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Non-contact detection of explosives by means of a tunable diode laser spectroscopy

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ABSTRACT As explosives are unstable, their decay products may be targeted for detection by means of tunable diode laser spectroscopy (TDLS). A model in which an explosive is placed inside an envelope with a hole in it has been studied. It has been shown that outside the envelope the concentration of the decay products may exceed that of the vapors of an explosive, by several orders.

Decay products of explosives have been investigated using Fourier-transform spectrometry and TDLS. The following decay products have been identified: NO, N₂O, CO, NH₃. Analysis of the temperature dependencies of their occurrence rates has allowed estimation of the activation energies, which appear to be close to 1 eV.

An experimental model of the diode laser spectrometer designed for noncontact detection of explosives has been developed. The possibility of such detection has been demonstrated experimentally.

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1 Introduction

Up until recent years the detection of explosives has mostly relied on the use of specially trained dogs. At present other techniques are available [1, 2] (and references therein), however, detection of explosives still requires further investigation. The most complicated scientific and technical task appears to be the development of non-contact detection methods. Such detection, and in particular in real time, is required in definite conditions, such as examination of complex structures probably containing a bomb (storehouses, industrial and residential buildings, offices, airports etc.). In such conditions it is not reasonable and, moreover, it is dangerous to directly approach a suspicious object, which therefore gives rise to a problem of not only non-contact but also remote detection (from the distance of 1–10 m). The most sensitive and commonly used techniques for explosives detection, is ion mobility spectroscopy and gas-chromatography but these cannot be applied effectively during search operations.

In this paper the possibility of solving the problem of non-contact and remote explosive detection by means of TDLS is analyzed and demonstrated. The TDLS technique is already currently used in many cases when it is required to detect trace amounts of gaseous substances in the atmosphere and other gas media.

2 Choice of markers

When analyzing the possibilities of TDLS relative to the task discussed, of principle importance is the choice of markers, i.e. gaseous substances released by explosives in the atmosphere – indicators of their presence. These markers may be both vapors of explosives themselves and products of their spontaneous decay. In physical terms, the spontaneous decay of explosives is caused by exothermicity of the process. The probability of decay, however, is low due to a relatively high level of activation energy. The half-life time of explosives generally lasts for tens of years.

Detection of products of spontaneous decay is a preferable task for several reasons. Firstly, as concerns diode laser spectroscopy, it should be mentioned that the most suitable objects to be detected are simple molecules containing approximately from two to five atoms and having relatively narrow absorption lines. Spectra of more bulky molecules of explosives contain only absorption bands with a bandwidth much broader than the spectral range of diode laser tuning [3]. Secondly, decay products can form a cloud with much higher concentration of particles in the vicinity of the explosive. The cause of this phenomenon becomes clear via analyzing the model in which an explosive is placed in an unsealed envelope (Fig. 1). The latter condition is of the most practical interest.

Let us estimate the flow of gaseous molecules of an explosive through the hole in the envelope.

In Fig. 1a large arrows schematically show evaporation and condensation processes. The flow of molecules ΔG through the hole in the envelope is the difference between the flows of evaporating (G_0) and condensing (G) particles. On the other side, flow ΔG results from diffusion of molecules through the hole in the envelope and can be calculated using the formula:

$$\Delta G = \pi D d N_0, \quad (1)$$

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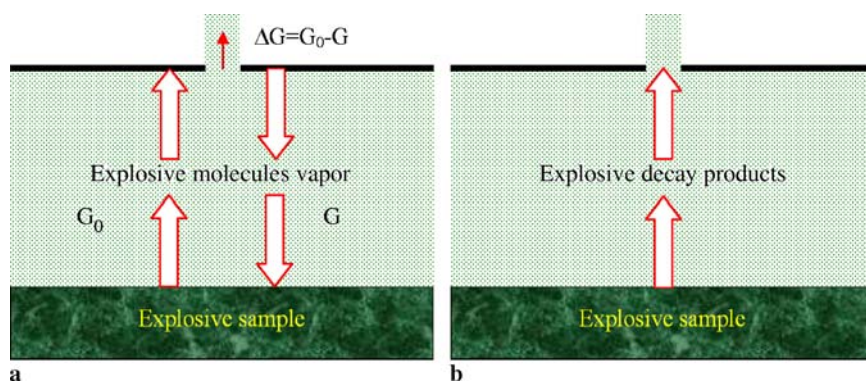


FIGURE 1 Model of particle flow through the hole in the envelope formed round the explosive: (a) for the flow of vapors of the explosive, (b) for the products of its spontaneous decay

where N_0 is the concentration of gaseous particles of an explosive, d is the diameter of the hole, and D is the diffusion coefficient.

We do not know experimental values of diffusion coefficients for molecules of explosives in the air, however, reasonable values for such bulky and heavy molecules are supposed to be $D \sim 0.01 \text{ cm}^2\text{s}^{-1}$.

Let us consider the most favorable case when the pressure of saturated vapors of an explosive is achieved in the air inside of the envelope. Then for such an explosive as trinitrotoluene (TNT) which has a concentration of saturated vapors at a room temperature equal to $N_0 = 3.2 \times 10^{11} \text{ molecules/cm}^3$ (13 ppb [4]) we can determine $\Delta G \approx 10^9 \dots 10^{10} \text{ molecules/s}$ provided that the diameter of the hole $d = 0.1 \dots 1 \text{ cm}$. At large hole diameters an increase in the flow of molecules would not be proportional to the diameter since in this case the pressure of saturated vapors could not be achieved in the vicinity of the hole inside the envelope. It should be noted that for other explosives of practical interest the pressure of saturated vapors appears to be even much lower than for TNT [1].

Now we consider the outflow of hypothetical decay products through the same hole. Assuming that the processes of their condensation (sorption) on an initial substance and on the envelope do not play a significant role (Fig. 1b). Then the concentration of decay products in the air inside the envelope will increase gradually until the flow of molecules through the hole is equal to that emanating from an explosive. In this case the flow through the hole will be independent of its diameter.

The results of our experimental studies on the products of spontaneous decay of explosives will be presented in the next section of this paper. Here we just note that for TNT there was a release of NO at a rate $W = 4 \times 10^9 \text{ molecules/g s}$ at room temperature. In the case of a sample with a mass $M = 1 \text{ kg}$ $\Delta G = G_0 = MW = 4 \times 10^{12} \text{ molecules/s}$. Thus, it should be expected that the concentration of NO in the vicinity of an explosive device based on TNT with a mass $> 1 \text{ kg}$ will be by several orders of magnitude higher than the concentration of TNT vapors.

3 Experimental studies on products of the spontaneous decay of explosives

Experiments involving detection and identification of products of spontaneous decay were conducted using Fourier-transform spectrometry. The vacuum Fourier-spectrometer IFS-66v/S (Bruker) with a multipass optical

cell was used. Samples of explosives with a mass from some tenths of gram to 100 g were placed in a sealed stainless steel vessel with a volume of 300 cm^3 . The vessel was equipped with a vacuum valve and connected to the multipass cell via a system designed for gas evacuation and leak-in. The optical path length in the cell was 4 m.

The vessel containing the sample of the explosive was evacuated down to a residual pressure of 0.1 Torr and then filled with pure nitrogen to a pressure of 1 atm. Then decay products were accumulated. The accumulation time at room temperature varied from several to tens of hours depending on the type and mass of the explosive. In some experiments the vessel containing the explosive sample was placed in a water thermostat which was held in the range $55\text{--}90^\circ\text{C}$. As a result, the rate of decay was increased while the accumulation time of decay products decreased significantly. The gaseous mixture that formed in the vessel was placed in the cell and an absorption spectrum from 3500 to 700 cm^{-1} at a resolution of 0.25 cm^{-1} was acquired. Figure 2 gives an example of the fragment of the spectrum with the marked decay products of plastic explosives containing 85% of RDX {1,3,5-trinitro-1,3,5-triazacyclohexane}. Along with the spectra of the substances marked, this fragment contains lines belonging to that of water which is of no interest in this case.

The decay products were analyzed for several types of pure explosives which contained NO_2 groups: TNT {2-methyl-1,3,5-trinitrobenzene}, Tetryl {2,4,6-trinitrophenyl-*N*-methylnitramine}, NG {nitroglycerin; propane-1,2,3-triyl trinitrate}, RDX {1,3,5-trinitro-1,3,5-triazacyclohexane}, HMX {1,3,5,7-tetranitro-1,3,5,7-tetrazocane}. All the above mentioned substances were characterized by the formation of nitrogen oxides either NO or N_2O ; for TNT – it was NO, for Tetryl, NG and RDX – both NO and N_2O and for HMX – only N_2O . The studies were performed not only on pure explosives, but also on two types of plastic explosives based (by $\sim 85\%$) on RDX and PETN {1,3-dinitrato-2,2-bis (nitratomethyl)propane}. Spectra of the decay products of these substances contained not only the lines attributed to nitrogen oxides, but also to those of CO. The latter probably resulted from the interaction of nitrogen oxides with the components of the binding material.

Spectra processing using the HITRAN spectral database [5] was used to obtain the values of the rates of the observed decay products formation. Figure 3 gives the values of the rates of NO formation depending on temperature. In terms of safety, these series of experiments were conducted

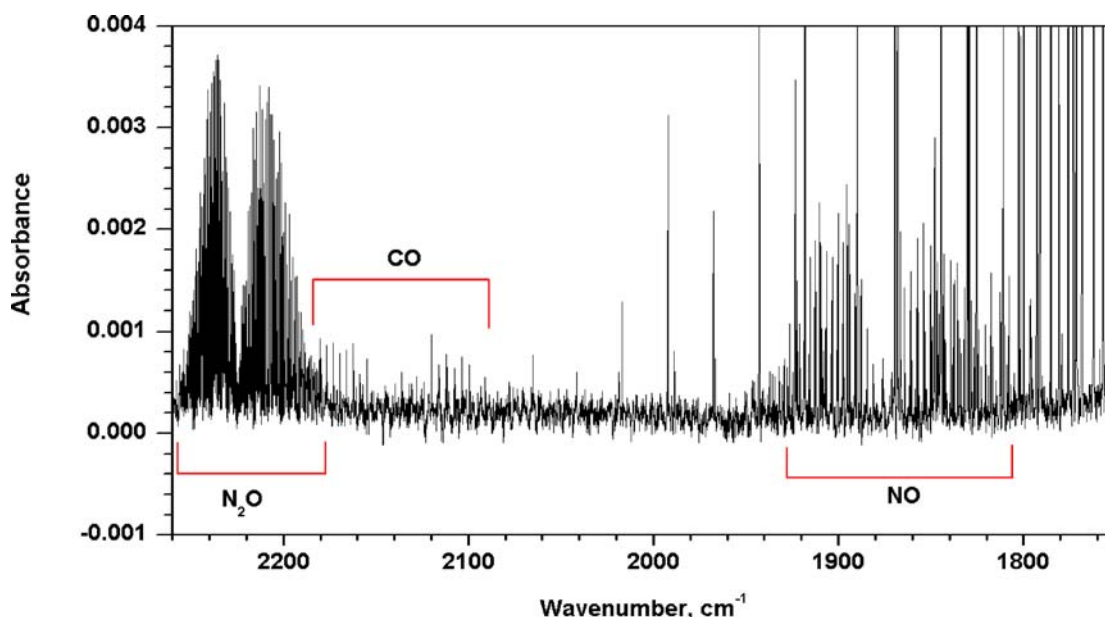


FIGURE 2 Fragment of the spectrum resulting from the analysis of the decay products of RDX-based plastic explosive. $M = 1.5$ g, $T = 90$ °C, $t = 2.5$ h

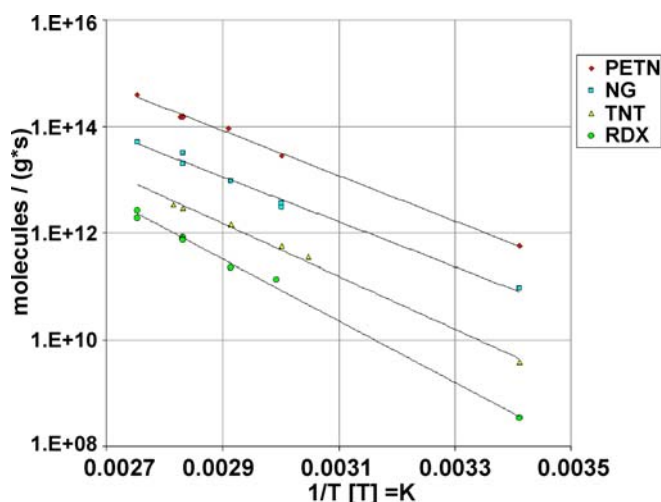


FIGURE 3 Rates of NO formation during decay of various explosives depending on temperature

using a small (< 4 g) amount of explosives, including the PETN and RDX-based plastic explosive samples.

Trend lines are the dependencies of the $Y = A \exp(-B/T)$ type. Parameter B is the activation energy required for NO formation due to the decay of the explosives specified. The values of activation energy were determined as follows: 9800 K for PETN, 9700 K for NG, 11 400 K for TNT, 13 300 K for RDX.

4 Model experiments on non-contact detection of explosives

The group of ammonium nitrate-based explosives was selected to be used in model experiments. The prime reason for selecting this group of explosives was related to safety reasons. Research also indicated that these explosives have been used on numerous occasions by various terrorist groups as extremely powerful ammonium nitrate-based explosive devices.

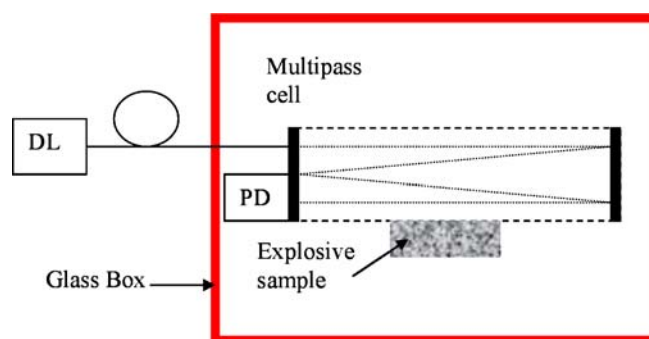


FIGURE 4 Diagram of the diode laser spectrometer used in experiments on explosives based on ammonium nitrate. DL – diode laser, PD – photodiode

The first stage of the Fourier-transform spectroscopy studies involved the analysis of the spectra of air samples collected in the vicinity of the ammonium nitrate specimen. The presence of ammonia was found in these samples, this led to the next stage of the studies using a diode laser spectrometer, its principal diagram is shown in Fig. 4.

The diode laser (NTT) equipped with a fiber output emitting in the vicinity of $1.51 \mu\text{m}$ was used. The multipass cell based on a four objective matrix system [6] with an optical path length of 39 m was used. The InGaAs-based photodiode served as a photodetector. The cell was placed in a glass box. During experiments the samples of ammonium nitrate and explosives based on it were put next to the cell inside the box. The ammonia detection limit of the equipment was 2.5 ppb with an averaging time of 1 s.

In the course of experiments the rate of ammonium nitrate decay to ammonia was determined to be approximately equal to $\sim 10^{12}$ molecules/g s.

In experiments with samples of ammonite (ammonium nitrate & TNT), ammonal (ammonium nitrate & TNT & aluminum powder) and ANFO (ammonium nitrate & fuel oil) ammonia was observed even if the above samples were placed inside of an unsealed envelope made of a polyethylene film.

Ammonia was also detected when the samples of explosives were located in a laboratory room in close proximity to the multipass cell which was open (the glass box was removed). The explosive samples did not exceed 100 g in these experiments.

Similar equipment was successfully carried out in open-field experiments with improvised explosive devices (IED) containing real explosives. This version of the spectrometer, designed as autonomous portable system was developed in the cooperation with Canberra Albuquerque Inc. In the open-field experiments possibility of remote detection was demonstrated, when the TDLS-system was placed downwind with respect to IED.

5 Conclusions

The results of these studies led to a conclusion that the concept of explosive detection by means of TDLS using rather simple decay products is feasible. The method dis-

cussed can be used for the detection of explosive devices, or at least, for those based on ammonium nitrate.

Further investigations of spontaneous decay of explosives will be required to extend the list of markers. This could yield additional opportunities in detection of explosives by means of TDLS.

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