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Semtex 1A and H negative ion resonances for explosives' detection

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ABSTRACT

We present the results obtained in dissociative electron attachment to Semtex in the gas phase by making use of a crossed electron-molecular beam experiment. Energy dependence of partial cross sections has been measured in an electron energy range from 0 to 12 eV with an energy resolution of ~80 meV. Semtex 1A and H are mixtures of two other explosives, i.e., royal demolition explosive – RDX (hexogen) and pentaerythritol tetranitrate – PETN (pentrite), appearing in different fractions. In fresh samples product anions from both explosives can be detected together with anions originating from volatile markers. After some time we only observe product ions formed upon dissociative electron attachment to PETN, which are not observed for a mixture of pure RDX and PETN. For both Semtex samples, an additional anionic feature at 210 *m*/*z* can be assigned to the binder butyl rubber.

1. Introduction

Due to the high risk of terrorist attacks during the last years, the interest in detection of explosives has raised considerably. The developments of fast and efficient techniques to discriminate explosives from other substances are fostered by the endeavour for personal safety and homeland security. In the last years a considerable number of techniques have been developed in order to detect in real time explosives, where several analytical methods have been used such as ion mobility spectrometry [1], GC/MS [2], mass spectrometry [3–12] and proton transfer reaction mass spectrometry [13], desorption electrospray ionization (DESI) [14], low-temperature plasma (LTP) ambient ionization mass spectrometry [15], among many others. Even small quantities of explosives can be used to trigger high levels of destruction. Some explosives, like plastic explosives, have been used frequently because they can be hardly detected. Semtex is a plastic explosive and consists of a mixture of two other explosives, PETN (pentaerythritol tetranitrate or pentrite) and RDX (royal demolition explosive or hexogen). Varying the proportion of these compounds, two different sorts of Semtex can be produced, 1A and H, with PETN/RDX composition ratios of 0.94/0.06 and 0.5/0.5, respectively. Semtex was produced for the first time in the 1950s for military purposes and was later used in high quantities during the Vietnam War. Nowadays, Semtex is still used for demolition of concrete and metal constructions or underwater blasting operations.

Dissociative Electron Attachment (DEA) experiments to PETN, $C_5H_8N_4O_{12}$ and RDX, 1,3,5-trinitro-1,3,5-triazocyclohexane $C_3H_6N_6O_6$ (chemical structures in Fig. 1) have been carried out recently in our group [7,16]. For both compounds, DEA was shown to be operative at very low energies close to ~0 eV showing unique features corresponding to a variety of fragment anions formed. For PETN the main fragment signal is due to NO_3^- followed by NO_2^- and O^- anions, whereas for RDX the most intense signal accounts for $C_2H_4N_3O_2^-$ and NO_2^-. In contrast to nitroaromatic compounds, PETN was shown to decay faster upon electron attachment and preferentially low-mass anions are formed [16]. Sulzer et al. [3–5,7,16], Mauracher et al. [6] and Havey et al. [10] have demonstrated that particularly NO_2^- and its resonance profile can serve as a fingerprint for the identification of the neutral compounds. DEA turns out to be even selective for isomers of nitrotoluene [3,10] and dinitrobenzene [4].

In the present work we investigate the negative ion formation from Semtex 1A and H at low energies (0–12 eV) by recording the ion yield curves with a high electron energy resolution (~80 meV). The by far dominant signal can be assigned to NO_3^- formation. It is shown that at threshold (~0 eV) a variety of intense DEA products are formed.

2. Experimental

Electron attachment to the two plastic explosives was investigated by means of a crossed electron-molecular beam set-up which

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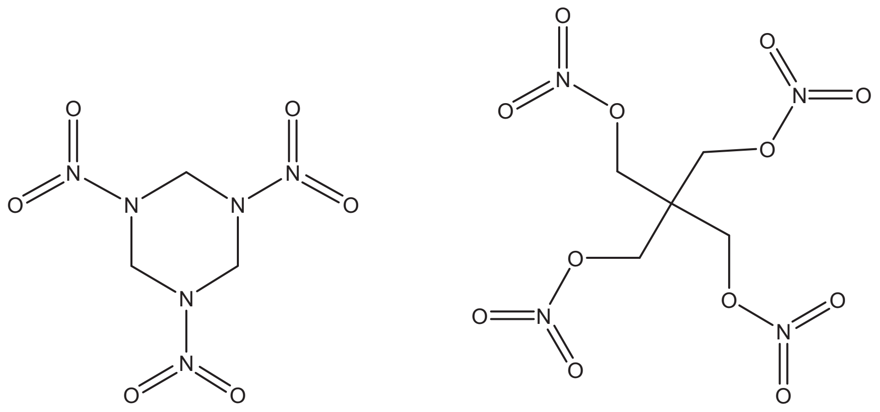

Fig. 1. Chemical structure of RDX (left) and PETN (right).

has been described elsewhere [6]. Briefly, a high resolution 80 meV full width at half maximum (FWHM) electron beam is formed in a hemispherical electron monochromator with typical currents of ~5 nA. Negative ions formed in the interaction region are extracted by weak electric fields, mass analyzed by means of a quadrupole mass filter and detected in a channel electron multiplier operated in pulse counting mode. The time window from the negative ion formation to the detection of an anion is in the order of few hundered μs. Negative ion yields are obtained as a function of the electron energy. Semtex 1A and H are solid at room temperature and therefore have to be heated in order to increase their vapour pressures so that at moderately elevated temperatures an effusive molecular beam can be generated. The effusive molecular beam emerges through a capillary from a heated oven operated at a temperature of around 90–100 °C which is well below the melting point of Semtex. Therefore, for the present oven temperatures we expect no thermal decomposition of the molecules. The electron energy scale as well as the electron energy resolution are calibrated using the well-known Cl^-/CCl_4 signal near 0 eV.

The Semtex samples have been provided by the defusing section of the Austrian ministry of interior in the autumn of 2006 and were analyzed a year after without further purification.

3. Results and discussion

Recent studies on electron attachment to RDX and PETN in our laboratory [7,16] have revealed that these compounds do not show any evidence of the parent molecular anion formation. The mass spectra for both explosives obtained close to 0 eV indicate strong decomposition into many low-mass anions via complex sequential processes driven upon low-energy electron attachment. This intense decomposition of molecules upon low-energy electron attachment apparently reflects the explosive nature of the molecules since it is less pronounced for other nitroaromatic compounds previously reported [3–7]. However, we notice that LTP experiments report the formation of stable $[M+NO_2]^-$ and $[M+NO_3]^-$ ions [15], whereas DESI measurements refer to the formation of RDX protonated ions [14].

In Fig. 2 we present the negative ion mass spectra for both Semtex 1A and H and for comparison the negative ion mass spectrum for pure PETN. These scans were obtained by summation over individual mass spectra obtained at different electron energies, from a value close to 0 eV up to 10 eV in steps of 1 eV. From these data it is possible to have a first survey of all fragment anions produced, though, for a mass spectrum recorded at one electron energy only those anions formed in a resonance close-by can be observed. Although the spectra look similar at a first glance, a close inspection reveals that for Semtex 1A the abundance of the fragment anion with 210 m/z is around five times greater than for Semtex H. For dissociative electron attachment to pure PETN and RDX the formation of this anion was not reported. The yield of 210 m/z is almost an order of magnitude lower than the less intense fragments presented in ref. [16]. Possibilities for the origin of this heavy anion are markers, plasticizers (~9%) or binders (~9% such as butyl rubber) added to Semtex. Other additives to Semtex samples may also contain 2,3-dimethyl-2,3-dinitrobutane, DMNB and 4-nitrotoluene, 4-NT.

In the anion mass spectra of a freshly introduced sample of Semtex H two anions, i.e., at 137 m/z and 182 m/z, can be assigned to volatile markers added to the plastic explosive. After heating the

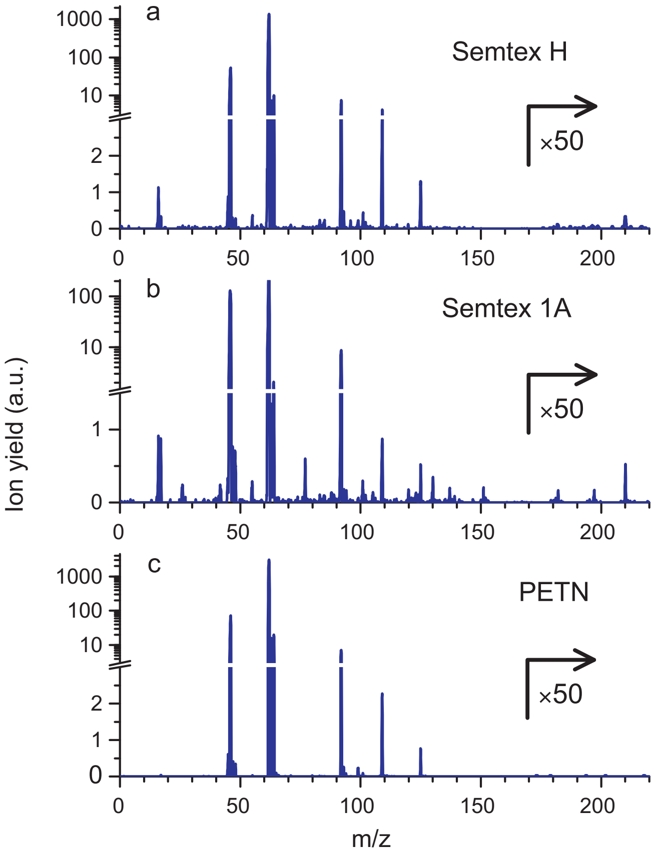

Fig. 2. (a) Negative ion mass spectrum of Semtex H (upper diagram), (b) Semtex 1A (middle diagram), and (c) PETN (lower diagram) obtained by the sum of individual mass scans measured at several different energies from 0 to 10 eV in 1 eV steps.

Table 1
Peak positions and relative intensities integrated from 0 to 10 eV for the most significant fragment anions of Semtex 1A and 1H obtained in the present experiment compared to previous studies in our laboratory on RDX [7] and PETN [17].

Mass (m/z)					Assignment	Peak position (eV)				
Semtex 1A (0.94 PETN + 0.06 RDX)	Semtex H (0.498 PETN + 0.502 RDX)	RDX	RDX-A3	PETN						
210	210	–	–	210	$(C_4H_8)_3C_3H_6^-$	~0	–	–	–	–
125	125	–	–	125	$NO_3HNO_3^-$	0.07	–	6	–	–
109	109	–	–	109	$NO_3HNO_2^-$	0.12	–	6.6	–	–
92	92	–	–	92	$(NO_2)_2^-$	0.02	–	6.4	–	–
62	62	–	–	62	NO_3^-	0.16	–	6.7	–	–
46	46	46	46	46	NO_2^-	0.15	4.4	6.5	8.8	–
16	16	–	–	16	O^-	–	1.7	6.8	8.5	11.1

sample for one night at 80 °C these anions completely disappeared. The anion efficiency curves of these two anions taken suggest that mononitrotoluene [3] and dinitrotoluene [17] was added to Semtex H. Furthermore, a contribution of both nitroaromatic markers is also observed on the dominant NO_2^- signal which disappears after heating the sample for some time. Apart from the anion with mass 210 m/z, anions with mass 125, 109, 92, 62, 46, and 16 m/z were identified as particularly dominant relative to their neighbouring peaks see (Table 1).

3.1. Energy dependence of partial cross sections

In Table 1 we show the position for the resonances in the different anions formed and in Fig. 3(a) the anion efficiency curves for $(NO_2)_2^-$, NO_3^-, NO_2^- and O^- formed upon DEA to Semtex 1A, while in Fig. 3(b) we show the anion efficiency curves for NO_3^-, NO_2^- and O^- formed upon DEA to Semtex H. The anion with mass 46 m/z is formed via DEA to RDX and PETN whereas those with masses 125, 109, 92, 62 and 16 m/z originate from PETN only. For all these anions we observe perfect agreement with the anion efficiency curves reported for the corresponding anions by Edtbauer et al. [16] upon DEA to pure PETN. Only the anion efficiency curve of O^- exhibits an additional asymmetric peak with a vertical onset at around 1.8 eV. In contrast to the cyclic explosives TNT [5] and RDX [7], delayed unimolecular decay reactions are strongly reduced for product anions of PETN, thus indicating a substantially faster decomposition of PETN upon low-energy electron attachment [16].

The anion efficiency curves of the fragment NO_2^- are shown in Fig. 4 for Semtex H (upper diagram) and Semtex 1A (middle diagram) in comparison to pure RDX (dashed line, data taken from [7]) and PETN (solid line, data taken from [16]), which are plotted in the lower diagram. The data shown were measured after heating both Semtex samples a few hours. The heating time turned out to be crucial for the shape of the resulting anion efficiency curves. Fig. 5 shows a comparison of the fragment NO_2^- from freshly introduced samples (solid lines) and the same samples measured after heating to 90 °C for a few hours (dashed lines) of Semtex H (upper diagram) and Semtex 1A (lower diagram). The close similarity of the NO_2^- anion efficiency curves from pure PETN and the heated Semtex samples indicates that RDX and markers that contribute to this anion are more volatile and disappear quickly at elevated temperatures. However, this contradicts the higher mass loss of PETN (172 pg/s at 110 °C) compared to RDX (49 pg/s at 110 °C), which was experimentally determined for pure samples [18]. A possible explanation is a different binding of PETN and RDX to the binder which contributes about 9% to both Semtex compounds. When all explosives from the sample are vaporized and the yield of NO_2^- and NO_3^- disappears, we observe a black rubber like material in the oven. A

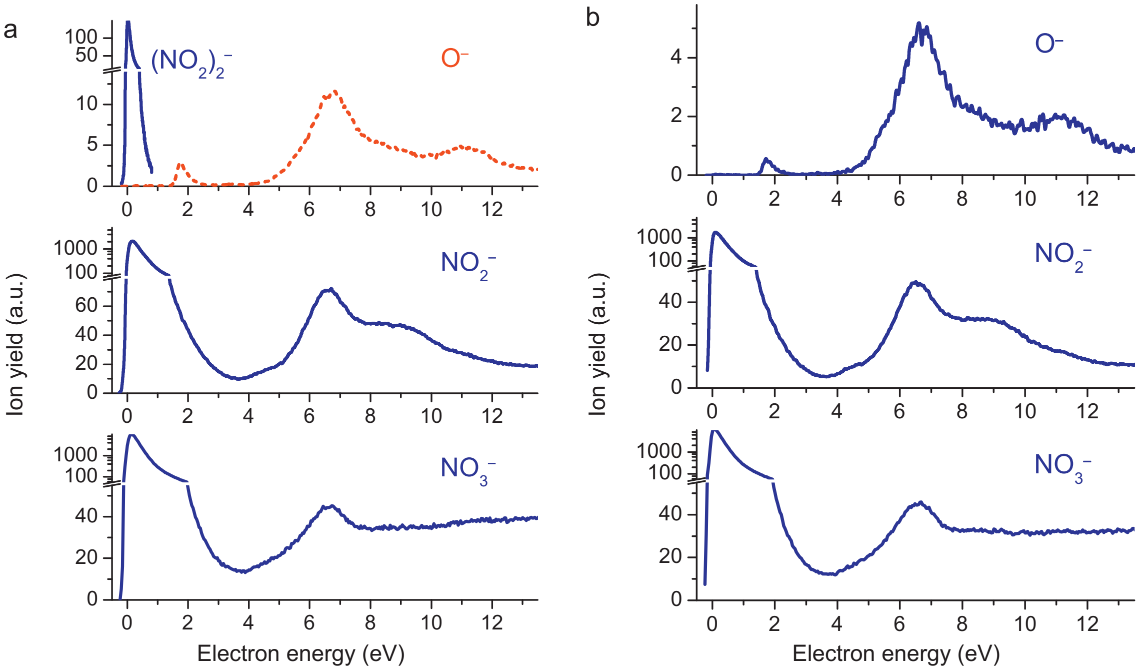

Fig. 3. (a) Anion efficiency curves for the most intense anions upon dissociative electron attachment to Semtex 1A, measured at 90 °C sample temperature. (b) Anion efficiency curves for the most intense anions upon dissociative electron attachment to Semtex H, measured at 90 °C sample temperature.

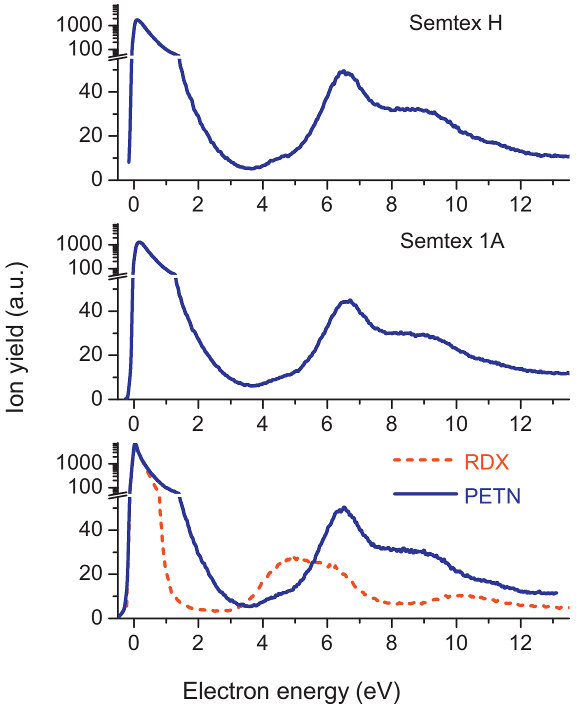

Fig. 4. Comparison of the NO_2^- anion efficiency curves for Semtex H, Semtex 1A, RDX (lower diagram, dashed line, data taken from [7]) and PETN (lower diagram, solid line, data taken from [16]) measured at 90 °C sample temperature.

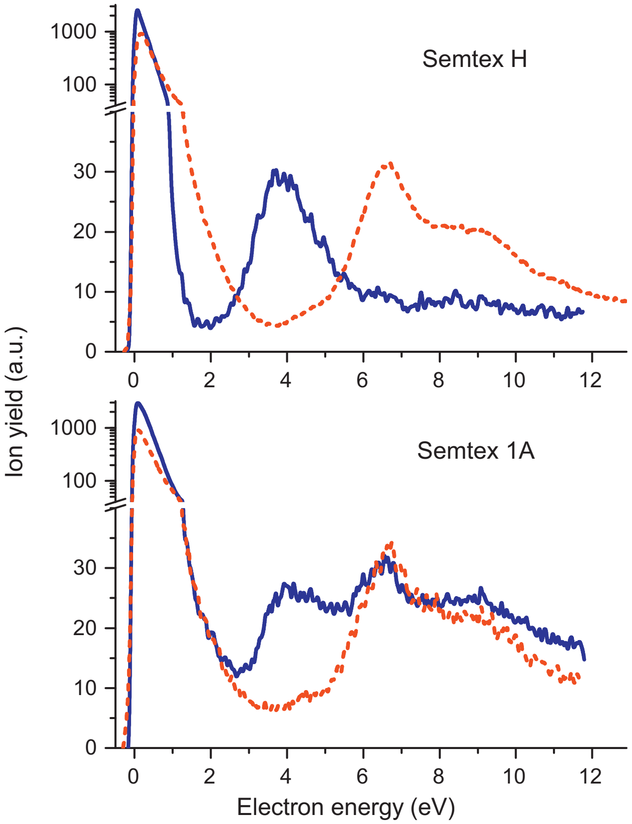

Fig. 5. Temperature dependence of the NO_2^- anion yield from Semtex H and Semtex 1A. For Semtex H the solid line shows the ion yield with a freshly introduced sample at 39 °C and the dashed line after heating the sample for 5 h to 90 °C. The lower diagram shows NO_2^- from Semtex 1A. The solid line shows the ion yield for a fresh sample that was heated to 90 °C and the dashed line after the sample was heated to 100 °C for 2 h.

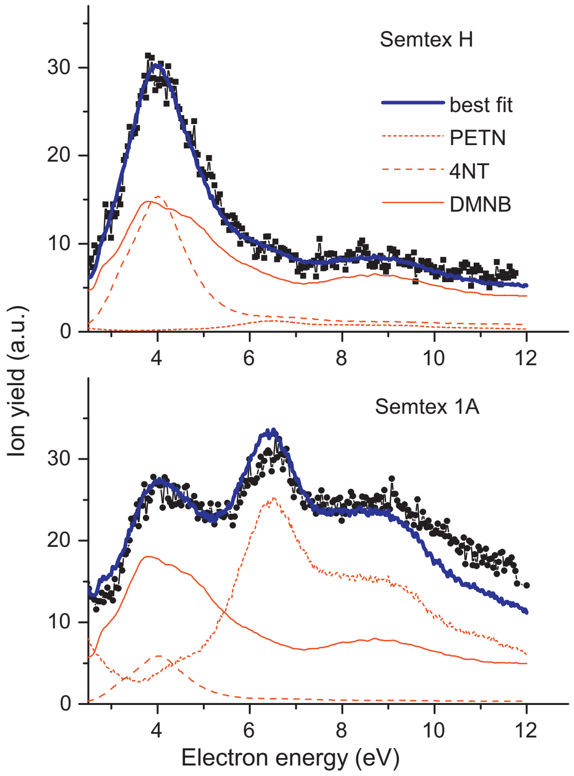

Fig. 6. Contributions of different nitro-compounds to the anion efficiency curve of NO_2^- from fresh Semtex H (line with full squares, upper diagram) and Semtex 1A (line with full circles, lower diagram). Thick solid line is a superposition of the four pure compounds indicated by the thin lines. The data for PETN [16], 4-NT [3] and DMNB are taken from the literature. The points correspond to the anion efficiency curve of Semtex 1A, measured for a fresh sample after heating to 90 °C (complete curve shown in Fig. 5).

detailed look at the NO_2^- anion yield from fresh samples (Fig. 6) indicates that besides PETN (dotted line; data taken from [16]) we assign a low-energy resonance at about 3.8 eV to 4-nitrotoluene (dashed line, data taken from [3]) and DMNB (thin solid line). The thick solid line represents the best superposition of the three compounds to match the Semtex data (solid dots). 4-nitrotoluene is a volatile marker that quickly disappears and also the contribution of RDX (not shown here) cannot be seen after heating the sample for a few hours. Even at very high temperatures (150 °C) RDX

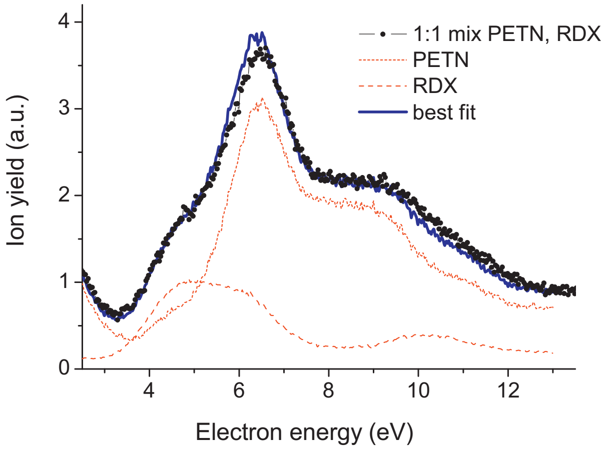

Fig. 7. NO_2^- anion efficiency curve for a 1:1 mixture of pure RDX and PETN (line with full points) heated to 95 °C. The thick solid line is a superposition of the NO_2^- anion efficiency curves of RDX (dashed line, data taken from [7]) and PETN (dotted line, data taken from [16]).

does not reappear. As expected, the relative contribution of RDX compared to PETN is higher in Semtex H (1.01 according to the composition) than in Semtex 1A (0.06 according to the composition). Please note, that the fraction of these two numbers is about 16 whereas the corresponding fraction of the relative ion yields turns out to be only 4.6. This indicates that already evacuation of the sample close to room temperature leads to a substantial loss of volatile RDX. After insertion of a new sample it takes typically 2 h to achieve suitable vacuum to turn on the filaments and another 2 h to tune the monochromator to high resolution.

In order to check the effect of the binder and plasticizer we introduced a 1:1 mixture of pure RDX and PETN into our instrument. Throughout the complete measurement series that was performed at a temperature of 95 °C both explosives are identified in a constant fraction. Fig. 7 shows the anion efficiency curve of NO_2^- of this mixture (data points) in comparison with a best fit (solid line) derived from a superposition of pure RDX (dashed line, data taken from [7]) and PETN (dotted line, data taken from [16]). This measurement clearly confirms a strong effect of the binder and plasticizer of the two Semtex samples, which leads to an enhancement of the contribution of PETN in the vapour released from these plastic explosives.

4. Conclusions

In the present DEA study on Semtex 1A and H we have determined the partial cross sections measured in the electron energy range of 0–12 eV with a high energy resolution of ~80 meV in a crossed electron-molecular beam setup equipped with a hemispherical electron monochromator. Although RDX and PETN in their pure form have comparable vapour pressures with PETN being even more volatile [18], both Semtex samples exhibit after some time exclusively fragment anions from PETN, which is not the case for a 1:1 mixture of pure RDX and PETN. We tentatively explain this surprising observation by a different interaction of the two explosives with the binder. A new anion at mass 210 *m*/*z* that has not been observed for pure PETN and RDX can be assigned to a fragment anion of the binder butyl rubber $(C_4H_8)_n$. For fresh samples an additional low-energy resonance in the anion efficiency curve of the fragment NO_2^- is observed slightly below 4 eV, which we assign to the presence of the volatile marker 4-nitrotoluene.

In previous studies it has been demonstrated that the anion efficiency curve of NO_2^- can serve as a fingerprint for the any pure nitro-containing compound. Even different isomers of nitrotoluene and dinitrobenzene can be clearly distinguished. However, composition of the two presently investigated plastic explosives somehow prevents a clear assignment. Instead of a well defined mixture of PETN and RDX we observe PETN only after heating the sample for a few hours. The only difference to PETN is an additional anion at mass 210 *m*/*z*, originating from the binder added to the Semtex plastic explosives.

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