

## Laser pyrolysis of explosives combined with mass spectral studies of the ignition zone

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### ABSTRACT

By combining a laser ignition technique with mass spectroscopic analysis we have developed a means of rapid determination of some of the molecules involved in the thermal ignition process of a high explosive. This technique also enables the study of how parameters such as initial gas pressure (0.1–5.0 MPa), type of gas (helium, air or nitrogen), laser wavelength (9–11  $\mu\text{m}$ ), laser pulse width (1 ms–1 s) and laser power (10–180 W) influence the production of major decomposition products ( $\text{N}_2\text{O}$ , HCN,  $\text{NO}_2$ ,  $\text{H}_2\text{CO}$ , NO and  $\text{CO}_2$ ) and some of the larger fragments in the reaction zone. It also permits the detection and identification of some of the larger molecule fragments involved in the ignition process. The experimental equipment consists mainly of a 180 W  $\text{CO}_2$  laser, an explosives test vessel, and a mass spectrometer. This paper describes in detail the techniques and apparatus used and gives an introductory study of the fast laser pyrolysis/laser ignition for 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX). The combined laser ignition/mass spectroscopy method gives advantages over earlier pyrolysis–MS methods in that it permits us to follow the transition from a slow thermal decomposition to a self-sustained deflagration. The method also makes it possible to study these processes at elevated pressures (up to 5.0 MPa). In the RDX pre-ignition zone some decomposition intermediates were identified: triazine ( $\text{C}_3\text{N}_3\text{H}_3$ ) and possibly  $(\text{CN})_2$ . In the pre-ignition zone of RDX we have also identified both condensed-phase and gas-phase processes. In order to show the general applicability of the method results are also presented for other high explosives: HNS, PETN, TNT and Teteryl.

Explosives; ignition zone; laser; mass spectrometry; pyrolysis; RDX.

### INTRODUCTION

The thermal decomposition of high explosives (HEs) has been successfully studied using many methods. The most common one is mass spectro-

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scopic detection of the decomposition products, combined with different methods for inducing thermal decomposition, such as infrared multi-photon absorption in molecular beams [1], heating in high vacuum [2], slow pyrolysis [3], laser-induced decomposition of crystals [4], and atmospheric pressure chemical ionization [5]. Other methods which have been used successfully include FT-IR spectroscopy [6], measurements of the kinetic isotope effect by DSC [7], emission spectroscopy [8], and X-ray photoelectron spectroscopy [9]. These methods have primarily been used to study the thermal decomposition itself, and then mainly the initial step of the decomposition, not the processes that lead to a self-sustained ignition. Very little work has been devoted to the study of processes in the pre-ignition/ignition zone [8,10,11].

All high explosives have an endothermic initial step (they are stable at room temperature), but for the development of a self-sustained reaction transfer to a set of exothermic reactions has to take place. This leads to the necessity of developing methods with which all processes from a slow decomposition to the ignition of a self-sustained reaction can be studied. Earlier work on laser ignition has shown it to be a very useful method for studying the influence of different parameters on the ignition of a pyrotechnic mixture [12,13]. This method applied to HEs has shown that the ignition energy is highly pressure dependent [12,14]. Similar results have been demonstrated for propellants [15] and pyrotechnics [16]. Results of the laser initiation of detonations in PETN have shown a strong gas-phase influence [17]. This indicates that the ignition process is a multi-phase process. Present work shows how mass spectroscopy (MS) combined with the laser ignition (LI) method can be used to study the pre-ignition/ignition reaction zone, and how it is possible to monitor changes in product formation in the transition from slow thermal decomposition to a self-sustained deflagration. The LI/MS method alone cannot give a very detailed description, due to its limited time and spatial resolution. The method will, however, with relative ease give some of the molecules and/or molecular fragments that are involved in the ignition processes. These can then be studied with other spectroscopic methods with better time and spatial resolution, e.g. laser Raman spectroscopy [10,18], LIF [19], or CARS spectroscopy [11]. The combined LI/MS method will also give a clue to the ignition process on a molecular level, due to the fact that it allows the study of how the concentration of certain molecules varies with different parameters (e.g. gas pressure, type of gas, laser wavelength, pulse width and laser power). In earlier laser ignition work [14] it has been shown that the ignition energy of a high explosive has two pressure regimes: one at low pressure, where the ignition energy strongly depends on the pressure, and one at high pressures (above 3 MPa), where the ignition is only slightly pressure dependent. This clearly demonstrates the necessity of being able to study the ignition processes at pressures of up to at least 4 MPa. At the same time, it was shown that

the ignition energy was different in air compared with in nitrogen, which shows the necessity of developing a method where different gases may be used at ambient and increased pressures. The explanation proposed for this behaviour was that a multi-phase ignition takes place where both the gas and condensed phases have to interact in order to start a self-sustained reaction. This was the starting point for developing the LI/MS method for measurements in the decomposition/deflagration zone. In the experimental section the LI/MS method is described in detail. After that follows a study of the pyrolysis/ignition products of RDX. In order to show the general applicability of the method some measurements were also conducted on other high explosives: HNS, PETN, TNT and Tetryl. This is followed by a discussion of the method.

## EXPERIMENTAL

The laser ignition method, fully described in earlier work [12–14], was primarily developed for ignition studies on pyrotechnical mixtures [12,13] but has been shown to be equally useful for studying high explosive ignition [12,14]. The experimental setup for the combined method of LI/MS is shown in Fig. 1. It consists mainly of a 180 W tunable continuous wave CO<sub>2</sub> laser (Edinburgh PL6), a mass spectrometer (JEOL 300D or Finnigan 1020), an explosive chamber, a laser power/energy meter, a photo detector, a digital oscilloscope and a deactivated fused silica capillary column. The useful pressure range for the explosive chamber is 0.1–10 MPa. The mass spectrometer was equipped with a PC-based program (Teqnivent Vector/2)

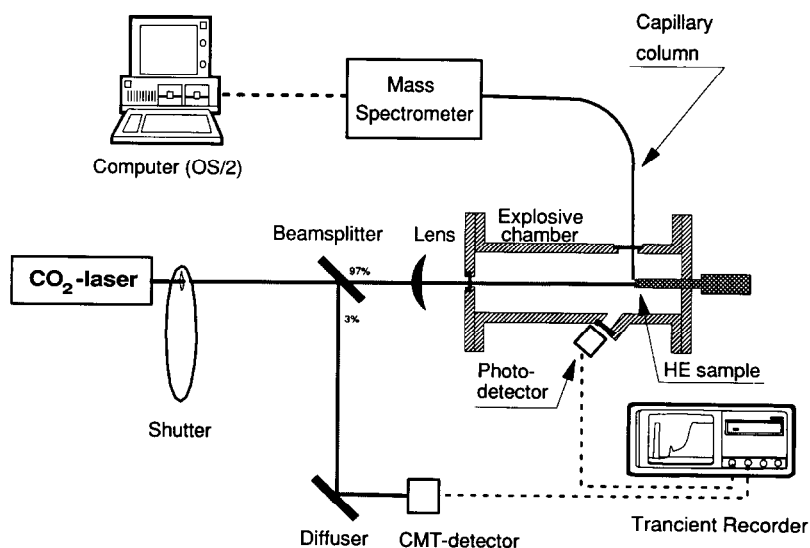


Fig. 1. Laser ignition/mass spectrometer setup.

for analysing the data. The samples were prepared by pressing about 300 mg of HE to a pellet with a diameter of 10 mm and a thickness of 2 mm. The density of the sample was 95% of the theoretical maximum density (TMD). The HE used was purified by several recrystallizations. The pellet was glued on to a sample holder in the explosive chamber. The beam from the laser was chopped to the desired pulse width either with a mechanical shutter or by electrically pulsing the laser. A beamsplitter then divided the laser beam into two parts; one part (3%) was for measuring the laser power with a cadmium mercury tellurid detector (CMT-detector), while the main part was focused by a zinc selenide lens through a window onto the explosive sample, hereby starting the desired reaction. The explosive chamber was interfaced to the mass spectrometer by means of a capillary column fixed in position by a capillary feed-through. Mass data was collected during and after the laser pulse. The position of the capillary column in the reaction zone is shown in Fig. 2. The sample holder was rotated for each laser pulse so that unreacted explosive was exposed to the laser beam. The position of the capillary column in the reaction zone had a large influence on the result. If the capillary was slightly misaligned the number of counts decreased rapidly and the distribution of counts between the different mass peaks changed. During experiments where self-sustained deflagration occurred, it proved necessary to move the capillary to a distance of approximately 2 mm away from the focus and the sample surface, as otherwise the capillary melted. This problem can alternatively be solved by using a steel sleeve on the capillary column. The capillary column used in the experiments was a deactivated (and thereby “nearly” chemically inert) fused silica capillary, with lengths varying in the range 1–30 m and an inner diameter of 0.1–0.35 mm. The use of a capillary column enabled us to use pressures of up to 2.5 MPa in the explosive chamber and, thus, to study the influence of pressure on the chemical reaction. In order to increase the highest usable pressure up to 5.0 MPa we used a Jet separator between the capillary column and the mass spectrometer (only possible with the JEOL 300D).

In order to get a deeper understanding of processes taking part in the laser pyrolysis/ignition experiment it is critical to know the amount of

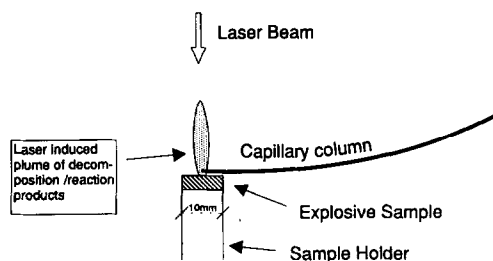


Fig. 2. Position of the capillary column in the decomposition zone.

CO<sub>2</sub>-laser energy actually absorbed by the sample and the depth of absorption. With a knowledge of the values of the reflection ( $R$ ) and absorption ( $\alpha$ ) coefficients, the interaction mechanism between the laser beam and the sample, and the influence of a possible gas phase, it is also possible to calculate the temperature in the sample as a function of time. The laser power ( $P_{\text{tot}}$ ) given in this paper should be corrected with the reflection coefficient ( $P_{\text{abs}} = (1 - R)P_{\text{tot}}$  with  $R = 0.71$  for RDX [20]) in order to get the absorbed power. In refs. 21 and 13, methods for measuring the absorption coefficient and the reflection coefficient are found. If the internal reaction energy release [21] is neglected, and assuming that no absorption of the laser beam in the vapour phase occurs, the maximum temperature ( $T_{\text{max}}$ ) and the maximum heating rate ( $H_{\text{max}}$ ) can be calculated as [21]

$$T_{\text{max}} = T_0 + \alpha I_0 \tau_p / \rho C_p = T_0 + \alpha (1 - R) P_{\text{tot}} \tau_p / \rho C_p \pi \omega^2$$

$$H_{\text{max}} = \left( \frac{\partial T}{\partial t} \right)_{\text{max}} = \alpha (1 - R) P_{\text{tot}} / \rho C_p \pi \omega^2$$

Here  $\omega$  is the beam radius and  $\tau_p$  the pulse width of the laser. By tuning the laser to a different wavelength it is possible to study the influence of the HE's IR absorption on the ignition processes [21].

## RESULTS

This paper concentrates on RDX studies, as the decomposition of RDX is fairly well known through numerous earlier studies [1–7,22,23], facilitating the data analysis and creating a background against which to test the applicability of our method and one of easier analysis of the MS data acquired in the pre-ignition/ignition reaction zone. None of these earlier studies are, however, conclusive, but the most modern one [1] shows that the decomposition of RDX can follow at least two different reaction channels. In order to test the general applicability of the method the following HEs were also studied, but to a lesser extent: HMX, Tetryl, PETN, TNT and HNS.

By varying the laser power it was possible to control the magnitude of reaction in each shot ranging from a weak decomposition to a self-sustaining reaction. The degree of reaction was measured with the photo detector shown in Fig. 1. For a weak decomposition no light was emitted from the reaction. In Fig. 3 is shown an example of a registration of one laser shot where a self-sustained reaction occurred, in which a pre-ignition reaction zone is clearly seen and, later, the ignition zone. For shots with laser power above that necessary to achieve a weak thermal decomposition and below the power necessary to achieve a self-sustained ignition, light emitted from

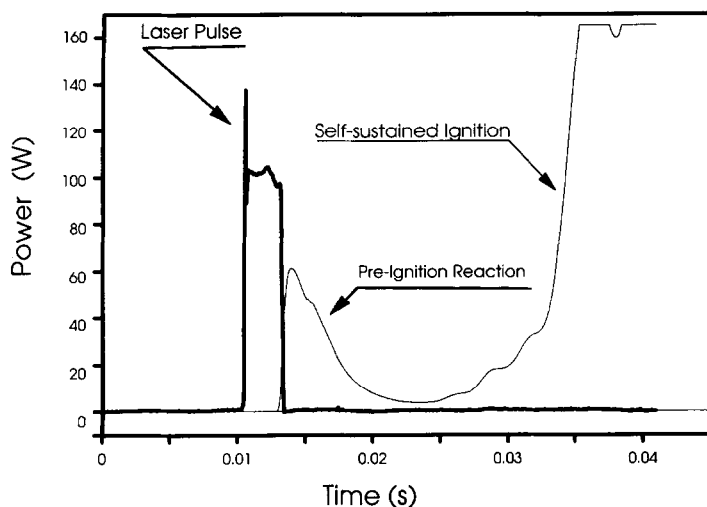


Fig. 3. Example of registration of the CMT- and photo-detector signals during an experiment.

a pre-ignition reaction zone could be observed, but this light was weaker than the one emitted at ignition.

A large number of experiments were conducted using the procedure outlined in the experimental section. As the method produces a large amount of data, only a selection of the most productive data is presented and interpreted in this paper. Most of the experiments were carried out in a helium atmosphere, and unless another gas is specifically stated below the gas used is helium. It is also possible to use air or nitrogen, but the use of helium minimizes the background in the mass spectrometer and increases the lifetime of some of the intermediates. Figure 4 shows a typical reconstructed ion chromatogram (RIC) from the pre-ignition reaction zone of RDX and the measurement conditions for acquiring this RIC. In this case two peaks may be seen, but anything from one to five peaks have been found, depending on the HE and the measurement conditions.

By plotting the intensities of some of the most interesting time-resolved masses, see Fig. 5 (same shot as in Fig. 4), some interesting observations can be made. Peak group one consists of at least two different peaks. In this case it is proved to be due to different retention times in the column. Peak group two consists mainly of the two mass peaks:  $m/z$  42 and  $m/z$  46. Bradley et al. [3] have pointed out that one of the gas-phase decomposition paths of RDX gives rise to the mass peaks  $m/z$  42, 46, 56, 75, probably derived from a molecule with  $m/z$  88, namely  $C_2H_4N_2O_2$  (with three isomeric forms, namely  $CH_2=CH-NH-NO_2$ ,  $(CH_2)_2N-NO_2$  and  $CH_3-CH=N-NO_2$ ). This leads to the conclusion that one of the possible origins of this second peak group is from an RDX decomposition in the gas phase as a ring-opening process [3]. The mass peak  $m/z$  81 (the origin of which was determined by

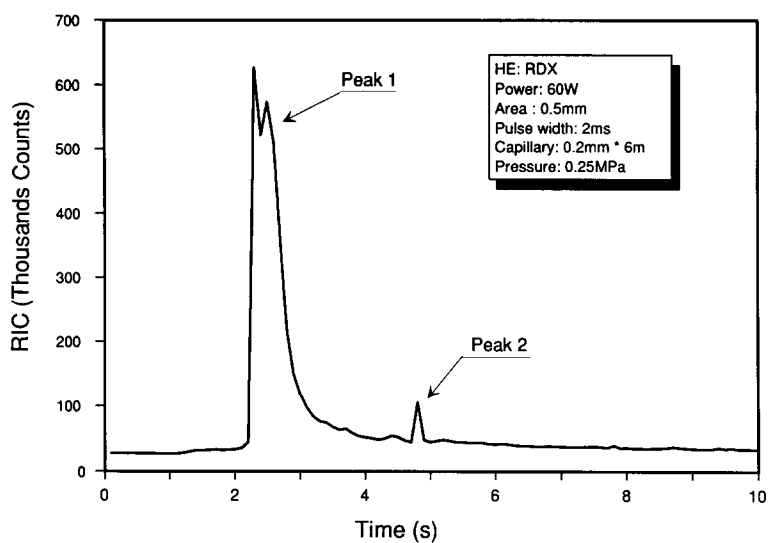


Fig. 4. RIC spectrum for RDX (pre-ignition reaction).

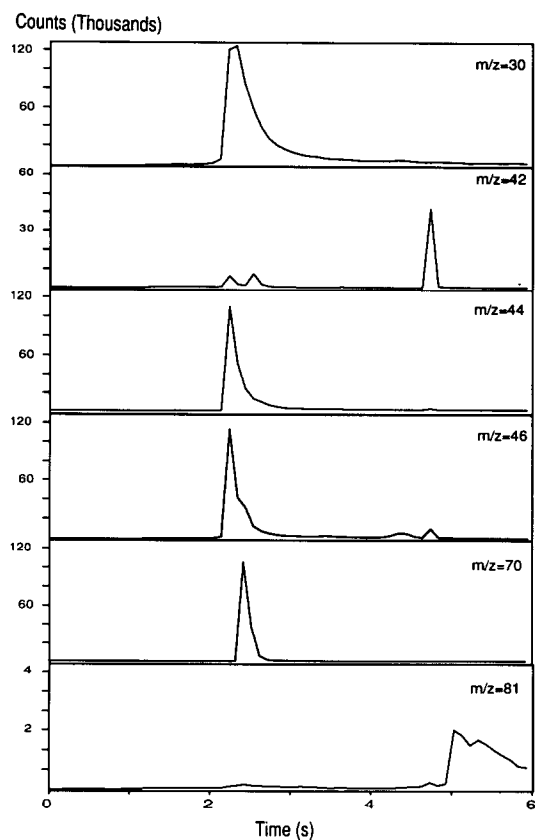


Fig. 5. Time-resolved mass spectra for RDX decomposition (selected masses).

the simultaneous occurrence of mass peak  $m/z$  54) could be identified as 1,3,5-triazine. The formation of triazine implies that the reaction to some extent occurs in the solid phase [3,5] (as a loss of side groups with the ring remaining intact).

Table 1 is a compilation of the total collected information on products in the pre-ignition reaction zone of RDX. The total data volume is 75 Mb. The table is divided into four parts: mass number ( $m/z$ ), possible assignment, strength (on a scale from 1 to 4, where 1 is very strong and 4 is just above the background), and comments. Substances that could be identified are shown with the masses they were identified by as one row. Observe

TABLE 1

Products in the pre-ignition reaction zone for RDX

$m/z$	Assignment	Strength	Comments
17/18	H <sub>2</sub> O	1	
26	CN	1	
26/27	HCN	1	See Fig. 6
28	N <sub>2</sub> , CO		
29/30	H <sub>2</sub> CO	1–3	Increases strongly with laser energy!
30	(NO)	1	Arises mainly from NO + NO <sub>2</sub> + N <sub>2</sub> O + H <sub>2</sub> CO
31		3	
40		2	
41		2	
42	N(CH <sub>2</sub> )N, (CH <sub>2</sub> ) <sub>2</sub> N	2	Ring fragments
42/46	(CH <sub>2</sub> ) <sub>2</sub> NNO <sub>2</sub>	2	Indicates ring opening in gas phase! [3]
43	NCOH or OCHN(?)	1	
44	N <sub>2</sub> O, CO <sub>2</sub>	1	
46	NO <sub>2</sub>	1	
52	N <sub>2</sub> C <sub>2</sub>	2	
54/81	C <sub>3</sub> N <sub>3</sub> H <sub>3</sub> (1,3,5-triazine)	3	Solid-phase decomposition reaction [5]
61/60/46/45	CH <sub>3</sub> NO <sub>2</sub> (nitromethane)	2	
61	?	3	
64/91/119	C <sub>6</sub> H <sub>5</sub> N <sub>3</sub> (?) (azidobenzene)	4	Occurs only at pressures above 0.5 MPa
70	Oxadiazole	1	Highest mass having an intense peak, see Fig. 7
76		3	
91		4	
95		4	



particularly the strong peak with  $m/z$  70, which could be identified as oxadiazole [24]. Different approaches were used in order to assign the detected mass peaks to different molecules. By varying the column length, some of the molecules could be separated by their different retention times. We are mainly interested in shortening the column, in order to detect some of the relatively short-lived molecules. Increasing the length of the capillary led to a decrease in the number of peaks, which means that this is only useful for identifying relatively stable molecules. For the main decomposition products ( $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{NO}_2$ ,  $\text{HCN}$ ,  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$ ) we used the fragmentation pattern of the molecules, which is caused by ionization in the mass spectrometer, to identify these [25]. Of these, it is possible to identify  $\text{NO}_2$ ,  $\text{HCN}$  and  $\text{H}_2\text{CO}$  more easily than the others. In some cases a change in the ionization voltage improved the possibility of identifying the reaction products. The  $m/z$  43 which, as can be seen in Table 1, is a very large peak, is not commented on in earlier RDX decomposition work. This peak could arise for several different molecules, namely hydrazoic acid ( $\text{N}_3\text{H}$ ), aziridine ( $\text{C}_2\text{H}_5\text{N}$ ),  $\text{HOCN}$ ,  $\text{OCNH}$  or from a fragment of a larger molecule. By comparison with the fragmentation pattern in ref. 25, hydrazoic acid and aziridine could be eliminated, along with any larger molecules. Thus, the peak is probably  $\text{HOCN}$ , which is the more stable of the two remaining possibilities. The  $m/z$  52 mass peak is probably ethanedinitrile ( $\text{CN})_2$ .

In order to study the influence of different parameters on the progress of the ignition, some parametric studies were conducted. By varying the laser power and recording the variation in intensity of the mass peaks of the decomposition products, it was possible to study the change in products from decomposition to a self-sustained deflagration. In Fig. 6 the peak intensity for selected mass peaks is shown as a function of laser power. The power level necessary to achieve a self-sustaining ignition is about 175 W.

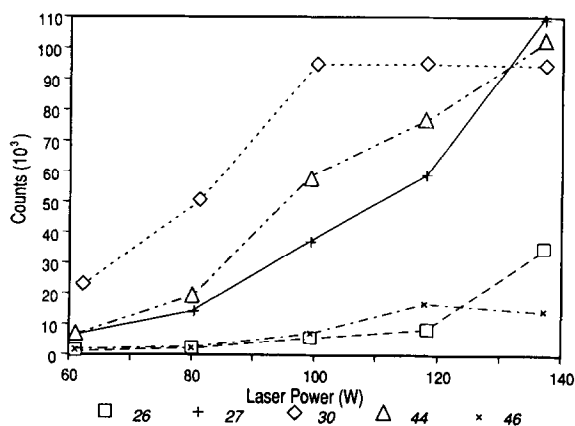


Fig. 6. Peak intensity as a function of laser power for selected masses: ( $\square$ )  $m/z$  = 26; ( $+$ )  $m/z$  = 27; ( $\diamond$ )  $m/z$  = 30; ( $\triangle$ )  $m/z$  = 44; ( $\times$ )  $m/z$  = 46.

Some interesting conclusions can be drawn from this Figure. The  $m/z$  30, which could arise from any or all of  $\text{NO}_2$ ,  $\text{NO}$  or  $\text{N}_2\text{O}$  (no  $m/z$  29, so it is not  $\text{H}_2\text{CO}$ ), increases approximately linearly for powers of up to 80–90 W and is the main product (of the molecules detectable with this column length) over the interval. Above this power level increasing amounts of  $\text{HCN}$  ( $m/z$  26 and 27) and  $\text{CO}_2$  ( $m/z$  44, and no increase in  $m/z$  30 so it is probably not  $\text{N}_2\text{O}$ ) are generated. Along with data shown in the Figure, one interesting observation was made: the concentration of  $\text{H}_2\text{CO}$  (determined by  $m/z$  29 [25]) is very low ( $\approx 1000$  counts) at power levels below 100 W, but increases strongly at power levels above this up to 50 000 counts. Rauch and Fanelli [22] have shown that  $\text{NO}_2$  is mainly derived from a gas-phase decomposition, and that  $\text{H}_2\text{CO}$  and  $\text{N}_2\text{O}$  arise from a liquid-phase decomposition. From this, from the data in Fig. 6, and from the observation that the amount of  $\text{H}_2\text{CO}$  increases and the amount of  $\text{NO}_2$  decreases as the laser pulse width (or possibly the energy) increases, we can draw the conclusion that the ignition of RDX is a multi-phase reaction. The gradual transition of the reaction from the gas phase to condensed phase, indicated by the increase in  $\text{H}_2\text{CO}$  and the decrease in  $\text{NO}_2$  as the laser pulse width (or possibly the energy) increases, together with the facts stated above, tells us that the gas-phase reactions play an important part in the ignition process, at least at pressures below 2 MPa, e.g. there is a transfer of reaction type as we approach ignition. Using the results of Zhao et al. [1] this can alternatively be explained as decomposition following a different reaction channel. These two interpretations do not necessarily exclude each other. One alternative interpretation would be that as ignition is approached, the  $\text{NO}_2$  is converted more rapidly to other products. To distinguish between these two explanations a method with better time resolution must be used. It is also necessary to examine these reactions at pressures above 3 MPa, where a break in the curve for ignition energy occurs [14], in order to gain a more complete understanding of the processes involved. The switch from the normal wavelength of the laser, 10.59  $\mu\text{m}$ , to 10.15  $\mu\text{m}$  shows two interesting characteristics: an almost 50% reduction in the  $m/z$  44 peak and an increase in the  $m/z$  27 peak of up to 30%.

In Fig. 7 the time delay for mass peak  $m/z$  70 (i.e. time between the first peak,  $m/z$  28, and peak  $m/z$  70) is shown as a function of the laser pulse width. The peak for  $m/z$  28 is chosen as reference as it arises from nitrogen, which can be assumed to have zero retention time and is probably produced in early decomposition, at least to some extent ( $m/z$  28 was always detected as the first peak). These measurements were made under otherwise constant conditions, which implies that we have here a time-dependent process producing the fragment with  $m/z$  70. The time is of an order of magnitude (seconds) that could only arise from a condensed-phase reaction. The  $m/z$  70 peak is probably an oxadiazole [24].

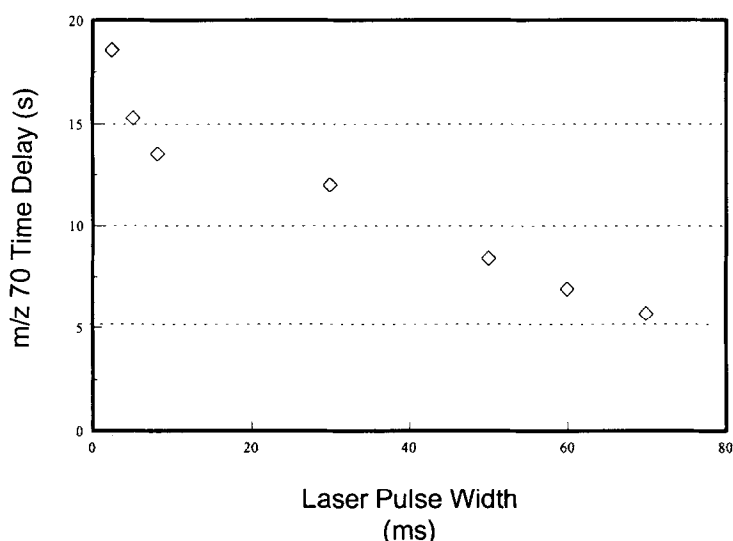


Fig. 7. Time delay for mass peak 70 vs. laser pulse width.

In the case where self-sustained ignition occurred, most of the information was hidden by the large amount of deflagration products formed, namely  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ; however,  $\text{N}_2\text{O}$ , HCN and a small amount of  $\text{H}_2\text{CO}$  could be identified in the ignition reaction zone in addition to the main decomposition products. The  $\text{H}_2\text{CO}$  concentration was fairly constant, about 1%, and did not seem to take part in any reactions. Both  $\text{N}_2\text{O}$  and HCN disappear, so they must be taking part in subsequent reactions. This is, surprisingly, not the case for  $\text{H}_2\text{CO}$ . Two peaks in the reaction zone remain unidentified, namely  $m/z$  27 (no  $m/z$  26, so it is not HCN) and  $m/z$  43. In order to conduct the measurements where a self-sustained ignition occurred (in He) a high-pressure level (1.8 MPa) has to be used and, consequently, a very long column (30 m), which naturally influenced the result in that only stable products could be detected, because of the long transition time in the column.

In order to show the general applicability of the method we present some LI/MS spectra for Tetryl and HNS. Figure 8 shows the time-resolved mass spectra for some of the most interesting masses in the pre-ignition reaction zone of Tetryl and the mass spectra for peaks 1 and 4. In these spectra one can distinguish at least five peaks. The spectra are interpreted as follows. The first peak is for the main decomposition products which consist of relatively small molecules with short retention times. The second to fifth peaks are for larger molecules with longer retention times (and not from slow processes in the reaction zone). These molecules are probably the most important ones as they can tell us which is the first step of the reaction. The decomposition of HNS gave rise to only two detectable peaks in the time-resolved spectra (Fig. 9) and very few mass peaks (namely  $m/z$  28, 30 and 44) in the first

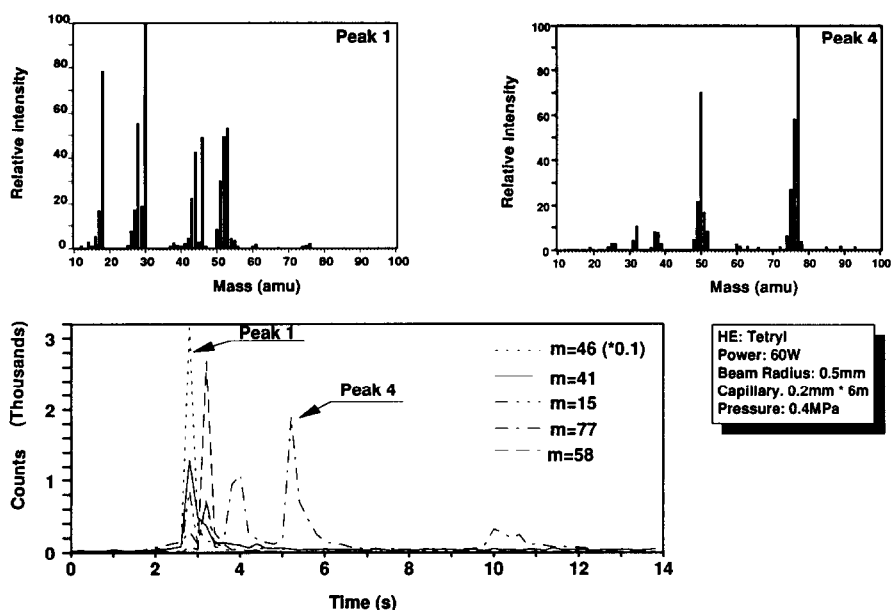


Fig. 8. Time resolved mass spectra for decomposition of Tetryl. Selected masses and complete mass spectra for peaks 1 and 4.

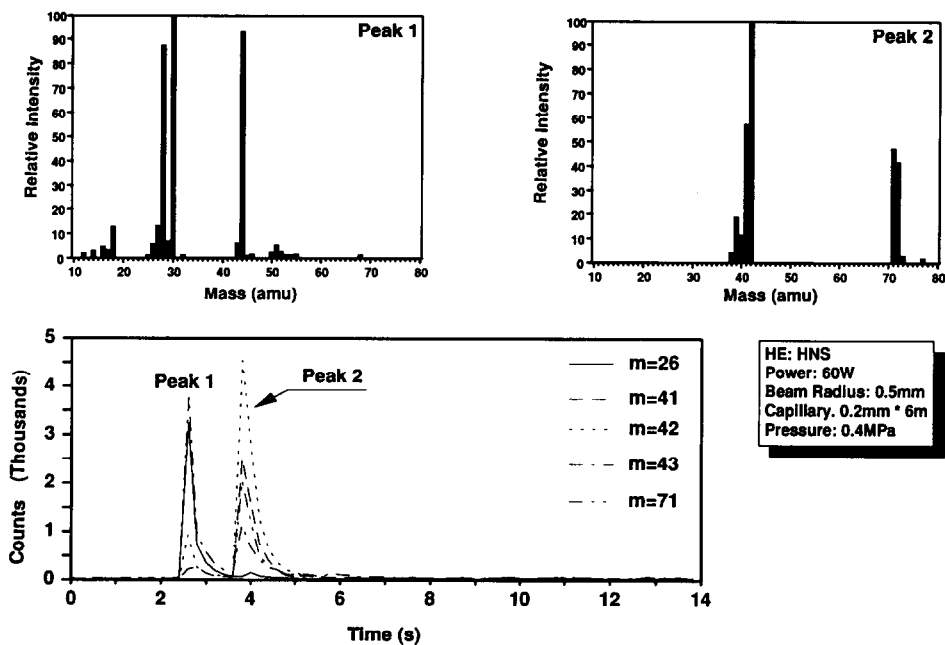


Fig. 9. Time resolved mass spectra for decomposition of HNS. Selected masses and complete mass spectra for peaks 1 and 2.

peak (main decomposition products). Mass spectra for the two peaks are also shown in Fig. 9. The decomposition of PETN gave rise to three peaks in the time-resolved spectra for the same set of parameters. In the pre-ignition reaction zone of TNT a lot of gas-phase TNT could be observed in conjunction with the main decomposition products. The spectra for HMX were very like those for RDX with one notable difference: a large mass peak at  $m/z$  26 (CN?) was found which could not arise from HCN (no mass peak at  $m/z$  27).

## DISCUSSION

The laser ignition method itself offers a route to a purely thermal start of a reaction, thereby getting rid of any mechanical and chemical disturbance of the reaction and measurement of the processes. This does not, however, mean that the ignition process is the same for a laser ignition as, for instance, for an ignition occurring in a fire; however, they are probably very closely related, so that one can use the results obtained with this method to draw conclusions which are valid at least for cases with the same time scale (1 ms–1 s), i.e. all thermal ignition in practice. The laser ignition method combined with a mass spectroscopic detection of reaction products/intermediates gives advantages over the pyrolysis–MS studies in other work (e.g. refs. 2–5), because it enables the control of the degree of reaction induced by the laser from a slow thermal decomposition to a self-sustained ignition. Thus, we can get a better understanding of the ignition process and may also be able to model it better. One other large advantage is that one can use an unmodified standard mass spectrometer for the measurements. The method alone cannot reveal the whole truth about the ignition processes, but it can give some clues to it. In particular, it gives, in a relatively easy way, some of the molecule fragments involved in the ignition process. These may then be studied with other techniques, e.g. laser spectroscopic methods, with better time and spatial resolution. The molecule fragments must have a lifetime greater than the transition time in the capillary in order to be detected. The most interesting results were obtained with the shortest column; most mass peaks were detected here. However, in order to start a self-sustained reaction a very long column was necessary, because of the need for high initial pressures.

The combined LI/MS method has some drawbacks, which also affect the results and conclusions of this work. The time resolution is limited (10–100 ms in this paper) and so is the mass number resolution (1 u here). Both of these factors could preferably be improved upon. We have also had difficulties in separating the delay of the occurrence of molecules in the reaction zone from the delay caused by the retention time of the capillary. Other difficulties involve the separation of the fragmentation incurred by the

decomposition process from the fragmentation taking place in the mass spectrometer. This uncertainty could be minimized either by using chemical ionization or by varying the ionization voltage (15–70 eV). Finally, the positioning of the capillary in the reaction zone is of great importance for quantitative measurements, and because of this the results presented in this paper should only be regarded as qualitative. The problem with a correct placement of the capillary in the reaction zone, which is probably the largest error source in our measurements, is in the process of being solved by positioning the end of the capillary with two micro translators placed in the explosive chamber, but operated from the outside.

The mass spectrometer has a maximum sweep speed of  $1200 \text{ u s}^{-1}$ , which makes it possible to obtain only real time measurements of the slow processes taking place at ignition. The real time measurements are to some extent corrupted by two facts: (i) even a chemically deactivated column has different retention times for some molecules; (ii) the molecule fragments must have a lifetime greater than the transition time in the capillary in order to be detected. The most interesting results were obtained with the shortest column; most mass peaks were detected here. The time resolution when acquiring full scans (100–200 u) is 0.1 s. By using the technique of selective ion monitoring it was possible to get down to a time resolution of below 10 ms.

Some of the molecules, especially  $\text{NO}_2$ , are absorbed very strongly by the GC columns. Because of this it is difficult to make any quantitative measurements of the decomposition products. However, this was not our aim. We sought to obtain a method to detect the molecules or molecule fragments occurring in the pre-ignition/ignition zone and to study the influence of pressure, laser pulse width, and laser power on the ignition process. The main reason for having a long capillary column was to reduce the pressure in the MS.

## CONCLUSIONS

The main conclusion of this paper concerns the method of combining laser ignition with mass spectroscopy (LI/MS) for studying the pre-ignition/ignition zone of explosives. This method has some distinct advantages over the earlier used method [2–5]. One advantage is the possibility of varying the laser power and the laser pulse width acting on the HE and thereby controlling the degree of reaction ranging from a very weak decomposition to a self-sustained deflagration. The other main advantage of using a capillary column before the mass spectrometer is that it becomes possible to study the ignition process at a pressure relevant to normal ignition conditions (0.1–5 MPa). Other findings can be summarized as follows.

(i) We have found that the LI/MS method is useful for parametric studies of the ignition process.

(ii) It is possible to detect and record mass spectra for large molecules or molecule fragments found in the pre-ignition reaction zones of RDX, HMX, Tetryl, HNS, and PETN.

(iii) The LI/MS method applied to the ignition of RDX has given the following interesting results about the ignition zone.

- (a) HCN and H<sub>2</sub>CO play important parts in the ignition process of RDX. The relative amounts of these molecules increase and the relative amount of NO<sub>2</sub> decreases with increasing energy/power.
- (b) The ignition of RDX is a multi-phase reaction (gas phase and condensed phases). All phases have to be considered in any attempt to model the ignition and the importance of the condensed phase increases as ignition is approached.
- (c) A molecule that gives rise to a mass peak  $m/z$  70 (possibly an oxadiazole) is formed in the condensed phase.
- (d) Some new reaction intermediates were identified in the pre-ignition reaction zone: triazine (C<sub>3</sub>N<sub>3</sub>H<sub>3</sub>), possibly ethanedinitrile (CN)<sub>2</sub> and HOCN.

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