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### Abstract

In this article, we present an overview of the various photonic aspects involved in different techniques for explosives detection on field and in the lab. We confine this synopsis to only laser-based techniques for detecting explosive molecules in point or proximal setup (laser source and detectors are in the proximity of sample) and in standoff mode (laser and detectors are at certain distance from the sample). The techniques considered in this overview are (a) laser-induced breakdown spectroscopy (LIBS), (b) Raman spectroscopy and its variants [surface-enhanced Raman spectroscopy (SERS), coherent anti-Stokes Raman spectroscopy (CARS), and spatial offset Raman spectroscopy (SORS)], (c) terahertz (THz) spectroscopy, and (d) photoacoustic spectroscopy (PAS). Various photonic aspects related to these techniques such as (i) laser sources used and the future requirements, (ii) detectors employed at present and improvements required, (c) design and advances in variety of optics used for illuminating, collimating, collecting, focusing, etc., and (d) integration of all these components for the creation of efficient portable devices for explosives detection in the laboratory and field are discussed in detail. We also present results obtained through some of our efforts toward trace and standoff explosives detection using SERS and femtosecond LIBS techniques, respectively.

**Keywords** *explosives detection; Raman; LIBS; SERS; SORS; photoacoustic spectroscopy; terahertz spectroscopy* 

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### 1 Introduction

Field detection of explosives in traces (or explosive mixtures) either in near regime or from a distance, rapidly/precisely, is essential for military, aviation, and security sectors [1-9]. Detection and identification of explosives and their associated mixtures/compounds prior to any potential blast is important as they can induce lot of damage to public and private properties as well as incur hundreds of human causalities. Identification of explosives from non-explosives is as well important to safeguard citizens by alerting and evacuating them from the suspected area. There are several scenarios wherein detection of explosives is important: (i) in the airport while screening the baggage or personnel, (ii) in the form of land mines buried in the field while the military personnel are moving, (iii) in the public places (e.g. malls) in terms of hazardous vapors/bulk explosives, (iv) moving containers/trucks and other vehicles at check posts or entry points, (v) post-blast case wherein only very small amounts of left out (unreacted) explosives need to be identified, and (vi) concealed explosives in opaque containers, wherein only traces will be at best available, that are left out while handling these sticky materials. In some cases, the samples can be brought to the lab and can be evaluated, whereas in some other cases the instruments need to be taken to the field for real-time assessment. Though the existing lab-based explosive detection techniques are sensitive enough to detect traces (approximately few picograms) they lack the selectivity and cannot be accommodated in real-time investigations. Moreover, chromatographic techniques such as gas chromatography mandate sampling procedure and are also time consuming, thus precluding their applications in in-situ investigations [10]. There are some extreme cases wherein neither the people nor the instruments can be taken close to the sample or sampling area, and sample collection is not possible. In such cases, standoff detection is

required (where the sources and detectors are at a distance away from the sampling region). There are several techniques reported in the literature and being used worldwide for detection of explosives in various forms [11–17]. The following laser-based spectroscopic techniques [18–20], exclusively used for explosives detection, are discussed in detail in terms of the photonic components (input lasers, detectors, optics, spectrometers, etc.) being used at present and the improvements required:

- 1. Laser-induced breakdown spectroscopy (LIBS) using femtosecond (fs) and nanosecond (ns) pulses in the proximal (near-field) and standoff mode.
- 2. Raman spectroscopy (normal and in the standoff mode).
- 3. Surface-enhanced Raman spectroscopy (SERS) for trace explosives detection, coherent anti-Stokes Raman spectroscopy (CARS) for standoff explosives detection, and spatial offset Raman spectroscopy (SORS) for detecting explosives inside opaque bottles (SERS, CARS, and SORS are lab based).
- 4. Terahertz (THz) spectroscopy in the near field and for imaging applications, especially for explosives detection.
- 5. Photoacoustic spectroscopy (PAS) in the near field and standoff mode for explosives detection.

Laser-based techniques are attractive for explosives detection as they (i) offer rapid real-time in situ investigation of sample, (ii) require only an optical accessibility of sample, (iii) utilize optics free path for investigation, and (iv) offer the capability of remote and standoff detection. Further, laser spectroscopy-based methods are ubiquitous, versatile, and sensitive [19]. Moore [21] has recently discussed about the instrumentation aspects required for trace detection of high explosives. The most important photonic components in laser spectroscopic experiments are (a) laser sources, (b) focusing/collection optics and fibers, (c) spectrometer, and (d) intensified charge

coupled device (ICCD) camera. Similarly, any standoff detection technique toward effective detection of explosives must meet two basic requirements: (i) capacity to detect the response generated from only a small amount of material located at a distance of several meters (high sensitivity) and (ii) the ability to provide easily distinguishable responses for different materials (high specificity). LIBS and Raman spectroscopy are probably the only two analytical techniques that share similar instrumentation and, at the same time, generate complementary data.

# 2 Laser-Induced Breakdown Spectroscopy (LIBS)

LIBS, over the past three decades, has evolved as one of the promising laser spectroscopic techniques in this direction with enhanced detection capabilities, particularly attractive for the detection of explosives and related hazardous materials due to its standoff detection capability, requirement of miniscule quantities of material, and rapid detection and analysis [22, 23]. Apart from explosive detection, the development of LIBS has benefited many fields such as environmental studies, nuclear waste management, biology, medicine, space applications, defense, and agriculture [24, 25]. Recently, LIBS rowers' instrument has been developed for MARS by the NASA (National Aeronautics and Space Administration), USA, and Chandrayan-2 by ISRO (Indian Space Research Organization), India, to analyze the constituents present in mars and moon atmosphere, respectively [26-28]. LIBS technique, an efficient tool for multielemental analysis, has its own advantages compared to other conventional methods such as inductively coupled plasma mass spectroscopy (ICP MS), atomic absorption spectroscopy (AAS), and atomic emission spectroscopy (AES). LIBS technique offers several advantages including (i) no or minimal sample preparation required, (ii) concurrent multiple element analysis for almost all the elements in the periodic table, (iii) real-time response with raw spectra available in less than a second, (iv) no limitation on the state of the sample (it can be in any form – solid, liquid, or gas), and (v) high sensitivity (parts per billion/to sub parts per billions can be detected, in principle). The technique also permits the detection of small molecular fragments such as CN and  $C_2$ . In fact, the ratios between the spectral emissions of these species and of the elements provide the possibility to correlate the emission lines to the molecular structure and to identify and discriminate the original compounds such as plastics and explosives [29-32]. This technique involves the interaction of an intense laser pulse with the sample, leading to the generation of dense plasma, termed as laser-induced plasma (LIP) or laser-produced plasma (LPP). Optical emissions from plasma, containing specific signatures of the constituent atoms from the material, are collected using a detector and fed to a spectrometer, resulting in laser-induced breakdown spectrum commonly known as LIBS signal. However, the transient evolution of LIP is complex as it involves various reactions within plasma constituents as well as with elements from surrounding ambiance into which plasma expands. ICCD cameras have become an integral part of the LIBS instrument as these cameras offer high gain and substantially increase the captured LIBS signal, thus improving the signal-to-noise ratio (SNR). A gated ICCD is useful in collecting the plasma emissions (signal) with respect to the input laser trigger or with respect to the plasma formation and thus eliminating the contribution from bright continuum generated in the process of plasma formation. In other words, it offers delay (when signal to be collected) and width (how far signal has to be collected) to capture optical emissions emanating from plasma. Usage of ICCD enables two types of LIBS spectra: (i) time-integrated spectra and (ii) time-resolved spectra. Signal can be recorded in particular time intervals so as to understand the evolution of plasma constituents as it expands. This technique is called as kinetic series where time-resolved

emissions are acquired by maximizing signal-to-background ratio.

Typical LIBS experiments are performed in the point or proximity [24] (near-field), and the detection is usually achieved by collecting the light using lenses configuration and/or optical fibers. LIBS technique has been used for qualitative as well as quantitate measurements. Proximal or point detection with LIBS technique has been utilized by numerous industrial as well as scientific communities for various analyses [33, 34]. Unlike those techniques, standoff LIBS experiments are executed for rapid analysis of distant samples, where optical emissions from plasma of a distant target are coupled using an array of lenses or a telescope attached with fibers to a spectrometer, for the investigation. In the case of collection optics, the following are important: (i) transmission window of the lenses, (ii) transmission as well as reflection wavelength region of the optics in telescope, and (iii) the fibers used should transmit the light in the (ultraviolet) UV-visible spectral region (ideally from 240 to 1100 nm, which most of the fibers do not work). Especially for explosive detection, this is even more significant since the CI peak at 247.8 nm appears in the UV region. In few cases, the dichroic mirrors (reflect particular wavelength and transmit complementary wavelength region) and UV-fused silica lenses (transmit UV-visible radiation) are used as delivering optics enabling simultaneous plasma emission collection. Spectrographs with wide wavelength range (for robust multi-elemental analysis in a single shot), with high resolution and high-throughput, are required for LIBS experiments. However, there exists a trade-off between resolution and throughput, i.e. the increase in slit size increases the throughput at the cost of resolution. Especially for trace explosives detection, efficient collection optics, spectrometers, fibers (for transmitting the signal), and ICCDs are required, which facilitate in collecting better signal and simultaneously enabling to record large number of spectra. Furthermore, advanced chemometric algorithms are

required for identification/classification of explosives by LIBS data [35].

The major challenge in identifying explosives is the presence of common elements (C, N, O, and H) in all these materials, which are also present in atmosphere, and invariably on-field detection needs to be performed in open atmosphere. Several reports, cited in the literature, have discussed various issues of explosives detection in bulk as well as traces on various organic and inorganic substrates including utilization of various algorithms for classification/identification in standoff configurations [36-49]. Apart from identifying explosives from non-explosives, distinguishing each among themselves is another mammoth challenge. It requires careful analysis of the data to conclude whether the given material is an explosive or not and importantly the exact identification of the explosive. LIBS technique has been successfully implemented/demonstrated in understanding of fundamental science, conservation of arts, industry, etc. The success of LIBS devices in Chadrayaan and ChemCam is an indication of the technique's maturity for various applications. Apart from application of LIBS in standoff analyses, several LIBS-based handheld devices utilizing compact ns lasers, for remote detection, are being designed and readily supplied by various companies in market. Few such links are provided, from the reader's point of view, in these references [50–53].

Two separate groups, led by Miziolek and coworkers [36-40, 54] and Laserna and coworkers [24, 41, 43-47], have performed several pioneering experiments using ns laser and proved the potential of ns-LIBS technique for standoff detection and discrimination of explosives. In 2005, De Lucia et al. reported the versatility of ns-LIBS for detection of hazardous materials and reported a prototype of man-portable laser-induced breakdown spectroscopy (MP-LIBS) backpack system (as shown in the Figure 1a) that was tested by recording LIBS spectrum of a bacteria [36]. In 2006,



**Figure 1** (a) Photograph showing a simulation of the MP-LIBS man-portable/backpack sensor in use by Dr. Richard Hark inside a Tyvek Biohazard Protective suit. Laser is in the handle. The computer, power supply, battery, and the high-resolution broadband spectrometer are in the backpack. HUD connected to the eyeglasses. Insert: LIBS 3000 spectrometer (opened). Copyright @IEEE. Reproduced with permission from IEEE SENSORS JOURNAL, VOL. 5, NO. 4, AUGUST 2005. (b) Photograph of the double-pulse ST-LIBS system developed by ARL in collaboration with Applied Photonics, Ltd. and Ocean Optics, Inc. Source: Copyright @IEsevier. Reproduced with permission from Spectrochimica Acta Part B 62 (2007) 1405–1411.

both these groups together reported a standoff laser-induced breakdown spectroscopy (ST-LIBS) sensor for detection of explosive residues on solid surfaces, which uses a Brilliant Q-switched Nd:YAG laser operating at 1064 nm and producing 350 mJ single pulses at 20 Hz [41]. Later on, a double-pulse ST-LIBS system was developed (as shown in Figure 1b) by De Lucia et al. for detecting a variety of hazardous materials including RDX, Composition-B, explosive residues, biological species such as the anthrax surrogate Bacillus subtilis, and chemical warfare simulants at 20 m with improved sensitivity and selectivity [37]. Furthermore, they have utilized multivariate analysis approaches such as partial least squares discriminant analysis (PLS-DA) to discriminate explosive residues. Gottfried et al. demonstrated the possibility of discrimination of various residues on organic and inorganic substrates, which is a cumbersome task [39]. Moreover, their preliminary studies with fs pulses showed that fs-LIBS has a few advantages compared to ns-LIBS for explosive residue detection [40, 55]. The second group led by Laserna also demonstrated progress in standoff detection of explosives using the ns-LIBS technique by analyzing various explosive and organic residues, detecting explosives behind barriers [24, 43, 44]. They have successfully combined the techniques of LIBS and Raman (fusion) for identification of explosives [45]. They also have demonstrated the possibility of detecting explosive molecules in fingerprints (on solid surfaces) using LIBS and supervised learning method [46, 47]. A few of the recent significant works including the deployment of different laser sources leading to hybrid techniques and advanced multivariate techniques for explosive detection in near and far-field from various other groups as well have been summarized in Table 1.

Our group (at ACRHEM, University of Hyderabad, India) has been working on the LIBS technique for explosives detection since 2009. Over the past decade, we have studied various aspects in detection/discrimination and identification of pure explosive molecules using ns and fs pulses. In our earlier studies, the effect of pulse duration [56] and the effect of ambiance (gas) surrounding the LPP [65] on CN and  $C_2$  molecular band emissions from explosives was investigated. Simultaneously, advanced chemometric techniques were developed and combined with LIBS data of pharmaceutical tablets for classifying

Table 1 Femtosecond and nanosecond LIBS studies for the detection of explosives.

Experimental details	Technique	Samples	Comments	Refs.
Two Nd-YAG lasers (Ultra Big Sky Laser and Big Sky CFR200) to provide different pulse energies	Man-portable LIBS and proximal LIBS	Chemical and biological agents, landmine detection, and first portable MP-LIBS system by ARL		[36]
Quantel Brilliant Twins laser (1064 nm, 10 Hz, 335 mJ/pulse, 5 ns/pulse width), Schmidt–Cassegrain telescope by Meade (LX200GPS) fitted with UV-coated optics, DP-ST-LIBS system	Double pulse ST-LIBS at 20 m	Various metallic and plastic materials, bulk explosives RDX and Composition-B, explosive residues, biological species such as the anthrax surrogate <i>Bacillus subtilis</i> , and chemical warfare simulants and nerve agents	Classification of aluminum and RDX, oil, dust and fingerprint residues on aluminum using PCA	[37]
Double pulse LIBS, two Nd:YAG lasers (Continuum Surelite),	Near-field LIBS only	Residues of RDX and Comp-B on Al		[54]
Quantel Brilliant Twins (1064 nm, 10 Hz, 335 mJ/pulse, 5 ns/pulse width) provide a collinear double pulse generator, designed for 30 m operation	DP-LIBS and PLS-DA	Explosive residues on Al, Arizona road dust, and oil residue	Multivariate analysis	[38]
Quantel Brilliant Twins (1064 nm, 10 Hz, 335 mJ/pulse, 5 ns/pulse width) provide a collinear double pulse generator, designed for 30 m operation 20 m using standoff laser-induced breakdown spectroscopy (ST-LIBS)	Double pulse technique and PLS-DA	Biological warfare agent surrogates <i>Bacillus subtilis</i> (BG) and ovalbumin and linear correlation	(2% false negatives and 0% false positives) (0% false negatives and 1% false positives)	[48]
Quantel Brilliant Twins (1064 nm, 10 Hz, 335 mJ/pulse, 5 ns/pulse width) provide a collinear double pulse generator, 25 m standoff spectra	Double pulse, PLS-DA different models	RDX residue, oil residue, Arizona dust residue on plastic, wood, cardboard, etc.	Individual PLS-DA models performed	[39]
Ti:Sapphire amplifier system (Coherent, Hidra-25), Nd:YAG (Big Sky, CFR400) laser at 1064 nm	Near LIBS	Bulk explosives (RDX, C-4, and Composition-B), RDX residue on aluminum substrate	No classification	[40]
Quantel Brilliant Twins Q-switched Nd:YAG laser (1064 nm, 350 mJ, 20 Hz)	Single pulse standoff setup. Algorithm based on the peak intensity ratios used	Classification between organic samples and inorganic samples including explosives	Decision-making strategy for standoff LIB spectral analysis of energetic materials.	[41]

Experimental details	Technique	Samples	Comments	Refs.
Two Q-Switched Nd:YAG lasers (Brilliant B, Quantel, 5 ns, 800 mJ, 10 Hz), up to 30 m	ns DP-LIBS for standoff	PMMA and a variety of glasses. Detection of organic (DNT, TNT, C4, and H15) and inorganic explosive (sodium chlorate)	Mimicking conditions of inside vehicles, industrial warehouses, and buildings	[43]
A Quantel Brilliant Twins Q-switched Nd:YAG laser (532 nm, 10 Hz, 400 mJ/ pulse, 5.5 ns/pulse width)	Raman-LIBS integration	DNT/TNT, NaClO <sub>3</sub> /KClO <sub>3</sub> DNT/Nylon, NaClO <sub>3</sub> /NaCl		[45]
A high-power double-pulse Nd:YAG laser system (10 Hz, 850 mJ/pulse, 5.5 ns/pulse width)	ns DP-LIBS for standoff	Detect chloratite, DNT, TNT, RDX, and PETN residues that have been deposited on the surface of aluminum and glass substrates	Explosive human fingerprint imaging	[46]
A Q-switched 1064 nm Nd:YAG twins laser system (10 Hz, 850 mJ/pulse, 5.5 ns/pulse width)	Standoff LIBS, supervised learning methods	Standoff LIBS spectra at 30 m corresponding to unquantified residues of RDX and fuel oil	_	[47]
Legend Ti:Sapphire fs amplifier (2W, Coherent Co.), INNOLAS ns laser (1.2 J at 1064 nm, 10 Hz)	Near LIBS, time-resolved studies	LIBS spectra of NTO, RDX, and HMX using ns and fs pulses recorded in ambient atmosphere	No discrimination or classification	[56]
Legend Ti:Sapphire fs amplifier (2W, Coherent Co.)	Near fs-LIBS	LIBS spectra of NTO, RDX, and HMX using fs pulses in air, argon, and nitrogen	No classification or discrimination	[56]
Legend Ti:Sapphire fs amplifier (2W, Coherent Co.)	Near-field LIBS (fs)	A set of nitropyrazoles varying with number of nitro groups	No classification	[57]
Ti:Sapphire fs amplifier and ns laser systems (~1.2 J at 1064 nm, 10 Hz)	Near LIBS, time-resolved studies	A set of nitroimidazoles varying with number of nitro groups	No classification	[35]
Ti:Sapphire fs laser system (amplitude, ~3 mJ, 1 kHz, ~50 fs, 800 nm), ns laser systems (INNOLAS, ~1.2 J at 1064 nm, 10 Hz)	Near-field LIBS (fs and ns)	Explosive molecules (structural and functional isomers of triazole-substituted nitroarene derivatives)	No classification	[58]
SpitLight 1200, InnoLas Laser GmbH, Germany (1.2 J at 1064 nm, 10 Hz), nongated Czerny-Turner spectrometer (MAYA 2000, Ocean Optics, USA)	Near-field LIBS using ns pulses	Isomers of pyrazoles (1-nitro-pyrazole, 3-nitro-1H-pyrazole, and 4-nitro-1H-pyrazole)	Classification through ANN and PCA	[59]

(continued overleaf)

#### Table 1 (Continued)

Experimental details	Technique	Samples	Comments	Refs.
Ti-sapphire laser with a chirped pulse amplifier system,	Remote filament LIBS	DNT coated on Al and Cu	No classification	[60]
Q-switched Nd: YVO4 laser	Filament LIBS	Chemical and biological agents, barley, corn, and wheat grains, aluminum (50 m away)	No classification	[61]
Nanosecond and femtosecond LIBS	Filament libs	Al, Brass (30 m), Military grade TNT	No classification	[62]
Remote fs filament libs (2 m focusing and 12 m collection)	Femtosecond filaments	Copper, graphite, and organic sample	No classification	[63]
Legend Ti:Sapphire fs amplifier (2W, Coherent Co.)	fs-LIBS in argon ambiance	ANTA, DADNE, HMX, NTO, and RDX using fs pulses in argon atmosphere	Classification with intensity ratios and kNN technique	[64]

and identifying them [66]. Our detailed studies revealed that the fs-LIBS spectra of explosives are dominated with molecular emissions, whereas the ns spectra are dominated with atomic emissions (compared to molecular emissions). This could be attributed to the difference in fs and ns ablation mechanism in turn to the pulse duration. fs pulse is extremely short lived when compared to ns pulse. Thus, during fs ablation, ideally there is no plasma-pulse interaction, and no reheating of plasma. Thus, fragmentation is dominated and results in molecular radicals, whereas in the case of ns ablation, plasma-plume reheating exists, and the fragments are broken down into the atomic constituents. However, at later time intervals (after the ns pulse ends), as the plasma cools down, molecular emissions dominate over atomic emissions (due to the recombination of atomic species) even in ns-LIBS. Further, we have performed several correlation studies wherein the LIBS spectra from various explosive molecules were collected using ns and fs pulses and correlated with the structures of the molecules, number of nitro groups, explosive properties of the explosive molecules, etc. in the near field [35, 57, 58]. Sreedhar et al. have utilized intensity ratios from ns-LIBS data for classification of inorganic nitrogen-rich high energy materials (HEMs) and oxidizers (ammonium perchlorate, boron potassium nitrate, and ammonium nitrate) [67]. Myakalwar et al. classified isomers of pyrazoles (energetic materials) using artificial neural networks and principal component analysis (PCA) [59] using ns pulses in proximity. Several recent review articles [23, 68] describe and explain the importance of fs-LIBS in comparison with ns-LIBS technique. fs pulses offer several advantages in LIBS and its applications such as (i) low breakdown threshold, (ii) precise interrogation with the material, (iii) efficient ablation, (iv) lower continuum emission, (v) small ablated mass and sample damage, (vi) minimal heat affected zones (vii,) absence of fractionation vaporization and (viii) improved spatial resolution for 3-D mapping applications. Furthermore, several recent studies have also shown that fs lasers may have advantages over ns lasers for LIBS analysis in terms of SNR, and it has been proved that the substrate effects are minimal in the fs-LIBS case when compared with ns-LIBS. Additionally, since fs pulses can travel through the atmosphere as a self-propagating transient waveguide, they have advantages over conventional standoff LIBS approaches [69]. Mirell et al.



**Figure 2** Femtosecond standoff (up to 2 m, configuration 1) and remote (~8.5 m, configuration 2) LIBS setup. In the figure, M, A, HWP, BP, L, D, P, and T stand for mirror, aperture, half wave plate, Brewster plate, lens, collection system, plasma, and target, respectively. Source: Copyright @OSA. Reproduced with permission from Optics Express, 26(7), 8069–8083, 2018.

utilized fs pulses for remote sensing of DNT (dinitrotoluene) coated on aluminum [60]. Chin et al. demonstrated the capability of fs filamentation for remote sensing of chemical and biological pollutants [61]. Brown et al. utilized filament LIBS for detection of military grade trinitrotoluene (TNT) [62], and Baudelet et al. demonstrated that the self-channeling of fs pulses can be utilized for remote interrogation of organic samples [63]. Recently, we have successfully demonstrated classification of metals, bimetallic alloy strips in standoff mode (at a distance of  $\sim 6.5 \,\mathrm{m}$  away from the plasma) using fs filament-induced breakdown spectroscopy (fs-FIBS) [70]. Our group has also reported discrimination methodologies for explosives (ANTA, DADNE, HMX, NTO, and RDX) recorded in argon atmosphere using fs-LIBS technique [64]. fs-LIBS technique offers several advantages compared to other spectroscopic techniques, and our initial studies have demonstrated promising results [71, 72] for utilization of fs pulses toward detection of explosives in remote ( $\sim 8.5 \text{ m}$ ) and standoff (up to  $\sim 2 \text{ m}$ ) detection. In these studies, we have reported remote and standoff detection of novel explosive molecules (nitroimidazoles and nitropyrazoles) using the fs filament-induced LIBS technique. In combination with fs-LIBS data, PCA was employed to discriminate/classify the explosives, and the obtained results were very promising. Figure 2 shows the schematic of the experimental setup, and Figure 3 shows some of the results obtained toward classification. Our efforts will now be focused toward standoff detection of trace explosive molecules utilizing fs pulses and study the substrate effects.

In summary, there are advantages of both ns-LIBS and fs-LIBS configurations. However, there are several challenges to be addressed before LIBS technique can be routinely used for standoff detection [73]. They are (i) miniaturization of lasers, (ii) stable beam profile at remote distances, (iii) design and optics of detector, (iv) relying only on the traces left out during the handling of explosives (e.g. while burying a landmine or someone carrying it in luggage/vehicle), (iv) scanning area, and (v) development of a library or database of all common explosives. The essential requirements of these versatile fs/ns laser sources are to deliver high intensities at the point of interest with a stable beam profile, should be compact, and portable. Over the past few years, ns and fs lasers have



**Figure 3** (a) Principal component scores plot; (b) the first three PCs for the processed LIBS spectra of explosives (nitroimidazoles and nitropyrazoles) obtained at 8.5 m; (c) PC scores plot; and (d) the first three PCs for R-LIBS of different metals obtained at 8.5 m. Source: Copyright @OSA. Reproduced with permission from Optics Express, 26(7), 8069–8083, 2018.

been subjected to several developments in terms of miniaturization, power, and their versatility. As mentioned earlier, backpack MP-LIBS systems were already designed using ns lasers. Though ns lasers are miniaturized, their beam profile is not stable at very long distances, so alternatively fs lasers have to be investigated. However, fs lasers are slightly bulky, and miniaturization of fs amplifiers is still in progress. As an example, Libra (M/s Coherent Ltd.) is a single box fs amplifier system with both seed and pump lasers being fixed in it. Owing to this, they can be portable and mounted on a vehicle/trolley for on-field applications. However, Pellegrino et al. [74] have demonstrated near-infrared (IR) low-energy ultrashort laser pulse fiber lasers for portable applications. Undoubtedly, fs amplifiers have niche applications, and exploiting the capabilities of these lasers such as delivering energy to long distances (few meters to few kilometers) for standoff detection of bulk/trace/vapor form of explosives is a massive challenge for all the scientists. Appropriate technique (either nsor fs-LIBS) has to be identified, and in some cases, it may require scanning a small area or even a larger area. In this case, time should not be a constraint. Further, once the data is obtained, one needs to do statistical analysis and arrive at an unambiguous decision on the presence/absence of the explosive. Investigations on the utilization of nanoparticles (NPs) in LIBS technique to achieve low limit of detection (LOD) by enhancing the signal of analyte molecule could also be extended for trace detection of high-energy materials (HEMs) [75, 76]. Nevertheless, lot more efforts are required to understand the LIBS data of several explosives, mixtures, composites, simulants, etc. Additionally, we need to develop robust algorithms for identification/classification/discrimination of these materials. Moreover, improvement of superior optics, fibers, lasers, detectors (ICCDs) is inevitable for development of compact, robust, cost-effective LIBS instrument for on-field applications. Further, the losses in the fibers should be minimal (coupling and propagation losses) for exceptional results.

# 3 Raman Spectroscopy and Coherent Anti-Stokes Raman Spectroscopy (CARS)

Several spectrometric techniques were established to detect explosives, but Raman-based detection became a promising potential tool for simple, quick, nondestructive, and label-free molecular identification of samples. The Raman effect was originally observed in 1928 by the great physicist Sir C.V. Raman. Two years after the report of "a new type of secondary radiation," i.e. in 1930, he received the Nobel Prize in Physics for his work on the scattering of light [77]. He used an astronomical telescope to focus sunlight in benzene liquid and observed the Raman scattering effect due to in-elastically scattered photons. Here, the photons of the incident light interact with molecules of a sample and are then scattered. The frequency of scattered photons is frequency shifted (up or down) in comparison with the original monochromatic frequency, which is called the Raman effect. This shift provides key information about vibrational, rotational, and other low-frequency transitions in molecules. Raman scattering, as such, is a weak process with extremely small cross sections (typically ranging from 10<sup>-31</sup> cm<sup>2</sup> to  $10^{-26}$  cm<sup>2</sup>), thus providing a poor SNR. This situation generally fails to deliver essential, useful information of the important molecular fingerprints under investigation. To prevail over the ambiguity caused by the poor scattering cross sections, many experimental techniques, for instance stimulated Raman scattering, CARS, and SERS, were developed. Using a combination of fs and picosecond pulses for broadband excitation and narrowband probing allows monitoring of the temporal evolution of a whole set of excited vibrational coherences with high spectral resolution. The Raman spectrometer components improved by replacing sunlight and human eyes via mercury arc lamp and photographic plate, the laser source, and multichannel detectors. The new-generation portable/handheld Raman microscopes are now far easier to operate and provide on-site detection and analysis in real time. The development of optical filter technology has also made it possible to manufacture the compact Raman spectrometers.

# 3.1 The Basic Components of Raman Spectrometer

1. Light sources (lasers): These are needed to excite the target species to obtain unique vibrational characteristic Raman frequencies. Over the years, Raman spectrometers have been subjected to various modifications and improvizations. Modern Raman spectrometers use standard monochromatic sources at various excitation wavelengths ranging from UV to near infrared (NIR) [266 nm (UV), 532 nm, 632 nm (visible), 785 nm, and 1064 nm (NIR)]. For shorter wavelength excitation, the Raman scattering efficiency increases, but simultaneously the possibility of fluorescence and burning/damage of sample may also increase. However, this is not always true as the emission

of fluorescence is specific to a molecule. In few cases, the Raman spectrum could be found just between the absorption and emission range because of the gap between absorption and fluorescence, where the latter appears at the longer wavelengths. The scattering efficiency will decrease with increasing excitation wavelength (from green to red to NIR). Therefore, longer integration times or higher power lasers are required for acquisition of the Raman spectrum. If the excitation wavelength is in the UV-Visible region and matches with the absorption wavelength of analyte, it can result in the increase in the scattering intensities by factors of  $10^2 - 10^6$ , called resonance Raman spectroscopy. It is necessary to use the laser that has stable frequency and narrow bandwidth to avoid the errors in the Raman shift. The quality of the Raman peaks is directly affected by the sharpness and stability of the excitation light source. Semiconductor lasers have the problem of "mode hopping," which is caused by laser temperature, injection current into the laser, and optical feedback.

- 2. *Sampling optics*: To transmit the light waves through the system with low power loss, optics should be extremely sensitive and suitable for the selection/choice of all laser wavelengths.
- 3. *Mirrors*: To guide light through the spectrometer and the system.
- 4. *Lenses*: To focus the light onto the sample and also to collect the scattered light from the sample. The solid angle of collection of light by wide-angle microscope objectives effect on the Raman spectra. The collection efficiency of the objective directly depends on it's numerical aperture (NA) i.e., the objective with high NA can suspend a large solid angle and thus collects maximum signal and vice-versa. However, using a higher NA we can observe a change in the relative intensities, and changing the input wavelength will manifest in the Raman peak shifts.

- 5. *Filters*: To collect the Raman scattered light (Stokes) which contains the sample signature and to filter out the intense Rayleigh scattering signal. Double or even triple monochromators were routinely used to reject the intense diffuse laser scattering and Rayleigh scattering. The efficient dielectric or holographic filters are also being developed.
- 6. Detectors: Detectors form an essential component of Raman spectrometers. Detectors should be very sensitive as they have to detect the weak inelastic scattered light from the sample. Various detectors have been used in Raman spectroscopy, such as CCD (charge coupled device), EMCCD (electron multiplying charge coupled device), InGaAs, and InGaAsP diodes. These array detectors pixel density will affect the resolution of the spectra. Each pixel of the detector array will collect and hold charge based on the number of photons that strike. The signal-to-noise (S/N) ratio is dependent on the construction and material quality of the pixel.
- 7. All the spectrometer components can be integrated through electronic hardware, and an interfaced computer makes it possible for automatic operation.

Bremer and Dantus [78] introduced a sensitive method for laser-based standoff detection of chemicals based on stimulated Raman scattering. Selective excitation of a particular Raman transition was detected by measuring the diffusely reflected laser light from a distant surface. The method simultaneously measured stimulated Raman loss and gain within a single laser shot and is insensitive to the optical properties (reflectivity/absorptivity) of the substrate. They demonstrated the specificity and sensitivity of the Raman spectroscopy technique by detecting and imaging nanogram analyte microcrystals on paper, fabric, and plastic substrates at 1–10 m standoff distance using only 10 mW of laser power from a single fs laser. Figure 4 shows typical standoff SRS

Figure 4 Standoff SRS images of NH<sub>4</sub>NO<sub>3</sub> on cotton (a) and blue textured plastic (b); and TNT on cotton (c). The sample distribution on each substrate corresponds to  $<100 \,\mu g \, cm^{-2}$ , although the local concentration is higher. With 20 laser shots per pixel in the  $30 \times 30$  images, the distribution of the analyte is recorded by observing SRL. Statistics were used to eliminate points less than 0.8 standard deviations of the mean above zero. The black lines are guides to the eye. On (off) resonance is 1043 cm<sup>-1</sup> (950 cm<sup>-1</sup>) for NH<sub>4</sub>NO<sub>3</sub> and 1360 cm<sup>-1</sup> (1043 cm<sup>-1</sup>) for TNT. Data for (a) and (c) were collected at 10 m and (b) at 7.5 m [78]. Source: Copyright @AIP Publishing. Reproduced from M. T. Bremer et al., Appl. Phys. Lett. 103, 061119 (2013); doi: 10.1063/1.4817248 with the permission from AIP Publishing.



images of the sample ammonium nitrate. Glenn and Dantus [79] have summarized the advantages of the technique of single ultrafast pulse excitation for remote-stimulated Raman scattering (SUPER-SRS) wherein they were able to simultaneously detect two explosives (TNT and RDX), which were deposited on a barcode.

# 3.1.1 Coherent Anti-Stokes Raman Spectroscopy (CARS)

One of the variants of the Raman spectroscopy, CARS, has emerged as a powerful technique for sensing of low concentration analyte molecules. In this technique, instead of the traditional single laser system, two powerful laser pulses irradiate a sample collinearly. The frequency of the first laser is usually constant, while the frequency of the second one can be tuned in a way that the frequency difference between the two lasers equals exactly the frequency of some Raman-active mode of interest. This particular mode will be the only extremely strong mode in the Raman signal. With CARS technique we can obtain a strong, desired Raman peak of interest. In this case, a monochromator is not really required. A wideband interference filter and a detector behind the filter would do the job. However, by scanning the Stokes laser pulse or by using a broadband (supercontinuum) source, it is possible to obtain a full spectrum. Two laser beams with frequencies  $v_1$  and  $v_2$  ( $v_1 > v_2$ ) interact coherently, and because of the wave mixing, produce strong scattered light of frequency  $2v_1 - v_2$ . If the frequency difference between the two lasers  $v_1 - v_2$  is equal to the frequency  $v_{\rm m}$  of a Raman-active rotational, vibrational, or any other mode, then a strong light of frequency  $v_1 + v_m$  is emitted. In other words, to obtain strong Raman signal, the second laser frequency should be tuned in a way that  $v_2 = v_1 - v_m$ . Then, the frequency of strong scattered light will be  $2v_1 - v_2 = 2v_1 - (v_1 - v_m) = v_1 + v_m$ , which is higher than the excitation frequency  $v_1$ and, therefore, considered to be anti-Stokes frequency.

In 1977, Tolles et al. [80] have presented the fundamental theory and its applications in surface studies, reaction dynamics, photochemistry, etc. Wallin et al. [18] have reported a section on CARS technique

toward explosive detection in their review (laser-based standoff detection of explosives) back in 2009. A schematic of energy level diagram illustrating the CARS principle has been depicted in this review. Imaging with CARS [81] technique in various configurations or schemes (such as E-CARS and F-CARS) has wide imaging applications in chemical and biological systems where vibrational imaging with high sensitivity, high spectral resolution can be obtained. Natan et al. [82] have recently reported demonstration of a single-beam coherently controlled fs pulse CARS technique for remote detection and identification of minute amounts of solids and liquids at a standoff (>10 m)distance. They had succeeded in rapidly resolving the vibrational spectrum of trace amounts of contaminants, such as explosives and nitrate samples, from the weak backscattered photons under ambient light conditions. In their single-beam technique, they carried out the multiplex measurement of characteristic molecular vibrations using a single broadband phase-shaped fs laser pulse, which supplied the pump, and Stokes and probe photons simultaneously. They have demonstrated that fs-CARS spectroscopy exhibited higher efficiency at low average powers compared to the longer (ns) pulses used in conventional CARS techniques - a merit for the nondestructive probing of sensitive samples such as explosives. Bremer et al. [83] recently presented a nondestructive and highly selective method of standoff detection. The method was found to be orders of magnitude more sensitive than previous coherent spectroscopy methods, identifying concentrations as low as  $2 \,\mu g \, cm^{-2}$  of an explosive simulant mixed in a polymer matrix as shown in Figure 5. The approach used a single amplified fs laser to generate high-resolution multiplex CARS spectra encompassing the fingerprint region (400-2500 cm<sup>-1</sup>) at standoff distance. Additionally, a standoff imaging modality was introduced, visually demonstrating similar sensitivity and high selectivity, providing promising results toward highly selective

trace detection of explosives or warfare agents. Li et al. [84] reported the detection of characteristic Raman lines for several chemicals using a single-beam CARS technique from a 12-m standoff distance. Single laser shot spectra were obtained with sufficient SNR allowing molecular identification. Background and spectroscopic discrimination were achieved through binary phase pulse shaping for optimal excitation of a single vibrational mode. These results provide a promising approach to standoff detection of chemicals, hazardous contaminants, and explosives. Katz et al. [85] demonstrated single beam standoff CARS (>10 m) and identified various components KNO<sub>3</sub>, RDX, sulfur, Teflon, urea, and chloroform under ambient conditions as shown in Figure 6 at 12 and 5 m standoff distances. Brady et al. [86] demonstrated the detection of several chemical warfare simulants (dimethyl methylphosphonate and 2-chloroethyl ethyl sulfide) using multiplex CARS and at a distance of 1 m. They claim that fs pulses can be used to obtain a complete Raman spectrum in milliseconds time with high chemical specificity. Portnov et al. [87, 88] have demonstrated detection of explosives (RDX) via backward coherent anti-Stokes Raman spectroscopy (B-CARS) in near as well as standoff regime. Their results showed that the signal intensity obtained in B-CARS technique was comparable to that of spontaneous Raman scattering, which implies that B-CARS allows favorable detection as compared to the Raman technique. Furthermore, Portnov et al. believe that the detection of trace amounts of samples from distances of  $\sim$ 10–200 m is possible with minimal pulse energies of the pump and Stokes laser beams, depending on the species investigated.

### 3.2 Standoff Raman Spectroscopy and Spatial Offset Raman Spectroscopy (SORS)

Hirschfield first proposed the standoff detection using Raman spectroscopy [89]. Standoff

Figure 5 CARS spectra acquired at 1-m standoff on <5-µm PS films (a), <2.5-µm PMMA films (b), and 200-nm PMMA film containing 10% DNT (c). Percentages refer to the concentration of 2,4 DNT in the film relative to polymer mass. Unprocessed (a) and processed spectra (b) show detection of the 1350-cm<sup>-1</sup> DNT feature at 2% concentration. Unprocessed spectra in (c) show signal from a blank substrate (bottom spectrum) and 200-nm film (middle) integrated for 100 s to clarify features in the low signal-to-noise 1 s exposure (top). CO<sub>2</sub> and the rovibrational features of  $O_2$  are also visible in (c) [83]. Source: Copyright @AIP Publishing. Reproduced from M. T. Bremer et al., Appl. Phys. Lett. 99, 101109 (2011); doi: 10.1063/1.3636436 with the permission from AIP Publishing.



Raman spectroscopy defined as Raman spectroscopy performed where the spectrometer is at a distance from the sample, i.e., no physical contact between a threat and the operator. This physical separation avoids the possible severe damage to individuals and the data acquisition device. The basic difficulty will be to record the weak Raman signal with high sensitivity and selectivity for identification of explosives due to interference from the background as well as the environment. Availability of powerful lasers and highly sensitive CCD detectors has overcome this problem. Unfortunately, the use of high-power lasers creates significant practical problems in the field, can inflict damage on target substrates (explosive), risk of eye injury, or skin injury to operators and bystanders. Hobro and Lendl [90] reviewed the standoff Raman instruments (laser, optical lay-out, wavelength dispersion, and detection) and overviewed its application in explosive detection. Wen



**Figure 6** Resolved femtosecond CARS vibrational spectra of several scattering samples (dashed blue), obtained at standoff distances of (a–c) 12 m and (d–f) 5 m. (a) <1000  $\mu$ g crystallized KNO<sub>3</sub>, (b) <500  $\mu$ g sulfur powder, (c) cyclotrimethylenetrinitramine (RDX/T4) explosive particles with a total mass of <4 mg, (d) bulk PTFE, (e) <4 mg of crystallized urea particles, and (f) 1-cm-long cuvette containing chloroform and scattering ZnTe particles (200 nm diameter). Each spectrum was resolved from a single measurement with an integration time of: (a–c) 3 s, (d) 1 s, (e) 300 ms, and (f) 350 ms. The Raman vibrational lines and their relative strengths are plotted by gray bars for comparison [85]. Source: Copyright @AIP Publishing. Reproduced from O. Katz et al., Appl. Phys. Lett. 92, 171116 (2008); https://doi.org/10.1063/1.2918014 with the permission from AIP Publishing.

et al. [91] performed deep-UV Raman spectroscopy for optical standoff trace detection of explosives. Hadi et al. [92] designed small standoff Raman spectroscopy system and detected ammonium nitrate, TNT, and urea nitrate at a 4-m distance and ammonium nitrate and nitromethane (NM), at distances of 20 and 12.5 m, respectively. Muhammed Shameem et al. [93] designed time-gated Raman system by assembling pulsed laser and high-resolution echelle spectrograph. He tested standoff distance at 5 m by providing high-quality Raman signals of sulfur with low background noise and lowered fluorescence. Zachhuber et al. [94, 95] demonstrated the detection of explosives and related compounds in standoff mode using SORS technique, wherein they employed 532- or 355-nm laser excitation wavelengths, operating at 10 Hz with a 4.4-ns pulse length and variable pulse energy (maximum of 180 mJ/pulse at 532 nm and 120 mJ/pulse at 355 nm). The scattered Raman light was

collected by a coaxially aligned 6" telescope and then transferred via a fiber optic cable and spectrograph to a fast gating ICCD camera capable of gating at 500 ps. Additional research was needed to develop the inevitable systems for high signal-to-noise, low signal acquisition time, and long operator distances with safe laser sources. Moros et al. [96] highlighted the fundamentals of standoff Raman for the detection of a wide range of high explosives and associated compounds under different analysis conditions. Gulia et al. [97] detected RDX (down to 100 ppm) and a mixture of RDX with KBr in standoff mode at a distance of 5 m using time-gated Raman spectroscopy technique.

Asher's group [98–102] have thoroughly investigated the capabilities of the UV resonance Raman spectroscopy for explosives detection. They achieved <1 ppm detection limit for common explosives such as  $NH_4NO_3$ , PETN (pentaerythritol tetranitrate), TNT, HMX, and RDX dissolved in

ACN/water solutions with 229-nm laser excitation. They did not observe any nonlinear spectral response or sample degradation at the input fluences, spectral accumulation times used. Further, they have reviewed the potential of deep UV resonance-Raman spectroscopy in the standoff mode [82]. They highlight the unique advantages of this technique: (i) deep UV excitation results in increased Raman intensities due to the short wavelength excitation, (ii) occurrence of resonance enhancement because of the Raman spectral coupling of vibrational motion with electronic transitions, (iii) absence of fluorescence interference, and (iv) damage threshold of the eye is higher for deep UV light when compared to that of visible and near-IR sources. They have also performed studies on the UV-excited photochemistry of PETN in acetonitrile and photoproduct hydrolysis. Gaft and Nagli [103] established that UV (248 nm)-excited Raman signals of explosives are 100-200 times stronger compared to Raman with green color excitation (532 nm). Malka and Bar [104] designed a home-built Raman spectrometer with line excitation for fast, compact, and low cost detection and mapping of explosive molecules. Malka et al. [105] also developed compact green laser pointer-based Raman spectrometer and measured the Raman spectra of different explosives (e.g. KNO<sub>3</sub>, AN, urea, urea nitrate, DNT, TNT, RDX, HMX, and PETN), liquid samples (hydrogen peroxide, acetone, methanol, and isopropanol), and even performed chemical imaging. Further, they could also detect explosive residues on latent fingerprints with concentrations as low as 1 ng in short timescales ( $\sim 10$  s).

SORS technique is based on the recording of Raman spectra from regions, which are spatially offset on the sample surface from the laser beam interaction point [106]. It has been shown that the Raman spectra from different spatial offsets contain different relative contributions from various depths due to the wider spread of photons interacting with deeper layers emerging onto the sample surface. Cletus et al. [107] have successfully developed a direct-coupled, inverse SORS spectrometer toward the detection of different chemical hazards even when the background light and daylight are present. Their device was efficacious in recognizing the disguised chemicals in different types of packaging (multilayer and nontransparent) systems. Eliasson et al. [108] used SORS for detection of hydrogen peroxide, which is a critical constituent of number of liquid explosives. Recently, Agilent [109] has developed SORS-based devices for use in airports. They have demonstrated a handheld system along with a bigger system (Insight200M weighing 25 kg only) for screening bottles, aerosols, and gels. Some of these systems apparently are being used in airports in the United Kingdom.

# 3.3 Surface-Enhanced Raman Spectroscopy (SERS)

The critical drawback of Raman spectroscopy is the low intensity of the inelastically scattered photons, which carries information about the sample. This weakness leads to its inability to detect trace contaminants, especially in real-life applications. SERS was discovered in 1974 by Fleischmann et al. [110], who observed high-intensity Raman spectra of the molecule pyridine adsorbed onto a specially prepared roughened silver surface than expected. Van Duyne and Albrecht et al. independently explained the electric field enhancement, which is responsible for Raman scattering [111, 112]. Several reports and reviews described the major enhancement mechanisms of (i) electromagnetic (EM) nature (which can be as high as  $\sim 10^{14}$ ) and (ii) chemical nature (which can reach values up to  $\sim 10^6$ ). EM enhancement attributed to the localized surface plasmon resonance (LSPR) in the near field metallic surface and chemical enhancement is due to charge transfer (CT) mechanism between the substrate and the analyte. Generally, the enhancement due to the CT is one to three orders of magnitude smaller than that of EM.

The interaction of the incident EM field with metal NPs possessing negative real and small positive imaginary (absorption) dielectric constants induces collective and coherent electron oscillations, called plasmons. The superior local field enhancement was present at the vicinity of the overlap of the near-field regions between adjacent NPs, called "hot spots" [113].

SERS has the potential to provide effective in-field detection of chemical warfare agents (CWAs) due to the combination of high label-free sensitive molecular fingerprinting ability [114]. Effective SERS detection requires that target substances are attached to suitably nanostructured noble metal substrates. The development of robust and cost-effective nanofabrication processes for the production of SERS substrates, in particular structures that contain the so-called EM "hot spots" is, therefore a key requirement toward the widespread use of this technique [17, 115]. The degree of control and reproducibility of commercial as well as research-based SERS substrates are still disputed, and it is likely that significant improvements regarding performance and standardization have to be made in order to transform SERS technique into a widespread technique for routine chemical quantification. Laser ablation in liquids (LAL) is a green technique for producing NPs and NSs (nanostructures) in a single experiment/exposure. Several recent advances have demonstrated the capability of LAL with ultrashort laser pulses in various applications [116]. Hot-spot generation is a key issue in SERS, which enables gigantic signal enhancements. Additionally, controllable aggregation of NPs to enable controllable hotspots is a critical issue to measure reproducible SERS signals of the analytes. It is important to identify the correct/appropriate substrate(s) for each analyte molecule (in this case different explosive molecules, e.g. TNT, AN, RDX, and PA). The enhancements for each molecule should be high for the same substrate so that a single substrate should enable us to detect multiple analytes, if not all the analytes. Further, the substrate should be recyclable for multiple usages to cut down the cost and make them versatile [117–119]. Several research groups were testing the SERS technique sensitivity in detecting traces of explosives, nerve agents, and other hazardous chemicals [120-126]. Ben-Jaber et al. detected RDX (nM) and vapor phase detection of DNT using silver nanocubes (AgNCs) [127]. Hakonen et al. detected femtograms of picric acid (PA) using Ag pillars as SERS substrates using a simple handheld Raman spectrometer [128]. Chen et al. demonstrated portable silicon sensor with AgNPs as a SERS analytical platform for signal-on detection of trace TNT explosive vapors [129].

Several techniques, including chemical and lithography based, have been employed to fabricate SERS substrates (nanostructured metal patterns). Some of them are electron beam lithography, focused ion beam lithography, atomic layer deposition, and ultrafast pulsed laser ablation. Over the past decade our group has been working on SERS to detect the explosives by employing different SERS substrates using ultrafast laser ablation technique. In our earlier works, we studied individual metals as SERS substrates including (a) aluminum by fs ablation [130], (b) copper by multiple/single line ps ablation [131], and (c) silver nanoentities through ultrafast double ablation [132] techniques. Furthermore, we have also investigated (a) the effect of oblique incidence on silver nanomaterials [133] and their applications for SERS, (b) the influence of nondiffracting Bessel beam on the Ag targets [134], and (c) Au NPs/NS by fs ablation for long-term stability [135]. Additionally, bimetallic/alloy NPs/NS were studied to adopt the advantage of the metals such as silver-gold NPs/NS (Ag<sub>0.65</sub>-Au<sub>0.35</sub>, Ag<sub>0.5</sub>-Au<sub>0.5</sub>, and Ag<sub>0.35</sub>-Au<sub>0.65</sub>) [136], and a detailed study on the various compositions of Ag-Au (Ag, Au<sub>20</sub>Ag<sub>80</sub>, Au<sub>30</sub>Ag<sub>70</sub>, Au<sub>50</sub>Ag<sub>50</sub>, Au<sub>70</sub>Ag<sub>30</sub>, and Au<sub>80</sub>Ag<sub>20</sub>, Au) [137], Ag@Au, and Cu@Au NPs was performed using the technique of fs laser ablation [138]. Likewise, Ag NPs decorated ZnO nanostructures

were synthesized by a two-step process (ion beam sputter deposition of Ag NPs onto the ZnO nanostructure grown on borosilicate glass by rapid thermal oxidation) and utilized as SERS substrates. Recently, we have also demonstrated the fabrication of eco-friendly filter papers embedded with aggregated Ag/Au NPs, which act as efficient SERS substrates toward the detection of various analytes including three explosive molecules [139]. The aggregation was achieved using NaCl and SERS signal was optimized for different concentrations of NaCl. Furthermore, commercially available SERS substrates are added advantage for handheld Raman spectrometers for various analyte detection [140]. A summary of these SERS studies used for the detection of explosives (with the limits of detection) is provided in Table 2. The challenge that remains to be conquered is preparation/development of simple, robust, recyclable, and versatile (should detect all common explosives with high sensitivity) yet cost-effective SERS substrates for practical applications. This has to be combined with compact and powerful spectrometers, which should be portable or handheld. Furthermore, powerful algorithms are needed, which can analyze and identify the Raman spectra of unknown compound(s) and/or compare them with common explosives/mixtures along with a library of the Raman spectra of all common and new explosives molecules/mixtures.

# 4 Terahertz (THz) Spectroscopy

Terahertz spectral region is important for explosive materials since in this region most of these materials have unique signatures. Several advantages of this technique include (a) capability to detect concealed weapons because many nonmetallic and nonpolar materials are transparent in the THz spectral range, (b) explosives have characteristic peaks in the THz spectral region, which can be used to identify these compounds, and (c) THz radiation as such does not pose any health risk even while scanning. There are several reports on the detection of explosives using THz radiation. Teraview group has done some pioneering work in this area. For example, see http://www.teraview.com/ applications/homeland-security-defenseindustry/explosive-detection.html [154], wherein they discuss about detection of explosives concealed by clothing and shoes. Further, they have also shown a standoff system (TPS spectra 3000) from their company.

The important components of a THz system include (a) fs laser source (typically, we are not touching upon other ways of generating THz radiation), (b) THz generator (photo-conducting antenna or thin films or nonlinear optical crystals, etc.), and (c) THz detector. For imaging applications there will be additional components involved. Puc et al. [155] utilized THz time-domain spectroscopy combined with imaging to study the effects of different paper and textile barriers while collecting the spectral features of drug, explosive simulants. They achieved rapid detection along with identification of concealed simulants in the 1.5-4.0 THz frequency range using an organic-crystal-based THz time-domain system. Davies et al. [156] examined the THz spectra of a wide range of pure and plastic explosives. Palka et al. [157] demonstrated a THz time-domain technique for extracting spectral fingerprints from materials, which was based on the frequency analysis of the reflected signal from the sample. They have successfully presented results obtained for the case of covered samples of RDX-based materials.

There are several review articles highlighting the various aspects of THz technology for explosives detection including (a) sources used, (b) different explosives data, (c) imaging capability of a few explosives, and (d) future prospects for THz technology to be applied in the field and airports. Federici et al. [158] have reviewed the techniques used for explosives detection using THz radiation. THz spectra of common explosives such as

 
 Table 2
 Summary of the identification of explosives by SERS studies using either micro or portable Raman
 spectrometers.

SERS substrate	Analyte	Enhancement factor (EF)	Raman spectrometer	Refs.
Ag NSs	ANTA (1 μM)	10 <sup>6</sup>	Micro-Raman spectrometer (532, 785 nm)	[133]
Ag–Au NSs	FOX-7 (5 μM)	10 <sup>6</sup>	Micro-Raman spectrometer (532 nm)	[136]
Ag NSs	CL-20 (5 µM)	10 <sup>6</sup>	Micro-Raman spectrometer (532 nm)	[134]
Ag NSs	RDX (50 mM)	10 <sup>4</sup>	Micro-Raman spectrometer (532, 785 nm)	[132]
Cu NSs	ΤΝΤ (100 μΜ)	10 <sup>5</sup>	Micro-Raman spectrometer (WITec-Alpha 300) (532 nm)	[141]
Au NS/NPs	PA (5 μM); AN (50 μM)	10 <sup>4</sup> ; 10 <sup>3</sup>	Portable (785 nm)	[135]
Ag–Au NS and NPs	DNT (1 μM)	10 <sup>5</sup>	Portable (785 nm)	[137]
Cu@Au and Ag@Au NPs	PA (5 μM); DNT (1 μM)	10 <sup>4</sup> ; 10 <sup>5</sup>	Portable (785 nm)	[138]
Electrochemical rough gold film	2,4DNT (3 × 10 <sup>-11</sup> M)	_	Portable 785 nm	[142]
Klarite	AN (75 pg)	—	Renishaw inVia Reflex Raman Microscope (785 nm)	[143]
i) Klarite ii) Au NPs (30 nm)	TNT (100 ppm)	i) 10 <sup>8</sup> ii) 10 <sup>6</sup>	Portable 780 nm	[144]
GO-Au nanocage	TNT (10 f M); RDX (500 fM)	$1.6 \times 10^{11}$	Portable 670 nm	[145]
Ag NPs with NaCl	TNT (10 <sup>-10</sup> M)	—	Confocal (LabRAM Aramis, Horiba Jobin Yvon) 532 nm	[146]
Au NPs on paper	TNT (94 pg); DNT (7.8 pg)	_	Portable (785 nm) Raman spectrometer	[147]
Ag nanofilm	NTO $(35 \ \mu g \ L^{-1}$ in DI and 0.35 mg $\ L^{-1}$ in aged tap water)	_	Nicolet Almega XR dispersive (785 nm)	[148]
Au popcorn NPs	TNT (10 <sup>-10</sup> M)	_	Portable (785 nm) Raman spectrometer	[149]
Au NPs	TNT (10 <sup>-7</sup> M)	_	830 nm	[150]
Monolayer of 5 nm Au NPs	AN (7.7 ppm); RDX (0.19 ppm)	$5 \times 10^4$	Jobin-Yvon micro-Raman (532 nm)	[121]
Au triangular nanoprisms	TNT (100 fM); RDX (10 fM); PETN (10 fM)	$6 \times 10^{6}$	Foster + Freman Foram 785 HP	[117]
			Raman system (785 nm)	
Au–Ag alloy nanoplates	TNT; RDX (10 nM)	_	Renishaw inVia (633 nm)	[118]

SERS substrate	Analyte	Enhancement factor (EF)	Raman spectrometer	Refs.
Ni–Au, Ni–Pd, Ni–Ag, Ni–Pt	TNT (10 <sup>-7</sup> M); DNT (10 <sup>-7</sup> M)	10 <sup>10</sup>	WiTec GmbH, Alpha-SNOM	[119]
nanostructures	RDX (10 <sup>-6</sup> M)		CRM 300 (633 nm)	
Ag nanocubes	DNT (10 <sup>-15</sup> M); RDX (10 <sup>-9</sup> M)	$8.7 \times 10^{10}$	Renishaw 1000 spectrometer (633 nm)	[127]
	DNT vapor			
Gold-coated sapphire	2,4-DNT; 2,4-DNCB;	_	Renishaw inVia	[120]
NS	p-Nitroaniline (vapor phase)		Raman microscope (785 nm)	
Klarite	TNT; RDX; PETN; EGDN (200 pg)	_	Portable (785 nm) Raman spectrometer	[122]
Au NPs	TNT (22.7 ng $L^{-1}$ )	_	Renishaw inVia Raman (785 nm)	[123]
Ag NPs on graphene sheets	TNT (10 <sup>-11</sup> M)	_	Renishaw 2000 model confocal (514.5 nm)	[124]
Ag nanopillars	PA (20 ppt)	_	Handheld Raman (785 nm)	[128]
Ag micro/nanopillar	PA (10 <sup>-12</sup> M); NTO (10 <sup>-13</sup> M)	$2.4 \times 10^9$	Portable Raman spectrometer	[125]
ZnO–Ag NWs	ANTA; Fox-7; CL20 (10 μM)	107	Confocal micro-Raman (532 nm)	[151]
Sea urchin-like nano ZnO-paper	Sulfite in wine	_	Portable (785 nm) Raman spectrometer	[152]
AgNPs decorated Si wafer chip	TNT–PABT ( $10^{-8}$ M: from lake water, soil, envelope, liquor, $10^{-6}$ M: from vapors diffusing from residues)	_	Portable handheld (785 nm) spectrometer	[129]
Si NW Ag NPs	ΑΡ (50 μΜ)	10 <sup>4</sup>	Confocal micro-Raman (632 nm)	[153]
Filter paper loaded with	MB (5 nM); PA (5 µM);	$3.4 \times 10^{7}$ ;	Portable (785 nm) Raman	[139]
aggregated Ag/Au NPs	DNT (1 μM); NTO (10 μM)	$2.4 \times 10^4$ ;	spectrometer	
		$2.0 \times 10^4$ ;		
		$2.1 \times 10^4$		
Ag nanopillar	Cyclosarin-(20 $\mu$ g mL <sup>-1</sup> );	40 ng;	Handheld Raman	[140]
	RDX -(2 ng mL <sup><math>-1</math></sup> );	4 pg;	spectrometer	
	Amphetamine- $(2 \text{ ng mL}^{-1});$	4 pg;		
	PA- $(0.4 \text{ ng mL}^{-1})$	0.8 pg		

CL-20, hexanitrohexaazaisowurtzitane; EGDN, ethylene glycol dinitrate.

RDX, TNT, PETN, Semtex-H, HMX, C-4, and ammonium nitrate are reported in the literature. Shen et al. [159] performed reflection THz spectroscopic imaging of RDX. Choi et al. [160] performed reflection THz time-domain spectroscopy of RDX, HMX in the 0.3-3 THz spectral region. Further, they successfully determined the refractive index and extinction coefficient accurately. Kemp [161] identified the potential problems associated with THz spectroscopy for practical applications. He argues that (a) explosives features in this spectral region are relatively weak and broad and, thereby, tend to be camouflaged by the combined effects of atmospheric water vapor absorption and barrier attenuation. Further, there are issues/challenges such as scattering from clothing and the target explosives. Chen et al. [162] measured the absorption properties of 17 explosive-related compounds using THz technique. The absorption spectra were obtained in the range of 0.1-3 THz. Their data clearly demonstrated that most of those compounds had THz fingerprints (caused by both the intramolecular and intermolecular vibrational modes). Leahy-Hoppa et al. [163] reported the THz absorption spectra in the 0.5-6 THz spectral range for four explosives (RDX, HMX, TNT, and PETN) and identified additional unique spectral features in those explosives and claim that their data may aid in their spectral identification. Further, Leahy-Hoppa et al. [164] also reviewed the pros and cons of THz technique for a wide range of explosives detection.

Though there are several advances in the THz technologies for detection and imaging of explosives, there remain several challenges: (a) efficient, robust, compact fs laser sources for generation of the THz radiation, (b) efficient materials for generating broad-band THz radiation design of basic components (detectors and optics) in the frequency range of 0.1–10.0 THz are relevant and important for spectroscopy and imaging applications, (c) understanding the THz spectral behavior of explosives mixed with common interferants (paper, wood, clothes, plastics, etc.), (d) extensive database of all explosive molecules and their compositions/mixtures, (e) combining the THz data with complementary techniques such as Raman for unambiguous detection of explosives, (f) efficient mechanism (including algorithms) for scanning large areas and for collecting the THz radiation in reflection geometry for imaging applications, and (g) propagation studies of THz radiation in atmosphere, reflection from various sources, and collimation/focusing of the reflected/scattered THz radiation are essential for developing THz-based devices for explosives detection, which can be used in the field (e.g. airports).

# 5 Photoacoustic Spectroscopy (PAS)

Photothermal spectroscopy has been used recently to detect trace levels of gases using optical absorption and following thermal perturbations of the gases. The fundamental principle involved is the measurement of physical changes (e.g. temperature, density, or pressure), which results from the photo-induced change in the sample's thermal state. Photothermal methods are classified as indirect methods because the transmission of the input light used to excite the sample is measured indirectly. A few examples of the photothermal techniques include (a) photothermal interferometry, (b) photothermal lensing, (c) photothermal deflection, and (d) PAS. In most photothermal techniques, one measures the refractive index using combinations of probe sources and detectors, whereas in PAS, one measures the pressure wave produced by heating of the sample. PAS is a particularly sensitive technique, capable of trace gas detection at parts-per-trillion (ppt) levels. Holthoff et al. [165] suggested that though the photoacoustic sensors are very sensitive, the total system size represents a large logistics problem in terms of cost, size, and power consumption. There are several reports on



**Figure 7** (a) Experimental setup at one end of 100-m distance and (b) long-distance LDV at the other end. Source: Copyright @Elsevier. Reproduced from Fu et al. [169], *Optics and Lasers in Engineering*, 107, 241-246 (2018) with permission.

the PAS of explosives in the near field as well as in standoff detection. Marcus et al. [166] recently reported on the PAS detection explosives such as RDX, PETN, and TNT at a distance of 1 m. They demonstrated and discussed the evaluation of an interferometric PAS sensor or these studies. They argue that the strength of PAS allows for the building of tailored spectroscopic sensors that are designed to achieve specific tasks. Holthoff and Pellegrino [167] recently summarized the results obtained during the development of photoacoustic sensing platforms at the Army Research Laboratory, USA. Chen et al. [168] reported the standoff detection of explosives using tunable quantum cascade lasers (QCLs) and the PA technique. They utilized a mid-infrared QCL (emission wavelength near  $7.35\,\mu\text{m}$ ) as the laser source. Direct standoff detection of TNT was achieved using an ultrasensitive microphone. With the aid of a sound reflector, narrow band-pass filters, and amplifiers, standoff detection at a distance of 8 ft was also successfully demonstrated.

Fu et al. [169] very recently reported detection of explosives at a distance of 100 m in the standoff mode using a QCL-induced photo-vibrational signal on explosives using a laser Doppler vibrometer (LDV). Figure 7 shows the experimental schematic and actual setup. They tested the trace samples of three high-explosive substances: (i) TNT, (ii) PETN, and (iii) a mixture of TNT and PETN with a ratio of 50:50% by weight. The results acquired from their experiments were compared with the standard absorbance spectra (achieved using a Perkin–Elmer Frontier (Fourier transfer infrared) FT-IR/NIR spectrometer), and the data obtained clearly demonstrated that an optical interferometer (e.g. LDV) is a decent noncontact sensor for detection of the photovibrational signal in the standoff mode and in an open environment.

There have been several other reports on explosives detection [170–173], which have successfully demonstrated isolated cases of detection. El-Sharkawy et al. [174–176] have recently performed remarkable experiments with PAS toward detection of explosive residues. They have reported instantaneous trace detection of TNT, RDX, and HMX using customized PAS technique by simultaneously validating the optical sensor signals with traditional piezoelectric transducer, where the customized optical sensor has shown fast response, high sensitivity with 10 cm standoff detection capabilities [174]. They have also

recorded PAS signal of explosive-related materials such as urea nitrate, ammonium nitrate, and ammonium perchlorate with distinguished peaks referring to good discrimination [175]. Furthermore, the presence of explosophorous bonds [nitrates (NO<sub>3</sub><sup>-</sup>) and perchlorates (ClO<sub>4</sub><sup>-</sup>)] has been investigated using phase-shift domain analysis between explosive and similar nonexplosive materials [176]. They have also demonstrated the capability of PAS technique to identify the residues of PETN, TNT, and AN with 1-s accumulations from a 3-m standoff distance. Thus, PAS can offer possibly fingerprint spectral option for each explosive material, with (a) novel discrimination capability and (b) real-time detection possibility along with standoff capability since there are no two materials with the same optical, thermal, and acoustical properties [177]. Patel et al. [178] have earlier demonstrated the capability of PAS technique, using QCLs, for the detection of CWAs and explosives with high sensitivity. They demonstrated detection capability of CWAs at parts-per-billion levels with false alarm rates of <1:108. However, concrete efforts are still required to arrive at usable devices for a variety of applications. The major applications for THz radiation identified include (a) screening of humans/baggage at airports and screening of moving vehicle at various places, (b) detection of land mines, (c) detection from minute quantities of samples (postblast scenario or forensics), and (d) screening for explosives in malls and public places. Further concerted efforts from scientists, engineers, and the users together will enable development of robust sensing technologies.

## 6 Concluding Remarks

In conclusion, there are several laser-based spectroscopic techniques reported in the literature, with some of them in advanced stages of research, capable of detecting explosives from a distance. However, none

of these techniques are ready to be used directly in the field for applications (though there a few devices based on THz and SORS that have been employed for detection in selected airports). The main and unresolved challenge still remaining today is the detection of trace explosives from a distance (e.g. detection of land mines is extremely difficult even today). Several factors need to be considered and researched before each of these techniques has full-fledged applications. No one technique can detect all the explosives and in different scenarios. One must identify the niche applications of each of these techniques and try to develop hybrid methods to fulfil most of the requirements. SORS can identify concealed explosives, while Raman and LIBS have the potential of standoff detection of more than 100 m, while THz technique has the capability of imaging hidden materials.

- 1. Novel laser sources (ns and fs) that are powerful, compact, robust, and cost-effective are need of the hour.
- 2. Compact/miniature detectors/spectrometers are again needed. They should not fully compromise on the resolution or detection capability even when the size is miniaturized.
- 3. Broad-band optics (which can transmit in the entire UV, visible, and NIR spectral range) with antireflection coatings are essential to collect the weak light signal from a distance.
- 4. Efficient telescope designs are warranted to collect tiny amount of light emanating from the traces of explosives (especially for LIBS and Raman cases).
- 5. Development of simple, robust, recyclable, and cost-efficient SERS substrates is necessary along with portable and handheld spectrometers with high efficacy.
- 6. Understanding of the interaction of THz radiation with several materials (clothes, paper, and wood) and in different atmospheric conditions (rain, humid, dry, snow, etc.) for propagation and collection of THz

radiation, especially for standoff configurations.

- 7. A complete database (Raman, LIBS, SERS, etc.) of all the explosive molecules, mixtures, interferants, liquids, etc. is desirable along with appropriate powerful algorithms to identify/detect/discriminate/ classify these molecules from others.
- 8. Ideally, for standoff applications, one wishes to have drones [179] fitted with laser source and detector and wireless network such that the drone can be sent to point of interest and collect the data (wireless connection) continuously.

### **Abbreviations**

CCD	charge-coupled device
CL-20	hexanitrohexaazaisowurtzitane
DNT	dinitrotoluene
EGDN	ethylene glycol dinitrate
FIBS	filament-induced breakdown
	spectroscopy
fs	femtosecond
FT-IR	Fourier transfer infrared
HMX	octahydro-1,3,5,7-
	tetranitro-1,3,5,7-tetrazocine
ICCD	intensified charge-coupled device
IR	infrared
LIBS	laser-induced breakdown
	spectroscopy
LOD	limit of detection
NM	nitromethane
NS	nanostructure
Ns/ns	nanosecond
PAS	photoacoustic spectroscopy
PCA	principal component analysis
PETN	pentaerythritol tetranitrate
QCL	quantum cascade laser
RDX	cyclotrimethylenetrinitramine
SERS	surface-enhanced Raman
	spectroscopy
SORS	spatial offset Raman spectroscopy
THz	Terahertz
TNT	trinitrotoluene
	1

### UV ultraviolet

## Glossary

- **ablation** The process of removing a material from the surface of a solid by irradiating it with a laser pulse. Irradiation results in the material getting heated by the absorbed laser energy and evaporates or sublimates.
- **explosives** Materials that store large amount of energy within them and release it within a short period of time when triggered.
- femtosecond A very short timescale that is equal to  $10^{-15}$  s.
- **laser ablation in liquids** The process of ablating a material/target placed in a liquid media and short laser pulses. The input laser pulse could be a nanosecond or a femtosecond pulse.
- **nanoparticle (nanopowder, nanocluster, or nanocrystal)** A microscopic particle with at least one dimension <100 nm.
- **Raman spectroscopy** A technique that provides information about the molecular vibrations and is generally used for sample identification. The technique is based on inelastic scattering of monochromatic light, usually from a laser source.
- **SEM (scanning electron microscope)** A type of electron microscope that produces very high-resolution (submicron) images of a sample by scanning it with a focused beam of energetic electrons.
- **TEM (transmission electron microscopy)** A technique capable of imaging at a considerably higher resolution than normal light microscopes.

## **Related Articles**

Raman Spectroscopy Instrumentation Geometric Optics Raman Scattering for Speciation and Analysis Molecular Spectroscopy Spectroscopy, Atomic

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