R3-C: Standoff Detection of Explosives: Infrared (IR) Spectroscopy Chemical Sensing

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II. PROJECT DESCRIPTION

A. Project Overview

The goal of the R3-C research component at the University of Puerto Rico at Mayagüez (UPR-M) is to develop chemical sensors for explosives detection based on mid-infrared (MIR) laser spectroscopy. The ideal end-
state of this project is to detect high energy materials (HEMs) residues on any substrate type at close, mid, and long standoff distances. To achieve this stage of development of the research, tunable quantum cascade laser (QCL) sources are explored for use in developing confirming chemical sensors for explosives residues left due to terrorist activities on real world substrates using various IRS modalities. Secondary sensors under development would be used in an orthogonal sensing scheme after remote detection of anomalies and devices under clothing and other substrates by millimeter wave radar sensing. Multivariate analysis routines are then coupled with the laser enabled detection step, providing target identification and discrimination from substrates and other interferences, and even quantification of HEMs and homemade explosives (HMEs). Addressable libraries of HE/HMEs will be built, tested, and made available to the Homeland Security community. The spectra in the library will be able to be modified or morphed according to models that consider the spectroscopic measurement conditions, the physical features of the HE/HME residues, and the characteristics of the substrates’ surfaces. These libraries are intended to be useful for both the identification of single target chemicals that are combined with many clutter species as well as the discrimination among multiple target chemicals that are mixed with each other and with additional clutter species.

The specific aims of the research include:

- Detection of explosives on metallic and mate substrates at close distances (~ 15 cm).
- Discrimination of explosives from interferences, including highly MIR absorbing substrates.
- Detection of explosives on substrates at mid-range distances (~ 1-10 m).

The challenges/obstacles that the research intends to address include:

- Establishing the differences between real samples vs. lab-prepared samples in detection of explosives.
- Detecting explosives traces with MIR lasers at off-normal incidence geometries.
- Detecting explosives with MIR laser spectroscopy of moving targets.

Overcoming these challenges requires transitioning from commercially available laser spectrometer operating at close distances (~15 cm) to a homebuilt system with the following characteristics:

- Highly collimated laser beams with capability for sensing at long distances (10-30 m).
- Higher power laser source systems: 50 – 200 mW.
- Wide spectral coverage: 1000 cm⁻¹: 830–2000 cm⁻¹ (5 – 12 µm).
- Fast scanning system: 5 seconds (or less).

The work performed under R3-C is different from other groups in that it addresses detection of explosives residues of masses from milligram to picogram deposited on real world substrates: bare and painted metal parts, clothing, travel bags, personal bags, laptop bags/cases, and other relevant substrates. Laser spectroscopy signatures obtained in this mass range allow for the identification/quantification of explosives.

B. State of the Art and Technical Approach

Vibrational spectroscopy, in its two main branches of infrared spectroscopy (IRS) and Raman scattering (RS), can be used for identifying and quantifying chemicals in complex matrices based of the fact that each substance has a unique vibrational spectrum [1-6]. IRS is a well-established discipline within science and technology fields, and has continuously evolved over the past 200 years [1-3]. Throughout this time, IRS gradually developed all of its major modalities: absorption/transmission, reflection, attenuated total reflection, and emission spectroscopies. It has benefited from technological developments in spectral sorting
capabilities (e.g. gratings in lieu of prisms, and interferometers in lieu of dispersive spectrometers), improvements in detection technologies, development of water resistant optical elements, and in fast processing data analysis (e.g. Fourier transformation) [1-6]. However, one area that has lagged in incremental developments and improvements until recently, is the energy sources used for excitation of infrared spectra. Only polychromatic thermal sources (e.g. globars), which are inherently low power sources, have been traditionally available [3].

The difference between the inherent strengths of the photonic mechanisms that enable IRS and RS as the dominant techniques of vibrational molecular spectroscopy limits their capabilities and use in applications of standoff (SO) detection of threat chemical compounds. Because IRS is a photonic absorption process, it’s much stronger than the inelastic scattering of photons in a Raman event. This enables SO-IRS with the capability of near-trace detection of target chemicals up to tens of meters. Conversely, RS is supported by important properties of laser technology that enables SO ranges as long as 1 km, but it has limited detection of bulk or semi-bulk amounts of samples (as low as several mg) and gaseous component of small molecules due to the weakness of the scattering event. Both IRS and RS, in their various modalities, have been shown to be useful for characterization, detection, identification, and quantification of threat chemicals, including HEMs and HMEs [6-17]. Over the past 25 years, the techniques have frequently been used in SO mode to deter terrorist threats by providing the basis for the required countermeasures to prevent explosives events. Fundamental and applied research in areas of interest to national defense and security focusing on remote detection of HEMs and HMEs that could be used as weapons of mass destruction has been reviewed regularly [7-17].

The need to develop more powerful MIR sources that enable detection at longer distances when a target hazardous threat chemical is located on a substrate in the form of a residue at trace or near-trace levels suggests the use of collimated, coherent, and polarized sources. These sources were first developed in 1994 at Bell Labs with the invention of quantum cascade lasers (QCLs) [18]. A QCL is a unipolar semiconductor injection laser based on sub-interband transitions in a multiple quantum-well heterostructure. As a semiconductor lasers that can produce varying wavelengths and operate at various temperatures, QCLs have various advantages over other types of lasers [19-23]:

- Produce from tens to hundreds of milliwatts of continuous or pulsed power under ambient conditions;
- They are commercially available; and
- They can be used to enable the development of ruggedized systems for the detection of hazardous chemical and biological (CHEM/BIO) threats.

The increase in output power has enabled the use of QCL-based spectrometers in long distance applications, making the detection of CHEMBIO threats possible at tens of meters from the source [24-25]. Furthermore, QCLs can be operated in field conditions, allowing for the sensitive detection of peroxide based explosives, such as triacetone triperoxide (TATP), of aliphatic nitrate esters such as pentaerythritol tetranitrate (PETN), of aliphatic nitrarnines such as RDX, and of nitroaromatic HEMs such as 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (TNT) in the vapor phase using photoacoustic spectroscopy [26-28]. TATP and TNT were also detected in the vapor phase using IRS with satisfactory results [28-29]. QCL sources have also been successfully used in remote detection of HEMs residues on surfaces [30-35]. Thundat’s group reported that nanomechanical IRS provides high selectivity for the detection of TNT, RDX, and PETN without the use of chemoselective interfaces by measuring the photothermal effect of the adsorbed molecules on a thermally sensitive microcantilever [36].

Most of the previous investigations have focused on the detection of HEMs residues deposited on ideal, highly reflective substrates, such as highly polished metallic surfaces [33]. There are very few reports published on
the effects of non-ideal, low-reflectivity substrates on the spectra of the target HEMs [35]. The work by Suter and collaborators, which measured the spectral and angular dependence of MIR diffuse scattering from explosive residue deposited on a painted car door using an external cavity QCL (EC-QCL), laid the foundation for part of our research [34]. However, our approach is significantly different because it comprises the detection, identification, and discrimination of explosives on highly interfering backgrounds such as a wood, natural and synthetic fibers, such as cotton shirts or pants, nylon and black polyester from laptop bags or travel cases, and simulated human skin [35]. The work also centers on using robust chemometrics techniques for “on-the-fly” pattern recognition and discriminant analysis, with an expected turnaround response time from milliseconds to a few seconds. The main difference between the contributions of this research and the current state-of-the-art research is in bridging the gap between lab experiments under well-controlled conditions and the real-world detection of explosives residues [36].

C. Major Contributions

C.1. Detection of HEM on Reflective Substrates using MIR laser spectroscopy (Year 1)

The first stage of this project involved validation experiments aimed at confirming the performance of a commercial QCL spectrometer (LaserScan™, Block Engineering) that would be used in HEMs detection experiments. The MIR spectroscopic system acquired reflectance spectra of films and deposits of chemicals on substrates. Some of the results obtained with the QCL system are included in Figure 1. The reflectance spectra measured with QCL and FTIR of: (a) TNT, (b) PETN, (c) RDX, and (d) TATP are shown in the figure [37,38]. The MIR laser spectra were collected on a smooth aluminum (Al) substrate.

![Figure 1: QCL and FTIR (reference) spectra of HEMs deposited on highly reflective polished Al substrates: (a) TNT, (b) PETN, (c) RDX and (d) TATP.](image)

These spectra serve the purpose of validating the technique for detection of HEMs, explosive mixtures/formulations, and chemical precursors. The MIR laser spectra were collected in open-air conditions, thus,
water vapor lines could be observed on some of the spectra. TATP samples had particularly evident water vapor lines because the samples sublimated rapidly, even at room temperatures. In other cases, the inherent strength of the MIR signatures of the HEMs made the water vapor lines imperceptible. There are operational parameters worth discussing: the LaserScan™ was designed for short focal length work (~15 cm). Highly reflective polished metallic substrates (e.g. Al, stainless steel, or gold) required a defocused MIR laser beam, since the specular radiation collected in back reflection mode saturated the detector. Alternatively, using an incidence angle of 9-10° avoided detector saturation.

C.2. Detection of HEMs on Non-Reflective Substrates using QCL Spectroscopy (Years 1-2)

The spectroscopic system based on QCL was next used to obtain MIR reflectance spectra of HEMs deposited on non-ideal, low reflectivity matte substrates such as travel bags (TB), cardboard (CB), and wood (W). We tested various deposition methods including spin coating, sample smearing, partial immersion, and spray deposition for preparing standards and samples used in the study. The HEMs used included nitroaromatic explosive 2,4,6-trinitrotoluene (TNT), aliphatic nitrate ester pentaerythritol tetranitrate (PETN), and aliphatic nitramine 1,3,5-trinitrohydro-1,3,5-triazine (RDX). Low surface concentrations (1-15 μg/cm²) of HEMs were used in the investigation. Figure 2 shows representative QCL spectra of TNT, PETN, and RDX on (a) Al, on (b) CB, on (c) W, and on (d) TB.

Figure 2. QCL spectra of HEM on substrates: (a) Al, (b) CB, (c) wood and (d) TB. Surface concentrations were 15 μg/cm². QCL spectra of substrates are included to establish the degree of spectral interference.
MIR laser reflectance spectra were used for the surface concentration profiles constructed in preparation to perform quantitative multivariate analyses (MVA). A total of nine different surface concentration profiles were assembled: 3-HEM x 3-substrates (plus three replicas of each combination). QCL spectra of clean Al substrates were used as backgrounds. Figure 3a shows some of the RDX spectra recorded on wood substrates; Figure 3b shows spectra for TNT on CB at various surface concentrations; and Figure 3c shows measured QCL reflectance spectra for PETN on wood. However, the QCL methodology used for detection of explosives on non-reflective substrates does not require the use of multivariate analyses for identification of HEM, but rather, as illustrated in Figure 3d, a single acquisition (3 s) of CB was subtracted from the corresponding QCL spectrum of PETN on CB to obtain the difference spectrum of PETN. Comparison with the QCL transflectance spectrum of PETN on Al demonstrates that several of the aliphatic nitrate ester signature bands can be readily assigned by comparison with the reference QCL spectrum. The only requirement for this type of remote detection experiment is be able to acquire a QCL spectrum of a non-contaminated (non-dosed) segment of the substrate.

The LaserScan™ spectroscopic system allowed the detection of HEM deposited at low surface concentrations (1-15 μg/cm²) on three types of non-ideal low reflectivity substrates: travel bag fabrics (TB), cardboard (CB), and wood (w). Spectral identification using spectral correlation algorithms were not efficient enough for identifying HEMs when present on non-ideal low reflectivity, highly mid-infrared absorbing substrates. However, multivariate analyses were efficient enough in attaining the goals of this investigation. Finally, PLS models demonstrated the capability of predicting surface concentrations of HEMs on the substrates tested using a maximum of 8 latent variables (LV) to obtain values of R² higher than 0.9 [35, 36].

Figure 3: Surface concentration profiles for (a) RDX on wood; (b) TNT on CB; and (c) PETN on wood. (d) Difference spectrum: PETN/CB minus CB and comparison with QCL transflectance spectrum PETN/Al (used as reference).
C.3. QCL Spectroscopic Library of Explosives (Year 2)

Spectral signatures of explosives were recorded by MIR spectroscopy using a QCL system. Explosive samples were deposited on aluminum and on real-world substrates such as travel baggage, cardboard, and others. Explosives used in this stage of the project were RDX, PETN, and 2,4-DNT. The deposition method utilized was sample smearing.

C.4. Classical Least Squares-Assisted MIR Laser Spectroscopy Detection of High Explosives on Fabrics (Yrs. 3-5)

MIR laser spectroscopy was used to detect the presence of residues of HEMs on fabrics. The discrimination of the vibrational signals of HEMs from a highly MIR-absorbing substrate was achieved by a simple and fast spectral evaluation, without preparation of standards, using the classical least squares (CLS) algorithm [39]. CLS focuses on minimizing the differences between the spectral features of the actual spectra acquired by MIR spectroscopy and the spectral features of calculated spectra modeled from linear combinations of the spectra of neat components: HEMs, fabrics, and bias. Samples in several combinations of cotton fabrics/HEs were used to validate the methodology. Several experiments were performed focusing on binary, ternary, and quaternary mixtures of TNT, RDX, PETN, and fabrics. The parameters obtained from linear combinations of the calculated spectra were used to perform discrimination analyses and to determine the sensitivity and selectivity of HEs with respect to the substrates and to each other; however, discrimination analysis was not necessary to achieve successful detection of HEs on cotton fabric substrates [40].

C.5. QCL Spectroscopy at Grazing-angle Incidence Using Fast Fourier Transform Preprocessing (Years 4-7)

A simple optical layout for a grazing-angle probe (GAP) mount for coupling to a MIR QCL spectrometer was designed and developed. This assembly enables reflectance measurements at high incident angles. In the case of optically thin films and deposits on MIR reflective substrates, a double-pass effect occurs, accompanied by the absorption of deposited samples in a reflection-absorption infrared spectroscopy modality. The optical system allows MIR light to pass through the sample twice. Applications to detection of traces of explosives using the QCL-GAP were also developed. Principal component analysis and partial least squares multivariate chemometrics methods were employed to analyze MIR spectra to evaluate an analytical methodology for confirming the presence of residues of pharmaceutically active ingredients (irbesartan) and of traces of explosives (RDX) that have been deposited on metallic substrates. The performance of spectral preprocessing via fast Fourier transform (FFT) analysis was evaluated for the ability to extract more powerful and accurate information from the obtained reflectance spectra. According to the figures of merit or distinguishing attributes of this new technique, FFT with chemometric routines can obtain sensitivity and specificity values of 1.000. The limit of detection obtained for RDX was 7 ng/cm². The experimental results demonstrate that the proposed system, when used together with proper chemometrics routines, constitutes a powerful tool for the development of methodologies that have lower detection limits for a range of applications that involve detecting traces of analytes that reside on substrates as contaminants [41].

C.6. Design and Construction of a Homebuilt MIR Laser Spectrometer System (Years 6-7)

Commercial MIR lasers (QCLs) are already predispersive systems: the grating selected wavelength of the output beam can be scanned very fast, maintaining high accuracy and precision. However, coupling to fast detection systems, in our case, was not a trivial problem to solve. The first approach to obtain data acquisition routines based on National Instruments (NI) LabView™ from researchers affiliated with National Labs or from other researchers in the field was not successful. A commercial solution to the problems was not within reach (>$35k). Thus, several members of our research team had to be involved in the solution of the problem. The first successful experiments are reported here. First, the development of an interface using LabView™ to
acquire spectroscopic data from a QCL source and a mercury-cadmium-telluride (MCT) cryocooled detector has not been fully discussed in the literature. A few research papers have focused on parts of the algorithms that can be employed [41-43]. However, none fully describe a procedure that can be programmed as a Virtual Instrument (VI) code in LabView™ including acquisition and data processing required to interface a fast laser with an equally fast data acquisition board (analog to digital card) and detector. A software developed on LabVIEW™ to implement the required interface was created for this purpose. The assessment of the routines programmed were used to determine the accuracy, data resolution, repeatability, and robustness of the measurements.

Figure 4 shows flowcharts of the Producer-Consumer architecture used in the data collection routines for interfacing a MIR pulsed laser system with a fast infrared detector. The Producer Loop deals with the control of the laser, of the detector, and the data acquisition (including spectral details). The Consumer Loop handles the data processing: signal averaging (background and samples), integration of pulses, spectral manipulations: ratios, smoothing of data, calculation of percent transmittance, absorbance, reflectance, and spectrum display.

The development of a customizable software for data collection and processing from experiments using an MCT detector and a MIR laser source that will assist researchers in the field will assist in the development of more applications has been successfully achieved. The LabView™ based software for data acquisition has the capabilities to acquire data from an MCT detector that receives light pulses from a MIR laser (QCLs). The schematic diagram of the simplest experimental setup is shown in Figure 5a. The validation of this software was done through measurements in transmission mode. Figure 5b shows the setup used for calibrating the QCL-detector assembly and testing the data acquisition routines based on NI-LabView™. A fast response cryocooled Vigo MCT (Boston Electronics, Boston, MA) was used to capture the QCL pulses. The validation of the setup and data acquisition routines used a polystyrene film (traceable to NIST standards) by operating the QCL and detector in transmission mode and comparing measurements with FTIR measurements.
An ultra-fast conversion (200 mega samples/s) data acquisition card (DAQ) was used to capture the signals from the preamplifier which is connected to the MCT detector. The system can acquire potential difference (volts) as a function of time and performs the signal processing required to obtain the spectroscopic information related to the samples. The advantage of developing this in-house system is that it facilitates the coupling with more IR accessories to perform more studies, such as diffuse reflectance, grazing angle RAIRS, attenuated total reflectance (ATR), transmission and absorbance. The schematic diagram of the simplest experimental setup is shown in Figure 5b.

![Schematic diagram of the transmission setup using QCL-MCT; and (b) calibration of QCL-MCT using a polystyrene film in transmission mode.](image)

**Figure 5:** (a) Schematic diagram of the transmission setup using QCL-MCT; and (b) calibration of QCL-MCT using a polystyrene film in transmission mode.

Figure 6 shows the QCL-MCT transmission spectrum of a thin film of polystyrene typically used for calibrating IR and FTIR spectrometers. The spectrum was recorded "live" (on the screen) of the display of the LabView Virtual Instrument (VI) Graphical User Interface (GUI) of LabView™.

![QCL-MCT transmittance spectrum of a polystyrene thin film.](image)

**Figure 6:** QCL-MCT transmittance spectrum of a polystyrene thin film.

Table 1 illustrates the comparison between the wavenumber listed by NIST for a polystyrene film used for calibrating FTIR and dispersive IR spectrometers and the data obtained with the Block Engineering MINI-QCL system coupled to the VIGO MCT fast detector. The accuracy of the data is good and the resolution of the spectral data is impressive.
Work will continue on this important sub-project during the Summer of 2019 and Year 7 as part of the Project R3-C contributions to the ALERT-II COE.

D. Milestones

D.1. Performance Metrics

The performance metrics of the project will be both formative and summative. The PI will have the responsibility to acquire quantitative and qualitative data as evidence of accomplishment of the objectives. Formative evaluation will ensure the quality of each collaborative effort by tracking the effectiveness of the research projects implementation and development. The continuous assessment will document the achievement of goals and objectives set by the DHS mission. The ongoing formative evaluation will ensure the timely modification of strategies, schedules, reallocation of resources, and revision of managerial decisions as needed to guarantee the attainment of project short- and medium-term outcomes. The plan involves the ongoing, systematic collection of information for determining the extent to which outcomes have been complying and use the information to make effective decisions to continuously strengthen and improve the project.

D.2. Year 6 Milestones

One of the most important outcomes and contributions from this research component is in the characterization of trace and near-trace to semi-bulk amounts of HEMs. Deposition methods of HEMs on substrates of interest to the Homeland Security Enterprise in general must be characterized both morphologically and spectroscopically.

It is also important to determine distributions of polymorphs on substrates. Although HEM traces commonly found on substrates in the field result from handling of bulk amounts of HEMs, which leave detectable HEM amounts in the form of solid residues, these are very hard to mimic under normal lab conditions. Research groups typically transfer from stock solutions (e.g. solvent mediated deposition). This and other deposition methods from solutions generally result in the formation of polymorphs which can lead to vibrational signals not accounted for in spectroscopic libraries. Targets for this sub-project will be RDX, PETN, TNT, nitrourea, urea nitrate, and ammonium nitrate (AN). Among the substrates to be studied are stainless steel (SS), aluminum, anodized aluminum, gold, silicon, fabrics, wood, cardboard, plastics, glass, and metal oxides (e.g.

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<th>QCL Wavenumber (cm⁻¹)</th>
<th>FTIR Wavenumber (cm⁻¹)</th>
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<td>967.019</td>
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<tr>
<td>1156.742</td>
<td>1154.613</td>
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Table 1: Wavenumber comparison for transmission measurements for polystyrene using a QCL spectrometer and a bench FTIR.
Al₂O₃, ZnO, ZrO₂, and silica gel). The following deposition techniques will be used in the characterization of samples/substrates combinations:

- Pipette transferred samples
- Smearred samples
- Spin coated samples
- Airbrush coated samples
- Inkjet printed samples
- Thumb transferred samples

This sub-project is still in progress. Most of it will be completed during summer 2019, but since it is a very comprehensive study, parts of it could carry over into Year 7.

D.3. Year 7 Milestones

Another important contribution of the R3-C research, education, and training component will be to disseminate the routines developed for interfacing MIR fast lasers to a detector and data acquisition module. The module should be available for dissemination by December, 2019 (ALERT-II YR-7). Key milestones for this include:

- Finish Evaluation of Setup 1 for Detection of HEMs on Reflective/Non-reflective substrates: Oct., 2019
- Couple Setup 1 to MIR fiber optics: December, 2019
- Finish Design and Development of Setup 2: February, 2019
- Evaluate the Effectiveness of Setup 2: May, 2020
- Finish the First Stage of Computational Chemistry of Target Chemicals: June, 2020

E. Future Plans/Project Completion (Year 7)

E.1. Sub-Project One: Implementation of Quantum Cascade Laser/Grazing Angle Probe Portable System Setup for Detection of Explosives on Non-reflective Substrates in Combination with Multivariate Analysis (MVA)

This project aims at further developing a portable explosives detection tool for use by first responders. A portable, fiber optics coupled mid-infrared (MIR) laser spectrometer which, when combined with MVA routines, improves detection accuracy for in situ analysis of target threats. Non-destructive spectroscopic methods for in-situ detection and identification of these compounds on non-reflective surfaces, such as fabrics and others, at trace level quantities are needed for implementing rapid and effective actions by first responders. During last year, this research team has been working in coupling a MIR quantum cascade laser (QCL) source to compact grazing angle probe (GAP) [36, 44-46]. Sensing at the grazing incidence (>80°) enables reflection-absorption infrared spectroscopy (RAIRS), which is one of the most sensitive MIR techniques. However, the majority of the materials used have high absorption coefficients in the MIR, which results in low reflection of radiation, thereby hindering the detection by conventional (thermal sources). Therefore, a MIR laser is required as an excitation source to produce a high number of reflected/scattered photons and to make the detection of the target compound on these surfaces.

The impact of developing QCL-GAP technology through this effort is essential to the explosives sensing community in security applications particularly, to detect individuals who have been in contact with explosive materials. It is clear that the QCL-GAP system operated in standoff mode with chemometrics-based MVA will be a new technology approach for versatile, rapid and early explosive detection. Figure 7A
describes the use of the first setup developed (Setup 1) for the QCL-GAP system. The optical system consists of a probe in which the MIR light passes twice through the same sampling area. An enlarged elliptical spot is generated on the sample surface by a reflection from a gold-coated mirror. Then, the light is back reflected the surface again producing a slightly larger elliptical spot on the same position. The second optical arrangement (Setup 2) can operate as a multipass system, increasing the RAIRS effect and in providing even more sensitive for the detection of analytes on surfaces (Figure 7B). This mount will be developed in YR-7 of the ALERT-II program.

The described effort deals with taking a technique that the ALERT-II project at the University of Puerto Rico-Mayaguez (R3-C project) has developed, used, and brought to its maximum level in direct (non-contact) sensing modality. Using QCL systems in direct and in grazing angle modes, the research team has detected micrograms to nanograms of explosives on fabrics other non-reflective substrates [6]. These studies show that robust calibration curves can be generated for the quantitative analysis of explosive materials on non-reflective substrates and with the implementation of other MVA methods could improve the performance of calibration and prediction models. Thus, operating a QCL in RAIRS mode promises to bring to the table a new portable trace remote detection technique: QCL-GAP.

A variety of non-reflective substrates (e.g., simulated skin, fabrics, cardboard, roughened aluminum, etc.) will be soaked in solutions that contain the desired HEM (e.g., TNT, PETN, RDX, TATP, etc.) in volatile solvents at different concentrations. The amount of HEM absorbed is then calculated by the difference between the soaked and standard mass of the non-reflective substrate determined by gravimetric or chromatographic techniques (HPLC). Attenuated total reflectance (ATR-FTIR) spectrometer and quantum cascade laser (QCL) in the direct mode (D) and grazing angle (GA) setup is used for spectra acquisition of substrates with and without the desired HEM. Multivariate analysis is then employed by chemometrics tools such as principal component analysis (PCA) and partial least squares (PLS) regression analyses with the use of the Unscrambler X® MVA suite.

Part of the efforts will concentrate in converting Setup 1 to a full fiber optics coupled, portable prototype, in preparation for commercialization and use by First Responders. Other efforts will focus on the development of Setup 2 for an even more sensitive trace analysis technology for explosives residues on surfaces.
E.2. Sub-Project Two: Laser Induced Thermal Imaging of Explosives

In our initial work on thermal excitation of emissions of TNT, our group demonstrated the level of high sensitivity that can be achieved by heating a metallic sample holder plate coated with target chemicals [7]. Later, sensitivity and selectivity were increased greatly by heating the sample and substrate at a distance using a CO2 laser [8-9]. Results from these experiments indicate that near-resonance absorption further decreases the detection limit for the case of PETN by coupling to a vibrational band of the nitro ester. Thus, instead of exciting the photothermal signal with a limited wavenumber coverage laser, using a tunable MIR laser leads to selective enhancement of detection as proven by several groups [8-9]. The R3-C component has teamed with VERLUZ, LLC (Humacao, PR), a subsidiary of Pacific Advanced Technologies, Inc. (PAT, Solvang, CA), to further develop this concept for a quick commercialization venture, based on the group's track record of detection of explosives on non-reflective substrates. Added to that, VERLUZ (PAT) has over 30 years of experience in development of MIR hyperspectral imaging. The combination of infrared hyperspectral imaging and real-time image processing with laser-induced thermal imaging will add significant sensitivity to detect low levels of explosives and other threat agents.

Initial experiments will begin by operating widely tunable QCL lasers in narrow windows corresponding to characteristic vibrations of RDX, PETN, HMX, and TNT in the regions between 850 and 1400 cm\(^{-1}\). Two to three strong vibrations for each HEM will be used for the experiments. Samples of the selected HEMs will be transferred to aluminum or stainless steel substrates (reflective surfaces) and non-reflective substrates (such as roughened aluminum, Teflon, cardboard, and fabrics) and the total emissions will be collected using a single element mercury-cadmium-telluride (MCT) cryo-cooled detector designed to operate in the MIR (3-12 µm).


Predicting the performance, IR and Raman spectra, and thermochemical properties of HEMs from a given molecular structure with or without using experimental measurements is critical in the research and development of new HEMs. Several relationships have been found that relate explosive characteristics with measured and predicted molecular properties. The proposed models can predict the detonation parameters without experimental data for a systematic set of energetic materials using the program package as EXPLO5. The program is based on the chemical equilibrium, steady-state model of detonation. It uses Becker-Kistiakowsky-Wilsons equation of state (BKW EOS) for gaseous detonation products together with Cowan-Ficketts equation of state for solid carbon. The calculation of the equilibrium composition of the detonation products is performed by applying modified White, Johnson, and Dantzig's free energy minimization technique. The program was designed to enable calculations of the detonation parameter at the Chapman-Jouguet point. Also, Unscrambler X® will be used to analyze the large and complex data sets obtained. This new strategy of computational study may be useful for designing new novel energetic materials before experimental attempts (i.e., synthesis and tests), which may be hazardous. This study is part of a systematic and comprehensive effort to predict and calculate the detonation parameters. According to our best knowledge, no evidence of similar studies has been reported in the open chemical literature to date.

Computational chemistry will be employed to predict specific properties of value (e.g., the heat of detonation, enthalpy of formation, density, NMR chemical shifts, by-products, etc.) to compare with experimental data for peroxide-based explosives. As a priority, ab initio methods are desired overall for each calculated property; i.e., all steps needed to attain set properties will be based solely with the theory-based background. Semi-empirical methods will be utilized in calculation mentioned properties using EXPLO5 (OMZ Research, Czech Republic) which involves the input of other properties. Once all models for every method and basis
sets have been run, data will be collected and plotted and compared with experimental data obtained from the literature.

Regarding thermochemical properties, density and enthalpy of formation are needed for using semi-empirical methods (EXPLO5). Due to this, the goal is to find a way to keep the entire process ab initio (i.e., without experimental reference needed). Through the calculation of both enthalpies of formation and density of a specific molecule, the thermochemical computer code EXPLO5 can be used to predict detonation (e.g., velocity, pressure, energy, heat, temperature, etc.) and combustion (e.g., specific impulse, force, pressure, etc.) performance of energetic materials. It uses Becker-Kistiakowsky-Wilsons equation of state (BKW EOS) for gaseous detonation products together with Cowan-Ficketts equation of state for solid carbon and the Murnaghan equation of state for condensed products. These equations allow calculation of chemical equilibrium composition and thermodynamic parameters of state along the shock adiabat of detonation products. Such analysis can be done to a specific molecule and mixtures as well as utilizing the detonation run parameters of calculating whole shock adiabat and expansion isentrope.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

The 2017 Explosives Incident Report (EIR) published by the United States Bomb Data Center (USBDC) reported 14,814 explosive related incidents, from which 687 were explosions and 355 out of them were bombings [47]. Over the years, incidents involving attacks have fortunately decreased due to technological advancements and rigorous security measures; however, threats still exist. The detection, identification, and quantification of highly energetic materials (HEMs), homemade explosives (HMEs), precursors, and new green explosives continue to be a high priority for security agencies.

1. Development of a methodology for detection, identification, discrimination, and quantification of explosives in the presence of highly interfering backgrounds.

2. Mass range from near bulk (0.1 g) to near trace (10 ng) at close distances (~15 cm) for potential operation at checkpoints and mid to long standoff distances.

3. The methodology under development will provide a positive/negative result or a confidence level indication to the operator for presence of explosives within (<3 s), with a goal of (1 s).

4. The methodology will operate effectively in field environments at multiple distances with varying humidity, air particulates, temperature, light, and wind.

5. The methodology would be useful in providing evidence of post-terrorist events by detecting explosives residues on dirt, concrete, wood, cardboard, bricks, and other surfaces.

6. Two invention disclosures for patent applications on coupling technology under development for robust separation and quantification methodologies.

The impact of developing QCL-GAP technology through this effort is particularly essential to the explosives-sensing community in security applications, which detects individuals who have been in contact with explosive materials. It is clear that the QCL-GAP system operated in standoff mode with chemometrics-based MVA will be a new technology approach for versatile, rapid, and early explosive detection. Figure 7A describes the use of the first setup developed (Setup 1) for the QCL-GAP system. The optical system consists of a probe in which the MIR light passes twice through the same sampling area. An enlarged elliptical spot is generated on the sample surface by a reflection from a gold-coated mirror. Then, the light is back reflected the surface again producing a slightly larger elliptical spot on the same position. The second optical
arrangement (Setup 2) can operate as a multipass system, increasing the RAIRS effect and in providing even more sensitive for the detection of analytes on surfaces (Figure 7B). This mount will be developed in YR-7 of the ALERT-II program.

B. Transition Pathway

B.1. Sub-Project 1

The subproject described in Task 1 will be either a “spinoff” small startup with alumni from the UPRM Chemistry doctoral program in Applied Chemical Sciences and former ALERT-II R3-C students in the form of an SBIR channeled through the Puerto Rico Science Trust. Another possible mechanism is to apply to DHS, DoD, or NSF for an SBIR together with Michele Hinnrichs and VERLUZ, LLC (PAT, Inc.). We have already submitted an invention disclosure for a patent (“Grazing Angle Probe Mount for Quantum Cascade Lasers.” Ser.#: 62/587,557; Filing Date: 11/17/2017). The planned prototype would be a portable explosives detection system (EDS), physically coupled to MIR fiber optics, user-friendly and completely contained in a small frame rugged box.

B.2. Sub-Project 2

Planning of a joint venture with Michele Hinricks (VERLUZ, LLC; Humacao, PR), a division of Pacific Advanced Technology, Corp. (Solvang, CA), Targeted SBIR: DHS (Jim Jensen, DHS Program Manager home-based in Edgewood Chemical Biological Center, Aberdeen Proving Grounds, Aberdeen, MD. Other possible sources of funding are DoD-DTRA, other DoD divisions, NSF.

B.3. Sub-Project 3

Intellectual property stemming from this task will be made available, cost-free, possibly through a mechanism similar to the one used by the University of Rhode Island, with its database of explosives properties.

C. Expected Outcomes

C.1. Sub-Project 1

The goal of Sub-Project 1 is to fully develop QCL-GAP setups coupled to MVA for detection of HEMs on reflective and non-reflective substrates. To transition the technology through an SBIR to build a portable system prototype.

The expected outcomes include:

- Development of portable QCL systems setups in the detection of HEMs on non-reflective substrates.
- Building a lab-based fiber optics coupled QCL-GAP.
- Completing the design and development of Setup 2.
- To strengthen our research, education, and training STEM facilities, focusing on explosives sensing concepts and data analysis at UPR. This ongoing process is visualized as continuous sustainable participation of undergraduate students and faculty development. BS in Technology in Industrial Chem. Processes students (UPRA) will be pipelined into UPRM MS/Ph.D. and further into DHS, US Government, and Private Sector internships, Postdoc, and work opportunities.
C.2. Sub-Project 2

The goal of Sub-Project 2 is to transition Laser Induced Thermal Imaging Spectroscopy (LITIS) together with VREL, LLC.

The expected outcomes include:

- Establishing the feasibility of LITIS on reflective and dielectric (i.e. non-reflective) substrates using various HEM/substrates combinations.
- Establishing the limits of detection and quantification of the technique.
- Establishing a joint venture with an industrial partner (VREL, LLC) for developing an instrument capable of detecting explosive residues at a distance using an active mode sensing modality.

C.3. Sub-Project 3

The goal of Sub-Project 3 is to predict the performance and thermochemical properties of new energetic materials from a given molecular structure without using experimental measurements using computational chemistry.

The expected outcomes include:

- Predicting the detonation parameters without experimental data for a systematic set of novel green energetic materials with high nitrogen and low carbon content as triazoles, tetrazoles, azidotetrazoles, triazene, nitro-substituted cage compounds, and oxygen-rich organic peroxides.
- Training students in computational chemistry to integrate the information provided by different programs of molecular modeling and chemometric routines for the prediction of explosive properties.

D. Customer Connections

- Commercialization partner: Daylight Solutions (Leonardo DRS) or other QCL manufacturer
- Planning of a joint venture with VREL, LLC (Humacao, PR), a division of Pacific Advanced Technology, Corp. (Solvang, CA), Michele Hinricks (Founder and CEO)
- DHS, Jim Jensen DHS Technical Contracts Manager in Edgewood Chemical Biological Center
- DTRA and other DoD divisions

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Student Internship, Job, and/or Research Opportunities
   b. Gabriela I. Padilla-Rivera, MS Student, Summer 2018, Research Internship, Army Corps of Engineers, Carlyle, IL.
d. Bianca M. López-Pagán, UG Student, Research Internship, Naval Surface Warfare Center – Indian Head Division, Indian Head, MD, Summer 2018.

2. Interactions and Outreach to K-12, Community College, and/or Minority Serving Institution Students or Faculty:
   a. Served as host for one high school student participating in Science Fair project.
   b. Served as collaborator and host for Follow-On Project of DHS SRTP-MSI Grant of Dr. Ricardo Infante-Castillo, University of Puerto Rico-Arecibo Campus ($50,000/1 year).

3. Training to Professionals or Others
   a. Puerto Rico Chemists Association Continued Education Program, Course in Chemistry of Explosives, February 2019, Southeastern Section, Aguadilla, PR, 45 attendees.
   b. Puerto Rico Chemists Association Continued Education Program, Course in Spectroscopic Standoff Detection of Chemical Threats, August 2018, Annual Convention, 70 attendees.

B. Peer Reviewed Journal Articles


Pending:


C. Peer Reviewed Conference Proceedings


D. Other Publications


E. Other Conference Proceedings


5. Medina, E., Olmo, J., Hernández-Rivera, S. P. Infante, R. “Application mid-infrared quantum cascade laser (QCL) and attenuated total reflectance (ATR) spectroscopy for detection of explosive particles in cotton and polyesters fabrics.” Puerto Rico Louis Stokes Alliance for Minority Participation (PR-LS-AMP) 39th Interdisciplinary Scientific Meeting & 54th Junior Technical Meeting, 4 May 2019, University of Puerto Rico, Mayaguez Campus, Mayaguez, PR.

F. Other Presentations

1. Seminars
2. Poster Sessions


G. New and Existing Courses Developed and Student Enrollment

<table>
<thead>
<tr>
<th>New or Existing</th>
<th>Course/Module/Degree/Cert.</th>
<th>Title</th>
<th>Description</th>
<th>Student Enrollment</th>
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<tbody>
<tr>
<td>Existing</td>
<td>Course in Certificate Program in Forensic Chemistry</td>
<td>Chemistry of Explosives</td>
<td>For students of Chemistry and Chemical Engineering</td>
<td>15</td>
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</tbody>
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H. Technology Transfer/Patents

1. Patent Applications Filed (Including Provisional Patents)

I. Software Developed

1. Databases:
   a. Ongoing: Library of vibrational spectra of HEMs, HMEs, and precursors.

2. Algorithms
   a. Fast Fourier Transform pre-processing programmed in in MATLAB® 8.6.0.267246 (R2015b; Math Works Inc. Natick, USA). This algorithm is being used to remove interference fringes from thin HEM films generated by GAP-QCL RAIRS measurements.
   b. Classical least squares (CLS) algorithm for assisted MIR laser spectroscopy detection of high explosives on fabrics and other non-reflective substrates.

J. Requests for Assistance/Advice

1. From Federal/State/Local Government
   a. Assistance from Dr. Marissa E. Morales-Rodríguez, from Oak Ridge National Lab is gratefully acknowledged. Dr. Morales-Rodríguez provided step-by-step guidance and assistance in implementing NI-LabView™ data acquisition routines.
V. REFERENCES


United States Bomb Data Center (2017), USBDC Explosives Incident Report (EIR).