxidation products (Atkinson, 2000; Barnes et al., 1990; Roberts, 1990).

However, measurements of organic nitrates during field campaigns remain rare preventing a precise evaluation of their impact on the NOy budget in a wide variety of environments. The main problems in analyzing organic nitrates in the atmosphere are first the great complexity of the mixtures due to the huge number of precursors and formation pathways and then the fact that organic nitrates are explosive compounds and only few of them are commercial. So standards have to be synthesized. These analytical difficulties also affect our capability to study the chemical processes in which organic nitrates are involved during lab experiments (e.g. in simulation chambers).

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Table 1 summarizes, without the intent of being exhaustive, some keystone articles concerning the organic nitrates analysis in field and laboratory studies.

Two approaches have been applied for the analysis of complex mixtures of organic nitrates during field and lab experiments: first, analyses at the molecular scale which is a powerful approach to elucidate mechanisms but has the drawback to be often limited to a low number of species and then, functional group analyses which are very useful to assess global budgets but bring poor information for the understanding of processes. The second approach allows to shortcut the complexity of the organic nitrates chemistry governing their production, transformation, and removal processes and assess directly the sum of peroxy nitrates ΣAN and alkyl nitrates ΣAN (Day et al., 2002; Perring et al., 2010). The thermal dissociation (TD) properties of different classes of nitrates was used as an analytical tool able to sketch the global chemistry of $RONO_2$, same as the Laser-Induced Florescence (LIF), cavity ring down spectroscopy (CRDS)(Paul et al., 2009), or cavity attenuated phase shift (CAPS)(Sadanaga et al., 2016), were used to quantify the NO_2 issued from the organic nitrates decomposition. In a similar way, the infrared spectroscopy (IR) was used to monitor the time dependent loss of organic nitrates and measure the rate of homolytic O−N bond cleavage (Francisco and Krylowski, 2005) employing specific absorption bands in IR (1638 cm^{-1}). Although notoriously powerful analytical techniques, the LIF, CRDS, CAPS and the IR exhibit poor capabilities in the individual quantification of organic nitrates mixtures due to their intrinsic conceptual operation mode.

Historically, measurements of individual organic nitrates have been conducted by gas chromatography coupled to electron capture detection - GC/ECD, both coupled or not (Atlas, 1988; Blake et al., 1999; Flocke et al., 2005; Fukui and Doskey, 1998; Muthuramu et al., 1993), to a pyrolysis/luminol chemiluminescence - CL detector (Buhr et al., 1990; Fischer et al., 2000; Flocke et al., 1991; Gaffney et al., 1999; Hao et al., 1994; Winer et al., 1974), to electron impact mass spectrometry EI-MS (Luxenhofer and Ballschmiter, 1994; Luxenhofer et al., 1994) or to negative ion chemical ionization mass spectrometry – NI/CI-MS (Beaver et al., 2012; Tanimoto et al., 1999) using thermal electrons (e^-_{th}). Abundant in marine environments, the halocarbons are highly sensitive towards the ECD detection (Fischer et al., 2002; Fischer et al., 2000) and may generate artifacts in the organic nitrates identification and quantification (Fukui and Doskey, 1998).

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Although the chromatographic separation represents an effective analytical tool, the organic nitrates identification relies mainly on the retention times, while the dedicated detectors are only able to confirm, in best case, the presence of the nitrate functional group in the molecule. Illustrative examples are given by the studies of Luxenhofer et al. (1994) and Kastler and Ballschmiter (1999) who succeed to analyze complex mixtures of alkyl and multifunctional organic nitrates by combining separation with liquid and gas chromatography and detection using the intense mass-to-charge (m/z) 46 fragment ion that corresponds to NO_2^+. The same study highlights possible interferences with dinitrophenols, nitro- and dinitrocresols, pentachloro-nitrobenzene and to a smaller extent nitrophenols.

Besides the poor temporal resolution, another major drawback of this method is represented by the recovery factor decline with longer times in the chromatographic columns. According to Roberts et al. (2002), the sensitivity of this method for PANs is characterized by a diminishing response factor proportional to the compounds retention time through the column. Measurement of functionalized (oxygenated) nitrates appears to be a greater challenge as the lower vapor pressures and stronger surface interactions of these molecules make sampling and chromatographic techniques less appropriate. Additionally, the detection of functionalized nitrates by electron impact mass spectrometry has proven to be difficult, mainly due to the instability and thus, the fragmentation, of the molecular ion formed (Mills et al., 2016; Roberts, 1990; Rollins et al., 2010).

Lately, the newly developed capabilities in Atmospheric Pressure / Chemical Ionization Mass Spectrometry (AP-CIMS; CIMS) (Huey, 2007; Perraud et al., 2010; Slusher et al., 2004; Teng et al., 2014) prone as potentially powerful tools in organic nitrates analysis. Several types of CIMS have been highlighted by the literature, the technique being currently in progress.

The AP-CIMS uses methanol as a proton source in order to generate RH^+ peaks of the parent ions. Therefore the nitrogen-containing ions are characterized by even m/z ratios, while the analytes containing only C, H, and O appear at odd m/z. Several PANs were identified as gas phase products of the α-pinene + NO_3 reaction with this technique (Perraud et al., 2010). The protonated molecular ions were identified and the most intense fragments in the MS/MS scan corresponds to losses of NO_2, HNO_3 and to a smaller extent $HOONO_2$. Hydroxynitrates and keto-nitrates have also been detected with this technique. For hydroxynitrates, RH^+ peaks as well as fragments corresponding to the losses of H_2O and NO_2 + H_2O in the MS/MS mode were detected (Perraud et al., 2010; Schoon et al., 2007; Tuazon et al., 1999).

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The thermal dissociation–chemical ionization mass spectrometry (TD-CIMS) technique has been used for measurement of PANs and other multifunctional organic nitrates by the means of I^- reaction (Lee et al., 2014; Slusher et al., 2004; Xiong et al., 2015). The obtained carboxylate ion is unique for each parent species, and the only significant interference that has been identified is at ppb levels of NO (Slusher et al., 2004). The CF_3O^- was equally successfully tested as ionizing source in a CIMS approach in order to identify hydroxy-nitrates formed during the OH oxidation of alkenes in the presence of O_2 and NO (Bates et al., 2014; Teng et al., 2014). The quantification of the nitrates formed was assured by a complementary TD-LIF technique after subsequent GC separation. Other polyfunctional organic nitrates were scarcely detected using this technique.

The Proton-Transfer Reaction Mass Spectrometry (PTR-MS) can be positioned as a subset of CI. Its use in atmospheric research has expanded rapidly these last years but few studies have tested this technique for the detection of organic nitrates (Aoki et al., 2007; Hansel and Wisthaler, 2000; Inomata et al., 2013).

The recent study of Müller et al. (2012) considers that the quantification of PAN by PTR-MS is difficult due to fragmentation. Less promising results are also reported by Aoki et al. (2007) concerning the PTR ionization of C_1–C_5 alkyl nitrates. Considerable fragmentation occurs, even at low field density (E/N) ratio (100 Td; *E* being the electric field strength and *N* the gas number density; 1 Td = 10^{-17} V cm^2), the signal intensities of protonated alkyl nitrates, $(ROH \cdot NO_2)^+$, being in best case, a few percent of those of the total ion signals. An increase of the E/N ratio increases furthermore the fragmentation, providing common ions such as NO_2^+ and more characteristic ones such as RO^+. Other low intensity signals corresponding to R^+ or $ROH \cdot H^+$ ions have been also recorded and could result from reactions of alkyl nitrates with $H_3O^+(H_2O)_n$ clusters.

Hansel and Wisthaler (2000) have measured several PANs (PAN, MPAN and PPN) with PTR-MS and have reported low detection limit (70 pptv, 15s integration time) and an overall accuracy of 15 %. Worth noticing that the reported analytical sensitivities (15-25 counts ppb^{-1}) have not been calculated for the molecular ion signal but for typical molecular fragments in the case of the alkyl nitrates or signals of speculative subsequent reaction products of the protonated molecular ions for PANs. These results are illustrative for the organic nitrates overall affinity towards fragmentation due to chemical ionization in a low pressure drift tube

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under high voltage. To our knowledge, polyfunctional organic nitrates have never been detected using this technique.

So, it appears useful to better explore the possibility of detecting organic nitrates in real-time with PTR-MS. In the present work, the detection of alkyl and multifunctional organic nitrates (PANs, ketonitrates, hydroxynitrates) by this technique was investigated. For this purpose, different organic nitrates were synthesized and mixtures at the ppb-ppm level were generated in a smog chamber. A commercial PTR-ToF-MS instrument was used but the operating mode as well as the chemical ionization reagent have been modified and optimized for each type of organic nitrate in order to gain sensibility in the detection and to reduce fragmentation of ions. Mass spectra have been carefully interpreted and detection limits have been also determined.

2 Material and methods

2.1 Instrumentation

A commercially available, high mass resolution PTR-ToF-MS instrument (Kore Technology - 'Series II' High Performance PTR-TOF-MS) was used in the present study. The mass resolution of this instrument is >5000 M/δM. The PTR-MS is equipped with the newly designed radio frequency ion funnel (RF) which is used to focus ions in the drift tube and hence to increase the detection sensitivity (Barber et al., 2012). This ion funnel uses a series of electrodes with progressively reducing aperture sizes. In addition to the standard dc electrical field, an ac electric field is provided at a radio frequency creating a strongly repulsive effective potential near the surface of the electrodes, which combined to the reducing aperture sizes, serves to focus the ions radially. This system has been shown to increase the sensitivity by one or two orders of magnitude (Barber et al., 2012).Worth notice that operating in the RF mode modifies the dynamic range over which the drift tube is operated and the contribution of the radiofrequency to the global effective E/N ratio remains difficult to estimate (Barber et al., 2012).

The PTR-MS sampling line was designed in order to assure the highest transfer efficiency of the compounds. This line is made of a 1.5 meter long Silcosteel® coated stainless steel tubing, which has been shown to be appropriated for the transfer of low-level polar organic compounds (Smith, 2003). This line was heated at 40°C in order to prevent adsorption of

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compounds in the line. With a sampling flow rate of ~3 cm^3 s^{-1}, the residence time in the line has been estimated to be lower than 2s. The PTR-MS inlet system is equally made with Silcosteel® coated stainless steel tubing and is equipped with a temperature control unit allowing heating up to 150°C.

2.2 Experimental strategy

In PTR-MS, proton transfer reactions with hydronium ions (H_3O^+) are typically used to ionize compounds having a proton affinity (PA) higher than the one of water (691 kJ mol^{-1}, Hunter and Lias, 1998):

$$H_3O^+ + R \rightarrow RH^+ + H_2O \qquad (R1)$$

In this case, the proton transfer reaction is exothermic and proceeds at a reaction rate close to the collision rate (10^{-9} cm^3 $molecule^{-1}$ s^{-1}; Flocke et al. (1991)). In order to avoid a massive fragmentation of the analyte and consequently a decrease of the intensity and the specificity of the analytical signal, the energy transferred during the reaction should be lower than the bond energies of the compound of interest.

Only few available data can be found concerning the PA of organic nitrates which were calculated using *ab initio* quantum mechanical methods exclusively. The PA of organic nitrates have been estimated to: 740 kJ mol^{-1} for methyl nitrate (Lee and Rice, 1992), 753 kJ mol^{-1} for ethyl nitrate (Kriemler and Buttrill, 1970), 748 kJ mol^{-1} for methylperoxy nitrate (Ravelo and Francisco, 2007) and 759–773 kJ mol^{-1} for peroxyacetyl nitrate (Tureček, 2000). These studies show that the PA of organic nitrates are higher than the one of water and so that proton transfer reaction may occur. Furthermore, the functionalized nitrates concerned by the current study are equally expected to easily protonate as it was shown that the presence of an additional oxygen atom in the molecule enhances the overall PA (Ravelo and Francisco, 2007).

It is well known that other chemical processes can also occur in the PTR reactor (Blake et al., 2009; de Gouw and Warneke, 2007). The H_3O^+ and R^+ can cluster with water molecules in the sampled air. The water cluster ions formation in the PTR cell is generally considered as problematic since their presence complicates the mass spectra treatment. Typically, their formation is limited by high kinetic energy of the ions into the drift tube at E/N ratios superior to 100 Td. However, the proton-transfer reaction of $H_3O^+(H_2O)_n$ clusters is more selective

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than the H_3O^+ due to a higher PA (808 kJ mol^{-1}, Goebbert and Wentold (2004)). This property may be valuable in our case as it allows a softer ionization of analytes. Recently Jacobs et al. (2014) have used $H_3O^+(H_2O)_n$ ions (distribution centered around n=4) in PTR-CIMS technique with the objective of monitoring isoprene derived hydroxynitrates and their oxidation products. In order to evaluate the efficiency of the protonation mode by $H_3O^+(H_2O)_n$ for the detection of other organic nitrates, a wide range of E/N ratios will be tested.

The NO^+ chemical ionization has also been tested for the detection of organic nitrates during our experiments. It has been shown to be a complementary, sensitive and reliable method for the detection of some organic compounds such as ketones, aldehydes and alkenes by CI-MS and SIFT-MS techniques (Knighton et al., 2009; Mochalski et al., 2014; Perraud et al., 2010; Wang et al., 2004). NO^+ ions are produced from the ionization of dry air within the hollow cathode discharge ion source. This process produces large amounts of NO^+ with only minor amounts of NO_2^+, O_2^+, and $H_3O^+(H_2O)_n$ impurities (Knighton et al., 2009). The intensities of O_2^+, and $H_3O^+(H_2O)_n$ are quite low, less than 1% of the primary NO^+ signal. In addition, it has been shown that the intensity of the NO_2^+ impurity is controllable and dependant on how the hollow cathode ion source is operated (Knighton et al., 2009). The ion source extraction voltage and the hollow cathode discharge current are the two most important parameters.

Previous studies interrelated the PA of water to the NO^+ chemical ionization binding energies (BE), creating an absolute NO^+ affinity scale (Cacace et al., 1997). The study used the H_2O-NO^+ binding energy as a reference anchor between the two conjugated parameters and concerned various classes of ligands (alkyl halides, alkyl nitrates, alcohols, nitro-alkanes, nitriles, aldehydes, ketones, aromatic and heterocyclic compounds). With the exception of the aromatic compounds, for which the NO^+ σ type complex structures are replaced by the π complexes, the overall data exhibit a highly correlated linear dependence (BE_{NO^+} = 0.367 PA – 174.5 kJ mol^{-1}). When compared with protonation energies, the binding energies characterizing the NO^+ chemical ionization are significantly lower (Cacace et al., 1997).

This characteristic offers the opportunity to generate soft ionizations with little fragmentation of the product ions, which is of high interest for the present study. Reactions which may occur are:

$$NO^+ + R \rightarrow R^+ + NO \qquad \text{(R2a)}$$

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$$NO^+ + R \rightarrow R \cdot NO^+ \qquad \text{(R2b)}$$

$$NO^+ + RX \rightarrow R^+ + XNO \quad (X=\text{-H, -OH, -}CH_3\text{, -OR}) \qquad \text{(R2c)}$$

As a function of the chemical affinity, NO^+ chemical ionization may follow several pathways. The charge transfer reaction (2a) seems to be the most common process for compounds having ionization energies slightly lower or close to that of NO (IE = 9.26 eV) (e.g. isoprene (Karl et al., 2012) butadiene, benzene (Knighton et al., 2009), monoterpenes, terpenoids (Amadei and Ross, 2011; Rimetz-Planchon et al., 2011) and phenols (Wang et al., 2004)). This hypothesis is confirmed by Smith et al. (2003) who reported for a series of ketones (C_3-C_{11}) that the yields of parent radical cation increase as the IE decrease.

The adduct formation pathway (2b) has been previously reported for the detection of C_3-C_4 alkanes, alkenes and terpenes (Diskin et al., 2002; Španěl and Smith, 1998), ketones (Smith et al., 2003; Wang et al., 2004) and flavoring esters (Iachetta et al., 2010) by selected ion flow tube mass spectrometry. The speculated mechanism which has been proposed to explain the formation of the adduct involves the formation of an excited intermediate complex $(R \cdot NO^+)^*$ which is then stabilized by collision with the carrier gas (Smith et al., 2003). Evidently the process is enhanced at upper PTR reactor pressure involving higher collision rates.

A third mechanism, similar to the protonation, involves the hydride, hydroxide, methyl or alkoxy abstraction (2c), as reported for aldehydes, ethers, alcohols (Smith and Španěl, 2005) terpenoids (Amadei and Ross, 2011) or several unsaturated alcohols (Karl et al., 2012; Schoon et al., 2007; Wang et al., 2004).

The O_2^+ ionization can generate artefacts, particularly when the PTR-MS is operated in dry air mode, as it proceeds via a dissociative charge transfer reaction producing parent cations M^+ but also fragment ions. In consequence, this process presents low interest for chemical ionization of large molecules.

To summarize, several parameters will be tested in order to establish the optimal conditions for the detection of each class of organic nitrates.

A thoughtful procedure was performed in order to establish the optimal measurement conditions for each class of organic nitrates:

- First, the instrument has been used in a dual mode, employing alternatively H_3O^+ and NO^+ as a reagent ion, by shifting the GD source gas from water vapor to dry air. Dry air was supplied to the hollow cathode ion source using the alternative GD ionization

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line. A third operation mode which consists in suppressing the GD source gas once the plasma is established has also been tested. This last operational mode implies hence the retro-diffusion of the sampling line dry air into the GD cavity and will be further referenced as the Retro-diffusion mode (RDiff).

- The ions intensity and distribution are sensitive to the extraction voltage used to inject the reagent ions into the drift tube and to the hollow cathode discharge current. The PTR-MS instrument was thus operated in a wide range of E/N (electric field to number density of the gas) ratios (30 – 180 Td), hence shifting the distribution between the different ionizing analytes in the protonation mode (H_3O^+/ $H_3O^+(H_2O)_n$) or into the dry air mode (NO^+/NO_2^+).
- The sampling line and the inlet system along with the drift tube was slightly heated (40°C) and the reactor pressure ranged from 0.7 to 1.6 mbar. The sampling flow rate (2.9 to 3.5 cm^3 s^{-1}) affects through the mass of the sampled analyte or through the third body collision processes the instrument response. An enhanced influence of this parameter may be noticed while operating in the RF mode.
- The influence of radio frequency ion funnel mode on the detection of the various organic nitrates has been tested by performing experiments with the RF mode on and off.

Ideally, little or no fragmentation occurs in the case of a soft ionization process. The large differences in ionization energy of the colliding species enhance the fragmentation of the organic molecule. Therefore the ionizing gas species should correspond, especially for labile molecules, to the analyte of interest in order to achieve the high yield ionizations with low excess energy.

In addition, the soft ionization processes demand the usage of uncommon settings of the PTR-MS device. The various effects of the altered PTR-MS tuning are termed in detail elsewhere (Hewitt et al., 2003; Knighton et al., 2009). Supplementary information relating the ion source discharge current and the extraction voltage influence are discussed in the Results section.

All reported signal intensities took systematically into account the background values, representing in most of the cases negligible low values of a few counts per minute. Background measurements are achieved before every single experiment by sampling the dry synthetic air of the reaction chamber.

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2.3 Normalizing analytical signal for H_3O^+ and NO^+ ionization

In this study, calibrated response factors of PTR-MS are determined for several types of organic nitrates in both H_3O^+ and NO^+ ionization modes. For that purpose, known amounts of organic nitrates are introduced in LISA simulation chamber (see section below). To quantify the PTR-ToF-MS response factors (S; ncpm $ppbv^{-1}$), the ion signal (I_{R+}; ncpm) is divided by the known concentration of organic nitrate ($ppbv^{-1}$), as measured by the FTIR in-situ technique. Corrections of the product ion signal (I_{R+}) due to changes of the operational conditions have to be taken into account, as shown by previous studies (Knighton et al., 2009):

$$I_{R^+} = \left(\frac{i_{R^+}}{f_{IA^+}}\right)\left(\frac{P_0}{P}\right)^2\left(\frac{T}{T_0}\right)^2 \qquad \text{(Eq. 1)}$$

The intensity of the product ion raw signal (i_{R+}) expressed in counts per minute is adjusted to the variabilities of the ionizing analyte (i_{IA^+}) normalized to its averaged values ($\langle i_{IA^+}\rangle$), ($f_{IA^+} = i_{IA^+}/\langle i_{IA^+}\rangle$; $IA^+ = H_3O^+$ or NO^+) as it has been shown that both signals (i_{R+} and i_{IA+}) are related. The drift tube temperature (T) and pressure (P) are also included in this expression to account for the small changes in the reaction time and gas number density that can occur during measurements. In our experiments, the temperature was very stable (± 1 K) but the PTR pressure was affected by the pressure in the simulation chamber which usually slowly decreases because of the sampling from in the constant volume of the rigid chamber.

Due to the high abundance of the ionizing species, the direct measurement of H_3O^+ and NO^+ reagents was not possible as the ion counting signals (m/z 19 and 30) were regularly saturated. The natural isotopic abundance properties of ^{17}O (0.038% of O), ^{18}O (0.200% of O) and ^{15}N (0.368% of N) are used to overcome this drawback and evaluate the primary H_3O^+ and NO^+ ion intensity using the m/z 21 ($H_3{}^{18}O$) and 31 respectively (Σ $^{15}NO^+$ and $N^{17}O^+$) (De Laeter et al., 2003). The $I_{H30+} = I_{m/z21} \times 500$ and $I_{NO+} = I_{m/z31} \times 247$ formulas were applied as a result of isotopic abundance probability calculations.

2.4 LISA Atmospheric Simulation Chamber.

Gaseous mixtures of organic nitrates at the ppb-ppm level were generated in the simulation chamber at LISA. This chamber comprises a Pyrex reactor of 977 L equipped with a multiple reflection optical system interfaced to a FT-IR spectrometer (Vertex 80 from Bruker). Details of this smog chamber are given elsewhere (Doussin et al, 1997).

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All experiments were conducted in the dark at 298 ± 2 K and atmospheric pressure. Mixtures of organic nitrates were generated in synthetic air (N_2 80% + O_2 20%) by introducing a known amount of the organic nitrate into the chamber and cross-monitored by long path *in situ* FTIR and PTR-MS techniques. Concentrations of organic nitrates were checked from their infrared spectral absorption bands. Integrated Band Intensities (IBIs; expressed in cm^2 $molecule^{-1}$ and calculated in decimal logarithm) and the spectral integration areas used to quantify PAN like compounds and other nitrates are: 9.50×10^{-18} for PANs (765–812 cm^{-1}), 8.30×10^{-18} for alkyl nitrates (820-900 cm^{-1}), 1.17×10^{-17} for hydroxynitrates (816-882 cm^{-1}) , 1.08×10^{-17} for ketonitrates (820-870 cm^{-1}). The IBIs values are given by the Beaver et al. (2012) and Bates et al. (2014) studies for the PANs and the hydroxynitrates respectively, whereas for the alkyl nitrates and ketonitrates the IBIs were calculated from repetitive injections of known amount of analyte, in the current study. Worth notice the weak disparity of cross sections concerning the characteristic -ONO_2 absorption band.

Before and after every single experiment, a cleaning procedure was applied in order to avoid memory effects from an experiment to the next one. It consists in vacuum clean-up down to 10^{-2} mbar for at least 10h and UV irradiation (340 and 360 nm fluorescent tubes) in order to heat the reactor and improve desorption of semi and low volatile compounds from the walls.

2.5 Chemicals and gases

The simulation chamber was filled with dry synthetic air generated with N_2 (from liquid nitrogen evaporation, >99.995% pure, <5ppm H_2O, Linde Gas) and O_2 (quality N45, >99.995% pure, <5 ppm H_2O, Air Liquide). Supplementary cylinder air was used for the dry air glow discharge generation in PTRMS (ALPHAGAZ™ 2; H_2O < 0,5 ppm; C_nH_m < 50 ppb; CO_2 < 0,1 ppm; CO < 0,1 ppm; NO_x < 10 ppb)

The alkyl nitrates considered in the present study (n-propyl nitrate - 97% Janssen Chimica; AlkC3 and isobutyl nitrate - 96 % Sigma Aldrich; AlkiC4) were used as commercially available, without further purification.

Ketonitrates were synthesized using Kames' method, (Kames et al., 1993): a liquid/gas phase reaction in which the corresponding hydroxyketone is reacted with NO_3 radicals released from the dissociation of N_2O_5 , at ice bath temperature, under dry condition. The carbonyl

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nitrates and nitric acid were separated by multiple headspaces vacuum procedure. The carbonyl nitrates' structure and purity were verified by FT-IR. The presence of HNO_3 is regularly noticed as injected as by product of the carbonyl nitrates synthesis. 1-hydroxy-2-propanone (95% Alfa Aesar) and 3-hydroxy-3-methyl-2-butanone (97% Sigma Aldrich) were used for the synthesis of 1-nitroxy-2-propanone and 3-nitroxy-2-propanone respectively.

The hydroxynitrate was synthetized starting from the commercially available 3-bromo-1-propanol (97% Sigma Aldrich). Its conversion to the analog iodide was performed by a Finkelstein reaction with sodium iodide (Baughman et al., 2004) and the subsequent mild conversion with $AgNO_3$ (Castedo et al., 1992) leads to the formation of 1-hydroxy-3-nitroxy-propane (1OH3C3).

The PAN type compounds were generated in the simulation chamber from the gas-phase oxidation of corresponding aldehydes by NO_3 radicals (Hanst, 1971). In our experiments, peroxyacetyl nitrate (PAN) was formed from the oxidation of acetaldehyde (>99.5% Sigma Aldrich). This reaction has been shown to produce mainly PAN with a yield close to 70% (Doussin et al., 2003).

3 Results and discussion

3.1 Influence of the operating conditions on the ionizing analytes signals

As already termed, intensities and mixing ratios of the ionizing species are dependent on the E/N ratio. For a standard drift tube, E/N is a well-defined quantity but when the instrument is run in RF mode, the influence of the additional ac electric field on the E/N ratio has to be taken into account and this is not obvious. Barber et al, 2012 have attempted to empirically estimate an effective E/N by running the instrument with the RF mode on and off and by seeking operating conditions for the RF mode on that match the performance obtained when the RF mode is off. The criterion used to estimate the performance is the ratio $[H_3O^+]/[H_3O^+(H_2O)]$. During our experiments, the additional ac electric field was fixed. Thus, variations of E/N ratio result only from variations of the dc component of the drift tube.

Typically recorded distributions over a relevant range of E/N are illustrated in *Figure 1* for both ionization modes, with and without the above described RF mode. When the RF mode is not employed, the water cluster ion distribution obtained in this study (*Figure 1*) is in

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reasonable agreement with those calculated and measured by de Gouw and Warneke (2007) asserting that i) the $H_3O^+(H_2O)_2$ cluster is abundant for E/N ratios < 60Td, ii) the $H_3O^+(H_2O)$ signal is maximum around 80Td and iii) the H_3O^+ signal is predominant for values larger than 100Td. In the RF mode, it has been observed that the signal of H_3O^+ ion is much higher than those of clusters for the entire range of E/N ratios. The $H_3O^+(H_2O)$ is one order of magnitude lower than the H_3O^+ and one order of magnitude more abundant than the $H_3O^+(H_2O)_2$. As the distributions of ions obtained with and without RF mode are quite different, it was not possible to estimate an effective E/N as proposed by Barber et al., 2012. So E/N ratios have been calculated without taking into account the RF contribution. In the case the RF mode is on, E/N ratios are indicated with * (E/N*).

The NO^+ ionization mode has been found more promising in the RF mode, since the abundance of the ionizing species is largely superior. Furthermore, the NO^+/NO_2^+ ratio exhibits the highest values around 40Td in the RF mode, increasing the probability to form the analyte-NO^+ adduct. Therefore, all further results presented in the current work in the NO^+ mode have been recorded with the RF mode and reported E/N* were calculated without taking into account the ac radiofrequency contribution.

3.2 Alkyl-nitrates

3.2.1 H_3O^+ ionization mode

A series of tests has been conducted in order to seek the optimum operating conditions for the measurement of alkyl nitrates with H_3O^+ ionization mode. In particular, the E/N ratio was spanned in the 50-140 Td range. The intensity of the main signals obtained for n-propyl nitrate (AlkC3) with the RF mode off has been plotted as a function of E/N in *Figure 2*. The recorded mass spectra of AlkC3 are characterized by a high degree of fragmentation, even for the lowest E/N (50 Td). The AlkC3 mass spectra recorded at the lowest extent of fragmentation of the protonated molecular ion is illustrated by *Figure S1 in S.I.*. The same result has been observed for AlkC4. Consequently, the sensitivity of the molecular ions formed is low (see Table 2). The protonated alkyl nitrates are expected to adopt the ion-dipole complex conformation ($ROH\cdot NO_2^+$; R1a) and not a covalently bound $RONO_2H^+$ one (Cacace and de Petris, 2000).

$$H_3O^+ + RONO_2 \rightarrow ROH\cdot NO_2^+ + H_2O \qquad (R1a)$$

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The bound energy of these complexes was calculated by *ab initio* methods to be around 82 kJ mol^{-1} in the case of methyl nitrate (Lee and Rice, 1992).

The only other study (Aoki et al., 2007) describing a tentative of alkyl nitrate detection with PTR-MS used E/N ratio spanning in between 96 and 147 Td. The low BE characterizing the formed complex enables its decomposition in ROH and NO_2^+ by collision induced dissociations. The recorded signals of NO_2^+ (m/z 46) and RO^+ (m/z 59 for AlkC3 and 73 for AlkiC4) are probably formed by the mechanisms:

$$ROH \cdot NO_2^+ \rightarrow ROH + NO_2^+ \quad (R3)$$

$$ROH \cdot NO_2^+ \rightarrow RO^+ + HONO \quad (R4)$$

This statement is supported by the decrease of the protonated signal in conjunction with the increase of the NO_2^+ with increasing E/N.

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.

Due to the abundance of water clusters, higher in our study than typically, the R5 mechanism is considered more likely, as proposed by Aoki et al. (2007). The formation of R-OH.H^+ ion can also be explained by reaction R6 as proposed by Spanel and Smith (1997) This ion is then expected to form the alkyl fragment (R^+) by reaction R7:

$$RONO_2 + H_3O^+(H_2O)_n \rightarrow R\text{-}OH \cdot H^+ + HNO_3 + nH_2O \quad (R5)$$

$$RONO_2 \cdot H^+ + H_3O^+ \rightarrow R\text{-}OH \cdot H^+ + HNO_3 \quad (R6)$$

$$R\text{-}OH \cdot H^+ \rightarrow R^+ + H_2O \quad (R7)$$

A third option is to consider the direct formation of the alkyl fragment from the collision induced dissociation of the protonated alkyl nitrates formed in reaction 1a into R^+ and HNO_3. Further collisions of the alkyl fragment ($R^+ = C_3H_7^+$) might generate the loss of two hydrogens and explain the weak signals at m/z 41 in the case of AlkC3.

$$C_3H_7^+ \rightarrow C_3H_5^+ + H_2 \quad (R8)$$

It should be noticed that the analog process for the m/z 55 in the case of AlkiC4 cannot be observed since it falls nearby a relatively abundant water cluster signal.

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457 Results obtained with the RF mode are shown in Figure 3 for the AlkC3. The ionization
458 pattern of the analyte is slightly different from the one obtained without RF mode and
459 enables, adjacent to the formation of the protonated alkyl nitrate, the identification of other
460 specific signals like the adduct AlkC3·H_3O^+ formation. Characterized by a high degree of
461 fragmentation, the spectra contain the protonated ion-dipole complex ROH·NO_2^+ at m/z = 106
462 (R1a) with the highest sensibility above 60Td. The E/N ratio is calculated without taking into
463 account the RF contribution. The m/z 124 signal can be assigned to the AlkC3-H_3O^+ adduct
464 formation. An analog process is described in the literature for long alkanes (> C6) providing
465 M·H_3O^+ signals (Španěl and Smith, 1998), in contrast with the alkenes which are readily
466 protonated due their higher PA.

467 The alkyl (R^+) intermediary parent ion, described in R5 and R6 (R-OH·H^+) is equally
468 recorded, corresponding in the case of AlkC3 to the m/z 61 signal. The increase of the E/N
469 ratio over 60Td contributes to a higher degree of decay of this intermediate ion in the
470 particular conditions of the RF mode. The RO^+ ion at m/z 59 is equally present in the case of
471 AlkC3 confirming the existence of the R4 mechanism conducting to HONO formation.

472 To summarize, the use of H_3O^+ ionization is not really suitable for the detection of alkyl
473 nitrates as it leads to high fragmentation, even at low E/N ratios, hence generating intense
474 signals of common organic analytes, unsuitable for a reliable identification of these
475 compounds. In addition, if considering the more characteristic signals of the protonated ion-
476 dipole complex ROH·NO_2^+, the H_3O^+ ionization mode exhibits poor detection limit: 5 ppb
477 min^{-1} for both AlkC3 (m/z 106) and AlkiC4 (m/z 120). This detection limit was estimated for
478 a mean signal/noise ratio of 3 at the chosen m/z.

479 In Table 2, are gathered the characteristic signals of each organic nitrate studied here as well
480 as their detection limits.

481

482 **3.2.2** NO^+ ionization mode

483 The performances of the NO^+ ionization were also evaluated. The most promising results,
484 enabling the identification of characteristic signals of the studied alkyl nitrates, were obtained
485 in the RF mode. The scan of a large range of E/N* ratios confirmed that the highest sensibility
486 towards NO^+ induced ionization and identification is obtained around 40Td as illustrated in

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Figure 3 for the AlkC3 case. As mentioned previously, the calculated E/N ratio does not take into account the RF contribution to the ion funnel field.

The recorded mass spectra of the analyte of interest in terms of relative peak intensities as a function of the m/z are represented by the thick black lines in Figure 4. It will be kept in mind that the NO^+ and NO_2^+ signals illustrated above are the sum of the corresponding nitrate fragments as well as the ions formed into the dry air plasma GD. The presence of O_2^+ (m/z = 32) and its interfering isotopic abundance signals at m/z = 33 and 34 has been observed and could result in interfering signals.

For both alkyl nitrates, the adduct formation (2b) appears to be the main ionization mechanism under these given conditions, leading to intense peaks at m/z = 135 (105+30) and m/z = 149 (119+30) for AlkC3 and AlkC4 respectively (see Figure 4 and Figure S2). The hydride abstraction $(R\ (-H))^+$ was also detected as a minor pathway (2c) at m/z = 104 and m/z = 118 for AlkC3 and AlkC4 respectively. Despite a weak intensity, this signal can be used as an interrelated identification signal for alkyl nitrates. The fraction of the abstraction channel is at no time higher than 10% of the intensity of the adduct formation channel.

An intense peak corresponding to the alkyl fragment (R^+) was observed in spectra at m/z 43 (AlkC3) and 57 (AlkiC4). The alkyl fragment signal is followed by a downward series of signals at m/z 41 and 39 in the case of AlkC3 and at m/z 55 and 53 for the AlkiC4. Considering the collisions of the alkyl fragment mechanism generating the loss of two hydrogens (R8), as proposed by Aoki et al. (2007) for the protonation mode, could explain the recorded signals.

In conclusion, the NO^+ ionization mode appears to be more suitable for the detection of alkyl nitrates than the H_3O^+ ionization mode as it produces two characteristic signals, corresponding to the adduct formation ($M.NO^+$) and the hydride abstraction ($M(-H)^+$). The detection limit for the $M.NO^+$ signal was estimated to be 205 ppt min^{-1} for AlkC3 (m/z 135) and 126 ppt min^{-1} in the case of AlkiC4 (m/z 149) (see Table 2). Although superior to the protonation mode, the NO^+ ionization exhibits a poor sensitivity. For measurements in real atmosphere where alkyl nitrates mixing ratios are usually in the ppt level, accumulations for several hours will be necessary.

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3.3 Hydroxy-nitrates

3.3.1 The H_3O^+ ionization

As for alkyl nitrates, the measurement of hydroxy-nitrates by PTR-MS has been tested with H_3O^+ ionization mode, with and without RF mode. For this purpose, 1-hydroxy-3-nitroxy-propane (1OH3C3) was synthesized and used as template. In the classical mode (RF off), the main signals which have been attributed to 1OH3C3 are: m/z 43 ($C_2H_3O^+$), m/z 104 ($M_{1OH3C3}(-OH)^+$), m/z 122 ($M_{1OH3C3}.H^+$), m/z 139 ($M_{1OH3C3}.H_2O)^+$). Intensities of these signals have been plotted as a function of E/N in *Figure 5*. As expected, the intensity of the signal m/z 43 increases with high E/N ratio while protonation and water adduct formation are favored by low E/N. A possible explanation for the formation of the ion $M_{1OH3C3}(-OH)^+$ is a loss of H_2O after protonation of the hydroxyl-nitrate, as suggested by several studies for alcohols (Schoon et al., 2007; Smith et al., 2012; Tuazon et al., 1999).

When the RF mode is on, the same signals (43, 104, 122, 139) were observed but with different relative abundance. The influence of E/N on the intensity of these signals has been plotted in *Figure 6*. Above 40 Td, the signal characterizing the water adduct formation (m/z = 139) is more abundant in the RF mode with a maximum around 45Td.

The water clusters are probably abundant in the PTR reactor due to the low E/N ratios and dissociate only into the RF region after the ionization occurs.

The mass spectrum illustrated by Figure S3 was recorded in absence of the RF funnel and is dominated by fragments like m/z 59, 60, 73, while the specific signal of the protonated molecule m/z 122 is present close to the noise limit.

The above described water adduct formation (m/z = 139) is competed by a H_3O^+ adduct (m/z = 140), equally present into the spectra. The ionization is probably induced by the expected high levels of water cluster, following an analogous process with the one described in R5. This involves the release of HNO_3 and arise the signal at m/z 77 (C_3H_6OH)-OH·H^+ and subsequently at m/z 59 with the loose of supplementary water (R7). Further collisions of the above mentioned ions may well explain the signals at m/z 75 and 57, generated by the loss of two hydrogens (R8).

In RF mode, the mass spectrum obtained for 1OH3C3 at E/N* =45 Td (corresponding to the operational condition for which the signal at m/z 139 is the most intense) was illustrated in

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Figure 7. It is worth to notice that all the other competitive ionization processes are strongly diminished in comparison to the spectrum obtained in classical mode. Only the specific signal at m/z = 104 exhibit a stronger signature compared to the case above. The fragmentation pattern is strongly diminished in this case.

To conclude, it has been observed that protonation of the hydroxynitrate is a minor process in comparison to fragmentation and to adduct formation. The use of the RF mode significantly reduces the fragmentation for the benefit of the $M.H_2O^+$ adduct formation. The lowest DL (80 ppb min^{-1}) was obtained at 45Td* in the RF mode for the signal corresponding to the water adduct formation at m/z 139. The same signal in absence of the RF effect is at least twice weaker in terms of sensibility. Sensitivities of other specific signals are equally proposed for comparison in Table 2.

3.3.2 The NO^+ ionization

The detection of hydroxy-nitrates in NO^+ ionization mode has been evaluated for the first time, by varying the E/N ratio (39 – 44 Td) and by studying the influence of the RF mode. As stated before the highest sensibility towards the NO^+ adduct formation are obtained in the RF mode, most likely due to the higher abundance of the ionizing species, as already seen in Figure 1.

Results obtained with RF mode have shown in *Figure 8*. Main signals which have been observed are: 151 and 167 which have been attributed to $M.NO^+$ and $M.NO_2^+$ adducts formation and 43 ($C_2H_3O^+$) which is characteristic of fragmentation. Although weak, the hydride abstraction (R2c) leading to a signal at m/z 120 has also been observed in the recorded spectra. This process has already been observed in previous studies for various saturated and unsaturated alcohols ($C_{1\text{-}10}$) and phenol (Karl et al., 2012; Schoon et al., 2007; Spanel and Smith, 1997) using SIFT and PTR-MS techniques. The hydride ion transfer of these compounds generates the corresponding carboxy ion (and HNO), while the hydroxide ion transfer gives the corresponding hydrocarbon ion (and HNO_2). Assuming the corresponding ionization of hydroxynitrate in the case of the 1OH3C3, would involve the formation of the $(O_2NO\text{-}C_3H_6)\text{-}O^+$ at m/z 120 and $(O_2NO\text{-}C_3H_6)^+$ at m/z 104 but their spectral signature is marginal into the spectra.

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As expected, the intensity of the signal 43 increases with increasing E/N ratio. The opposite tendency was observed for adducts. The mass spectrum obtained at E/N* = 41 which corresponds to the highest sensitivity for the m/z 151 signal is shown in *Figure 9*.

Beside the above mentioned characteristic signals, other specific mechanisms could be associated to the spectral signature of 1OH3C3. The mechanism is reviewed and suggested by (Harrison, 1999) for the particular case of NO^+ ionization of primary alcohols. In this study, an additional product (R (-2H) + NO^+) has been observed which would correspond in our case to an m/z = 149, hypothetically formed by the oxidation of the alcohol to the corresponding aldehyde and its subsequent ionization. Although relatively weak the signal is systematically recorded in the mass spectra of the hydroxy-nitrate. The 45 and 67 ions are equally present in mass spectra and can be attributed to fragmentation.

The detection limit obtained in NO^+ ionization mode at E/N ratio of 41 Td* for the $M.NO^+$ signal at m/z 151 was quite low (37 $ppt.min^{-1}$) showing that this ionization mode is more suitable than H_3O^+ mode for the measurement of hydroxy-nitrates. As shown in Table 2, the hydrogen abstraction signal (m/z 120) is at least one order of magnitude less sensitive.

3.4 Keto-nitrates

3.4.1 The H_3O^+ ionization

Two distinct keto-nitrates were synthesized and characterized in the current study, 3-nitroxy-2-propanone (KnC3) and the 3-nitroxy-3-methyl-2-butanone (KnC5).

In order to identify the optimal conditions for the detection of ketonitrates in H_3O^+ ionization mode, tests were performed by varying E/N ratios into a large domain, from 45 to 170 Td (*Figure 10*).

Several signals which can be attributed to keto-nitrates have been detected, as illustrated in *Figure 10* for KnC3: At low E/N ratios, which correspond to the $H_3O^+(H_2O)_2$ controlled regime, the formation of two keto-nitrate water cluster adducts, $M_{kn}\cdot H_3O^+$ (m/z=138) and $M_{kn}\cdot H_3O^+(H_2O)$ (m/z=156) has been observed. Worth notice the reduction of these specific signals with the decay of the preeminent ionizing analyte $H_3O^+(H_2O)_2$ (m/z= 55) signal. The literature available data expect that for polar compoundsthe ionization process may follow

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two similar pathways, by proton-transfer (R9a) and by ligand–switching reaction (R9b) (de Gouw et al., 2003).

$$M_{kn} + H_3O^+(H_2O)_n \rightarrow M_{kn}H^+ + (n+1)\,H_2O \qquad (R9a)$$

$$M_{kn} + H_3O^+(H_2O)_n \rightarrow M_{kn}H^+(H_2O)_m + (n-m+1)\,H_2O \qquad (R9b)$$

The bound energy of the cluster ions formed in the reaction above (R9b) is weaker than the water cluster bond. In the given conditions, there is a high probability that the drift tube dissociative effect can split the formed cluster ions and lead to the formation of MH^+ and $MH^+\cdot(H_2O)$. Since the cluster ion distribution may be governed by the water vapor drift tube loads, the detection efficiency can be humidity reliant in this particular case (de Gouw et al., 2003).

Redistribution processes among the various precursor ions formed into the glow discharge can equally occur, leading to the formation of auxiliary hydrated ions such as $NO^+(H_2O)_n$, able to produce ligand-switching reactions alike the ones presented above (R9b).

For intermediate E/N ratios, where $H_3O^+(H_2O)$ water cluster is the key analyte, we notice that the signal corresponding to $M_{kn}\cdot H^+$ (m/z=120) is maximum. In addition, two other signals corresponding to $M_{kn}\cdot NO^+$ (m/z=149) and $M_{kn}\cdot NO_2^+$ (m/z=165) adducts formation have also been observed and rise up to a maximum for these intermediate E/N ratios. These adducts can be explained by the formation of NO^+ and NO_2^+ analytes in the GD, which increases with the increasing E/N ratios.

For high E/N ratios, the m/z 43 ($C_2H_3O^+$) signal which is a common fragment of organic compounds, strongly increases. This reveals that mainly fragmentation occurs, making this region not suitable for the detection of ketonitrates.

From these results, the intermediate E/N ratios (70 - 80 Td) appear to be the most suitable for the detection of keto-nitrates in H_3O^+ ionization mode. Mass spectra obtained at E/N=75Td which corresponds to the highest sensibility of the $M_{kn}\cdot H^+$ signal are shown in *Figure 11* for KnC3 and in S.I. Figure S4 for KnC5 respectively.

For KnC3, the most intense signal corresponds to $M_{kn}\cdot H^+$ (m/z=120). As discussed above, additional processes occur which are responsible for other signals: $M_{kn}\cdot NO^+$ adduct formation at m/z 149 and fragmentation at m/z 43 ($C_2H_3O^+$). These characteristic signals are tailed by their corresponding isotopic abundance signals mainly due to ^{13}C isotope at m/z=121 and 150.

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635 The already discussed reactions R5 and R6 could explain the intense signal of m/z 75 since
636 the resulting (C_3H_5O)-$OH\cdot H^+$ ion seems the accurate match of this signal.

637 Worth notice that due to the low E/N ratios, imposed by the breakability of organic nitrates, in
638 the above illustrated mass spectra examples, the intensities of the signals m/z 19 (H_3O^+) and
639 37 ($H_3O^+(H_2O)$) are of the same order of magnitude while the m/z 55 ($H_3O^+(H_2O)_2$) is one or
640 two orders of magnitude lower.

641 In the case of KnC5, the $M_{kn}\cdot H^+$ (m/z=148) signal is not the most intense one, suggesting that
642 fragmentation is more favored that for KnC3 under similar conditions. The characteristic
643 fragmentation pattern of this analyte exhibits a characteristic m/z 85 signal corresponding to
644 the $C_5H_9O^+$ group after the cleavage of the NO_3 fragment. An analogous process is described
645 by Aoki et al. (2007) asserting the alkyl group as the main signal in the mass spectra of alkyl
646 nitrates. The abundant m/z 59 fragment ($C_3H_7O^+$ or $C_2H_3O_2^+$) is most probably a result of
647 subsequent fragmentation/recombination processes.

648 The intense m/z=103 signal could be ascribed to the already mentioned R5 and/or R6, both
649 conducting to the formation of a (C_5H_9O)-$OH\cdot H^+$ ion with release of HNO_3 and water. Worth
650 notice that the elimination of supplementary H_2O from the resulting complex could also
651 contribute to the m/z 85 signal ($C_5H_9O^+$).

652 In the RF mode, the water clusters distribution is dominated by the H_3O^+ ion, for the entire
653 range of E/N* ratios. Its signal is the most abundant, while all the other $H_3O^+(H_2O)_n$ species
654 are at least one order of magnitude lower. The redistribution of water cluster in the RF mode
655 modifies obviously the keto-nitrates' fragmentation pattern and the burden of each ionization
656 channel in a similar way as in the case of hydroxy-nitrates. No straightforward correlation can
657 be made in between the two modes, showing the complexity of the ion funnel influence.

658 The most noteworthy difference in the RF mode resides in the presence of an intense signal
659 corresponding to a H_2O adduct formation (m/z 137 and 165 respectively), similar to the
660 hydroxy-nitrate, with a maximum intensity around 48 Td (Table 2) as calculated without
661 taking into account the RF contribution.

662 With the same PTR entry voltage, the RF mode activation induces the enhancement of the
663 fragmentation due to higher input energies and the maximum of the protonated ketonitrate
664 signal glides towards 48 Td. Making the assumption that the highest sensibility is related in
665 the two modes to an analogous E/N state, a coarse assessment of the RF mode contribution is

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estimated (25 - 35 Td) as the difference between the two modes maximum sensibility for the protonated molecular ion signal.

To conclude, it has been observed that protonation of ketonitrates is the main ionization process in the absence of a RF field. The use of the RF mode modifies the fragmentation patern and enhances the mechanism leading to the $M.H_2O^+$ adducts formation. The recorded sensitivities listed in Table 2 for the H_3O^+ ionization mode, to a DL of 70 - 80 ppt min^{-1} for the protonated signal of KnC3 (m/z 120). A similar DL is reached by the water adduct signal at m/z 137 under the influence of the RF ion funnel. The highest sensibility for the KnC5 identification is attained by the water adduct signal at m/z 165 recorded at 48Td in the RF mode with a DL of 20 ppt min^{-1}. Sensitivities of other specific signals are equally proposed for comparison in Table 2.

3.4.2 The NO^+ ionization

For the first time, the detection of keto-nitrates using NO^+ ionization was tested. In a similar way as for the protonation process, mass spectra of KnC3 and KnC5 were recorded as a function of E/N ratios. The previously proven affinity of NO^+ coupling -C(O) functional group in ketones to form adducts (Smith et al., 2003) was for the first time tested in a PTR reactor. The adduct formation was successfully achieved in the presence of NO^+ for both studied ketonitrates, for which very similar IE are expected.

In the given ionization mode and considering the higher IE of ketonitrates, the adduct formation is expected to prevail over the charge transfer, the literature stating that the yield of parent radical cation formation seems to be anti-correlated with the IE of the ketones, the lowest IE analytes, presenting the highest probability for the charge transfer reaction (Smith et al., 2003).

Following the same approach as in the previous case, the E/N* region was set in order to provide the highest NO^+/NO_2^+ ratio. The *Figure 12* is presenting the influence of the E/N ratio variation in the RF mode over the analyte signal of interest. We notice that the NO^+ profile sharply increasing together with the NO^+/NO_2^+ ratio is joint by the adduct signal.

We plot as an example, the KnC5 adduct signal at m/z=177 (147+30) as a function of two fragments (m/z= 43 and 85) having potentially, as explained above, different formation pathways. A decrease of the fragmentation yield in favor of the adduct formation in the PTR

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reactor is observed over the 35 Td shoulder. The high sensitivity of the instrumental setup for the identification of ketonitrates is quantified in Table 2.

Due to the rising incidence of the NO^+ and NO_2^+ ions, simultaneously formed in the GD, the signals corresponding to the $M_{kn}\cdot NO^+$ and $M_{kn}\cdot NO_2^+$ adducts formation is equally strengthened (m/z=149 and 165 for the KnC3 - *Figure 13* and m/z=177 and 193 for the KnC5 – see S.I. Figure S5 respectively). All these characteristic signals are tailed by their corresponding isotopic abundance signals due mainly to ^{13}C isotope at m/z=121, 150, 166, 178 and 194 respectively.

The KnC3 spectrum was recorded at E/N* = 40Td as shown in *Figure 13*. We notice a low fragmentation pattern of the analyte with a major adduct signal contribution at m/z= 149. The existence of a secondary (water controlled) competitive process might be revealed by the existence of the minor protonated signal at m/z 120 backed by the characteristic fragment at m/z =75 as described by R5-7.

In an analog way, in *S.I. Figure S5,* the mass spectrum of KnC5 is plotted for the instrumental setup corresponding at the lowest fragmentation (E/N = 36 Td). We notice the distinct signal of the formed adduct (m/z =177) as well as, to a lower extent, the characteristic signals described above (m/z= 59, 85, 103) which are most likely formed following the mechanisms described in the previous paragraph, since the water is ubiquitously present in the system.

The best results related to the NO^+ ionization are related typically to the highest NO^+/NO_2^+ ratios in the RF mode as seen in Table 2. The NO^+ high affinity towards adduct formation is confirmed by the low DL achieved for these highly characteristic signals, 30 and 40 ppt min^{-1} for the adducts formed at m/z 149 and 177 respectively at an E/N* ratio < 45 Td.

3.5 PANs

The detection of PANs with PTR-MS has been tested by generating the peroxyacetyl nitrate (PAN) from the well-known NO_3-oxidation of acetaldehyde in the simulation chamber. The disadvantage of this procedure despite the 70% PAN formation yield (Doussin et al., 2003) is that it generates several bi-products (nitric acid, formaldehyde…) leading to more complex mass spectra. The PANs family analytes were all obtained by in-situ generation using the corresponding aldehydes. In order to overcome any judgment error, the present study will

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only illustrate the PAN mass spectra while for the other analogous formed PAN like products (P2MCrN and P3MCrN) we will only discuss about the mass spectra signals which are assigned to them.

3.5.1 The H_3O^+ ionization

The optimal conditions for the detection of PANs in H_3O^+ ionization mode were explored by varying the E/N ratios from 55 to 120 Td. The most promising results were obtained in the case of PAN around 85Td where the protonated signal of PAN was recorded as we can depict from Figure S6 in S.I.

In an analogous way with the reaction R1a, the protonated peroxy-nitrates are equally expected to form low energy gas phase ion-dipole complexes ($ROOH \cdot NO_2^+$) with bound energies of 92 kJ mol^{-1} in the case of methyl-peroxynitrate (Ravelo and Francisco, 2007). Previous studies (Hansel and Wisthaler, 2000) have proposed a speculative decomposition of the protonated PAN:

$$RC(O)OONO_2H^+ + H_2O \rightarrow RC(O)OOHH^+ + HNO_3 \qquad (R10)$$

The same mechanism is equally indicated by later studies (Aoki et al., 2007), giving the mass spectral signal at m/z = 77, as recorded in the case of the PAN (Figure S6). According to their statements the other protonated PANs parent compound generated in our study (C_4H_7-$C(O)OONO_2H^+$, m/z = 162) should lead to representative ionic signals of type C_4H_7-$C(O)OOHH^+$, m/z = 117, which are indeed present in the deconvoluted mass spectra of our analytes. Moreover, the fact that this signal is absent during the NO^+ ionization mode (characterized by inferior H_2O levels) may support this hypothetic decomposition of the PANs.

Another likely mechanism which, unexpectedly, may lead to the same analytical signal is reviewed by (Roberts, 1990) proposing the unimolecular decomposition of PANs to form the corresponding C_{n-1} alkyl nitrate. In our particular case the reaction may be written as:

$$C_5H_7\text{-}C(O)OONO_2 \rightarrow C_4H_7\text{-}ONO_2 + CO_2 \qquad (R11)$$

Assuming the presence of both processes, the resulting alkyl nitrate may interfere with the above mentioned m/z=117 signal in the case of a charge transfer reaction. More likely, in the case of a protonation process, the obtained m/z=118 signal derived from the alkyl nitrate will enhance the isobaric signal due to the ^{13}C isotopic abundance of the analyte obtained by PAN

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decomposition. The signal of m/z 118 seems indicative of the presence of a double peak which might confirm the occurrence of both processes. This fact is equally confirmed by the I_{118}/I_{117} measured ratio (0.19 - 0.23 for the P2MCrN and 0.52 - 0.57 for the P3MCrN) which is significantly different from the expected ^{13}C isotopic abundance for a $RC(O)OOHH^+$ type compound (0.06). This difference suggests the presence of this kind of analytical interference, more pronounced in the case of P3MCrN.

However the PAN decomposition path is considered to be several hundred times slower than the bond homolysis channel:

$$C_4H_7\text{-}C(O)OONO_2 \rightarrow C_4H_7\text{-}C(O)OO^{\cdot} + NO_2 \qquad (R12)$$

The recombination of $C_4H_7\text{-}C(O)OO^{\cdot}$ (m/z = 115) with highly abundant $H^+(H_2O)$ and $H^+(H_2O)_2$ could generate the signals at m/z 133 and 151 respectively. Additionally, the high levels of NO_2^+ (m/z = 46) may favor the presence of $NO_2^+ \cdot H_2O$ (m/z = 64) which can potentially quench the $C_4H_7\text{-}C(O)OO^{\cdot}$ radical to give an adduct signal at m/z = 179.

In order to certify the mono-nitrogen containing analytes for several ion signals in the spectrum, an analysis similar to the one performed by Inomata et al. (2013) which consists in subtraction of the isotopic effect of ^{13}C by calculating I_{even} / I_{odd} ratios of an ion signal at an even m/z [M] to the adjacent ion signal at an odd m/z [M+1].

As described by Table 2 the normalized sensitivity for the protonated PANs is weak spanning few counts ppb^{-1} min^{-1} for all three considered PANs.

3.5.2 The NO^+ ionization

Unlike the keto-nitrates, the PANs present a low sensibility towards detection in NO^+ ionization mode and generally a complex chemical equilibrium in classical PTR analysis.

In the NO^+ ionization mode, the signals corresponding to the adduct formation is barely noticed for the entire range of E/N considered. However the presence of weak signals at m/z = 191 and 207 for both P2MCrN and P3MCrN, are indicative of the presence of PAN NO^+ and PAN NO_2^+ adducts respectively.

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4 Conclusions

Organic nitrates play a key role in atmospheric chemistry as they act as reactive nitrogen reservoir species. The use of PTR-MS for the measurement of VOCs has expanded a lot in atmospheric research these last years but few studies have investigated the performances of this instrument for the detection of organic nitrates. These studies have shown that this technique exhibits poor performances (high fragmentation and poor sensitivity) when it is run in classical mode. In the present work, the detection of alkyl and multifunctional organic nitrates (PANs, ketonitrates, hydroxynitrates) by this technique has been studied by operating the instrument in the classical mode (H_3O^+ as ionizing species) but also by testing an ionization induced by NO^+. This study has shown that a soft ionization by NO^+ using low E/N ratios (<50 Td) promotes the R-NO^+ adduct formation and minimizes the fragmentation, favoring the identification of molecular composition. In addition, the versatility of the instrument allows an easy change of the chemical ionization source, from H_3O^+ to NO^+ by simply replacing water vapor by dry air in the glow discharge. This is very useful for a double identification of the organic nitrates. In terms of sensitivity, the NO^+ adduct ionization mode appears to be the most sensitive for the detection of hydroxy- and ketonitrates with detection limits in the range of tens ppt/min. This sensitivity is suitable for measurement of organic nitrates during lab studies but also in ambient air. The detection of alkyl nitrates and PANs with PTR-MS is less sensitive, with detection limits in the range of hundreds ppt/min, whatever the ionization source used. For these two classes of nitrates, accumulations over longer periods will be necessary for measurements in ambient air.

A crucial aspect to be taken into account in further studies for lab and field measurements deployment of the method will be the effect of the humidity of the sampled air. In addition, longer acquisition time, elimination of interfering ionization paths by selective ionization sources and softer ionization sources could improve the technique's performances.

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1 *Table 1 Summarized analytical approaches into the organic nitrate analysis*

Type of study	Analytes	DL / time or normalized sensitivity	Ionizing species	Experimental setup	Study
Synthesis	PAN	< 40 ppb	O_3+NO KOH / O_3+NO	CL NO_x IC KOH / CL NO_x	Winer et al. (1974) Grosjean and Harrison (1985)
Field campaign	PAN	10-80 ppt / 1 min	luminol	CL NO_2	Gaffney et al. (1999)
Synthesis	C_3-C_5 alkyl nitrates C_2-C_4 hydroxy nitrates C_2-C_4 dinitrates		e^- / luminol	GC-ECD –CL NO_2	Hao et al. (1994)
Laboratory / Field campaign	ΣAN, ΣPN	30-90 ppt	-	TD-LIF	Day et al. (2002)
Field campaign	ΣAN, ΣPN	30-90 ppt	-	TD-LIF	Perring et al. (2010)
Field campaign	C_3-C_5 alkyl nitrates	10 ppt	e^- e^-_{th}	GC-ECD GC-NICI-MS	Atlas (1988)
Field campaign	C_2-C_3 Alkyl nitrates PAN, PPN,	10 ppt	e^-	GC-ECD	Fukui and Doskey (1998)
Synthesis; **cis-2-butene+OH (NO)**	Alkyl nitrates α, β -hydroxynitrates, dinitrates	-	e^-	GC-ECD	Muthuramu et al. (1993)
Peroxyalkyl +NO_2	PAN, PPN, PiBN, MPAN, APAN, PnBN, PBzN	2 ppt	e^-	GC-ECD	Flocke et al. (2005)
Field campaign	C_4-C_{14} alkyl nitrates (C_2-C_8)-alkyl- and phenyl-alkyl-nitrates	1 ppt	e^-	GC-ECD GC-EI-MS	Luxenhofer and Ballschmiter (1994) Luxenhofer et al. (1994)

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Field campaign	C_6-C_{13} alkyl nitrates C_3-C_6 dinitrates C_2-C_6 hydroxynitrates		e^-	HPLC / GC-ECD GC-EI-MS	Fischer et al. (2000) Kastler and Ballschmiter (1999)
Field campaign	PAN, PPN, MPAN,	15 ppt / 10 min	e^- e^-_{th}	GC-ECD GC-NICI-MS	Tanimoto et al. (1999)
Synthesis; alcohols+N_2O_5	C_1-C_8 alkyl nitrates, ketonitrates, hydroxynitrates, dinitrates	-	e^- CH_5^+	GC-ECD GC-NO_y CI-MS	Kames et al. (1993)
NO_3 + α-pinene	Carbonyl hydroxi-nitrates or PANs	-	H^+ (MeOH)	APCI-MS	Perraud et al. (2010)
Peroxyacetyl +NO_2	PAN, PPN, MPAN	10 ppt /15s	I^-	TD-CIMS	Slusher et al. (2004) Huey (2007)
C_2-C_8 alkenes + OH (O_2, NO)	β -hydroxy-nitrates	19-50 counts/ppb	CF_3O^-	ToF CIMS MS-MS CIMS	Teng et al. (2014)
Field campaign	PAN, PPN, MPAN,	25 counts/ppb	O_2^+, H_3O^+, $(H_2O)_2H^+$ H_3O^+	SIFDT* PTRMS	Hansel and Wisthaler (2000)
Synthesis	C_1-C_5 alkyl nitrates	15† counts/ppb	H_3O^+	PTRMS	Aoki et al. (2007)
C_3-C_6 Cycloalkanecarbaldehydes	nitroperoxycarbonyl cycloalkyl nitrates	20† counts/ppb	H_3O^+ $H_3O^+(H_2O)_n$	PTRMS	D'Anna et al. (2005)

1 * Selected Ion Flow Drift Tube; † as specific alkyl (-R^+) fragment

2 PAN = peroxyacetyl nitrate; PPN =peroxypropionyl nitrate; PiBN = peroxyisobutyryl nitrate; MPAN = peroxymethacryloyl nitrate; APAN =
3 peroxyacryloyl nitrate; PnBN = peroxybutyryl nitrate; PBzN = peroxybenzoyl nitrate

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Table 2 Organic nitrates normalized sensitivity as a function of the ionization mode

Compound	MW (g mol^{-1})	H_3O^+ ionization			NO^+ ionization		
		Signal (m/z)	Sensitivity (ncpm) ppbv^{-1}	E/N (Td)	Signal (m/z)	Sensitivity (ncpm) ppbv^{-1}	E/N (Td)
AlkC3	*105*	*43*	35	70	*104*	1.1	34*
propyl nitrate		*59*	18.8		*135*	48.8	
		106	2				
Alk*i*C4	*119*	*57*	43.4	70	*118*	8.3	34*
isobutyl nitrate		*73*	23		*149*	78.9	
		120	2				
KnC3	*119*	*75*	45.4 – 88.4	73 – 75	*149*	320 - 331	45*
nitroxyacetone		*120*	119 – 144	73 – 75			
		137	127	48*			
KnC5	*147*	*103*	38.3	74	*177*	249 - 265	39*
3-nitroxy-3-methyl-2-butanone		*148*	8	74			
		165	538	48*			
PAN	*121*	*122*	7.7	90	*151*	weak	
1OH3C3	*121*	*104*	0.2	62	*120*	22.8	34*
1-hydroxy-3-nitroxy-propane		*120*	0.2		*151*	268	
		122	2		*167*	10.2	
		139	52.6				
		140	38				

* Without taking into account the RF contribution

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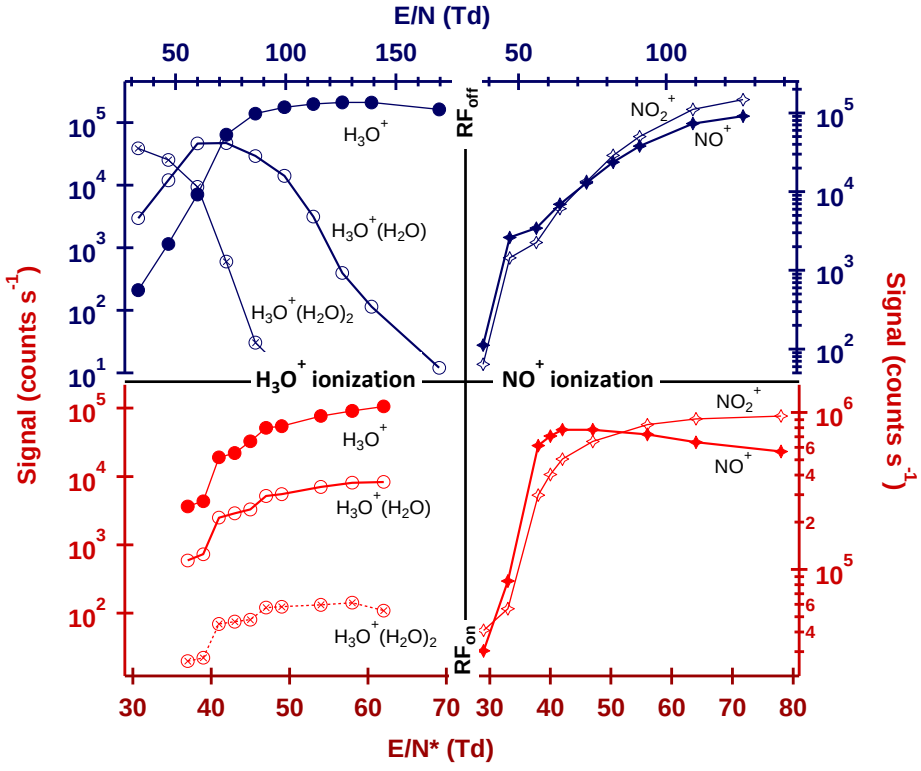

Figure 1. Typical ionizing species distribution as a function of the E/N ratio, in the two ionization modes with RF mode on and off. When the RF mode is on, E/N* ratio were calculated taking into account only the contribution of the dc electric field while the additional input of the ac electric field remains difficult to estimate.

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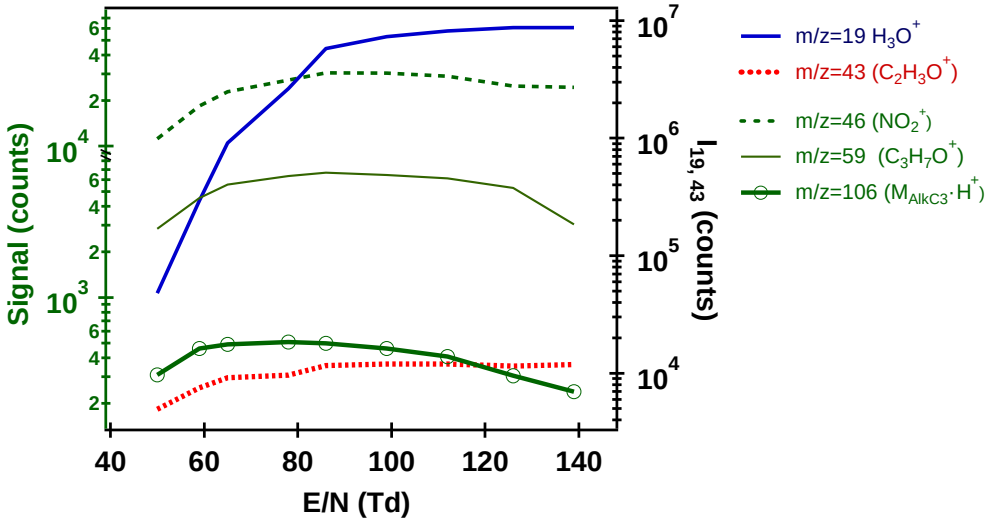

Figure 2. The E/N ratio influence over the AlkC3 identification for several representative signals as recorded in absence of a RF funnel (left axis). The H_3O^+ ion is equally illustrated in order to point the water cluster ions distribution influence, while the common signal at m/z=43 is a fragmentation mark (right axis).

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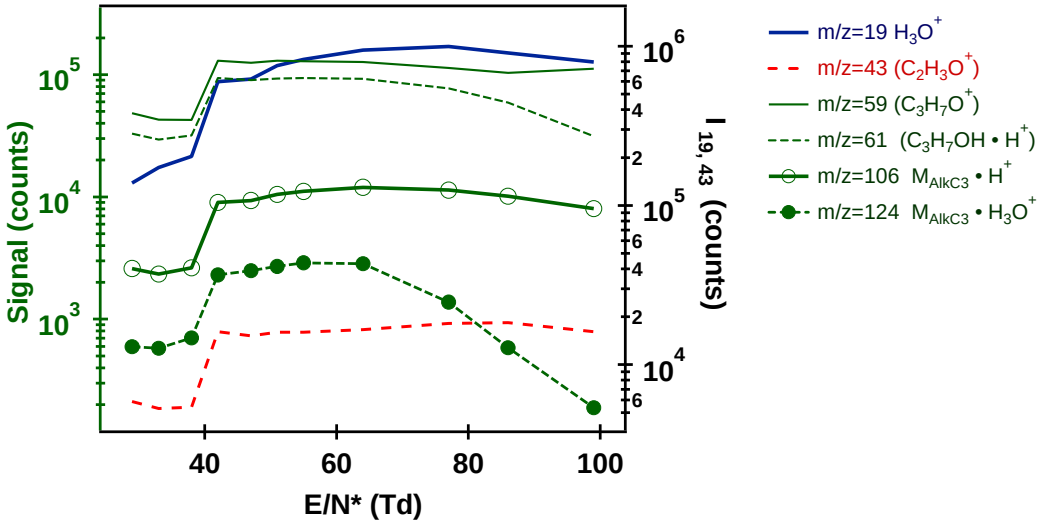

Figure 3. The E/N ratio influence over the AlkC3 identification for several representative signals as recorded with the RF mode (left axis). The H_3O^+ ion is equally illustrated in order to point the water cluster ions distribution influence, while the common signal at m/z=43 is a fragmentation mark (right axis).

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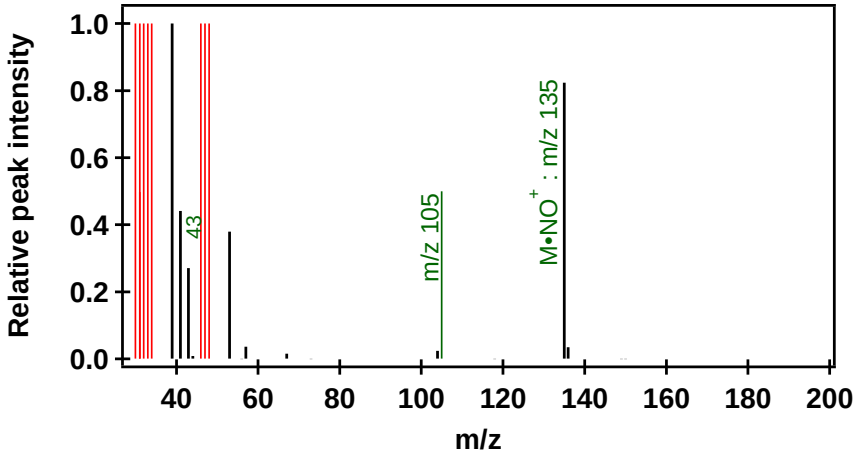

Figure 4. Recorded mass spectrum of AlkC3 (black bars) at the lowest extent of fragmentation (E/N* = 34 Td) in the NO^+ ionization mode. The green thin line represents the expected molecular ion of the analyte and the intense signals depicted by the red thin bars represent the ionizing analytes at m/z = 30 (NO^+) and 46 (NO_2^+) and their isotopic abundance signals at m/z = 31 and 47, 48 respectively.

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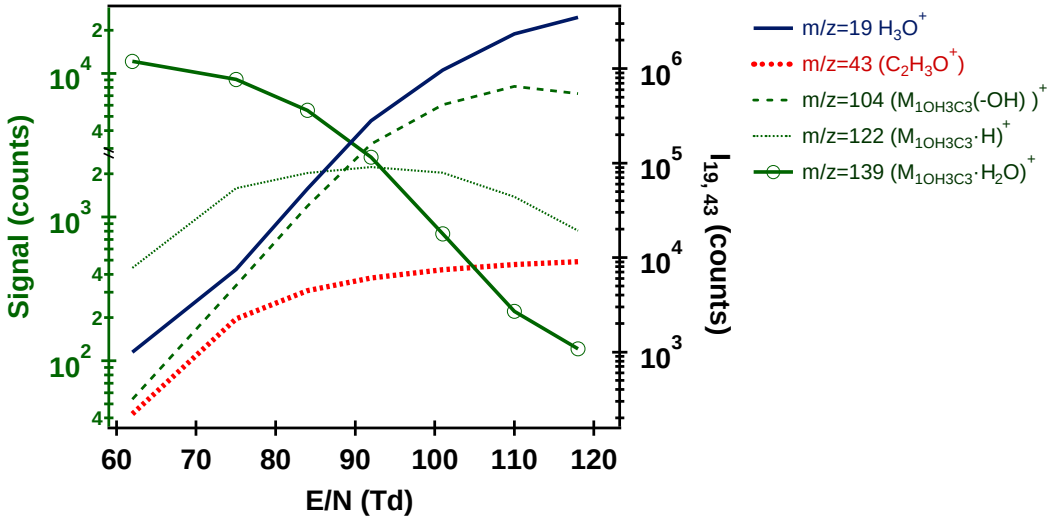

Figure 5. Typical signals due to the 1OH3C3 soft ionization and their behavior as a function of the E/N ratio variation (left axis) in absence of a RF mode. The fragmentation intensity depicted by the m/z=43 ion is illustrated together with the H_3O^+ ion onto the right axis.

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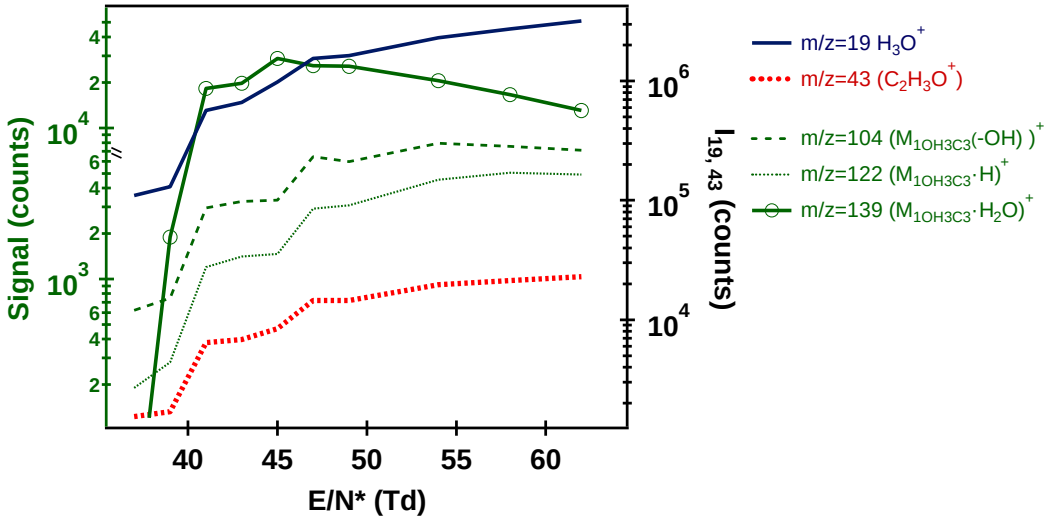

Figure 6. Typical signals due to the 1OH3C3 soft ionization and their behavior as a function of the E/N ratio variation (left axis) in the RF mode. The fragmentation intensity depicted by the m/z=43 ion is illustrated together with the H_3O^+ ion onto the right axis.

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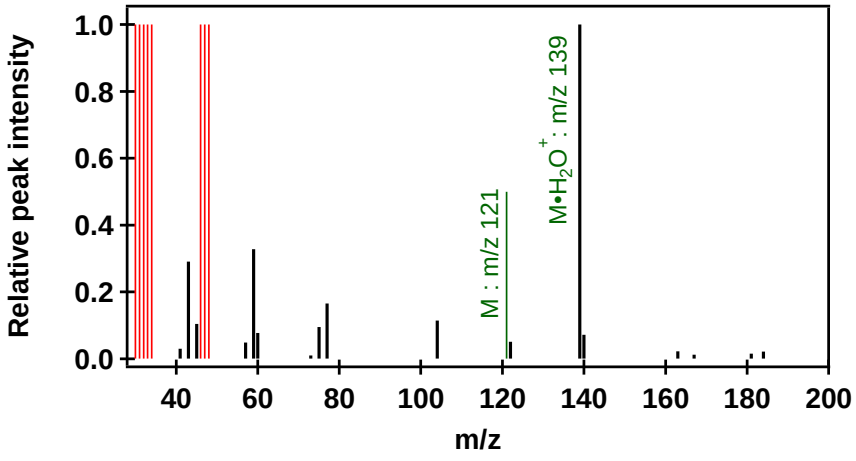

Figure 7. The recorded mass spectrum of 1OH3C3 (black bars) at the lowest extent of fragmentation (E/N* = 45 Td) in the H_3O^+ ionization mode under the influence of the RF mode.

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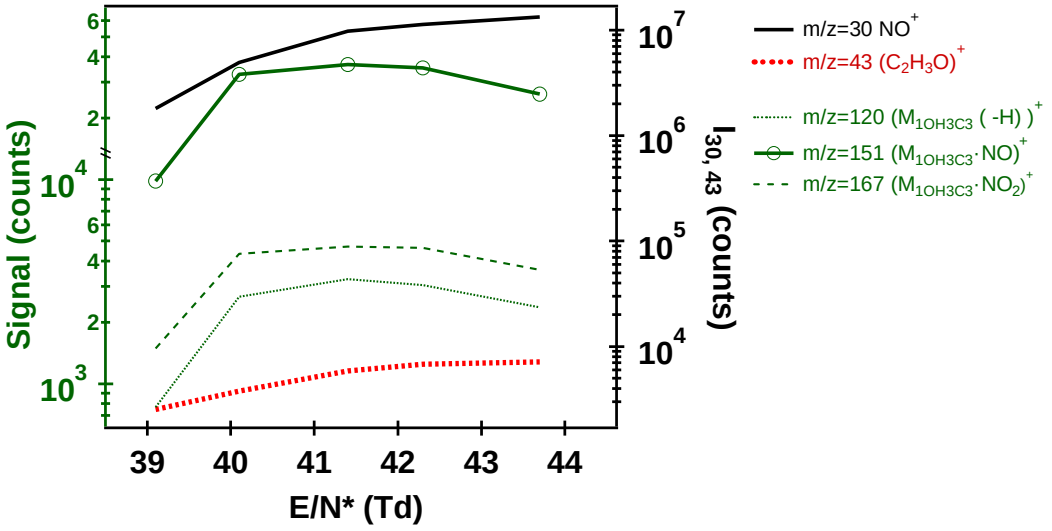

Figure 8. The E/N ratio and their influence over the 1OH3C3 ionization and identification pathways, for several characteristic signals.

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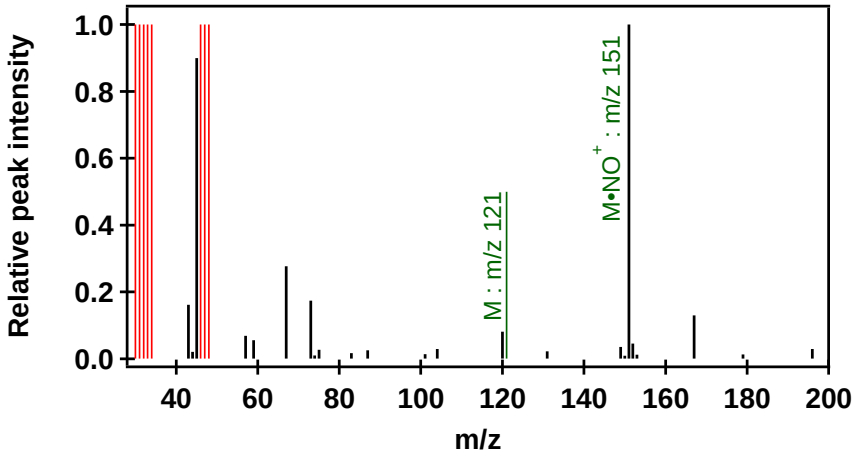

Figure 9. Recorded mass spectrum of 1OH3C3 (black bars) at the lowest extent of fragmentation (E/N* = 41 Td) in NO^+ ionization mode.

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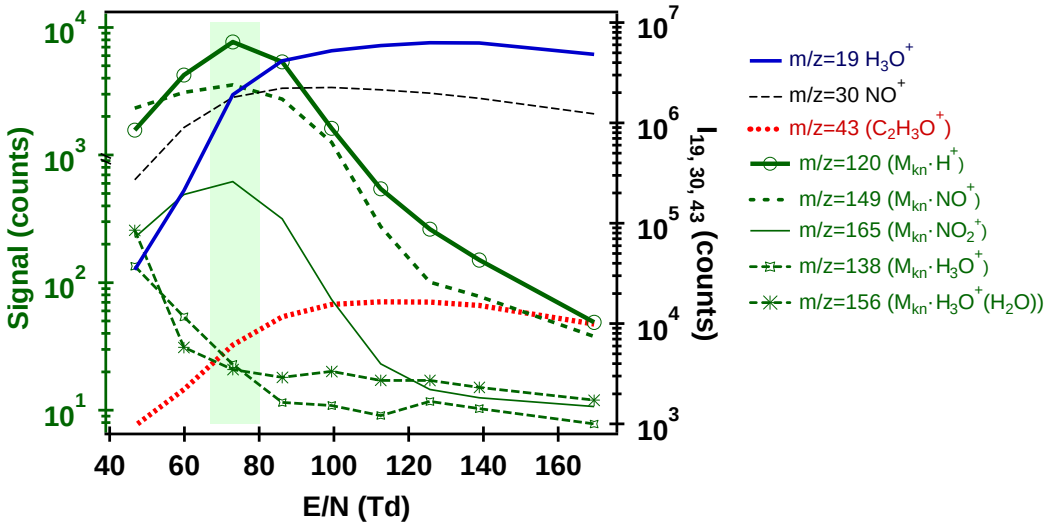

Figure 10. The KnC3 typical signals distribution over a wide range of E/N ratios (left axis), illustrating the water cluster ions distribution impact over the keto-nitrates identification. The fragmentation representative, m/z=43 signal, together with the H_3O^+ and NO^+ ionizing species are equally plotted onto the right axis.

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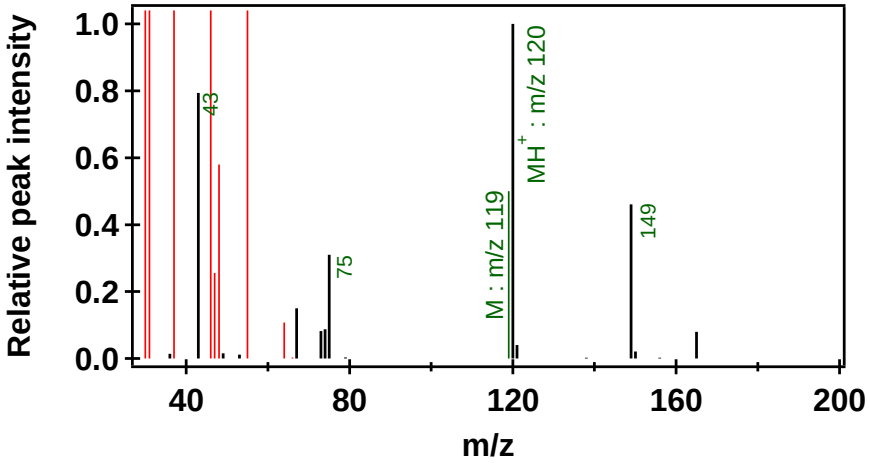

Figure 11. Recorded mass spectrum of protonated KnC3 (black bars) for E/N = 75 Td, corresponding to the highest sensibility for the protonated analyte signal detection (m/z 120).

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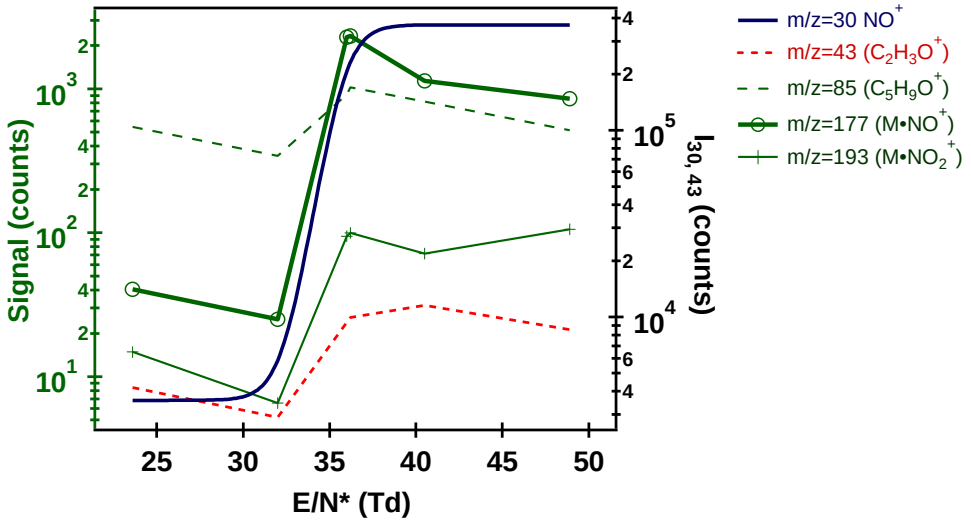

Figure 12. The RF mode behavior of typical NO^+ ionization signals of keto-nitrates (KnC5) under the E/N ratio influence (left axis). Typical distribution of the NO^+ ions and $C_2H_3O^+$ fragment into the given E/N interval (right axis).

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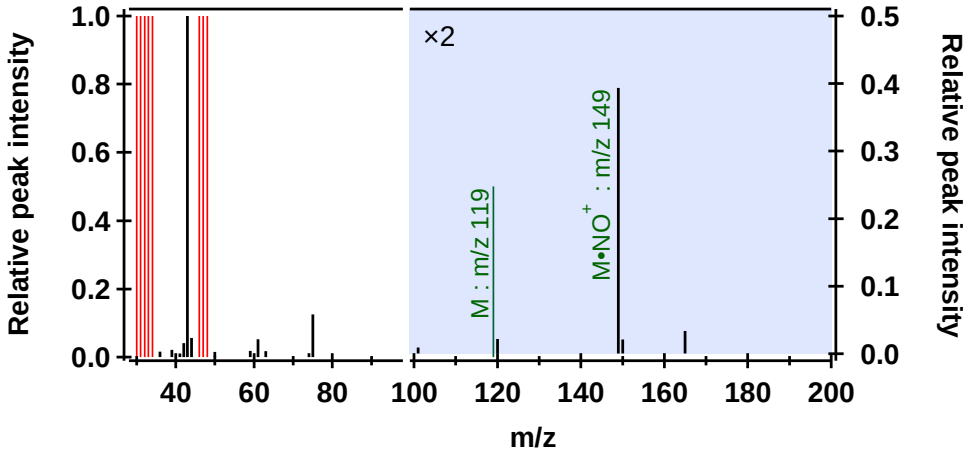

Figure 13. Recorded mass spectrum of KnC3 adduct (black bars) at the lowest extent of fragmentation (E/N* = 40 Td) in the NO^+ ionization mode.