

REVIEW

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Laser methods for detecting explosive residues on surfaces of distant objects

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Abstract. The basic methods of laser spectroscopy that are used for standoff detection and identification of explosive traces in the form of particles on the surfaces of objects tested under real or close-to-real conditions are briefly considered. The advantages and drawbacks of all methods are discussed and their characteristics are compared. Particular attention has been given to the prospects of development and practical implementation of the technologies discussed and justification of their most preferred applications.

Keywords: laser spectroscopy, standoff detection, detection of explosive traces in the form of particles.

1. Introduction

The number of studies devoted to the detection and identification of explosive traces has significantly increased in the last decade for quite clear reasons. These studies were mainly devoted to the methods of chemical analysis of materials in the gas phase. Examples are classical chromatography [1, 2] and ion-mobility spectrometry [3, 4]. Analysis of materials by these methods has a point character and includes several stages, in particular, selection of a test and its transport to the analysis site [5].

Concerning the remote detection of explosive traces, it is fairly difficult to perform it in the gas phase because of extremely low vapour pressure of most of known explosives at room temperature [5, 6]. For example, the equilibrium vapour pressures of TNT (trinitrotoluene) and RDX (hexogen) at a temperature of 25 °C are, respectively, $\sim 1.7 \times 10^{-3}$

and $\sim 4 \times 10^{-6}$ Pa [5, 7]. Simple ways of hiding explosives (for example, in a plastic packet) reduces the vapour pressure by three more orders of magnitude [8]. At the same time, most explosives are known to adhere well to materials with a high surface energy (for example, metals and their oxides), i.e., are strongly bound to the substrate by adhesion forces. Therefore, even when explosives are carefully treated, it is difficult to avoid transfer of their particles to door knobs, footwear, walkways, vehicle surfaces, etc. In particular, the amount of explosives in a fingerprint on object surfaces is $\sim 10 \mu\text{g}$ [9]. For comparison, one 5- μm RDX grain with a mass of ~ 90 pg contains ~ 300 billion molecules, i.e., approximately the same amount as in the gaseous state in 1 L of air under normal conditions [5]. Thus, the possibility of detecting explosive traces of a given type by remote probing the object surface is quite real. And, since it is extremely difficult to remove explosive particles adhering to the surface, remote detection of explosive traces in the form of solid particles on the object surface should be more efficient [10].

Two approaches to distant detection of explosives are distinguished in the literature. These are standoff detection, where examiners and the corresponding equipment are located at a safe distance from the examination site (10–100 m) [6, 11], and remote detection [6], where only the operator is at a safe distance. In the latter case a robotic platform with the necessary equipment is placed in the close proximity of a suspicious object. Generally, detection is carried out contactlessly in both cases. At the same time, point analysis implies contact or near-contact examination of unknown materials.

Obviously, among all approaches to the detection of explosive traces, standoff detection is preferred, although it is more complex for practical implementation [6]. Laser spectroscopy methods [6, 12] are most promising for solving the problem of standoff detection and identification of particle traces of both known and new types of explosives that are present on the surfaces of objects in a multicomponent

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medium. A great variety of laser methods are being developed in this context. Most of them were discussed in recent reviews [5, 6, 13–18].

In this paper we will not consider in detail the numerous original studies, as, for example, in [13, 14, 16], where one can find an extensive bibliography on different methods of standoff detection of explosives. We will restrict ourselves to the consideration of the basic (in our opinion) laser technologies that have been most developed and are promising for practical use. Concerning original studies, we will refer to the ones we believe to be of fundamental importance for the problem under consideration and to some new studies that were not considered in the aforementioned reviews. Emphasis will be on the comparative analysis of the advantages and drawbacks of the methods presented, discussion of the recent results, justification of possible fields of application, and consideration of the prospects of their development.

Since the review volume is rather limited, the results are reported only briefly. To get acquainted with details, we will refer the reader to original studies, reviews, and monographs, which contain a large amount of data on individual aspects of the problem under consideration.

2. Spectral features of explosive molecules

Explosives are divided into two classes: those containing at least one nitro/nitrate group and explosives without them. The latter belong to peroxides [for example, TATP (triacetone triperoxide)], perchlorates, or azides. The most widespread explosives are nitrogen-containing ones: TNT (trinitrotoluene), RDX (cyclotrimethylenetrinitramine), PETN (pentaerythrol tetranitrate), etc. They contain not only nitrogen but also hydrogen, carbon, and oxygen [5, 6]. The general property of these materials is that the content of nitrogen and oxygen in their molecules exceeds significantly that of carbon and hydrogen [5, 6, 12]. The relative nitrogen content is several times higher than in conventional materials (silk, polyurethane, Nylon, etc.).

As was noted above, molecules of nitrogen-containing explosives include either nitro (NO_2) or nitrate (NO_3) groups. The vibration frequencies of these groups depend on the type of the atom a group is added to in the explosive molecule; the absorption cross section at these frequencies is rather large. For example, a typical peak absorption cross section σ_m for stretching vibrations of the NO_2 group in the well-known explosives is within $(1 - 10) \times 10^5 \text{ cm}^2 \text{ mol}^{-1}$ ($\sim 10^{-17} \text{ cm}^2$ per molecule) [5].

The UV and visible absorption spectra of explosives are characterised by the presence of wide bands without any characteristic features. At the same time, in the mid-IR range, from 2500 cm^{-1} ($4 \mu\text{m}$) to $\sim 1100 \text{ cm}^{-1}$ ($9 \mu\text{m}$), the vibrational–rotational absorption spectra of explosive molecules have a high specificity, which is determined by their symmetry and chemical composition, due to which separate spectral lines can be assigned to certain chemical compounds with a sufficiently high accuracy [19]. Specifically this spectral range contains the fundamental vibrational–rotational transitions of molecules of almost all known explosives. One would believe the methods of IR laser spectroscopy to be most promising for detecting and identifying explosives for this reason. However, as will be shown below, most of the methods under consideration are based on radically different approaches, because there are no tunable laser sources

with a sufficiently high power in the mid-IR spectral range. The situation changed when quantum-cascade lasers (QCLs) were designed, as a result of which the new directions in remote detection of explosive traces on object surfaces based on the IR laser spectroscopy methods are being rapidly developed [17, 18].

3. Laser-induced breakdown spectroscopy

One of promising methods for standoff detection of explosives is laser-induced breakdown spectroscopy (LIBS) [20–22]. This method is more often called the laser-spark emission spectroscopy in the Russian literature [23, 24]. LIBS is an analytical method for determining the elemental composition of materials, based on recording the emission spectrum of laser plasma [20–24]. The radiation of laser plasma contains information about the elemental composition of the material, because atoms and ions of each element have a certain set of characteristic emission lines. The signal recorded by a spectrograph makes it possible to determine not only the elemental composition of the material but also identify it with the aid of special algorithms [25–27].

Figure 1 shows a scheme for detecting explosives based on the standoff LIBS system. A lens is used to focus laser radiation into a spot (generally less than 0.1 cm in diameter) on a surface studied. As a result, a small amount of material is removed from the surface (laser ablation) with subsequent formation of a plasma plume above the surface. The light emitted by the plasma is collected by special optics and focused into an optical fibre connected to a spectrograph, which records characteristic spectra with a high resolution. A personal computer is used to analyse the spectrum and display the results on a monitor screen.

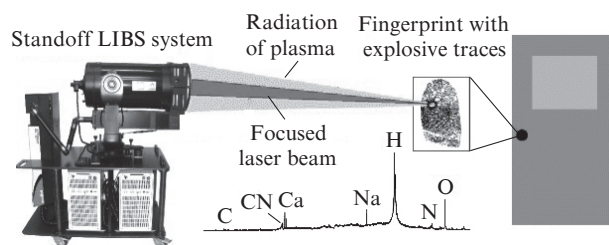


Figure 1. Schematic for detecting explosives using a standoff LIBS system [26].

The evolution of laser plasma is fairly complex; therefore, when recording the signal, one must choose a corresponding time window to reduce the effect of continuous background and select spectral lines of sufficient intensity. To this end, standoff LIBS systems use a gated intensified CCD detector (iCCD). This approach, along with the signal amplification, provides a necessary delay of the onset of spectral measurements with respect to the laser pulse beginning and the measurement duration (the strobe-pulse width). The choice of optimal time conditions for detecting signals also appears to be important to reduce the effect of spectral interferences from foreign elements, which are observed at the same or similar wavelengths but in different time intervals [23, 27].

As was noted above, the common property of explosives is that the content of nitrogen and oxygen molecules in them

exceeds significantly that of carbon and hydrogen. Therefore, having determined the amount of nitrogen and oxygen in a sample with respect to other elements, one can find out if the given chemical compound belongs to explosives [28]. However, some difficulties arise in this case. The presence of atmospheric oxygen and nitrogen in laser-induced plasma complicates recognition of explosives, because it affects significantly their emission spectra [29]. It is extremely important to reduce significantly this influence in order to determine the stoichiometric composition of materials studied, i.e., the real amount of oxygen and nitrogen with respect to hydrogen and carbon, from the LIBS data. Recently the possibilities of the LIBS method, where a target with explosive traces is successively irradiated by two laser pulses, were demonstrated in [30, 31]. This double-pulse irradiation makes it possible not only to reduce significantly the influence of plasma atmospheric oxygen and nitrogen on the emission spectrum but also increase considerably the recorded signal.

The laser radiation wavelength plays an important role in the formation of ablation plume both in the stage where the laser radiation interacts with the target surface and in the stage where it is absorbed in the plasma. Although explosives absorb most strongly in the UV range (electronic transitions), the best signal-to-noise ratio was obtained in the near-IR range [32], because plasma is heated more efficiently in this case (the inverse bremsstrahlung absorption coefficient in laser plasma is proportional to the cube of radiation wavelength). It is likely that for this reason most existing standoff LIBS systems work at a wavelength of 1064 nm (the fundamental harmonic of YAG:Nd³⁺ laser radiation) [27]. Another important factor is the high optical quality and availability of optical elements and units of YAG:Nd³⁺ lasers.

Technological LIBS measurements are generally performed using nanosecond laser radiation. At the same time, the specific features of laser irradiation by femtosecond (10^{-12} – 10^{-15} s) pulses have been studied for different LIBS applications. To date, there are only few studies devoted to detection of explosives based on femtosecond LIBS measurements [33–35]. As was noted in these studies, except for the minimum substrate destruction, they showed no other significant advantages in comparison with the nanosecond range (for example, decrease in the radiation background and influence of environment on the emission spectrum of plasma).

Femtosecond pulses are used not only in the conventional LIBS schemes for detecting explosives. The recent technique (Remote Filament-Induced Breakdown Spectroscopy, R-FIBS) is based on the so-called filamentation. Filaments arise in the radiation channel as a result of dynamic equilibrium between such phenomena as Kerr self-focusing and the defocusing effect of the plasma formed as a result of multiphoton or tunnel ionisation of air molecules during propagation of ultrashort laser pulses in it [36]. Rohwetter et al. [37, 38] performed remote R-FIBS analysis of metal samples (copper, aluminium, and steel) using IR lasers at distances up to 90 m. It was shown that in the filamentation regime the spectra induced by femtosecond pulses are ‘purer’ (independent of the environment) than those recorded in the classical scheme of standoff LIBS analysis.

Concerning the application of R-FIBS technology for detecting explosives, we know only few studies on this subject [39, 40]. In [39] the technology considered above was

used for standoff detection of DNT (dinitrotoluene) and perchlorate ammonium traces during irradiation of a target by UV (266 nm) and IR (795 nm) lasers. The distance to the target was ~3 m. Experiments on thin organic films were performed in [40]; their results also indicate that the R-FIBS technology can also be used for remote detection of organic materials. According to [40], the main advantage of R-FIBS is as follows: depending on the laser beam profile, femtosecond filamentation can be implemented in atmosphere at large distances (up to several kilometres); in this case, one can do without focusing optics.

Nevertheless, it is early to speak about the practical use of this technology for standoff detection of explosives, because the method is in the initial stage of development. The R-FIBS method was reviewed in detail in [41], with consideration of possible fields of its application and prospects of development.

In our opinion, the main advantages of LIBS are its relatively high sensitivity (in comparison with the other methods of laser spectroscopy), simple design of the analytical system, availability of the element base, and deep elaboration of the physical and technical features of the method and the algorithms for identifying explosives in multicomponent mixtures by determining their elemental composition. These advantages are confirmed by the spectra of some explosives (Fig. 2), which were recorded under field conditions at a distance of 30 m using a mobile LIBS system [42]. The possi-

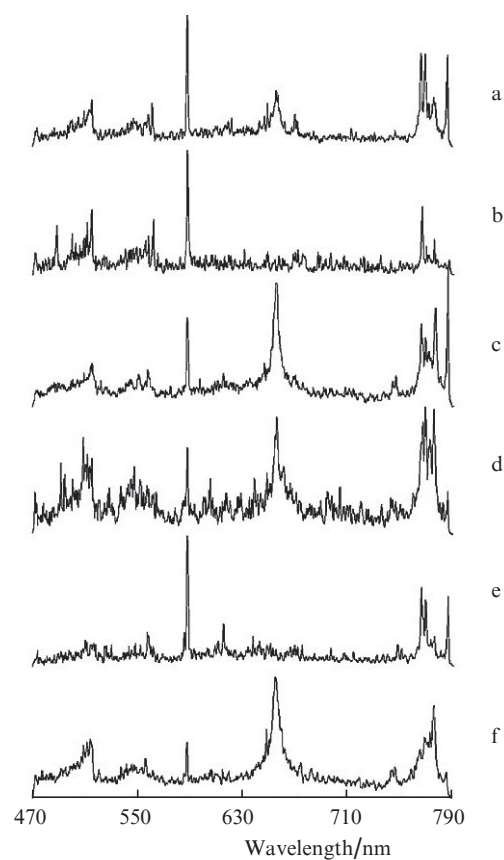


Figure 2. LIBS spectra recorded at a distance of 30 m under single-pulse laser irradiation of (a) acetone, (b) a fingerprint, (c) a TNT solution (100 ppm), (d) a fingerprint with TNT traces, (e) a pure substrate, and (f) a fingerprint with C4 traces [42].



Figure 3. Mobile standoff LIBS system [43].

bilities of LIBS technology, fields of its application, and prospects of development were considered in detail in [43]. Prototypes of portable devices and mobile standoff LIBS systems (Fig. 3), designed for detecting and identifying explosive traces on surfaces of objects at distances more than 100 m, were also demonstrated in [43].

At the same time, this method has a number of drawbacks. First, it is destructive and, therefore, cannot be used to examine people and vehicles. Second, since laser radiation is generally focused into a small spot to form plasma, it is fairly difficult to apply standoff LIBS technology to examine real large objects ($\sim 1 \text{ m}^2$). In addition, the working wavelength of existing LIBS devices is generally 1064 nm [27], which is not eye-safe, whereas the operation in the visible range (532 nm) is unfavourable for security reasons. Finally, this method is sensitive to external interferences (chemical contaminations), which can change the nitrogen/oxygen ratio in the materials examined.

4. Raman spectroscopy

Raman spectroscopy is a powerful analytical tool for studying the molecular spectra that are due to vibrational–rotational transitions. Since these transitions are specific for each molecular structure, the Raman spectrum of inelastically scattered radiation from a particular chemical compound is its characteristic individual mark. Within the classical concepts, a Raman spectrum can be considered as a result of modulating the induced dipole moment of a molecule by the vibrations of nuclei of the atoms entering this molecule under irradiation by monochromatic UV or visible light [44].

The basic advantages of Raman spectroscopy are its nondestructive character and high selectivity. The main experimental difficulties in recording Raman spectra are related to the very low intensity of scattered radiation. It is from 10^{-5} to 10^{-6} of the excitation line intensity for the strongest Raman lines, whereas weak Raman lines may have intensities even several orders lower (the scattering cross sec-

tion is $\sim 10^{-30} \text{ cm}^2$ at $\lambda = 532 \text{ nm}$ [45]). For comparison, the intensity of elastically scattered Rayleigh component is $\sim 10^{-3}$ of the light intensity incident on the scattering medium. In addition, scattered light is emitted into an angle of $4\pi \text{ sr}$, which leads to significant losses during its collection. Since the Raman process has a low probability, it is fairly difficult to observe it even in condensed media. To this end, it is necessary to use modern lasers, sensitive instruments for detecting scattered light, and effective light collection systems. Therefore, a Raman spectrometer operates generally in the signal accumulation regime, as a result of which measurements cannot be performed in real time in most cases. In addition, since Raman signals are weak, this method is sensitive to external illumination and radiation from the object examined, as well as to other chemical compounds around it [46, 47]. To decrease the influence of the aforementioned factors, a high-resolution spectrometer equipped with a gated intensified CCD camera is generally used.

Despite all these drawbacks, standoff detection and identification of bulk explosive samples has recently become an important application of the aforementioned method [45, 48–58]. This is due to a great extent to the development of portable high-resolution Raman spectrometers, where scattered light collected by a telescope is fed to a spectrograph through an optical fibre. As a result, not only the spectrometer sizes were reduced, but also the design became sufficiently reliable to be used under field conditions (Fig. 4) [59].

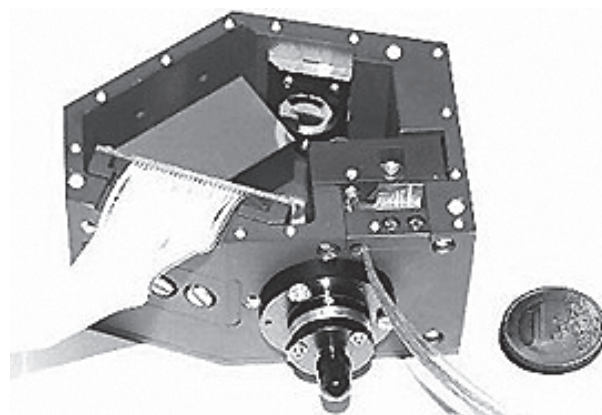


Figure 4. Portable high-resolution Raman spectrograph [59].

Since a Raman signal is inversely proportional to the fourth power of the incident laser radiation wavelength, the latter must be in the UV range to yield the strongest Raman intensity [45]. This increase is even more significant in the case of resonant effect of radiation on molecules in the deep UV region. For example, it was shown in [56] that the Raman scattering cross section at a radiation wavelength of 229 nm for the explosives under study exceeds its value in the visible spectral range by about three orders of magnitude. Thus, the deep UV region was considered as most promising for standoff detection of explosives. Another advantage of the UV region is the much smaller influence of spurious fluorescence. Generally, it does not manifest itself at laser wavelengths shorter than 250 nm [52, 59]. The day-light (external-illumination) effect is also absent when measuring under irradiation with a wavelength shorter than 300 nm. Solar

radiation is known to be almost completely absorbed by the ozone layer in this spectral region.

At the same time, most of portable standoff Raman spectrometers use the second harmonic (532 nm) of YAG laser radiation. Apparently, this choice is conditioned to a larger extent by practical considerations [58]. Indeed, the wavelength of 532 nm falls in the visible spectral region. The optical details and units for this region are the most available ones, due to which the spectrometer design is simple and reliable. The application of pulsed lasers in Raman spectrometers with signal scanning allows one to reduce the influence of external noise on the measurement results to minimum even in the day time. As an example, Fig. 5 shows the characteristic Raman spectra of some explosives, which were recorded using a portable Raman spectrometer located at a distance of ~ 30 m from the object [45].

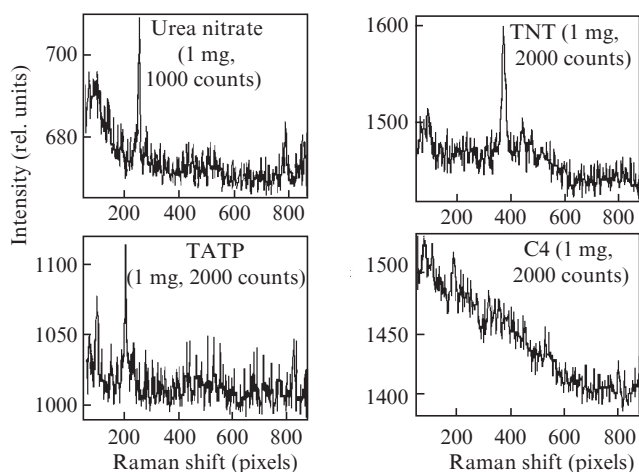


Figure 5. Standoff Raman spectra (distance to the target 30 m, laser wavelength 532 nm) [51].

The absence of inexpensive and compact laser radiation sources of sufficient power in the deep UV ($\lambda < 250$ nm) region is most likely to be the main factor limiting the development of portable Raman spectrometers operating in the optimal spectral range.

5. Coherent anti-Stokes Raman spectroscopy

Coherent anti-Stokes Raman spectroscopy (CARS) is a modern analytical tool for studying the structure and constitution of materials based on scattered light spectrum; it has a number of significant advantages in comparison with spontaneous Raman scattering [44]. CARS can be considered as a nonlinear optical analogue of Raman spectroscopy. This method is based on the concept of phasing molecular vibrations in a resonant biharmonic pump field and subsequent coherent scattering of a probe wave from these vibrations [60].

As for any resonance, the efficiency of energy exchange between interacting waves depends on the phase relations between them. Therefore, the scattered wave intensity will be maximum only in certain directions, along which matching conditions are satisfied. However, the requirements to laser beam alignment are not so severe in some cases. Using sharp

focusing of a laser beam into a focal volume with a length $l_{\text{foc}} \ll l_{\text{cog}} = 2\pi/\Delta k$, one can compensate for the phase mismatch Δk , i.e., obtain a CARS signal of the same intensity as in the case of exact phase matching [60].

Explosive residues on surfaces of objects look like formations, whose thickness h generally does not exceed 1 mm. Therefore, they almost always satisfy the condition $h \ll l_{\text{coh}} = 2\pi/\Delta k$, due to which one can apply CARS for standoff detection of explosive traces on surfaces of objects when applying the collinear scheme of wave interaction. The back-scattered signal recorded in this case is due to the reflection of an anti-Stokes wave from the substrate surface; therefore, it lies in the spectral range that is free of the influence of excitation radiation and spurious incoherent effects, such as luminescence [61]. The high degree of collimation of coherently scattered beam facilitates also effective selection of the useful signal against the background of incoherent illumination and interferences. The application of lasers with a narrow lasing band yields a high spectral resolution for Raman bands. Scattering from coherently excited phase-matched vibrations leads to a significant increase in the signal, to a level much above the Raman scattering intensity: from 25 times for HMX (cyclotetramethylenetetranitramine or octogen) to 250 times for PETN [61]. In turn, elimination of the effect of the nonresonant component makes it possible to obtain CARS spectra containing all characteristic features that are observed in spontaneous Raman spectra. Having approximated the results obtained, Portnov et al. [61] estimated the range of distances for standoff detection of different solid explosive residues. At a laser pulse energy of ~ 10 mJ, it turned out to be from 8 m (HMX) to 20 m (PETN).

An attempt to extend the possibilities of the method using femtosecond pulsed laser radiation was performed in [62–64]. The so-called one-arm CARS technique [65] was applied, where a broadband ultrashort laser pulse is used simultaneously for broadband pumping and as a Stokes component, whereas the narrow-band part of this pulse, which is in antiphase with the former two, serves as a probe pulse and determines the spectral resolution of the method (which is below 1 cm^{-1}) (Fig. 6). This technique, providing automatically a spatial overlap of the pump beam, probe wave, and Stokes component, can be used to study thin (~ 1 mm) layers of materials on substrates. These studies demonstrated a possibility of standoff detection of explosive traces in the solid state (KNO_3 , RDX) at a distance up to 12 m, when detecting backscattered radiation. As was stated in [62–65], femtosecond CARS is more efficient in comparison with the conventional CARS, due to which the laser intensity on a target can be reduced, and samples can be probed nondestructively. Possible ways of developing femtosecond CARS were also considered in [62–65]. For example, Li et al. [64] predicted a possibility of detecting explosive traces (few μg) at a distance of 50–100 m by increasing the laser pulse energy to 100 μJ (by a factor of 10 in comparison with the value obtained in [64]); using more efficient optics for collecting scattered radiation; and applying a cooled photoelectron multiplier in the photon-counting regime. It was also proposed to use jointly the LIBS and CARS methods, which make it possible to measure independent explosive characteristics (the so-called orthogonal technologies); this approach was believed to reduce significantly the false-alarm probability [6].

It follows from the aforesaid that the CARS technology has a number of undoubted advantages over the spontane-

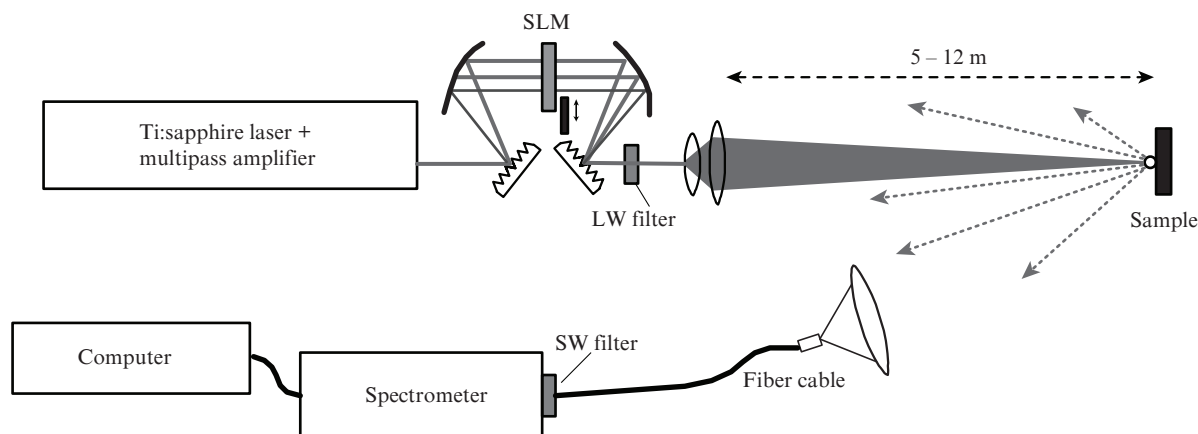


Figure 6. Schematic of the one-arm experimental CARS setup (30 fs, 1 kHz): SLM is a spatial light modulator and LW and SW are, respectively, long- and short-wavelength cutoff filters [62].

ous Raman scattering. However, it still remains complex for technical implementation, and, therefore, expensive. Hence, it is problematic to use it in commercially produced portable devices, designed, for example, for standoff detection of explosive residues when examining people and vehicles.

6. Photofragmentation followed by laser-induced fluorescence

Large structural aggregates, to which molecules of most explosives belong, are generally characterised by weak and poorly resolved transitions in the UV and visible spectral regions, a circumstance that hinders their spectroscopic detection. At the same time, most of small molecules (composed, for example, of two or three atoms) exhibit strong and well-resolved transitions. This fact suggests a possibility of indirect detection of explosives: their large molecules are first decomposed into small characteristic fragments, and then their presence is determined by spectroscopic methods.

Photofragmentation (photodissociation) followed by laser-induced fluorescence [PF-LIF (PD-LIF)] is a relatively new technique, which is based on decomposition (dissociation) of polyatomic molecules into characteristic fragments [66–71]. In contrast to LIBS, where atoms and ions are formed during dissociation of complex molecules, the dissociation products in the PF-LIF method are fragments of two- and triatomic molecules. In this context, the laser power used in PF-LIF is much lower than in LIBS.

The essence of the aforementioned method is as follows [66, 68]. Molecules of most explosives are known to contain characteristic functional groups, in particular, NO_2 . Under UV laser irradiation these explosives undergo photofragmentation with the formation of free NO_2 groups, because they have the lowest binding energy. Then NO_2 molecules rapidly dissociate into atomic oxygen and NO groups, which are excited under UV irradiation. Since explosive molecules have a wide absorption band in the UV region, one can use the same radiation source for their fragmentation and excitation of NO molecules. In turn, NO molecules can be detected using laser-induced fluorescence (Fig. 7).

Nitrogen oxide NO can also be present in contaminated air. However, there is a significant difference between the NO molecules existing in air in the form of contaminations and the molecules formed as a result of dissociation of NO_2

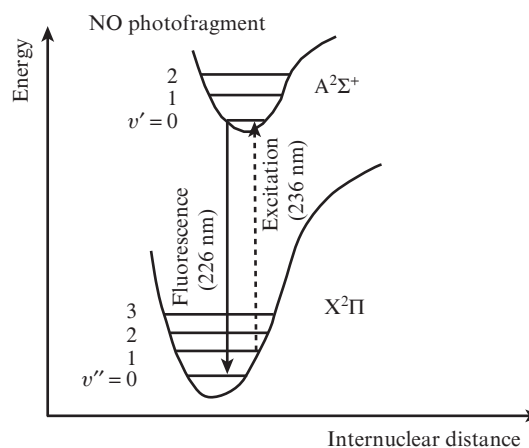


Figure 7. Schematic of formation of PF-LIF signal [68].

fragments. Almost all nitrogen oxide molecules that are present in atmosphere are in the ground energy state, whereas a considerable part of NO molecules that are explosive photodissociation products are first in the vibrational excited state ($\sim 30\%$ in the case of TNT molecules). This difference is extremely important, because it allows one to distinguish contaminated air from the air containing explosive traces. Since some part of these molecules are initially vibrationally excited, their fluorescence is observed at a smaller wavelength than that of the excitation laser radiation. All these features indicate that the process under consideration differs from scattering or conventional fluorescence, which are single-photon processes, yielding light photons with energy equal to the excitation photon energy or lower.

Thus, the high selectivity (peculiarity) of the detection technique discussed here is due to the presence of characteristic wavelengths in the fluorescence spectrum, which are determined with a high accuracy. The fact that the signal is recorded at a wavelength that is shorter than the laser wavelength is decisive for minimising possible optical interferences. Another advantage of this method is the relatively strong fluorescence signal, which can be obtained using UV laser radiation with an eye-safe power. In particular, the effective cross section of the entire PF-LIF process per TNT molecule was estimated to be $\sim 4 \times 10^{-23} \text{ cm}^2$, which exceeds

the Raman scattering cross section in the UV range by a factor of $\sim 4 \times 10^4$ (for $\lambda = 248$ nm) [68].

As an example, Fig. 8 shows the experimental dependences of the 226-nm fluorescence signal from DNT, TNT, C4 (is known as plastid with an active RDX component), and PETN on the pump wavelength; the pump energy density is 10 mJ cm^{-2} [68]. Each point of the curves is obtained by averaging over six measurements (pulses). It can be seen that the spectra of all explosive samples contain many peaks,

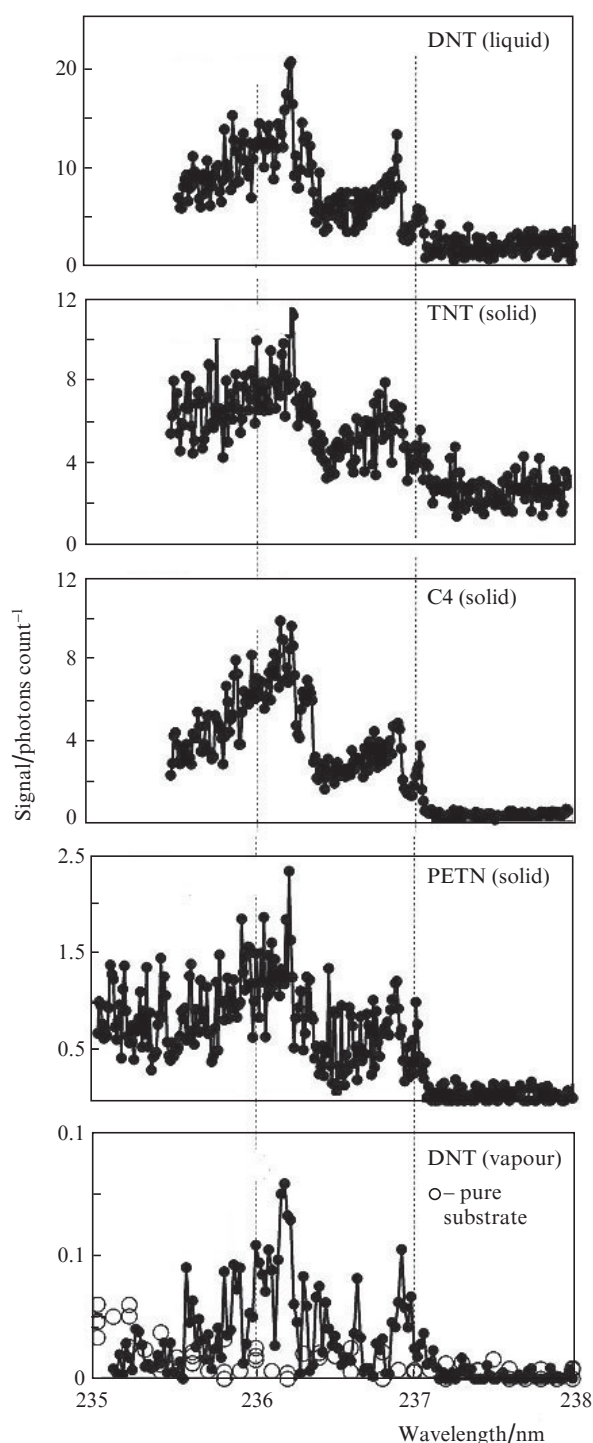


Figure 8. PF-LIF signals at a wavelength of 226 nm for different explosives [69].

with a maximum signal under excitation radiation wavelength 236.2 nm, which corresponds to the $X^2\Pi (v'' = 1) \rightarrow A^2\Sigma^+ (v' = 0)$ transition. As was believed in [68], the signal-to-noise ratio is larger in this case than upon excitation of NO molecules from the second vibrational level of the ground state ($\lambda \sim 248$ nm), which occurred in [66, 67].

At the same time, the PF-LIF method has a fundamental drawback: it can be used to determine only nitrogen-containing explosives, without making any difference between them. Its another drawback is the need for laser radiation sources that must be tunable in the UV range and have sufficiently high energy parameters. Generally, these sources are tunable parametric light generators [68–70] or KrF excimer lasers [66, 67]. These instruments are too complex, cumbersome, and expensive to be used in portable mass-produced sensors.

7. Pulsed laser fragmentation mid-IR spectroscopy

The essence of detection of explosives by this method (MIR-PF) is as follows [72–75, 77]. When an object is exposed to pulsed laser radiation, explosive traces are heated to decompose into characteristic fragments; the latter are desorbed from the surface and pass to the gas phase. Studies with different explosives showed that it is optimal to perform fragmentation using the eye-safe radiation with a wavelength of about $1.5 \mu\text{m}$ [73]. During laser fragmentation of explosives, a ‘cloud’ of NO_x molecules is formed in the immediate vicinity of the sample surface, and these molecules are detected by different methods of IR spectroscopy. To this end, the explosive decomposition products are synchronously irradiated with another laser, for example, a tunable QCL. The QCL tuning range includes characteristic absorption bands of NO_x molecules in the mid-IR (MIR) range. The signal in the form of reflected (scattered) radiation is recorded by an IR camera (Fig. 9). Explosives are generally identified using the HITRAN database [76], which contains the most complete information about the molecular spectra used for comparison.

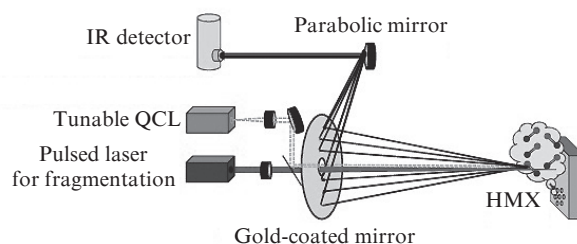


Figure 9. Schematic for detecting explosives using a standoff MIR-PF system [72].

It is noteworthy that Bauer et al. [72] observed no radiation from NO_x groups in the surrounding air when studying a pure aluminium surface. Thus, they concluded that the ratio of NO and NO_2 concentrations can serve as a criterion for assigning materials under study to explosives. It was also demonstrated in [72] that the method under consideration can be used for standoff detection of HMX residues on a

metal surface at a distance of 5 m. It was also predicted in [72] that the detection limit can be increased to 20 m by improving the parameters of the optical system receiving the scattered radiation from the object.

However, it should be noted that the MIR-PF technique (as well as PF-LIF) can detect only nitrogen-containing explosives. At the same time, as was shown in [77], the explosives belonging to peroxides (for example, well-known TATP) can be detected by direct application of IR spectroscopy using tunable QCLs, because the explosives of this class have a high vapour pressure (~ 7 Pa at 25°C ; for comparison, the corresponding value for TNT is 4.2×10^{-4} Pa [14]). The MIR-PF technique, in contrast to PF-LIF, does not require UV tunable lasers: it is based on the two-laser scheme. Nevertheless, modern laser technologies make it possible to implement a compact version of the MIR-PF system with a work range of 10 m or more. A prime problem to be solved is to eliminate the influence of interferents for MIR-PF [77].

8. Discussion

In this review we briefly considered the main methods of laser spectroscopy that are developed for standoff detection and identification of solid explosive traces on surfaces of objects. Some of them (LIBS, Raman spectroscopy) have been implemented in experimental devices and tested under real field conditions. In this context, they can be considered as the most advanced technologies. At the same time, one cannot but mention a number of new methods (for example, Active Spectral Imaging), which are promising for standoff probing of object surfaces to detect explosive traces [17, 18, 78–81].

Table 1 contains the comparative characteristics of some laser methods for standoff detection of explosive particle traces on the surfaces of objects. In our opinion, these methods are most likely to be implemented in devices in the nearest future. The table contains the summed results of the analysis performed in this study and in [17, 18]. Based on them, some generalisations can be made. When compiling the table, we proceeded from the following quantitative criterion for detecting explosives: $\sim 10 \mu\text{g cm}^{-2}$; this amount approximately corresponds to a typical mass of a first fingerprint after touching explosives [9].

We did not include Raman spectroscopy in Table 1, because, even in sight, it is not realistic for this technique to satisfy the requirements imposed on the standoff technologies for detecting explosive traces on surfaces of objects [6]. The prospects of standoff Raman spectrometers are directly related to the development of deep-UV lasers and increase in their power (energy) with a simultaneous decrease in size. However, even in this case one can hardly expect full-fledged

on-line standoff devices, aimed at detecting explosive traces on surfaces of objects [14]. At the same time, compact Raman systems can also be of interest for special problems of standoff detection of explosive traces, in which the analysis time is of little importance. It is most likely that the Raman spectroscopy, which is characterised by high selectivity, is the best tool for standoff examination of bulk explosive samples, which can be performed at large (more than 50 m) distances in the close-to-real-time regime, and for standoff analysis of liquids in plastic or glass vessels [51, 55]. The development of combined systems for standoff analysis on the basis of different physical principles is also of interest. For example, one would expect combination of the LIBS technology with Raman spectroscopy to increase the selectivity of analysis in multicomponent media [82–84]. However, this combination will complicate the entire system in any case, and the gain in selectivity will inevitably lead to a decrease in the detection limit.

The data in Table 1 suggest that the standoff LIBS technology (as the most sensitive technique of all known) must be used for standoff detection of explosives at large distances (100 m or more), where the potential of this technique is open completely. None of existing laser technologies can compete with it in this context. Apparently, for this reason, the efforts of the developers of LIBS systems are primarily aimed at designing far-ranging mobile complexes and solving related questions (construction of an effective algorithm for identifying explosives in multicomponent media on different substrates, study of the influence of environmental conditions, etc.) [31, 42]. At the same time, other laser techniques can compete with LIBS at smaller distances.

CARS spectroscopy has a high selectivity and exceeds significantly spontaneous Raman scattering in sensitivity. Thus, it is a promising tool for detecting explosive traces at intermediate distances (20–50 m). At the same time, one can state with a high degree of confidence that CARS can hardly be of commercial use in the nearest future in view of its complexity and high price as a whole.

The PF-LIF technology is undoubtedly interesting for detecting explosive particle traces at intermediate distances. It is rather simple and highly selective when applied to multicomponent media. However, it has one fundamental drawback. PF-LIF can be used to detect traces of only the explosives containing functional NO_2 groups. At the same time, the explosives belonging to peroxides (for example, well-known TATP), cannot be detected by PF-LIF. Obviously, this circumstance narrows the range of problems to be solved. In addition, we should mention another trouble with this method. It is technical to a greater extent and is related to application of rather high-power tunable UV lasers in PF-LIF sensors. According to the estimates of [69], to obtain a detection limit of ~ 25 m in the PF-LIF method, one needs

Table 1. Comparison of the laser methods of standoff detection of explosive traces ($\sim 10 \text{ mg cm}^{-2}$) in the form of particles on the surfaces of objects.

Detection method	Obtained detection distance/m	Predicted detection distance/m	Selectivity	Safe for eyes	References
LIBS	45	> 100	intermediate	no	[42, 43]
PF-LIF	2.5	25	high (nitrogen-containing explosives)	yes	[67, 69]
MIR-PF	5	20	high (nitrogen-containing explosives)	yes	[72, 76]
CARS	12	50–100	high	no	[64]
Active Spectral Imaging	~ 1	10–20	high	yes	[79]

a pulsed laser with an average power of 10 W. However, such lasers are currently absent, and it is not quite clear if they arise in the nearest future. It is likely to be the main reason for the absence of working prototypes of portable standoff PF-LIF devices, despite the large number of experimental studies on this subject.

The MIR-PF technique, as well as PF-LIF, has a fundamental limitation: it can be used to detect only nitrogen-containing explosives. At the same time, MIR-PF solves the problem of UV-tunable lasers by applying the two-laser scheme. Nevertheless, modern laser technologies make it possible to implement a standoff system based on MIR-PF in a compact version, working in the range of distances up to 10 m or more. Direct application of IR spectroscopy allows one to use this method to detect such explosives as the well-known TATP, which belongs to peroxides and has a high vapor pressure. At the same time, it is possible that the best way of applying this technique (as well as PF-LIF) to a number of problems is to integrate it into a compact combined sensor system, along with Raman scattering [85].

Although some promising laser technologies were not considered in this study, we should mention them for completeness sake. First of all, we mean the rapidly developing technique referred to as Active Spectral Imaging [18]. This method is in many respects based on the well-known passive technology of Spectral Imaging (SI), which is actively developed in view of the monitoring of the Earth's surface from space. Combination of SI with tunable QCLs gives grounds to expect compact portable devices to arise in the nearest future. One might expect the working range of these devices, operating in real-time or close-to-real-time regimes, to be 10–20 m, with a possibility of detecting explosive traces in multicomponent media. We estimated the detection distance (Table 1) taking into account the real possibilities of increasing the average QCL power by a factor of at least 5–10 (to 80–150 mW) and applying an IR camera with NETD (Noise Equivalent Temperature Difference) in the range of 50–80 mK. In addition, it is necessary to increase several times the collection coefficient of scattered IR radiation.

One of the drawbacks of this method is the need for powerful software to process large data arrays in real time. It is necessary to solve this technical question and increase the tunable QCL power to an average value in the range of 0.1–1 W, with a simultaneous decrease in the QCL cost. As a result, this technology will become a basis of compact portable devices with a coverage range of several tens of meters, aimed primarily at examining personnel, luggage, and vehicle surfaces [18].

9. Conclusions

Our analysis of the data in the literature leaves no doubts that the laser spectroscopy methods are most promising for solving problems related to standoff detection of explosive particle traces on surfaces of objects. At the same time, none of the methods considered here satisfy completely the requirements imposed on standoff sensors [6]. The analysis shows that the standoff sensors (operating in real-time or close-to-real-time regimes), designed for detecting explosive traces on surfaces of objects, can be separated into three classes.

(1) Short-range devices with a detection distance of 10–20 m. These instruments include universal Active SI systems and compact systems of limited application: PF-LIF

and MIR-PF. Devices of this type can become most widespread, because their prime task is the examination of personnel, luggage, and vehicles.

(2) Intermediate-range devices with a detection distance of 20–50 m, which include systems based on the CARS technology. These systems can be used to solve special search and examination problems, for example, monitoring of vehicles and detection of suicide bombers.

(3) Long-range devices with a detection distance above 50 m. Representatives of this class are mobile LIBS systems. The latter can primarily be used, for example, to search for and detect vehicles carrying explosive materials.

Further development of all systems for standoff detection of explosive traces on surfaces of objects is directly related to the design of compact lasers with improved operating parameters at room temperature and to the expansion of the lasing and tuning ranges. The problem of designing inexpensive and highly sensitive photodetectors and effective optical systems for collecting light remains urgent. Finally, a large amount of work must be done to construct reliable algorithms for recognizing explosives in multicomponent media in the presence of interferents. In addition, the corresponding studies aimed at expanding the library of spectra of both explosives and their possible interferents must be carried out. Success in the aforementioned fields will allow one to search more efficiently for new approaches to the design of combined systems, based on application of 'orthogonal' technologies. Specifically these systems are most likely to play the decisive role in future [6].

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