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

3

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

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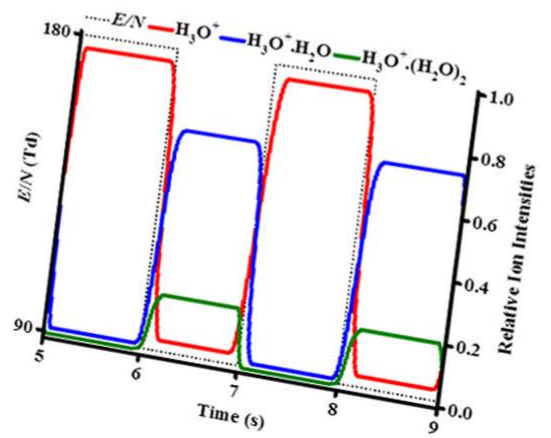
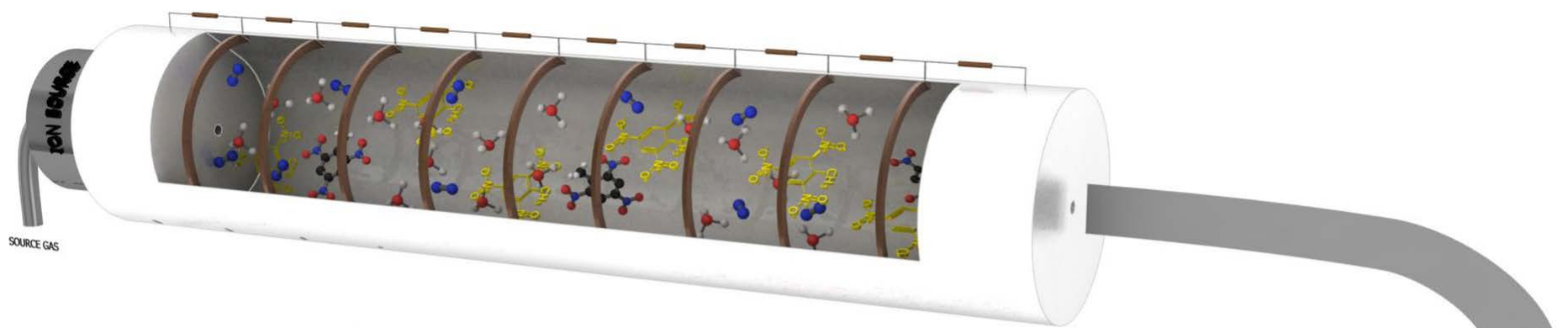
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34 Graphical abstract

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38 **Abstract (250 words)**

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

58

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

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

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

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

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

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

106 The simplest way to provide a rapid change in E/N is to alter the E field by changing
107 the voltage applied across the drift tube. In this paper we present details of a collaborative
108 project involving Kore Technology Ltd. (Ely, UK), the Defence Science and Technology
109 Laboratory and the University of Birmingham on new hardware and software modifications
110 for such a purpose. We illustrate the application of this new development to a number of
111 explosive, or explosive-related compounds, namely 2,4- and 2,6-dinitrotoluene (2,4- and 2,6-
112 DNT, m/z 182.03, $C_7H_6N_2O_4$), hexamethylene triperoxide diamine (HMTD, m/z 208.07,
113 $C_6H_{12}N_2O_6$), and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX, m/z 222.04, $C_3H_6N_6O_6$). These
114 have been selected to show the application of the system for chemical compounds with
115 different physical properties, such as vapour pressures, and chemical functional groups.

116 Finally, we comment that it may be even more beneficial for selectivity improvements
117 to have the combined operation of a radio frequency ion-funnel PTR-MS and fast drift tube
118 voltage switching. This is exemplified in this study for 2,4,6-trinitrotoluene (TNT, m/z
119 227.02, $C_7H_5N_3O_6$).

120

121 **Methods**

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

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

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

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

158 At the end of the drift tube there is an exit plate which has at its centre a $400 \mu\text{m}$
159 aperture, through which a proportion of the reagent and product ions enter the ion transfer

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

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

173 The circuitry for the switching has been added to an existing set of electronics that
174 was not designed for switching. Oscilloscope traces of the power supply output (only) show
175 asymmetry in the rise and fall times of the voltage. This is due to built-in diode circuitry on
176 the output of the power supply. If we define the period between a stable low voltage and a
177 stable high voltage after switching as the rise and fall times, we observe times of ~ 10 ms and
178 ~ 25 ms, respectively. When the power supply is connected to the reactor, thus adding
179 resistors and capacitors to the output, by the same criterion we observe greater time
180 differences in the rise and fall times of the product ions (see section 3.1 for details).
181 Analytically what is important is that data are acquired when the product ion signal is
182 constant in the two phases. This is accomplished by means of using purposely written
183 software that censors the data between voltage changes.

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

194 Passivated (SilcoNert®) stainless steel inlet lines were used in order to minimise
195 adsorption effects. All measurements were taken under the same operational conditions. The
196 TDU, inlet tubing and drift tube were maintained at 150 °C. The drift tube pressure was set at
197 1.1 mbar. The only variable was the operating drift tube voltage, which was changed to
198 provide the appropriate reduced electric fields to yield the product ion(s) of interest for each
199 explosive investigated.

200 For the fast switching experiments, the acquisition time per point was set to 40 ms.
201 Such short acquisition times imply that ion counts fluctuations will be at the level of 15 to
202 20% due to ion count statistics. However, in real operation it is not necessary to present a
203 signal that has not been processed. It is better to show for each individual cycle average ion
204 signals outside of the circuit's time constants (i.e. after the rise and before the fall time), and
205 that is what is presented in this paper, other than for one data set to illustrate the typical level
206 of fluctuation observed in the signal intensities for 40 ms acquisition times over a cycle (see
207 section 3.1).

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

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

217

218 **Results and Discussion**

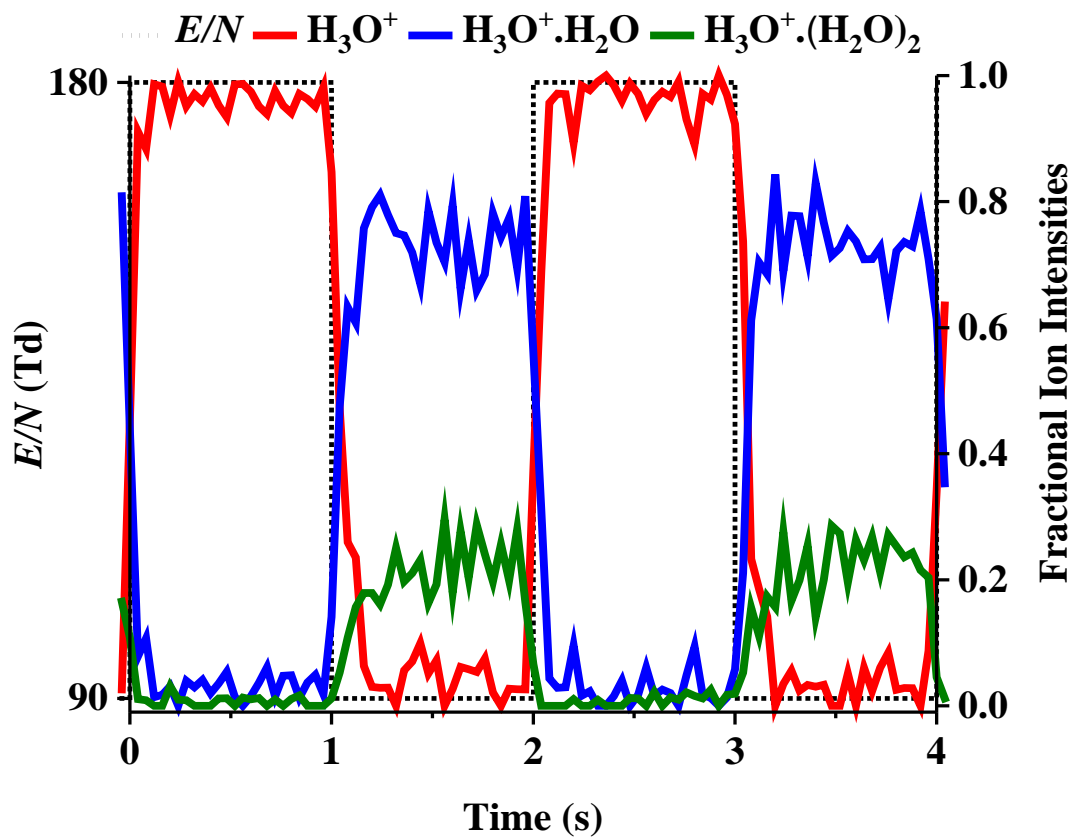
219 **Reagent Ions.** Before conducting any switching experiments with samples, it was
220 important to characterise the time constants associated with the rapid change of voltages
221 applied to the drift tube. To investigate this, we examined the temporal profile of the
222 protonated water H_3O^+ (m/z 19.02) and the dimer and trimer protonated water clusters,
223 $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ (m/z 37.03) and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ (m/z 55.04), respectively. These were chosen
224 because their individual concentrations in the drift tube are very sensitive to the E/N value
225 used. For example, at 90 Td protonated water clusters are the dominant reagent ions, whereas
226 at 180 Td these have negligible intensities because the collisions occurring in the drift tube
227 are sufficient to break-up protonated water clusters to the H_3O^+ monomer. It should however

228 be appreciated that the relative intensities of the reagent ions recorded are those measured at
229 the detector. The actual distribution of reagent ions in the drift tube may be different owing to
230 possible break-up of the protonated water clusters in the transfer optics from the DT to the
231 mass spectrometer and as a result of the dependence of the transmission of the ions on m/z .

232 Figure 1 shows measurements of the fractional reagent ion signals (total ion signal
233 adds up to 1) for H_3O^+ , $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ and $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2$ for 180 Td and 90 Td switching at a
234 frequency of approximately 1 Hz, starting with 180 Td at $t = 0\text{s}$. Figure 1(a) shows the raw
235 data obtained from the instrument to illustrate the noise associated with 40 ms data
236 acquisition and (b) the processed averaged data over the part of the cycle for which the ion
237 signals have reached stability. The measured transition time when switching from a low to a
238 high E value to result in 95% of the maximum ion signal was measured to be 60 ms. For
239 changing from high to low E values the transition time was measured as 140 ms to reach
240 within 5% of the stable lowest ion signal for that E/N phase. In practice this limits the
241 switching frequency to less than 5 Hz. However, we will demonstrate that that is more than
242 adequate for applications to explosive detection, and hence to applications where the
243 concentration of an analyte is changing over the time period of seconds.

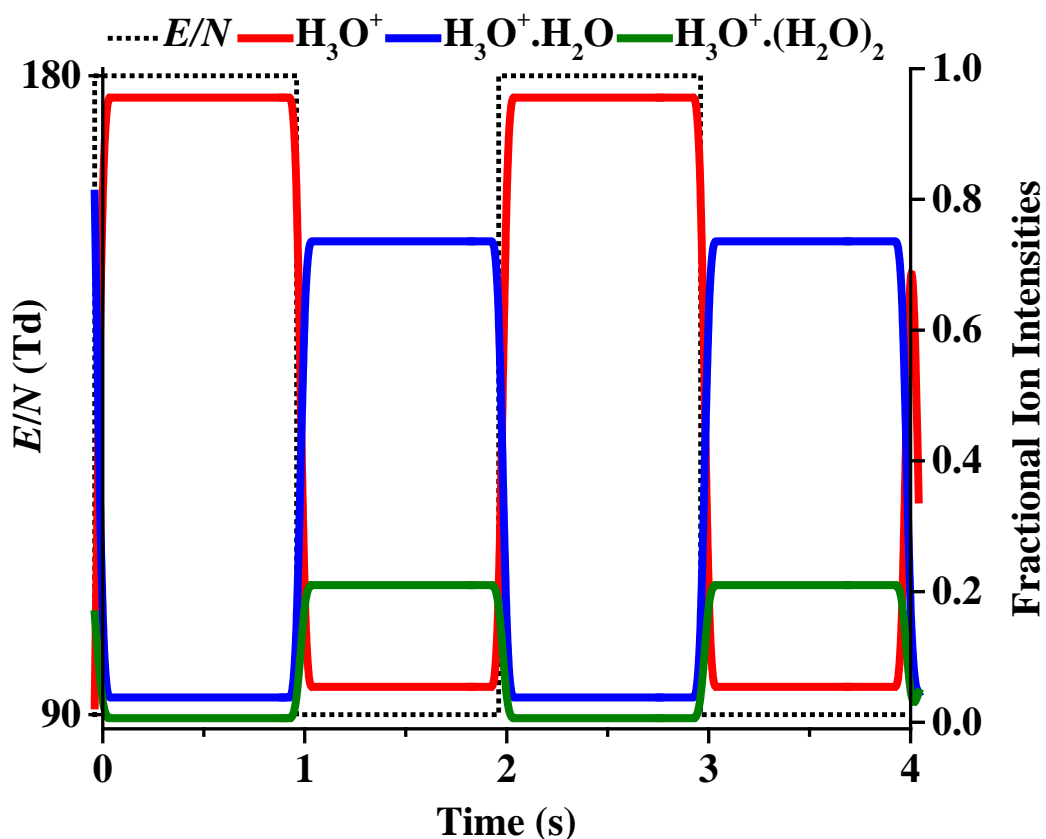
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245 (a)



246

247 (b)



248

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

252

253 **Examples of Improved Selectivity: Explosive compounds**

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

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

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

276 **2,4- and 2-6 dinitrotoluene ($C_7H_6N_2O_4$).** Figure 2 shows the PID plot as a function of
277 E/N (70 - 230 Td) for (a) 2,4-DNT and (b) 2,6-DNT. (The product ion branching ratios for
278 2,6-DNT have already been published in another paper by us dealing with the applications of
279 a radio frequency field in the drift tube.¹⁸ However, for ease of comparison with the 2,4-DNT
280 isomer the results are reproduced in this paper. The only difference is that the second water
281 cluster (2,6-DNTH⁺. $(H_2O)_2$) is not shown in figure 2(b), because its intensity is insignificant.)
282 From figures 2(a) and (b) it can be seen that monitoring product ions at m/z 183.04 (the
283 protonated parent) and 201.05 (DNTH⁺. H_2O) is sufficient for assigning 2,4-DNT, but that the
284 presence of m/z 136.04 (elimination of HONO from the protonated parent) and m/z 91.06
285 (elimination of two nitro groups) observed at the high E/N setting indicates the presence of
286 2,6-DNT. Another common ion detected for both isomers at high reduced electric field values
287 is at m/z 165.05, which results from the elimination of H_2O from the protonated parent. Given
288 that this is observed for both isomers, it cannot be used to differentiate the isomers.¹⁸ A
289 summary of results from the fast switching experiment for 2,4-DNT and 2,6-DNT are shown
290 in figure 3, which show how the two isomers can be readily distinguished.

291

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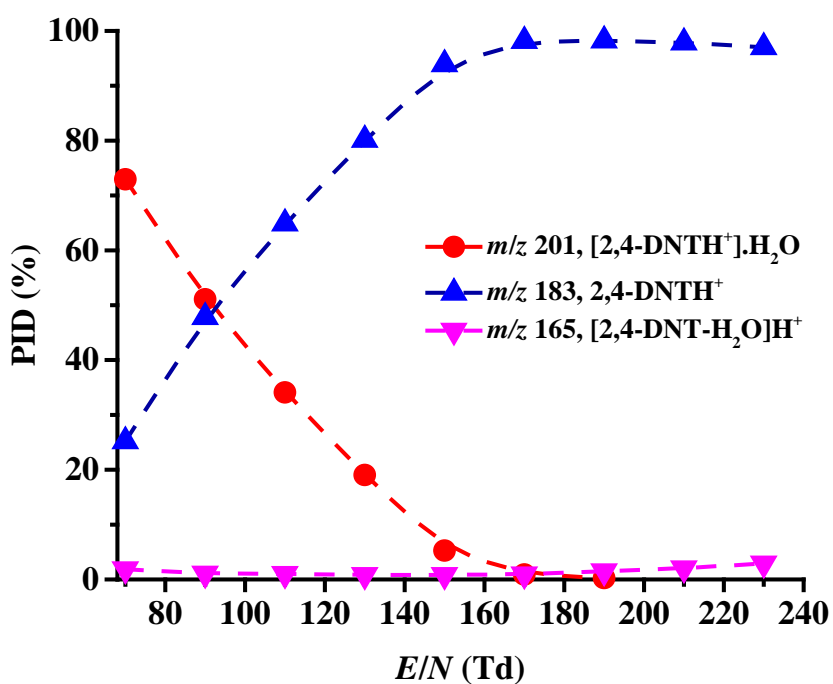
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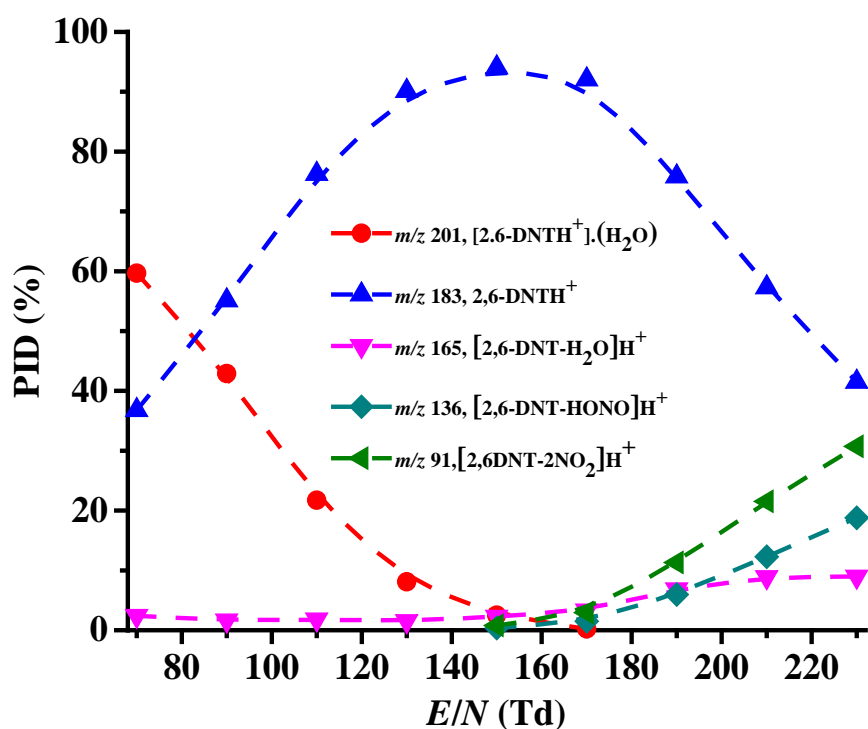
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298 (a)

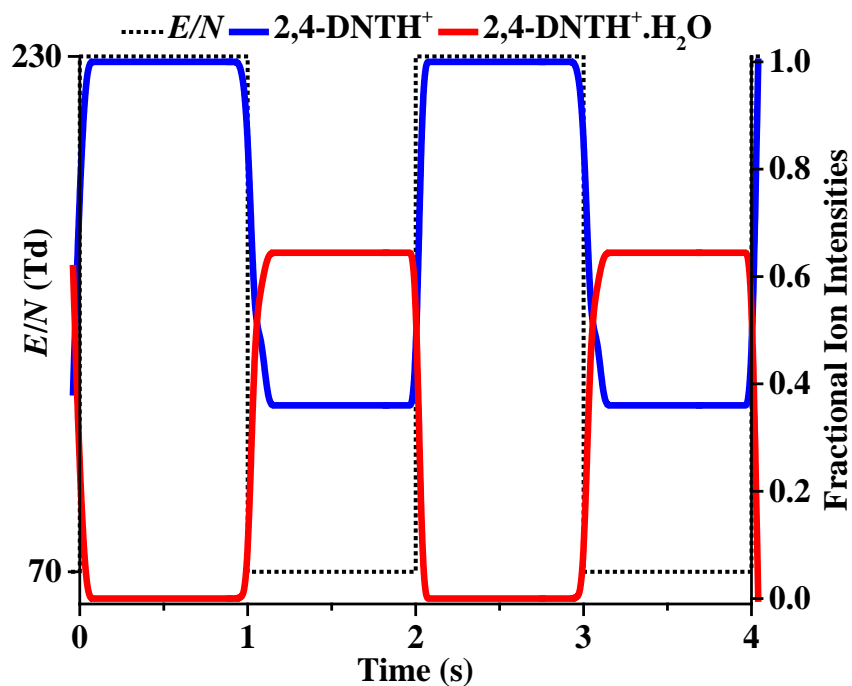


(b)

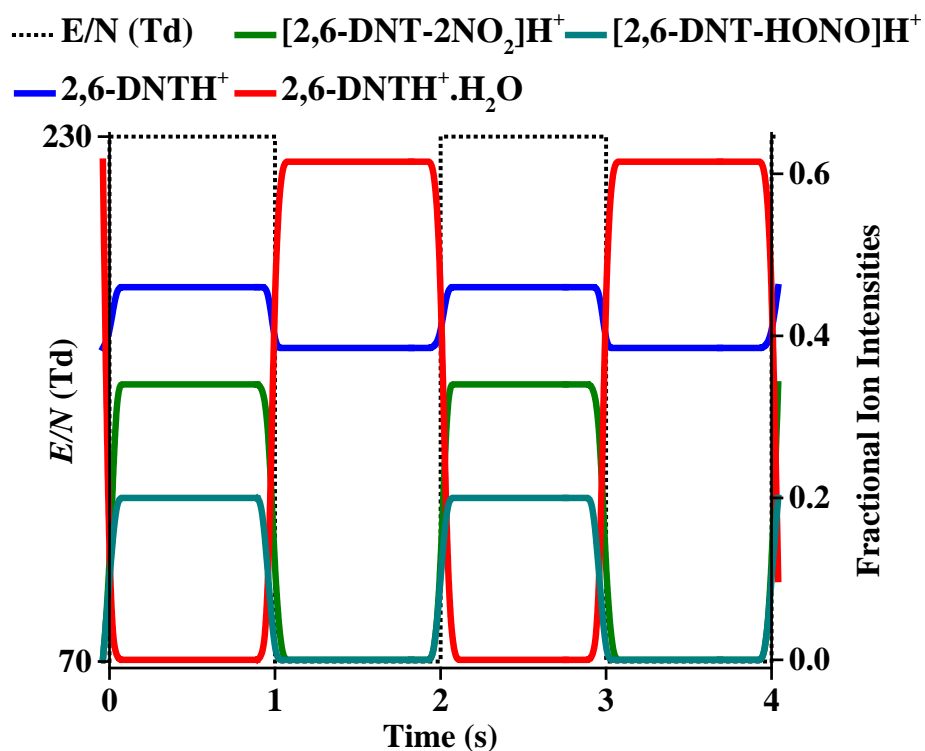


299 **Figure 2.** (a) Percentage product ion distribution (PID) results for (a) 2,4-DNT and (b) 2,6-
 300 DNT as a function of reduced electric field (70 to 230 Td).

301 (a)



302 (b)



303

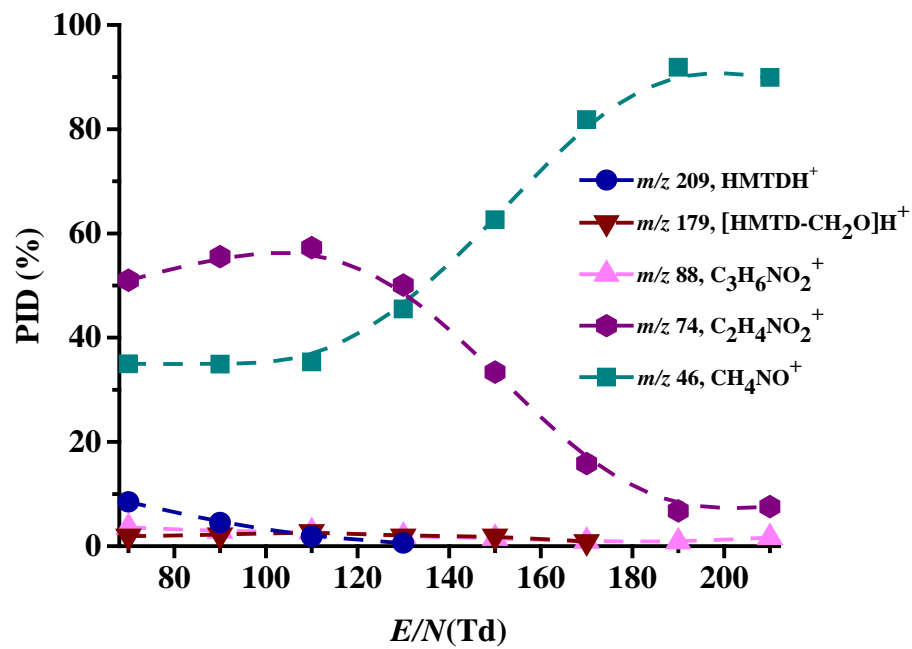
304 **Figure 3.** Changes in the fractional ion intensities averaged over each cycle using 1 Hz E/N
 305 switching between 70 Td and 230 Td for (a) 2,4-DNT and (b) 2,6-DNT. The product ions at
 306 m/z 91.06 and m/z 136.04 are distinctive of 2,6-DNT.

307 **HMTD (C₆H₁₂N₂O₆)**. For HMTD five product ions are observed at m/z 46.03, 74.02,
308 88.04, 179.07 and 209.08. The product ions at m/z 88.04 and m/z 179.07 have negligible
309 intensities at all E/N values, and are therefore not considered further. m/z 209.08 is the
310 protonated parent, but only has a reasonable intensity at low E/N (< 90 Td). DFT calculations
311 give 877 kJ mol^{-1} and 844 kJ mol^{-1} as the proton affinity and gas-phase basicity, respectively,
312 for HMTD. Thus proton transfer from not only protonated water but also from the protonated
313 water clusters is exoergic. Given the high proton affinity of HMTD, the reaction of H_3O^+
314 would most probably be dissociative, and the protonated parent is almost certainly a result of
315 a reaction with $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$. The product ion at m/z 179.07 corresponds to the loss of
316 formaldehyde (CH_2O) from the protonated parent, leaving $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_5\text{H}^+$. m/z 88.04
317 corresponds to $\text{C}_3\text{H}_6\text{NO}_2^+$ and m/z 74.02 to $\text{C}_2\text{H}_4\text{NO}_2^+$. By taking advantage of the high mass
318 resolution associated with KORE PTR-ToF-MS, we can rule out that the ion at m/z 46.03 as
319 being NO_2^+ , because the peak position of that ion is at m/z 45.99. CH_4NO^+ agrees with m/z
320 46.03. Given the significant rearrangement and eliminations required to produce this ion, and
321 the fact that it has a high branching percentage even at low E/N (see figure 4(a)), it is possible
322 that CH_4NO^+ does not directly result from dissociative proton transfer to HMTD. It is
323 probable that this ion is a consequence of the reaction of H_3O^+ with a neutral product
324 resulting from the thermal decomposition of HMTD in the system. Decomposition of HMTD
325 could have resulted in the formation of other neutrals that then react with the reagent ions.
326 However, initial temperature dependent measurements have not shown any dependence on
327 the product ion distributions. The mechanism for the production of the product ions needs
328 further exploration, but that is not the aim of this paper. Independent of the source of the
329 product ions under the operation conditions we have used, and especially for m/z 46.03, they
330 are still specific to HMTD and hence we can use them to specify the presence of HMTD.
331 Figure 4 (a) shows the PID obtained for HMTD as a function of the reduced electric field (70
332 - 210 Td). Under the experimental conditions used the product ions that dominate are at m/z
333 46.03 and m/z 74.02. However, the presence of the protonated parent observed at low E/N is a
334 useful ion for identification although it is observed with a low branching percentage. Thus we
335 have selected the product ions at m/z 46.03, 74.02 and 209.08 for use in identifying HMTD
336 with a high specificity under our operational conditions. The switching results using these
337 three product ions are shown in figure 4(b).

338
339
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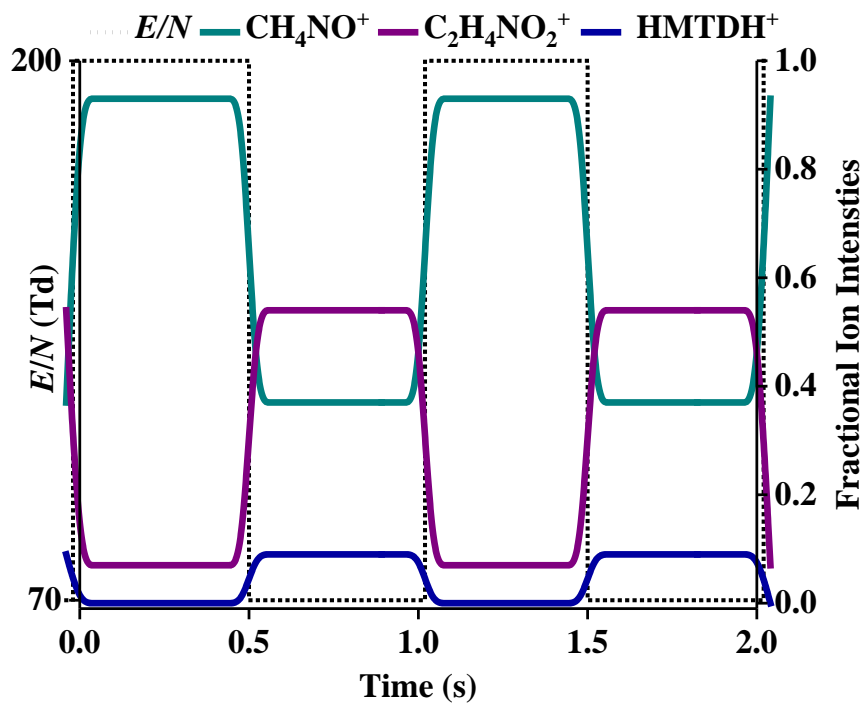
341

342 (a)



343

344 (b)



345

346 **Figure 4.** (a) PID for HMTD as a function of reduced electric field covering the range 70-210

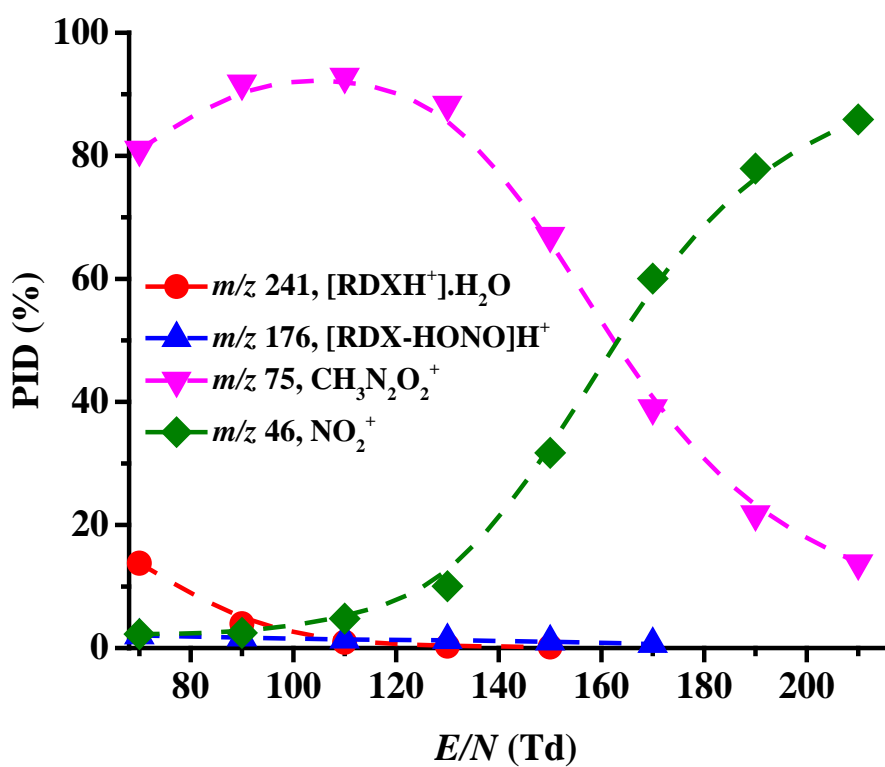
347 Td and (b) changes in the fractional ion intensities averaged over each cycle for a reduced

348 electric field switching 2 Hz. (2 Hz is presented here to illustrate the operation of the system
349 as a different frequency.)

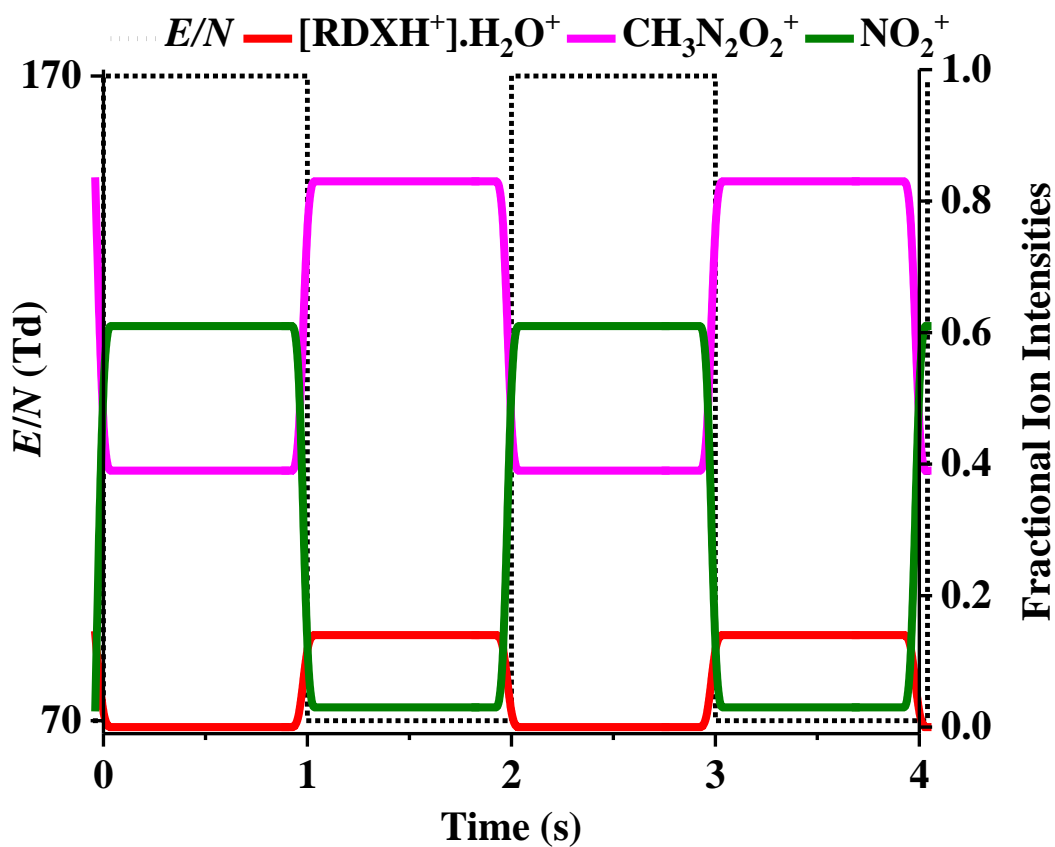
350 **RDX (C₃H₆N₆O₆)**. Major product ions are observed are at m/z 45.99 (NO₂⁺) and m/z 75.02
351 (CH₃N₂O₂⁺). m/z 75.02 dominates for $E/N < 160$ Td, whereas m/z 45.99 dominates at for E/N
352 > 160 Td. Another product ion is also observed at m/z 176.04 ([RDX-HONO]H⁺) throughout
353 the E/N range investigated, but it only appears at a low intensity compared to the other two
354 primary product ions. At the lowest E/N an ion is observed at m/z 241.05. This is assigned to
355 be RDXH⁺.H₂O. Given the observation of this, it is surprising that no protonated monomer is
356 detected. We propose that as the reduced electric field is increased to the stage where no
357 water clustering occurs the protonated parent has too much internal energy for it to survive
358 before detection. DFT calculations give the PA and GB of RDX to be 764 kJ mol⁻¹ and 734
359 kJ mol⁻¹, respectively, and therefore only H₃O⁺ can efficiently react with RDX via proton
360 transfer. Figure 5 (a) shows the PID for RDX as a function of E/N (70 – 210 Td) under the
361 operational conditions we have used. A separate study is being undertaken to investigate
362 temperature effects on the PID. For our operating temperatures, the PID shows that product
363 ions at m/z 45.99, 75.02 and 241.05 are sufficient to identify the presence of RDX with a high
364 level of confidence. Figure 5(b) shows the reduced electric field switching results for 70 Td
365 and 170 Td.

366

367 (a)



368
369 (b)

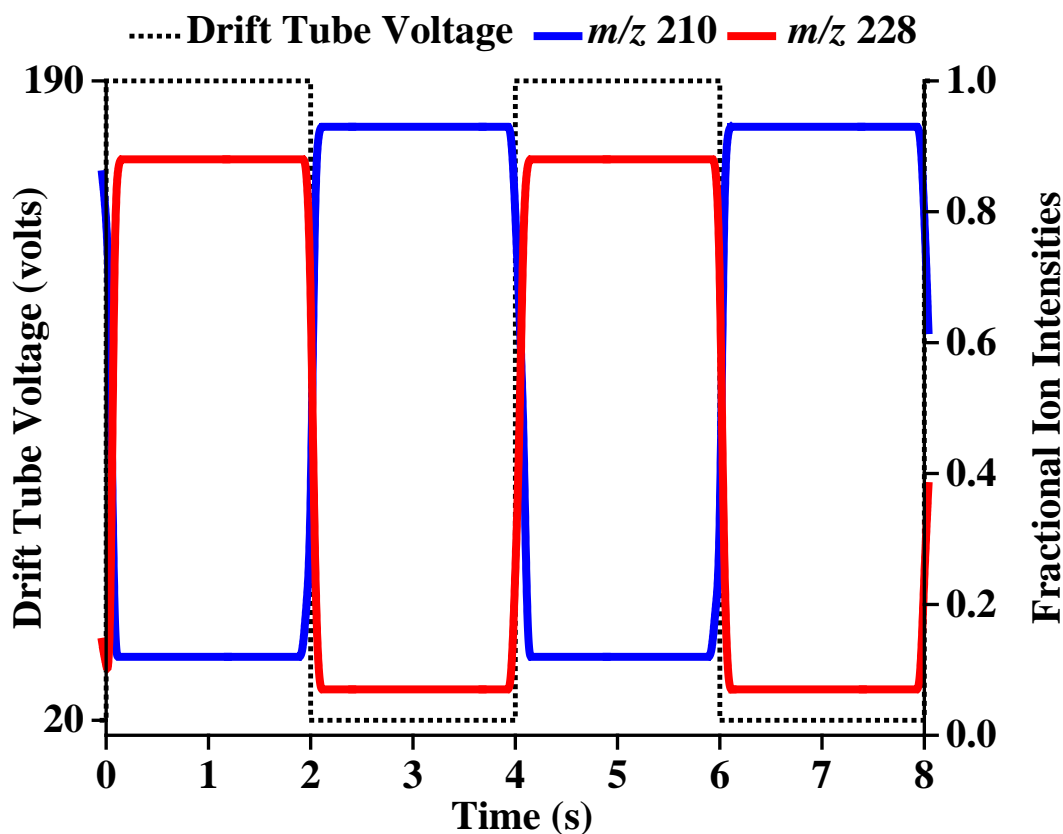


370

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

373

374 **Radio Frequency Ion Funnel and Drift Tube Voltage Switching: an Application to**
375 **TNT.** Recently, we demonstrated how a radio frequency ion funnel-drift tube (RFIF-DT) can
376 be employed in a novel way to modify the product ions resulting from the reaction of H_3O^+
377 with TNT through changes in collisional induced dissociation.¹⁸ In DC-only mode, and for all
378 E/N values investigated, the reaction of H_3O^+ with TNT leads to only one product ion,
379 namely protonated TNT at m/z 228.03.⁸ However, in RF-mode, another fragment ion is
380 observed at m/z 210.02, corresponding to the elimination of water from the protonated
381 parent,¹⁸ with the intensity of this product ion increasing relative to the protonated parent
382 with decreasing drift tube voltage (i.e. decreasing E/N in DC mode). In that work we
383 proposed that the dominance of m/z 210.02 at low drift tube voltages is a result of the
384 protonated TNT spending a longer time in the RF region of the drift tube. Through numerous
385 collisional processes this allows it to gain sufficient internal energy until it reaches a level
386 that leads to the elimination of H_2O . In this study we illustrate how improvements in
387 selectivity can be achieved by combining RF-mode with fast drift tube voltage switching for
388 TNT (figure 6). We therefore propose that by combining the RFIF and drift tube voltage
389 switching techniques an even higher confidence in the assignment of an analyte in a complex
390 chemical environment may occur than is possible in DC-only mode.



391 **Figure 6.** Application of combining radio frequency and fast drift tube voltage switching at
 392 0.5 Hz between 20 and 190 V (equivalent to 30 and 180 Td in DC-mode only) for reactions
 393 of H_3O^+ with TNT.
 394

395

396 **Conclusions**

397 We have successfully implemented new hardware and software to enable the rapid switching
 398 of the reduced electric field, E/N , with transition times less than 140 ms at frequencies of 0.1-
 399 5 Hz in the drift tube of a KORE Technology PTR-ToF-MS. This switching results in the
 400 rapid modification of product ions from the reactions of reagent ions with chemicals through
 401 changes in collisional energies. We have demonstrated in this paper how this technique
 402 provides an improved selectivity for a number of explosives, thereby leading to a higher
 403 confidence in identification.

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

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

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

421

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429

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