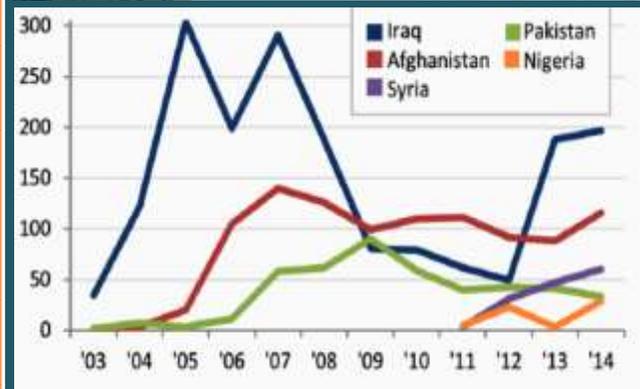


2015

Laser-Based Standoff Explosives Detection Technologies



Laser-Based Standoff Explosives Detection Technologies

August 2015

Homeland Security Research Corp. (HSRC) is an international market and technology research firm specializing in the Homeland Security (HLS) & Public Safety (PS) Industry. HSRC provides premium market reports on present and emerging technologies and industry expertise, enabling global clients to gain time-critical insight into business opportunities. HSRC's clients include U.S. Congress, DHS, U.S. Army, U.S. Navy, NATO, DOD, DOT, GAO, and EU, among others; as well as HLS & PS government agencies in Japan, Korea, Taiwan, Israel, Canada, UK, Germany, Australia, Sweden, Finland, Singapore. With over 750 private sector clients (72% repeat customers), including major defense and security contractors, and Fortune 500 companies. HSRC earned the reputation as the industry's Gold Standard for HLS & PS market reports.

**Washington D.C. 20004, 601 Pennsylvania Ave., NW Suite 900,
Tel: 202-455-0966, info@hsrc.biz, www.homelandsecurityresearch.com**

Table of Contents

1	Standoff IED, PBIED & VBIED Detection Pipeline Technologies	4
1.1	Laser-Based Standoff Explosives Detection	4
1.1.1	Introduction.....	4
1.1.2	Standoff Laser-induced Breakdown Spectroscopy (LIBS)	7
1.1.3	Next Generation Standoff LIBS Systems.....	9
1.1.4	Laser-Based Molecular Signatures Technologies	10
1.1.5	Laser-Based Stimulated Raman Adiabatic Passage (STIRAP) Technologies.....	11
1.1.6	External Cavity Quantum Cascade Lasers Standoff IED Detection	12
1.1.7	Standoff Laser Induced Fluorescence (PLP/LIF) Technology.....	14
1.1.7.1	PLP/LIF Standoff Explosives Detection: Principle of Technology	14
1.1.7.2	Next-Generation Standoff PLP/LIF Systems.....	15

List of Tables

Table 1 - Comparison of Laser Based Standoff Explosives Detection Technologies	6
--	---

List of Figures

Figure 1 - Short Range Standoff Vehicle-Borne Explosives Detection Setup	4
Figure 2 - Vapor Pressure of Important Explosives.....	5
Figure 3 - LIBS Principle of Operation	7
Figure 4 - Standoff Laser-Induced Breakdown Spectroscopy Real-time Explosive Detection	8
Figure 5 - LIBS Emission Temporal Resolution as a Tool to Discriminate Between Different Explosives.	9
Figure 6 - Absorbance Spectra of Various Explosives and Tuning Range of External Cavity Quantum Cascade Laser Source.....	13
Figure 7 - PLP/LIF Technology: Principle of Operation.....	14
Figure 8 - Fluorescence Energy Levels	14

1 Standoff IED, PBIED & VBIED Detection Pipeline Technologies

1.1 Laser-Based Standoff Explosives Detection

1.1.1 Introduction

Standoff explosives trace detection methods aim to detect traces from handling explosives or the vapors surrounding an explosive material associated with the vapor pressure of the explosive. The technologies described are mostly laser-based trace detection technologies such as:

- Laser-induced-breakdown spectroscopy
- Raman spectroscopy
- Laser-induced-fluorescence spectroscopy
- IR spectroscopy

This chapter includes field-evaluated, novel techniques, as well as those not yet tested in realistic environments.

Figure 1 - Short Range Standoff Vehicle-Borne Explosives Detection Setup

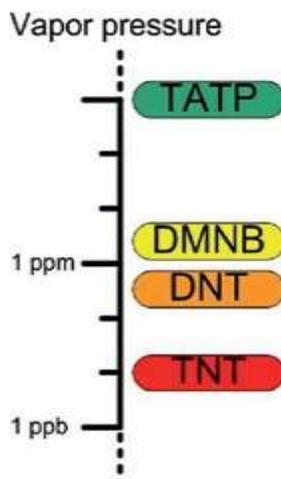


(Source: S. Wallin)

All the laser-based technologies reviewed below are not expected to be ready for use before 2013. They need further RDT&E (research, development, testing & evaluation) to be useful in a real environment. However, some of them are more mature than others. MMWave-based systems are deployed for active use while Standoff Explosives & Weapon Detection is an area of research under rapid development.

(Source: Sara Wallin et al)

Figure 2 - Vapor Pressure of Important Explosives



Several of the Standoff Vehicle-Borne Explosives & Weapon Detection methods discussed below have detection limits too high for detection of explosives under realistic conditions. A definition of required detection limits is beyond the scope of this report. However, an understanding of the required levels can be obtained by the study of vapor pressures and the amount of material available in fingerprints. Any laser-based, Standoff Vehicle-Borne Explosives & Weapon Detection method (except for very limited scenarios) must be sensitive enough to detect explosive traces in the vapor phase or in the form of particles. Many detection technologies have problems with their selectivity not being sufficient to handle the presence of interferents in a non-laboratory environment. To avoid excessive false alarms, detection methods need to be reasonably immune to these interferents.

The better the method's selectivity, the less susceptible it is to interferents. Although further RDT&E can probably increase both the sensitivity and the selectivity of some of these methods, it is unlikely that one technology will be the sole solution. The integration of several technologies using their respective strengths is most likely the fastest way forward. In real-life scenarios, imaging technologies can be expected to provide warnings to be followed up by more specific technologies based on spectroscopic identification. PF-LIF and PF-MIR are limited to detection of molecules with NO₂ functional groups. These must be complemented by other technologies for detection of a full range of explosives.

The Raman-based methods have good potential to be upgradeable to new threats as the LIBS. LIBS however, is very much dependent on a type of data processing that requires full knowledge of threat substances as well as possible interferents. However, if this shortcoming can be dealt with, it can also be upgraded.

The information obtained from PF-LIF and PF-MIR spectroscopy is not specific enough to identify the explosive and is limited to detection of molecules with NO₂ functional groups. Therefore, they are not upgradeable. This report has discussed several laser-based Standoff Vehicle-Borne Explosives & Weapon Detection technologies for explosives. Some technologies such as LIBS, Raman spectroscopy and PF-LIF have been field tested and should be considered as more mature technologies, even though they are still in the research stage.

Some detection technologies measure molecular properties in the vapor phase, others measure molecular properties directly from the particulate form and some of them measure the properties of fragments of these molecules. Therefore, direct comparisons of these technologies are difficult to make.

The properties of a detection method should also be assessed by stringent testing for a certain setup. The technologies addressed in this review have not been subjected to such testing and many properties can therefore not be objectively assessed. The table below shows a comparison of some key properties. This is based on data from referenced reports as well as a somewhat subjective assessment based on knowledge of the scientific basis on which the technologies are based. The objective of this comparison is not to give exact scientific data but to at least place these methods in some kind of perspective relative to each other.

Table 1 - Comparison of Laser Based Standoff Explosives Detection Technologies

	Sensitivity	Sample Type ^a	Molecular Selectivity	Sensitivity to interferents	Distance (m) ^b	Tested in Real Environments	Eye Safe ^c	Detection Time (s)	Complexity
Raman Spectroscopy	Medium	B	Good	Low to medium ^d	470	Yes	N	~1	Low
LIBS	High	B, P	Medium	Medium to high	>45 ^e	Yes	N	~1	Low to medium
PF-LIF	Medium	B, P, G	Medium	Medium	~30 ^f	Yes	Y	~1	Medium
RRS	High	P, G	Very Good	Low	>30 ^f	No	Y	~10 ^g	Medium
PF-LIF IRRRS Spectroscopy	Low	B, P	Poor	High	~20 ^h	No	P	<30	Medium
CARS	Very High	P	Good	Low	>12	No	P	~10 ^g	Very high

LIBS laser-induced-breakdown spectroscopy, **PF** photo-fragmentation, **LIF** laser-induced fluorescence, **RRS** resonance Raman Spectroscopy, **CARS** coherent anti-stokes Raman spectroscopy

^a **B** bulk, **P** particles, **G** gas phase

^b As shown so far

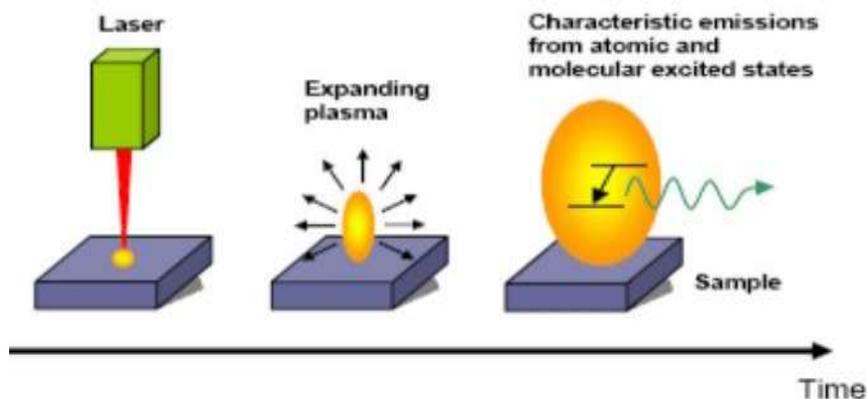
- c **Y** yes, **N** no, **P** has potential to be depending on the choice of wavelength and laser power/pulse energy required
- d Sensitive to possible fluorescing interferents in the nanosecond range
- e Estimate from Lopez-Moreno et al. and the fact that LIBS emission is compared with e.g., Raman signals
- f Estimated from experiments at shorter range
- g Scanning method-depends on the number of substances searched for
- h Estimated from experiments at 5 m

(Source: Sara Wallin et al.)

1.1.2 Standoff Laser-induced Breakdown Spectroscopy (LIBS)

Laser Induced Breakdown Spectroscopy (LIBS) is a detection method that uses a laser with high energy to break down the sample into plasma. This plasma emits light with characteristic frequencies from ionic, atomic and molecular species that can be detected with a spectrometer thus allowing identification of the elemental composition.

Figure 3 - LIBS Principle of Operation

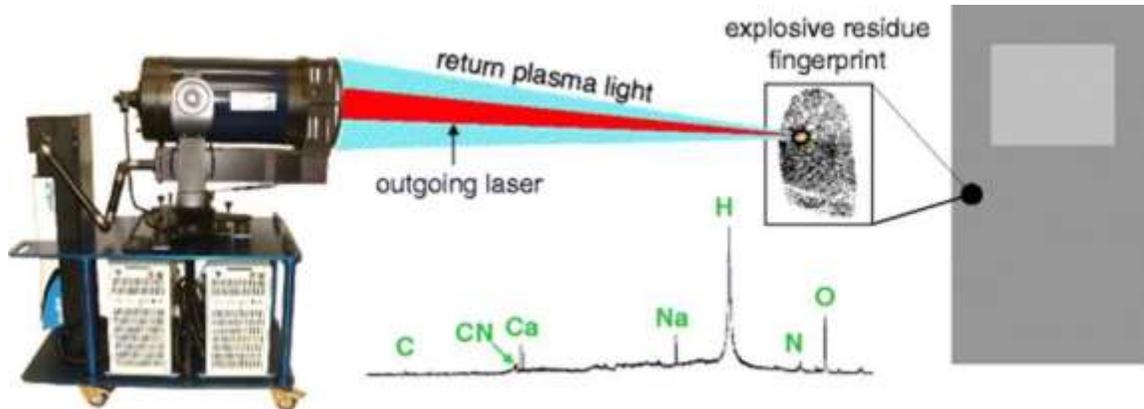


Laser-induced breakdown spectroscopy (LIBS) offers the capability for real-time, Standoff IED, PBIED & VBIED Detection of explosive trace amounts on various surfaces. Research in this area is presented in open literature. Both laboratory and field-tested standoff LIBS instruments have been used to detect explosive materials. LIBS technology uses double-pulse LIBS to reduce air entrainment in the analytical plasma and the application of advanced chemo-metric techniques such as performing partial least-squares algorithms analysis to discriminate between residues of explosives and non-explosives on various surfaces.

A number of challenges associated with detection of explosives residues using LIBS are still under research along with their possible applications. A few

research teams have investigated methods for improving the sensitivity and selectivity of LIBS for detection of explosives including the use of femtosecond-pulsed lasers, supplemental enhancement of the laser-induced plasma emission and complementary orthogonal techniques. Although RDT&E is not completed, researchers have demonstrated the high potential of LIBS for real-time detection of explosives residues at standoff distances.

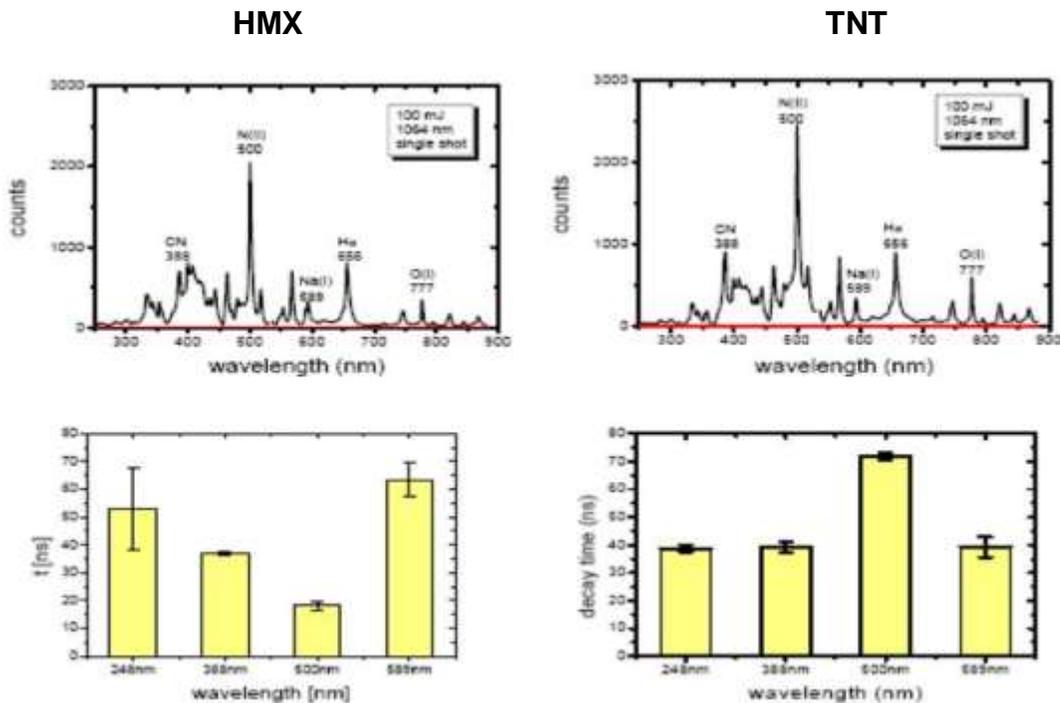
Figure 4 - Standoff Laser-Induced Breakdown Spectroscopy Real-time Explosive Detection



(Source: Jennifer L. Gottfried et al)

The open problem with the practical use of LIBS is whether it is possible to accurately identify the detected explosives in a real environment. In a real environment, there will be many interfering substances. The explosive surface may not be exposed so the detection may be made on surface trace particles. Therefore, other dust particles and dirt, as well as parts of the surface may interfere with reliable detection. There can also be contributions from nitrogen and oxygen in the air. Another possible problem is peak intensity variations depending on plasma temperature variations from shot to shot. De Lucia et al. has investigated some of these issues. They identify two possible ways to identify the origin of a LIBS spectrum. The first is to make a spectral matching with a predetermined spectral library and the second is to use the stoichiometry of the compound by taking the intensity ratio between peaks of interest. For explosives, these ratios would be C: H and N: O.

Figure 5 - LIBS Emission Temporal Resolution as a Tool to Discriminate Between Different Explosives.



(Source: Schade

1.1.3 Next Generation Standoff LIBS Systems

Next generation standoff LIBS systems will have the following features:

- Limit of detection: Nano to Pictograms
- Speed: fast
- Selectivity: high
- Applicability: Standoff detection
- Cost outlook: approximately \$20- 50K
- Sample type: solid, liquid, gas, aerosol
- Operator Skill: medium
- Configuration: no limitation to develop a rugged and field portable device

1.1.4 Laser-Based Molecular Signatures Technologies

Every optically based sensing method requires a prior knowledge of the molecular signature, or in this case, wave-length specific signature, for the species of interest. For many species, high quality, low spectral resolution ($\sim 0.1 \text{ cm}^{-1}$) databases are sufficient. There are literally person-decades of effort contained in these infrared databases. And, for many small molecules, spectral resolution of this magnitude is sufficient for achieving rotationally resolved vibrational spectra. When greater specificity or discrimination is required, high spectral resolution signatures are needed.

Fortunately, there are also a number of high quality, high spectral resolution databases that have been developed and maintained. The HITRAN database is one example of such a database. However, many of these high-resolution databases contain spectral information for a limited number of species. For example, although the current HITRAN database contains over 7 million rotationally resolved transitions, only 47 different molecular species (and their isotopic variations) are represented. Nevertheless, most of the major species relevant for atmospheric analysis are contained in this high resolution spectral database.

In the case of explosives, it is often not the energetic compound that is of interest, but rather a volatile impurity or perhaps a photo fragment. For TNT-based explosives the volatile explosive bouquet consists of toluene, nitrobenzene, and the mononitrotoluene (MNT). A detailed database containing the high-resolution spectral signature for such compounds is extremely limited, in part due to the fact that each is an asymmetric top and is expected to exhibit fairly complex spectra when examined at high spectral resolution and room temperature conditions.

For many bouquet species, again, high quality low resolution infrared data is widely available. To a significant extent, we have used these databases as a starting point for our high resolution infrared measurements. All of the infrared measurements shown here were collected using the spectrometers. For the longer wavelength measurements, various Pb-salt diode lasers were utilized as the primary light source. At shorter wavelengths, a combination of Pb-salt diode lasers and cw external cavity quantum cascade lasers (QCLs) was used.

While a comprehensive table of nitrobenzene rovibrational absorptions near 700 cm^{-1} has been generated, we have not been successful assigning a complete set of rotational quantum numbers to these transitions. Certainly, the complex nature of the spectra contributes to the challenging nature of generating accurate assignments. Another contributing aspect however is the discrete tuning limitation associated with Pb-salt diode lasers and this limitation is particularly true at longer wavelengths where He cooled cryogenic cooling is necessary for laser operation. Continuous tuning is accomplished over a single longitudinal mode of the laser. Helium cooled diodes typically

possess very short longitudinal mode tuning ranges in frequency space ($<1 \text{ cm}^{-1}$ in many cases) with adjacent modes being separated by $3\text{--}5 \text{ cm}^{-1}$.

The molecular signatures for species associated with RDX-based explosives do not typically contain nitro groups. In fact, based on a series of GC/MS measurements, the explosive bouquet for RDX-based contains cyclohexanone, ethylhexanol, and isobutylene. Of these compounds, isobutylene lends itself to high-resolution spectroscopic study most readily. Several rovibrational bands of isobutylene occur at shorter wavelengths and these bands have been successfully investigated with Pb-salt diode laser technology. For example, the band at 11 microns has been observed, analyzed, and assigned, at least for the torsion-free vibrational bands. Some headway has also been achieved on the band centered near 1380 cm^{-1} . What is interesting about these two bands is the observed regularity associated with the P, Q, and R branches.

1.1.5 Laser-Based Stimulated Raman Adiabatic Passage (STIRAP) Technologies

Laser induced fluorescence is a very sensitive technique for monitoring molecular species. Unfortunately, it is not very useful for many of the species of interest for threat detection in the atmosphere. These relatively small molecules frequently require excitation in the ultraviolet and there are many other trace species in the atmosphere that are also excited in the UV, significantly complicating result interpretation. Techniques that use two photons for excitation allow much more selectivity in targeting the molecule of interest but at a cost of more instrument complexity. One such technique is Stimulated Raman adiabatic Passage or STIRAP.

In its most basic form, STIRAP requires three energy levels of an atom or molecule with good electric dipole coupling between an initial state and an intermediate state as well as good electric dipole coupling between the intermediate state and a final state

In order to perform ordinary sequential excitation or stimulated emission pumping (SEP) the first laser (pump) excites the molecule from level $|i\rangle$ to level $|j\rangle$ after which the second laser (Stokes) excites from level $|j\rangle$ to level $|k\rangle$. STIRAP differs in that the order of the laser pulses is reversed, albeit with partial temporal overlap. This counterintuitive sequence is capable of transferring 100% of the atoms or molecules from the initial state to the final state, whereas SEP transfers a smaller fraction to the final state. STIRAP can be performed with any ordering of the atomic/molecular energy levels with lambda, (initial and final states lower than the intermediate state) and ladder (final state higher than the intermediate state which is higher than the initial state) being the most common.

1.1.6 External Cavity Quantum Cascade Lasers Standoff IED Detection

In the case of explosives detection, this distance is around 5–25 m. For standoff detection of trace amounts of material, only laser-based techniques have the potential to provide sufficient sensitivity. Indeed, optical detection techniques based on IR-laser spectroscopy represent a promising approach because almost all explosive chemicals typically exhibit strong, characteristic absorbance patterns in the mid-IR spectral range. Transparency of the atmosphere is another crucial prerequisite for detection techniques designed to work over distances of at least a few, preferably some tens of, meters. Thus, the atmospheric transmission window of $\lambda > 7.3\mu\text{m}$, where (by chance) most organic chemicals exhibit strong light absorbance, is a suitable spectral region for this purpose. Here, we describe the design and assessment of a new mobile imaging standoff detector.

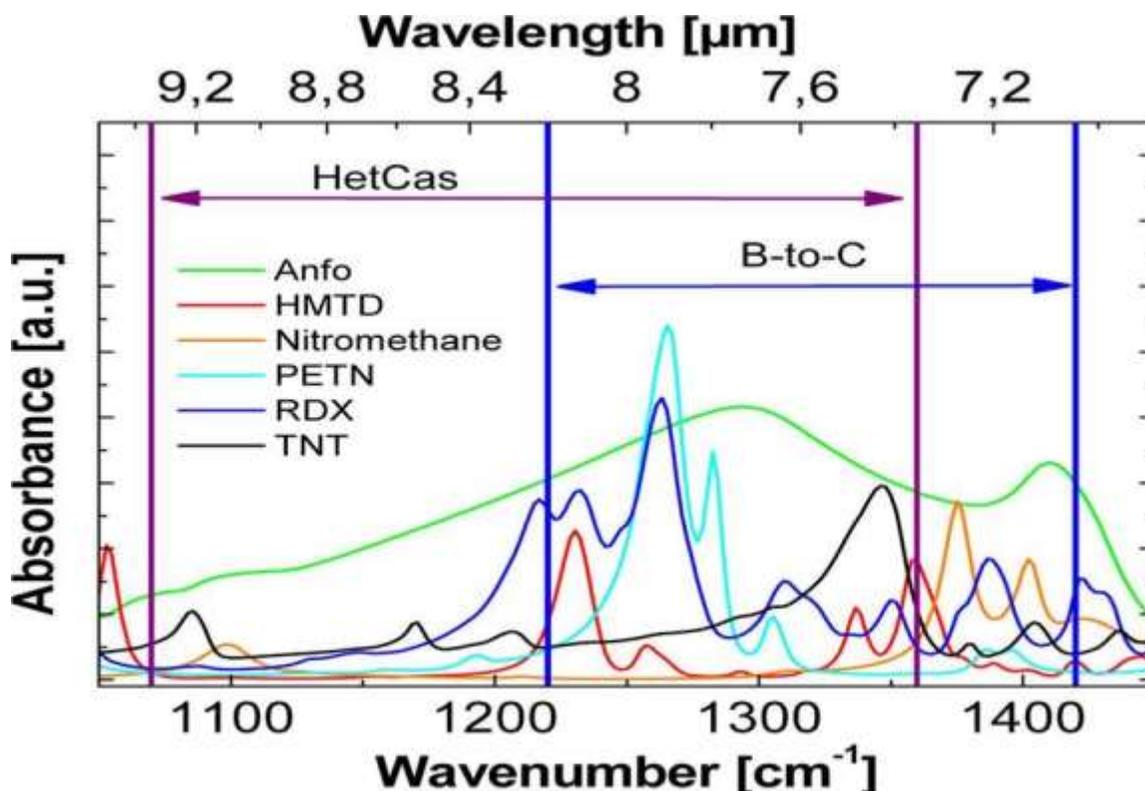
The key element of our system is the quantum cascade laser. These new unipolar semiconductor laser sources are based on inter-subband transitions in indium gallium arsenide and aluminum indium arsenide hetero-structure superlattices grown on indium phosphide. The gain characteristics of the laser can be optimized for high-power operation as well as for broad spectral tuning. For the present application, it is beneficial to design the quantum well system such that the initial state of the laser transition is a bound state. The broadening of the gain curve is achieved with a super-lattice design offering a broadened mini-band for the final state. This type of laser design is called 'bound-to-continuum.'

With these lasers, high power levels that are eye-safe can be generated in the IR spectral region. In the past, semiconductor lasers operating in this spectral range had to be operated using cryogenic cooling. However, new classes of IR lasers are small, rugged, and can operate at room temperature. This makes real-world applications like standoff detection outside a laboratory situation possible. Additionally, quantum cascade lasers are highly wavelength-versatile semiconductor lasers owing to their gain properties, which can easily be tuned over a wide range. For spectroscopy of explosives, the range of the laser source needs to cover wavelengths of the fingerprint absorbance of the chemical species being measured.

The broadly tunable quantum cascade lasers used are based on a bound-to-continuum design with a central wavelength of $\sim 7.5\mu\text{m}$. To further increase the spectral range covered by a single chip, we also grew lasers comprising two different active regions with central emission wavelengths of ~ 7.8 and $\sim 8.8\mu\text{m}$, respectively. We refer to this as a heterocascading, or HetCas, design. The gain characteristics of two B-to-C lasers centered at wavelengths of 7.3–9.5 and 9.5 μm are combined, resulting in enhanced spectral tuning. This band is ideal for concealed observation because wavelengths of $\sim 8\mu\text{m}$ cannot be seen with the naked eye. Only a person equipped with an IR imager would be able to see that a measurement was being performed.

An external cavity quantum cascade laser serves for active illumination with a maximum tuning range of about 300cm^{-1} . By a commercially available IR imager for collecting the diffusely backscattered radiation. Using this setup, we demonstrated the contactless detection of the IR fingerprints of a variety of explosives – such as pentaerythritol tetranitrate (PETN), trinitrotoluene, and cyclotrimethylene-trinitramine – on different substrates, such as pieces of factory-painted sheets from the body of cars as well as the polyamide commonly used in backpacks. The software processing of the hyperspectral data cube enables fully automatized identification against a background of nonhazardous materials.

Figure 6 - Absorbance Spectra of Various Explosives and Tuning Range of External Cavity Quantum Cascade Laser Source



(Source: Fraunhofer Institute for Applied Physics)

1.1.7 Standoff Laser Induced Fluorescence (PLP/LIF) Technology

For nitro compound-based explosives, it is possible to combine photo fragmentation and the detection of photo dissociated NO radicals. A laser pulse is used to fragment the explosive (pulsed laser photo dissociation, PLP sometimes also referred to as PF, photo fragmentation).

1.1.7.1 PLP/LIF Standoff Explosives Detection: Principle of Technology

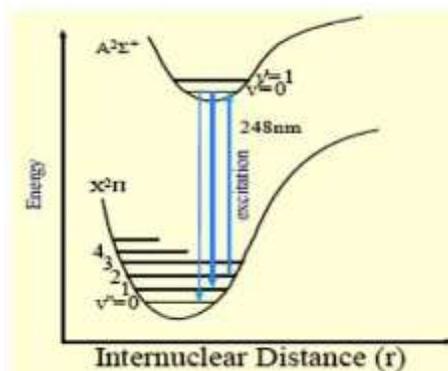
Figure 7 - PLP/LIF Technology: Principle of Operation



The fragmentation of nitro-based explosives leads to the formation of NO-radicals. Thus, the explosive can be detected through monitoring of NO concentrations. This is not a species selective detection method, rather it will alert for any nitro containing compound. Since NO is frequently present in the atmosphere, interference of background NO and explosives originating NO can cause a sensitivity problem.

The monitoring of NO-radicals is managed with LIF (Laser Induced Fluorescence) which is a high sensitivity, spectroscopic detection method. LIF can be used to monitor NO by probing its vibration levels in the ground electronic state. A reported method 122 uses the same laser pulse, wavelength 248 nm, for fragmentation and LIF-spectroscopy. The monitoring is done by excitation in the $A_2\Sigma^+(v' = 0) \leftarrow X^2\Pi(v'' = 2)$ transition. The fluorescence originates from $A_2\Sigma^+(v' = 2) \rightarrow X^2\Pi(v'' = 0,1)$ transitions. This means that the excitation is done from a vibrationally excited level of the NO radical.

Figure 8 - Fluorescence Energy Levels



(Source: Arusi-Parpar)

Since atmospheric NO is not excited above $v'' = 0$ to any noticeable extent at room temperature, atmospheric NO interference is significantly reduced (Boltzmann distribution gives the relative populations of NO in the $v'' = 0, 1, 2$ states as 1, 10^{-4} , 10^{-8} , respectively, at room temperature). In dissociated TNT molecules, at least 30% NO is produced with a $v'' = 0, 1, 2$ ratio of 1, 0.5, 0.1, respectively. Thus in this detection scheme, interference from atmospheric NO is greatly reduced.

Another contributing factor for interference reduction is that the fluorescence is measured at shorter wavelengths than the excitation wavelength, rejecting fluorescence from TNT and other molecules in the air. A sensitivity for 2, 4, 6-trinitrotoluene of 15 ppb at near ambient conditions (atmospheric pressure and explosive sample holder at 28°C) and at a range of 2.5 meters was reported.

Other publications have reported sensitivities of 40 ppb 124 or low ppm 125 levels. However, the detection schemes used were not chosen for suppressing background interference and measurements were conducted in a low pressure, controlled environment.

This method has potential for remote detection. However, sensitivity must be enhanced.

1.1.7.2 Next-Generation Standoff PLP/LIF Systems

Next-generation standoff PLP/LIF systems will have the following features:

- Limit of detection: low ppb
- Speed: fast
- Selectivity: poor – detects nitro containing compounds
- Applicability: n/a
- Cost: n/a
- Sample type: gas, liquid, solid

More information can be found at:

[Standoff IED, Person-Borne & Vehicle-Borne Explosives & Weapon Detection: Technologies & Global Market - 2015-2020](#)