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# Use of Rapid Reduced Electric Field Switching to Enhance Compound Specificity for Proton Transfer Reaction-Mass Spectrometry

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Key words: PTR-MS; explosives; reduced electric field; collisional induced dissociation

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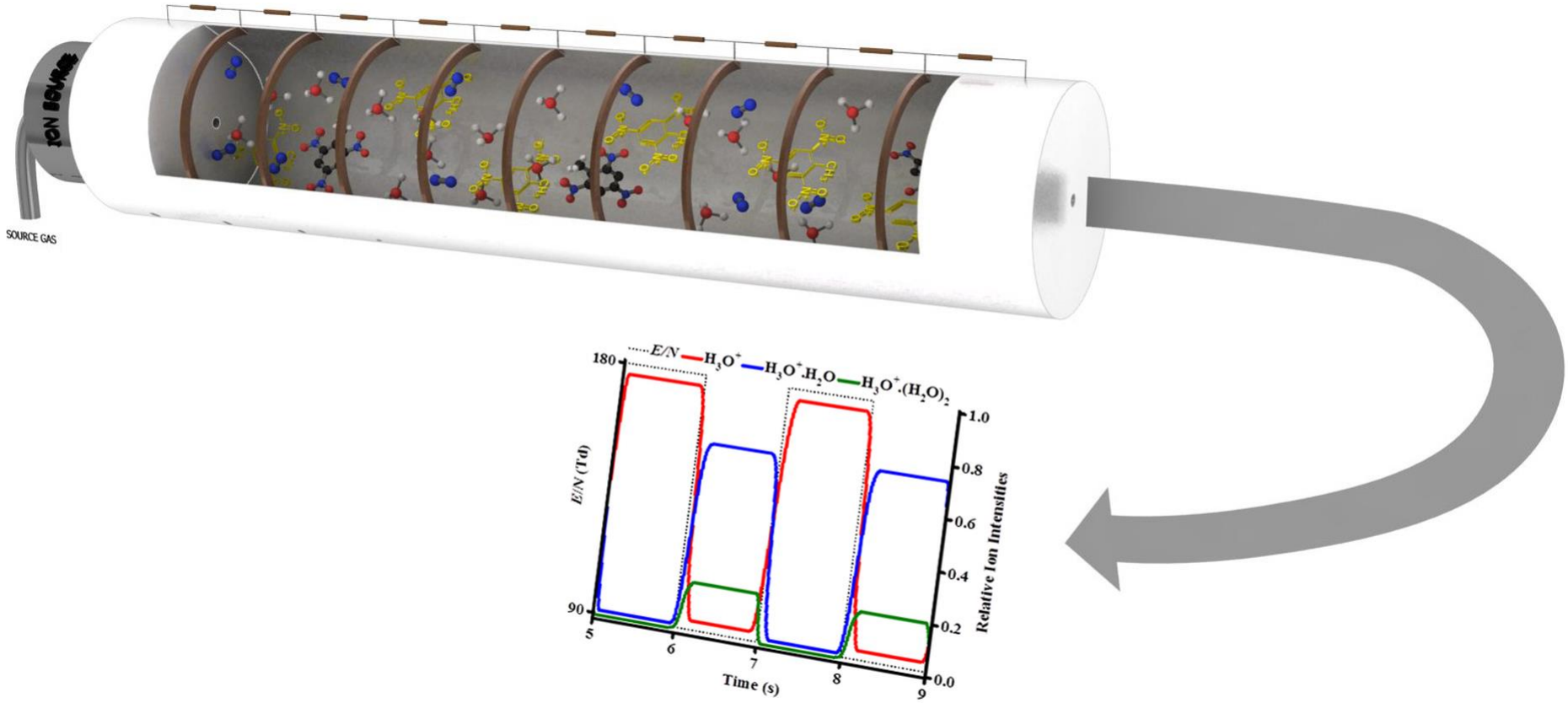
## Graphical abstract



**Abstract (250 words)**

The high sensitivity of Proton Transfer Reaction-Mass Spectrometry (PTR-MS) makes it a suitable analytical tool for detecting trace compounds. Its specificity is primarily determined by the accuracy of identifying the *m*/*z* of the product ions specific to a particular compound. However, specificity can be enhanced by changing the product ions (concentrations and types) through modifying the reduced electric field. For current PTR-MS systems this is not possible for trace compounds that would only be present in the reaction chamber of a PTR-MS for a short time (seconds). For such circumstances it is necessary to change the reduce electric field swiftly if specificity enhancements are to be achieved. In this paper we demonstrate such a novel approach, which permits any compound that may only be present in the drift tube for seconds to be thoroughly investigated. Specifically, we have developed hardware and software which permits the reaction region's voltages to be rapidly switched at a frequency of 0.1-5 Hz. We show how this technique can be used to provide a higher confidence in the identification of compounds than is possible by keeping to one reduced electric field value through illustrating the detection of explosives. Although demonstrated for homeland security applications, this new technique has applications in other analytical areas and disciplines where rapid changes in a compound's concentration can occur, e.g. in the Earth's atmosphere, plant emissions and in breath. Importantly, this adaptation provides a method for improved selectivity without expensive instrumental changes or the need for high mass resolution instruments.

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) is a broad-based technique that has proved its analytical use in many fields including atmospheric chemistry, food science, breath analysis and Homeland Security.[1] Within the Homeland Security area, PTR-MS is capable of detecting a wide range of dangerous substances, and a number of studies have been published dealing with chemical warfare agents, illicit drugs and explosives.[2-19] A key criterion for any analytical instrumentation is sensitivity. The high sensitivity of PTR-MS, which can now reach levels of parts per quadrillion by volume in seconds,[20] permits the relatively easy detection of many chemical compounds in trace amounts.

While high sensitivity is necessary for a range of applications, high selectivity is also required so that chemical compounds can be identified with a high level of confidence in real-time. Higher selectivity is particularly needed with increasing sensitivity because the number of possible interferents at detectable levels increases. High chemical specificity is of considerable importance to the military, to emergency responders and for applications in security areas such as airports, harbours and train stations, where false alarms can cause significant cost and disruption to the public.

Without a pre-separation stage (e.g. a Gas Chromatography (GC) stage), PTR-MS primarily relies on the value of *m/z* of the product ion(s) to identify a given chemical compound. This results in an uncertainty in identification. Fast GC systems are being developed for use with PTR-MS to reduce any ambiguity in assignment, but these still take away from a major advantage of PTR-MS, namely real-time measurements.

A possible way to improve selectivity without losing the real-time capability advantage of PTR-MS is to manipulate the ion chemistry occurring in the reaction chamber. Thus different product ions (or changes in their intensities) can be used to aid in compound identification. A number of methods to achieve this have been proposed and adopted. One method is to use different reagent ions, e.g. changing from $H_3O^+$ (proton transfer reactions) to $O_2^+$ (charge transfer) to produce different product ions.[13] This is achieved by switching the reagent gas from water to air. Given that the reactions of $O_2^+$ and $H_3O^+$ with a neutral compound results in different product ions, rather than switching reagent ions,[13-16] it may be more beneficial for improved selectivity to have both (or more) reagent ions injected into the reaction chamber simultaneously, as recently illustrated by Amador-Muñoz et al.[21]

A more recent proposition to improve selectivity is the use of a RF ion funnel system to enhance collisional induced dissociation (CID).[18,19] Changes in CID can also be achieved by changing the reduced electric field, which is the key operational parameter in PTR-MS, and is the ratio of the electric field $E$ in the drift tube to the total neutral number density $N$. By

changing the reduced electric field from a low value, for example 80 Td, to a high value, for example 180 Td (or vice-versa) differences in product ion distributions will occur. This can aid in the identification of the trace neutral responsible for those ions. This approach was used in the early investigations using PTR-MS,[22,23] where changes in the reduced electric field were used to distinguish isomeric compounds. More recent examples exploiting this technique can be found in the literature,[24-26] and this same approach was used by González-Méndez *et al.* to discriminate between nitro-glycerine (NG) and the isobaric compound 2,4,6-trinitrotoluene (TNT).[17] For that study the drift tube voltage was changed manually. However, for the switching of the reduced electric field to be analytically useful, the reduced electric field needs to be changed at a frequency whose reciprocal is comparable to the sample time of a compound in the drift tube. This is particularly the case for areas of application where the sample is present in the reaction chamber of a PTR-MS for short periods of time, e.g. a real-time breath sample (< 10 s) or for thermally desorbed materials such explosives (< 20 s).

The simplest way to provide a rapid change in *E/N* is to alter the *E* field by changing the voltage applied across the drift tube. In this paper we present details of a collaborative project involving Kore Technology Ltd. (Ely, UK), the Defence Science and Technology Laboratory and the University of Birmingham on new hardware and software modifications for such a purpose. We illustrate the application of this new development to a number of explosive, or explosive-related compounds, namely 2,4- and 2,6-dinitrotoluene (2,4- and 2,6-DNT, *m/z* 182.03, $C_7H_6N_2O_4$), hexamethylene triperoxide diamine (HMTD, *m/z* 208.07, $C_6H_{12}N_2O_6$), and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX, *m/z* 222.04, $C_3H_6N_6O_6$). These have been selected to show the application of the system for chemical compounds with different physical properties, such as vapour pressures, and chemical functional groups.

Finally, we comment that it may be even more beneficial for selectivity improvements to have the combined operation of a radio frequency ion-funnel PTR-MS and fast drift tube voltage switching. This is exemplified in this study for 2,4,6-trinitrotoluene (TNT, *m/z* 227.02, $C_7H_5N_3O_6$).

## Methods

**Experimental Details.** A Kore Technology Ltd. Proton Transfer Reaction-Time of Flight-Mass Spectrometry (PTR-ToF-MS) was used, details of which have been comprehensively described elsewhere.[27, 28] In brief, a needle valve is used to introduce water vapour from a container into a hollow cathode discharge source where, after ionisation via electron impact and subsequent ion-molecule processes, the terminal reagent ions are predominantly $H_3O^+$ (or

at low *E/N* < 80 Td protonated water clusters). These ions are transferred from the ion source into the reaction chamber, also referred to as the drift tube (DT), of the PTR-ToF-MS, where they encounter the analyte. $H_3O^+$ efficiently reacts with an analyte M through proton transfer providing M has a proton affinity greater than that of water ($PA(H_2O)$ = 691 kJ $mol^{-1}$). Proton transfer from the protonated water clusters will only occur if PA (M) is higher than that of the water clusters, which possess higher proton affinities than $H_2O$. For example, the proton affinity of the water dimer is 808 kJ $mol^{-1}$. If $PA(H_2O) < PA(M) < PA(H_2O)_2$, as is the case for many explosives, then as the concentration of $H_3O^+$ decreases at low *E/N* then the concentrations of the product ions must also decrease, but this is somewhat compensated by the increased reaction time. In this study, only HMTD has a proton affinity greater than that of water clusters.

Proton transfer can be non-dissociative (resulting in the protonated parent molecule $MH^+$) and/or dissociative. Dissociative proton transfer results in product ions which, depending on their *m/z* values, may be useful for the identification of a compound. Fragmentation may be spontaneous upon proton transfer or may require additional energy which is supplied through numerous collisions with the buffer gas during the migration of the product ions down the drift tube under the influence of the electric field, *E*.

The instrument's DT used in this study also incorporates a radio-frequency ion funnel (RFIF).[18, 29] In brief the RFIF consists of 29 stainless steel plates of 0.2 mm thickness, mounted on precision-machined ceramic rods at an even spacing of 3.2 mm per plate. Tabs on the electrodes permit a resistor chain on a ceramic strip to be connected in addition to two capacitor stacks which allow the RF to be applied to the second half of the reactor. The orifice diameters of the plates through the first half of the stack is 40 mm, as used in the standard drift tube reactor. In the second half of the DT the orifice diameter steadily decreases to 6 mm at the final plate before the exit aperture. Across the complete ion-funnel a DC voltage is applied driving ions axially. When just operating with only this voltage we shall refer to the instrument as operating in DC-only mode. To the second part of the drift tube a RF field can applied. The resonant frequency used is ~760 kHz and the voltage amplitude (peak-to-peak) is 200 V. The RF field is superimposed on the DC voltage gradient across the complete drift tube. We shall refer to operating the instrument with the RF on as RF-mode, and its use in this paper is exemplified for TNT only.

At the end of the drift tube there is an exit plate which has at its centre a 400 µm aperture, through which a proportion of the reagent and product ions enter the ion transfer lens

section and then, after appropriate lensing, onwards to the pulser section, from which ions are pulsed into to the time-of-flight mass spectrometer for detection.

**Fast Reduced Electric Field Switching.** New electronics were developed by Kore Technology Ltd. for the purpose of providing fast reduced electric field switching that can be retrofitted into any Kore PTR-ToF-MS. The fast reduced electric field switching is accomplished by software control of a programmable +500 volt power supply unit (PSU). This can be controlled over the range 50 to 450 volts (covering typically the *E/N* range of between approximately 10 and 250 Td). It is possible to switch the output voltage according to the two required *E/N* values. This is achieved using a digital-to-analogue converter that allows a new software interface to set the two voltage values between which the power supply will switch. In addition to the voltage control, the software also provides the facility to alter the frequency of switching between two voltages. The data are saved as two separate, cumulative spectra from the two *E*/*N* states.

The circuitry for the switching has been added to an existing set of electronics that was not designed for switching. Oscilloscope traces of the power supply output (only) show asymmetry in the rise and fall times of the voltage. This is due to built-in diode circuitry on the output of the power supply. If we define the period between a stable low voltage and a stable high voltage after switching as the rise and fall times, we observe times of ~ 10 ms and ~ 25 ms, respectively. When the power supply is connected to the reactor, thus adding resistors and capacitors to the output, by the same criterion we observe greater time differences in the rise and fall times of the product ions (see section 3.1 for details). Analytically what is important is that data are acquired when the product ion signal is constant in the two phases. This is accomplished by means of using purposely written software that censors the data between voltage changes.

**Operational parameters.** Explosives measurements were obtained through the use of PTFE swabs (ThermoFisher Scientific) doped with known quantities of explosives and placed into a Kore Technology Ltd. thermal desorption unit (TDU), which was connected to the inlet of the PTR-ToF-MS. Details of the TDU have been given elsewhere.[17] The swabs came prepared from the manufacturer mounted on rectangular cardboard for easy insertion into the TDU. Once a seal was created, a carrier gas (in this study laboratory air) was heated to the temperature of the TDU before it flows through a series of holes in a heated metal plate. This heated air then passed through the swab and into the inlet system driving any desorbed material through to the drift tube creating a concentration “pulse” of typically between 10 – 20 seconds of an explosive in the drift tube.[17]

Passivated (SilcoNert®) stainless steel inlet lines were used in order to minimise adsorption effects. All measurements were taken under the same operational conditions. The TDU, inlet tubing and drift tube were maintained at 150 ºC. The drift tube pressure was set at 1.1 mbar. The only variable was the operating drift tube voltage, which was changed to provide the appropriate reduced electric fields to yield the product ion(s) of interest for each explosive investigated.

For the fast switching experiments, the acquisition time per point was set to 40 ms. Such short acquisition times imply that ion counts fluctuations will be at the level of 15 to 20% due to ion count statistics. However, in real operation it is not necessary to present a signal that has not been processed. It is better to show for each individual cycle average ion signals outside of the circuit's time constants (i.e. after the rise and before the fall time), and that is what is presented in this paper, other than for one data set to illustrate the typical level of fluctuation observed in the signal intensities for 40 ms acquisition times over a cycle (see section 3.1).

**Explosive Compounds.** Explosive standards were purchased from AccuStandard Inc., New Haven, CT. and diluted in the appropriate solvent(s) (HPLC grade) to provide the required quantity. Typically, the measurements were undertaken with between 1 and 50 ng of explosives deposited on the swabs prior to their insertion into the TDU to give an idea of realistic measurements.

**Density Functional Theory Calculations.** Density Functional Theory (DFT) calculations have been undertaken to determine the proton affinities and gas-phase basicities for the reactions of HMTD and RDX. These were obtained using the Gaussian09W program with the GaussView05 interface,[30] and the B3LYP functional with 6-31+G(d,p) basis set.

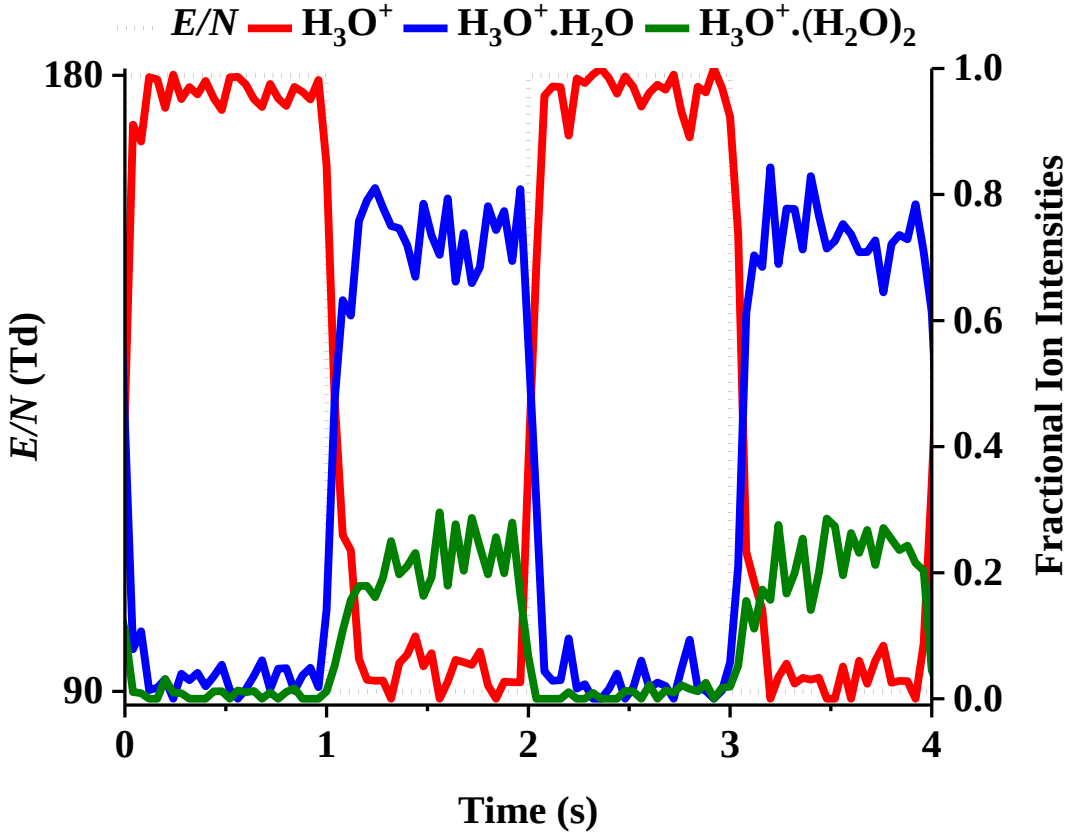
## Results and Discussion

**Reagent Ions.** Before conducting any switching experiments with samples, it was important to characterise the time constants associated with the rapid change of voltages applied to the drift tube. To investigate this, we examined the temporal profile of the protonated water $H_3O^+$ (*m/z* 19.02) and the dimer and trimer protonated water clusters, $H_3O^+.H_2O$ (*m/z* 37.03) and $H_3O^+.(H_2O)_2$ (*m/z* 55.04), respectively. These were chosen because their individual concentrations in the drift tube are very sensitive to the *E/N* value used. For example, at 90 Td protonated water clusters are the dominant reagent ions, whereas at 180 Td these have negligible intensities because the collisions occurring in the drift tube are sufficient to break-up protonated water clusters to the $H_3O^+$ monomer. It should however be appreciated that the relative intensities of the reagent ions recorded are those measured at the detector. The actual

distribution of reagent ions in the drift tube may be different owing to possible break-up of the protonated water clusters in the transfer optics from the DT to the mass spectrometer and as a result of the dependence of the transmission of the ions on *m/z*.

Figure 1 shows measurements of the fractional reagent ion signals (total ion signal adds up to 1) for $H_3O^+$, $H_3O^+.H_2O$ and $H_3O^+.(H_2O)_2$ for 180 Td and 90 Td switching at a frequency of approximately 1 Hz, starting with 180 Td at t = 0s. Figure 1(a) shows the raw data obtained from the instrument to illustrate the noise associated with 40 ms data acquisition and (b) the processed averaged data over the part of the cycle for which the ion signals have reached stability. The measured transition time when switching from a low to a high *E* value to result in 95% of the maximum ion signal was measured to be 60 ms. For changing from high to low *E* values the transition time was measured as 140 ms to reach within 5% of the stable lowest ion signal for that *E*/*N* phase. In practice this limits the switching frequency to less than 5 Hz. However, we will demonstrate that that is more than adequate for applications to explosive detection, and hence to applications where the concentration of an analyte is changing over the time period of seconds.

(a)



(b)

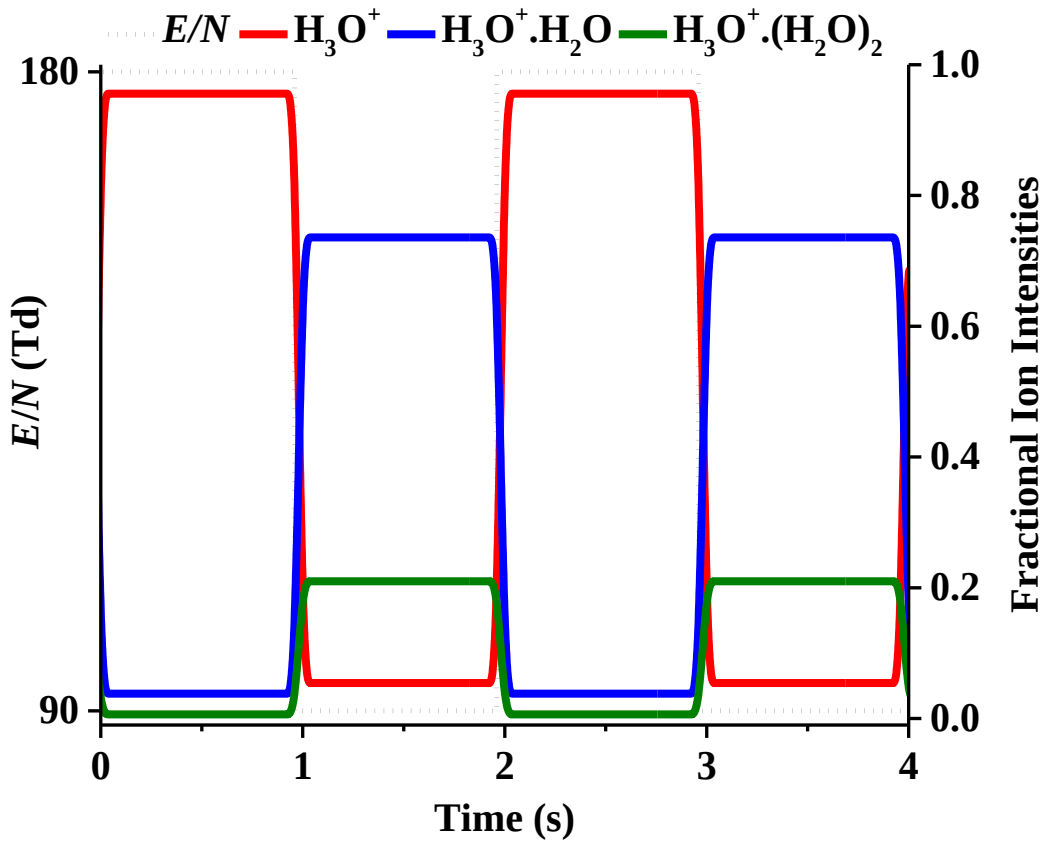



**Figure 1.** Changes in the fractional ion intensities of protonated water and protonated water clusters as *E/N* is switched between 180 Td and 80 Td at a frequency of 1 Hz showing (a) raw data and (b) averaged ion intensities.

**Examples of Improved Selectivity: Explosive compounds**

**Product ion distributions as a function of the reduced electric field.** For any given explosive, it is first necessary to ascertain the dependence of the product ion intensities as a function of *E*/*N*, and hence determine which two *E*/*N* values should be used to enhance selectivity. The dependences of the product ion distributions (PIDs) on *E*/*N* are required. Therefore, in the following, not only are the characteristics of the switching reported, but also details on the PIDs for 2,4-DNT, 2,6-DNT, HMTD, and RDX. However, it is important to appreciate that the PIDs we have determined for different reduced electric fields are specific to the KORE PTR-ToF-MS instrument and the operational conditions we have used. Owing to *m/z* dependence transmission of ions from a drift tube at a specific *E*/*N* to the transfer optics and then through the mass spectrometer, differences in operational conditions (i.e. pressure and

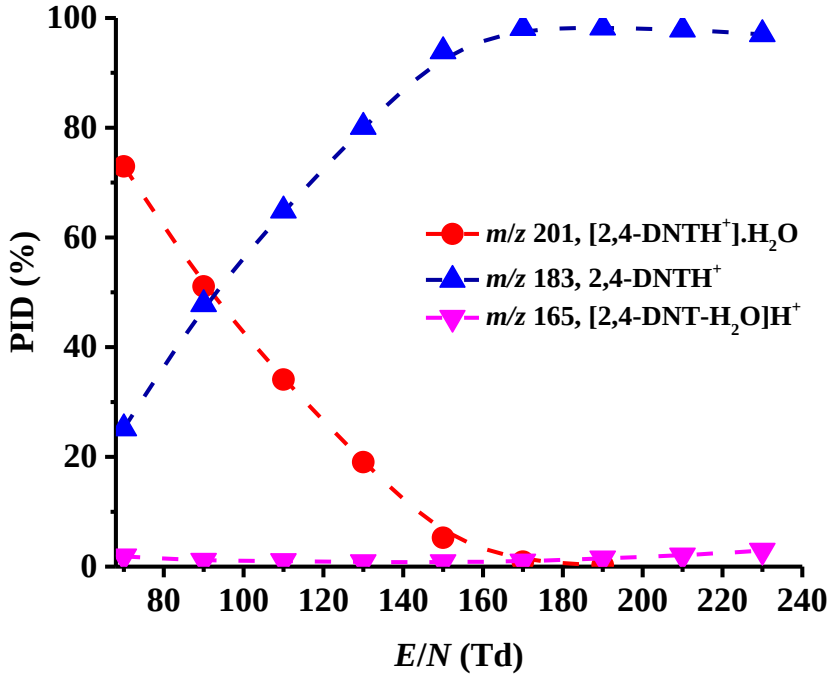
temperature), potential surface effects (e.g. stability of compounds e.g. reactions on metal surfaces or decomposition) and the rate of heating used for the thermal decomposition, different PIDs will result from the use of different conditions and instruments. Hence for a PTR-MS instrument to be of analytical use, the PIDs will need be determined for a given instrument under the set of conditions being used. The PIDs obtained and reported from PTR-MS studies should therefore include as much detail as possible, including information on any allowances used for transmission dependencies etc. For use in determining the probability of a given reaction pathway full details on *m/z* dependent transmission and detection sensitivity, thermal or reactive decomposition of the parent molecule, and effects of differences in operational conditions are required.

In the following the explosives' product ion distributions as a function of *E*/*N* have been obtained from the average of three background subtracted scans for each *E*/.

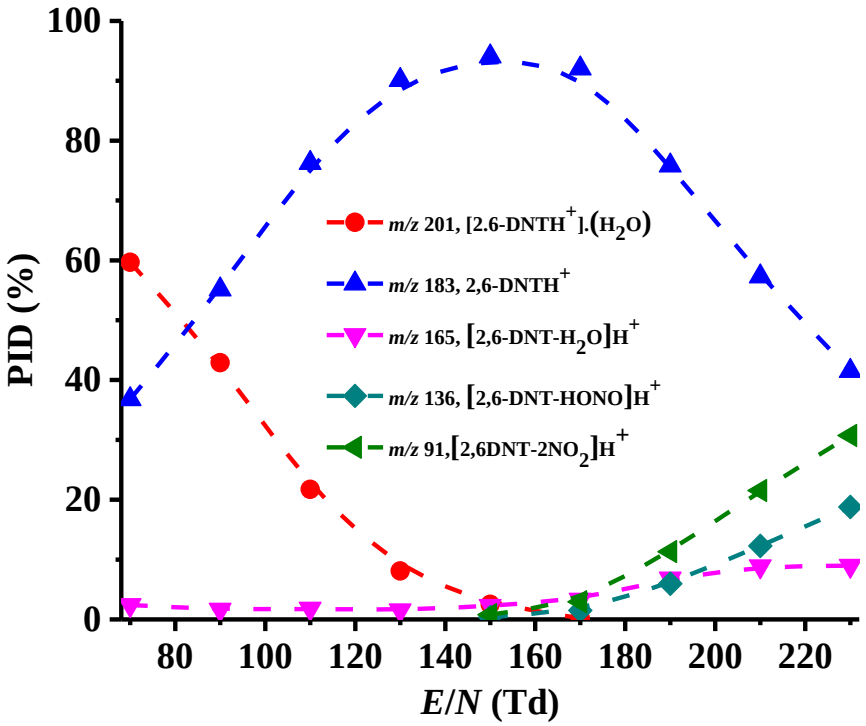
**2,4- and 2-6 dinitrotoluene ($C_7H_6N_2O_4$).** Figure 2 shows the PID plot as a function of *E*/*N* (70 - 230 Td) for (a) 2,4-DNT and (b) 2,6-DNT. (The product ion branching ratios for 2,6-DNT have already been published in another paper by us dealing with the applications of a radio frequency field in the drift tube.[18] However, for ease of comparison with the 2,4-DNT isomer the results are reproduced in this paper. The only difference is that the second water cluster ($2.6\text{-}DNTH^+.(H_2O)_2$) is not shown in figure 2(b), because its intensity is insignificant.)

From figures 2(a) and (b) it can be seen that monitoring product ions at *m/z* 183.04 (the protonated parent) and 201.05 ($DNTH^+.H_2O$) is sufficient for assigning 2,4-DNT, but that the presence of *m/z* 136.04 (elimination of HONO from the protonated parent) and *m/z* 91.06 (elimination of two nitro groups) observed at the high *E/N* setting indicates the presence of 2,6-DNT. Another common ion detected for both isomers at high reduced electric field values is at *m/z* 165.05, which results from the elimination of $H_2O$ from the protonated parent. Given that this is observed for both isomers, it cannot be used to differentiate the isomers.[18] A summary of results from the fast switching experiment for 2,4-DNT and 2,6-DNT are shown in figure 3, which show how the two isomers can be readily distinguished.

297 (a)

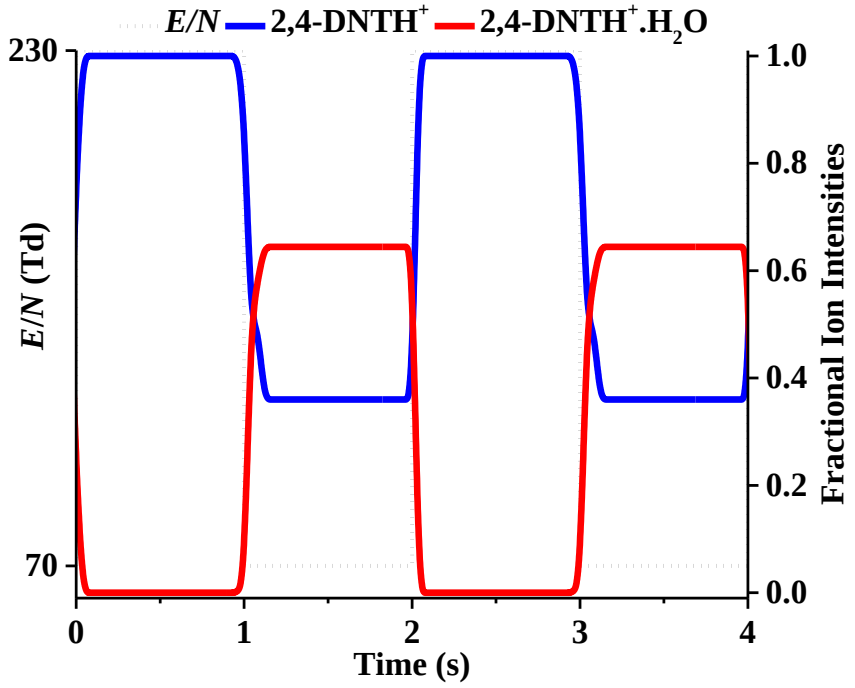



(b)




298 **Figure 2.** (a) Percentage product ion distribution (PID) results for (a) 2,4-DNT and (b) 2,6-
299 DNT as a function of reduced electric field (70 to 230 Td).

(a)




(b)

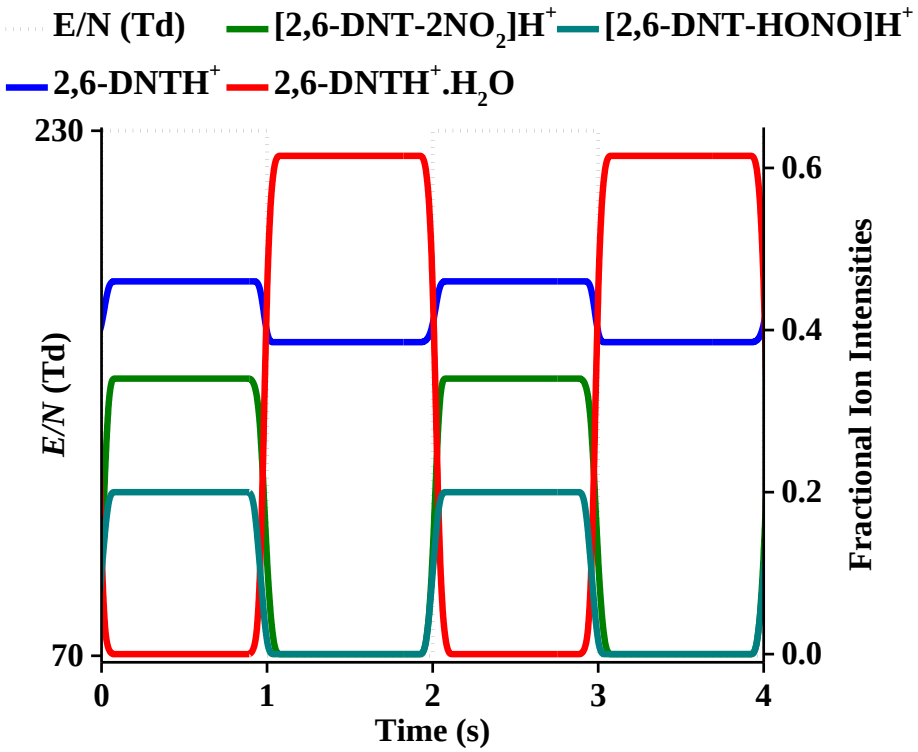
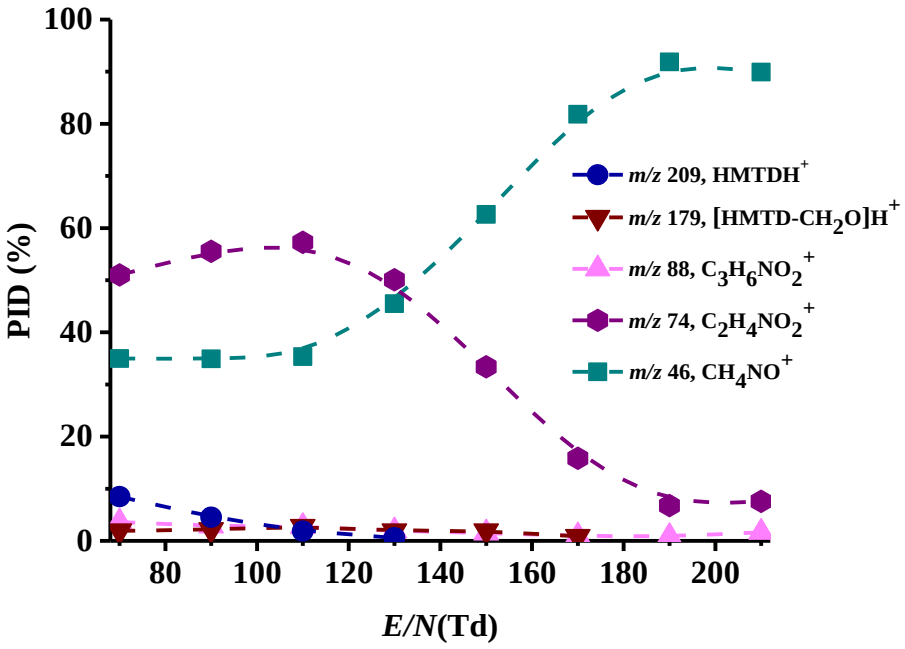



**Figure 3.** Changes in the fractional ion intensities averaged over each cycle using 1 Hz *E/N* switching between 70 Td and 230 Td for (a) 2,4-DNT and (b) 2,6-DNT. The product ions at *m/z* 91.06 and *m/z* 136.04 are distinctive of 2,6-DNT.

**HMTD ($C_6H_{12}N_2O_6$).** For HMTD five product ions are observed at *m/z* 46.03, 74.02, 88.04, 179.07 and 209.08. The product ions at *m/z* 88.04 and *m/z* 179.07 have negligible intensities at all *E/N* values, and are therefore not considered further. *m/z* 209.08 is the protonated parent, but only has a reasonable intensity at low *E/N* (< 90 Td). DFT calculations give 877 kJ $mol^{-1}$ and 844 kJ $mol^{-1}$ as the proton affinity and gas-phase basicity, respectively, for HMTD. Thus proton transfer from not only protonated water but also from the protonated water clusters is exoergic. Given the high proton affinity of HMTD, the reaction of $H_3O^+$ would most probably be dissociative, and the protonated parent is almost certainly a result of a reaction with $H_3O^+.(H_2O)_n$. The product ion at *m/z* 179.07 corresponds to the loss of formaldehyde ($CH_2O$) from the protonated parent, leaving $C_5H_{10}N_2O_5H^+$. *m/z* 88.04 corresponds to $C_3H_6NO_2^+$ and *m/z* 74.02 to $C_2H_4NO_2^+$. By taking advantage of the high mass resolution associated with KORE PTR-ToF-MS, we can rule out that the ion at *m/z* 46.03 as being $NO_2^+$, because the peak position of that ion is at *m/z* 45.99. $CH_4NO^+$ agrees with *m/z* 46.03. Given the significant rearrangement and eliminations required to produce this ion, and the fact that it has a high branching percentage even at low *E*/*N* (see figure 4(a)), it is possible that $CH_4NO^+$ does not directly result from dissociative proton transfer to HMTD. It is probable that this ion is a consequence of the reaction of $H_3O^+$ with a neutral product resulting from the thermal decomposition of HMTD in the system. Decomposition of HMTD could have resulted in the formation of other neutrals that then react with the reagent ions. However, initial temperature dependent measurements have not shown any dependence on the product ion distributions. The mechanism for the production of the product ions needs further exploration, but that is not the aim of this paper. Independent of the source of the product ions under the operation conditions we have used, and especially for *m/z* 46.03, they are still specific to HMTD and hence we can use them to specify the presence of HMTD. Figure 4 (a) shows the PID obtained for HMTD as a function of the reduced electric field (70 - 210 Td). Under the experimental conditions used the product ions that dominate are at *m/z* 46.03 and *m/z* 74.02. However, the presence of the protonated parent observed at low *E/N* is a useful ion for identification although it is observed with a low branching percentage. Thus we have selected the product ions at *m/z* 46.03, 74.02 and 209.08 for use in identifying HMTD with a high specificity under our operational conditions. The switching results using these three product ions are shown in figure 4(b).

(a)




(b)

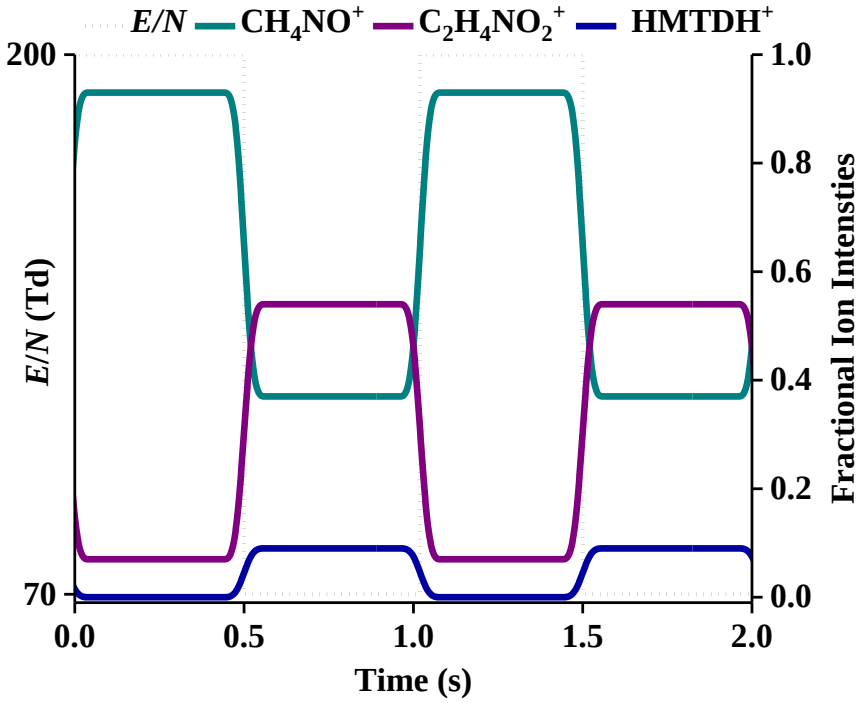
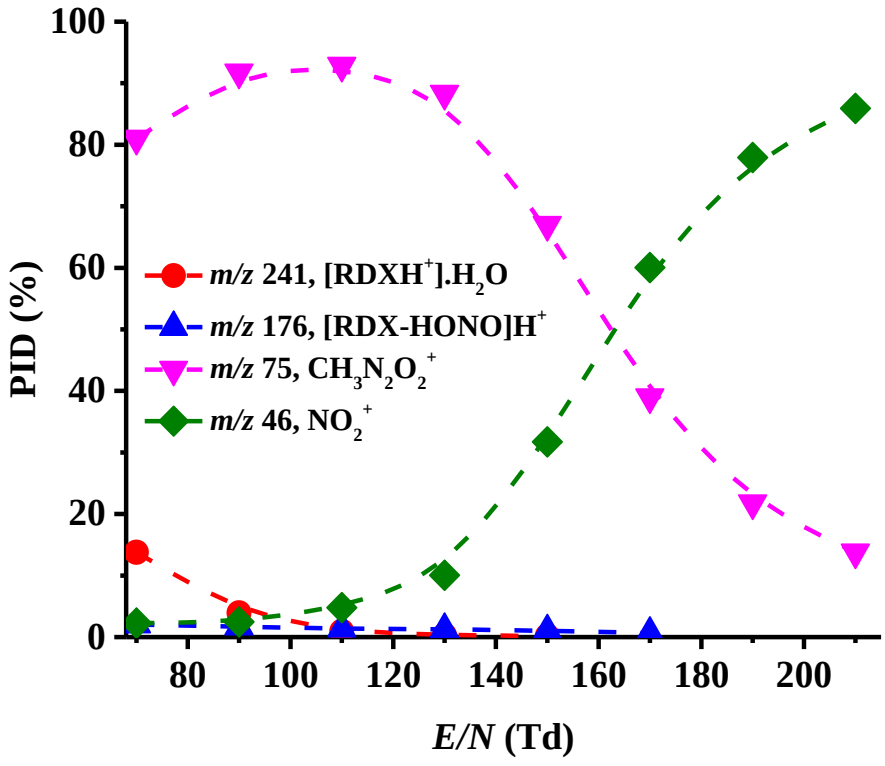



**Figure 4.** (a) PID for HMTD as a function of reduced electric field covering the range 70-210 Td and (b) changes in the fractional ion intensities averaged over each cycle for a reduced electric field switching 2 Hz. (2 Hz is presented here to illustrate the operation of the system as a different frequency.)

**RDX ($C_3H_6N_6O_6$)**. Major product ions are observed are at *m/z* 45.99 ($NO_2^+$) and *m/z* 75.02 ($CH_3N_2O_2^+$). *m/z* 75.02 dominates for *E/N* < 160 Td, whereas *m/z* 45.99 dominates at for *E/N* > 160 Td. Another product ion is also observed at *m/z* 176.04 ([RDX-HONO]$H^+$) throughout the *E/N* range investigated, but it only appears at a low intensity compared to the other two primary product ions. At the lowest *E/N* an ion is observed at *m/z* 241.05. This is assigned to be $RDXH^+.H_2O$. Given the observation of this, it is surprising that no protonated monomer is detected. We propose that as the reduced electric field is increased to the stage where no water clustering occurs the protonated parent has too much internal energy for it to survive before detection. DFT calculations give the PA and GB of RDX to be 764 kJ $mol^{-1}$ and 734 kJ $mol^{-1}$, respectively, and therefore only $H_3O^+$ can efficiently react with RDX via proton transfer. Figure 5 (a) shows the PID for RDX as a function of *E/N* (70 – 210 Td) under the operational conditions we have used. A separate study is being undertaken to investigate temperature effects on the PID. For our operating temperatures, the PID shows that product ions at *m/z* 45.99, 75.02 and 241.05 are sufficient to identify the presence of RDX with a high level of confidence. Figure 5(b) shows the reduced electric field switching results for 70 Td and 170 Td.

(a)



(b)

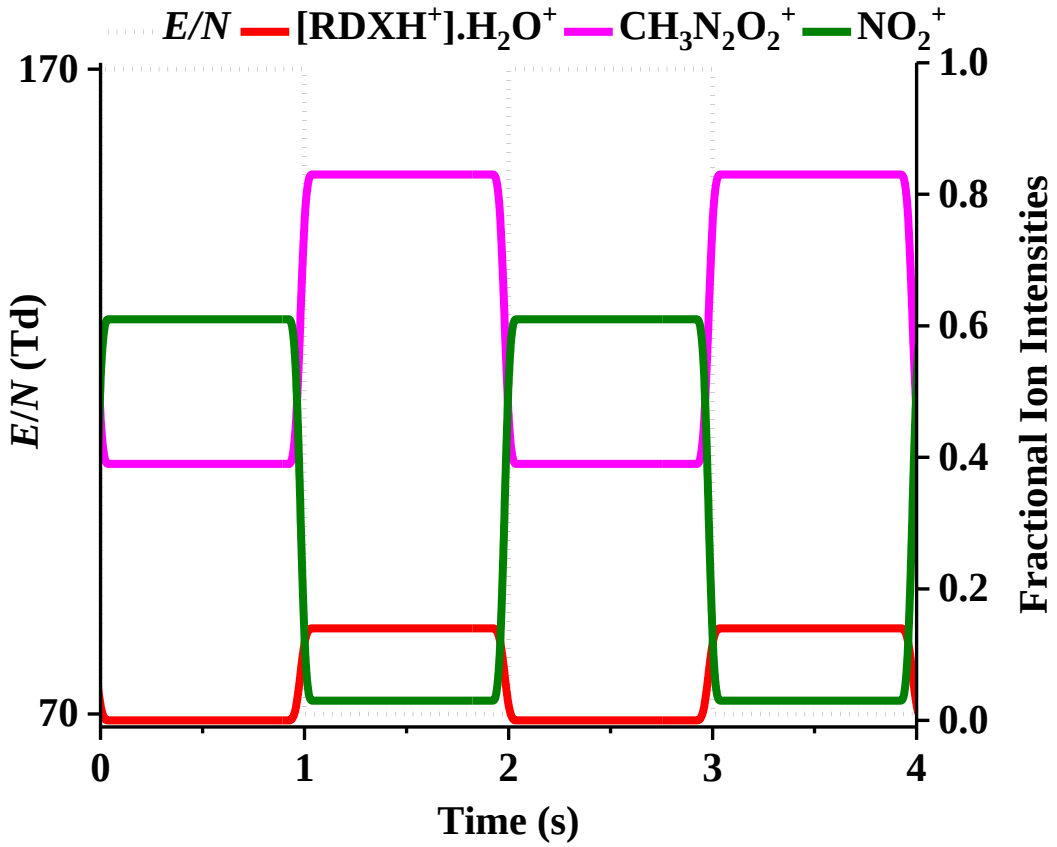



**Figure 5.** (a) PID for RDX as a function of reduced electric field covering the range 70-210 Td and (b) results for the reduced electric field switching at 1 Hz.

**Radio Frequency Ion Funnel and Drift Tube Voltage Switching: an Application to TNT.** Recently, we demonstrated how a radio frequency ion funnel-drift tube (RFIF-DT) can be employed in a novel way to modify the product ions resulting from the reaction of $H_3O^+$ with TNT through changes in collisional induced dissociation.[18] In DC-only mode, and for all *E*/*N* values investigated, the reaction of $H_3O^+$ with TNT leads to only one product ion, namely protonated TNT at *m*/*z* 228.03.[8] However, in RF-mode, another fragment ion is observed at *m*/*z* 210.02, corresponding to the elimination of water from the protonated parent,[18] with the intensity of this product ion increasing relative to the protonated parent with decreasing drift tube voltage (i.e. decreasing *E*/*N* in DC mode). In that work we proposed that the dominance of *m*/*z* 210.02 at low drift tube voltages is a result of the protonated TNT spending a longer time in the RF region of the drift tube. Through numerous collisional processes this allows it to gain sufficient internal energy until it reaches a level that leads to the elimination of $H_2O$. In this study we illustrate how improvements in selectivity can be achieved by combining RF-

mode with fast drift tube voltage switching for TNT (figure 6). We therefore propose that by combining the RFIF and drift tube voltage switching techniques an even higher confidence in the assignment of an analyte in a complex chemical environment may occur than is possible in DC-only mode.

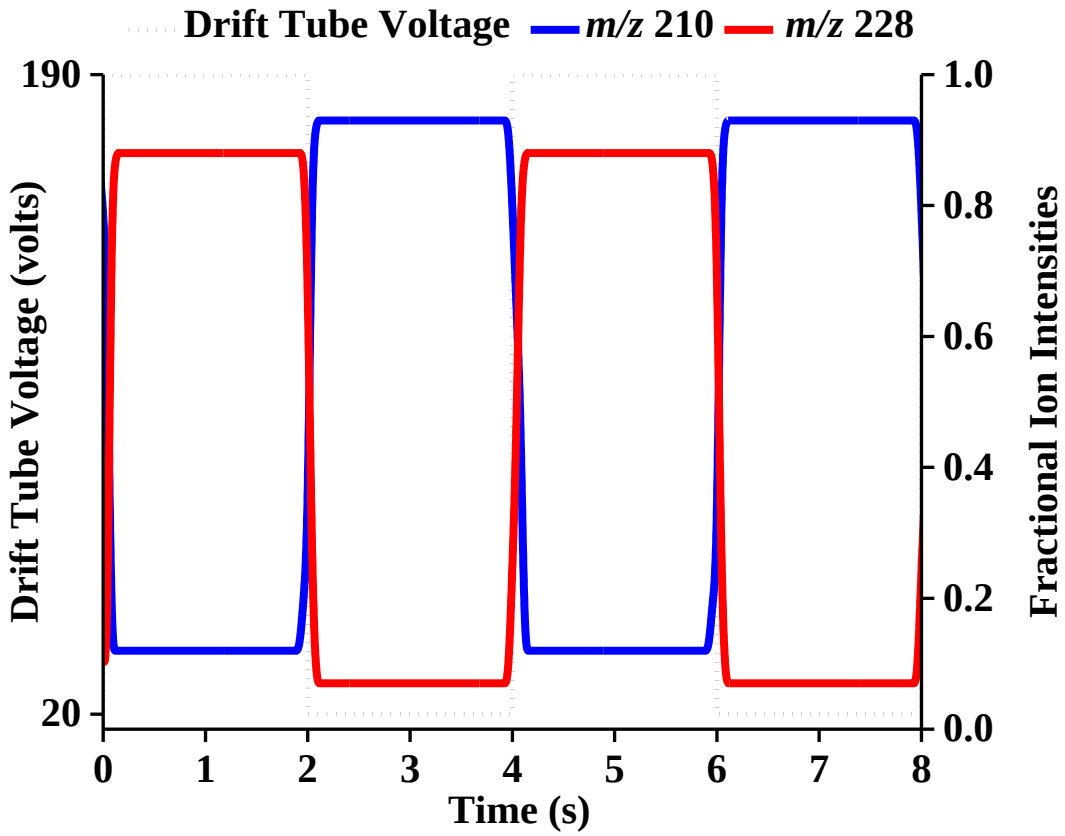



**Figure 6.** Application of combining radio frequency and fast drift tube voltage switching at 0.5 Hz between 20 and 190 V (equivalent to 30 and 180 Td in DC-mode only) for reactions of $H_3O^+$ with TNT.

## Conclusions

We have successfully implemented new hardware and software to enable the rapid switching of the reduced electric field, *E/N*, with transition times less than 140 ms at frequencies of 0.1-5 Hz in the drift tube of a KORE Technology PTR-ToF-MS. This switching results in the rapid modification of product ions from the reactions of reagent ions with chemicals through changes in collisional energies. We have demonstrated in this paper how this technique provides an improved selectivity for a number of explosives, thereby leading to a higher confidence in identification.

The results show that for all explosive compounds investigated switching between for example 80 Td and 200 Td is sufficient for analytical purposes. Slightly different *E/N*s have been used in some of the examples provided in this paper, simply because they were found to provide the maximum signal, but in reality differences in intensities between 70 Td and 80 Td and 200 Td and 220 Td, for examples, are not significant.

By using TNT as an example, we have indicated how the combination of the new drift tube voltage switching capabilities with an RFIF DT provides further improvement in selectivity. This combination of switching capabilities and RFIF to PTR-MS opens up other possibilities for improved selectivity at little cost to the manufacture of the PTR-MS instrument.

The main conclusion that can be drawn from this work is that rapid reduced electric field switching adds a new dimension to the analytical capabilities of PTR-MS. And although demonstrated for explosive compounds in this paper, this innovation has of course applications outside of those for homeland security and can be used for any other sampling protocol where there are time restrictions in compound concentrations, e.g. where there are transient processes of where volatiles are present for a short period, such as occurs in real-time breath sampling, atmospheric pollution or emissions from leaf wounding.

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