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

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II. PROJECT DESCRIPTION

A.   Overview and Significance

This project deals with the use of infrared spectroscopy in standoff mode and coupled to laser sources operating in the mid-infrared (MIR) to develop confirming (orthogonal chemical sensors) for detecting explosives residues on clothing, travel bags, personal bags, laptop bags/cases, skin and other substrates. The main

hurdle to overcome is discriminating the nitro- or peroxide-based explosives from highly interfering, MIR absorbing substrates (matrices) in which explosives are found. Quantum cascade lasers (QCL) will be used as energy sources. QCL have revolutionized MIR spectroscopy applications. Techniques evaluated will provide positive/negative or a confidence level indication to the operator for the presence of explosives within 1 min (in most cases a few seconds) while operating effectively in a field environment at multiple distances with varying levels of relative humidity, air particulates, temperature, light and wind.

A main objective of the tasks performed by this research and education component at the University of Puerto Rico at Mayaguez (UPRM) is to lay the foundation for the standoff detection of explosives on highly MIR absorbing substrates, including cotton, cardboard, wood, plastics, and create a library of adaptable infrared absorbance/reflectance spectra for a variety of highly energetic materials (HEM) on various substrate surfaces. An addressable library of HEM will be built, tested and made available. 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 HEM residues and the characteristics of the substrate surfaces. This library is 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 library can include as many as 30 target HEM and 7 or more substrate types. Target chemicals will include high explosives, explosives formulations, non-nitrogen-based, home-made explosives and co-indicator compounds and precursors of these various chemicals. Substrates could be metals or non-metals and could have high infrared transmittance of reflectance or absorbance; they could also have low infrared transmittance, reflectance or absorbance. The concentration of a given dilute solid on a surface can be 1 $\mu g/cm^2$ or lower. Single target chemicals can represent as little as 0.1% of the overall residue. Mixtures can have as many as 5 to 10 target components plus 15 or more additional background chemicals, with a given target component representing as little as 1% of the overall amount of residue on a surface. Development of this library will include the preparation of samples comprising chemical residues on the surface of a substrate, spectroscopic characterization of samples like the ones prepared and the investigation and modeling of various measurement effects and residue/substrate effects. The measurements performed at UPRM will make use of several spectroscopic measurement instruments available, including an FT-IR spectrometer, tunable QCL sources and photodetectors.

B.   State-of-the-Art and Technical Approach

Vibrational spectroscopy consists of two main techniques: infrared spectroscopy (IRS) and Raman scattering (RS). Spectra obtained by means of these techniques can be used for identifying and quantifying samples in complex matrices because each substance has a unique spectrum in the fingerprint and fundamental vibrations regions of the MIR region and corresponding Raman shift regions [1-5]. The two techniques are, in general, complementary in the information they provide. When coupled to multivariate chemometrics routines, IRS and RS can be used for discriminating between interfering substrates and other analytes, even when the target analyte is in very small quantities [6].

IRS is a well-established discipline within science and technology fields and it has continuously evolved during 200 years [1-3]. Throughout this time, IRS has gradually developed all of its major modalities: absorption/transmission, reflection, and emission spectroscopies and benefited from technological developments in spectral sorting capabilities (gratings in lieu prisms; interferometers in lieu of dispersive spectrometers); improvements in detection technologies; in development of water resistant optical elements; and in fast processing data analysis: Fourier transformation [1-5]. However, one area that has lagged in incremental developments and improvements until recently has been in the energy sources for excitation of infrared spectra: only polychromatic thermal sources (globars) have been traditionally available [3].

The difference in inherent strength of the photonic mechanisms that enables IRS and RS as dominant tech-

niques of molecular spectroscopy limits their capabilities and use in applications of standoff (SO) detection of threat chemical compounds: IRS being a photonic absorption process is a much stronger process 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. On the other hand, RS is supported by important properties of lasers which enable SO ranges as long as 1 km, but limited to bulk amounts of samples (as low as several mg) and gaseous molecules of small molecules due to the weakness of the scattering event. Both IRS and RS, in their various modalities, have been shown useful for characterization, detection, identification and quantification of threat chemicals, among them HEM and homemade explosives (HME) [8-17]. 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 explosive events. Fundamental and applied research in areas of interest to national defense and security focusing on remote or SO detection of high explosives and homemade explosives (HME) 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 level 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 (QCL) [18]. A QCL is a unipolar semiconductor injection laser based on sub-interband transitions in a multiple quantum-well heterostructure. As a semiconductor laser that has the ability to produce varying wavelengths and to operate at various temperatures, this type of laser has various advantages over other types of lasers [19-23]. QCLs are capable of producing from a few tens to hundreds of milliwatts of continuous mode or pulsed power under ambient conditions, are commercially available and have enabled the development of ruggedized systems for the detection of hazardous chemical compounds. Recent developments in QCL technology include size reduction, which has enabled the transition from tabletop laboratory instruments to easy-to-handle, small instrument designs, and portable units that can be used by first responders and military personnel outside the confinement of a sample compartment. Moreover, the increase in output power has enabled the use of QCL-based spectrometers in long distance (range) applications, making the detection of chemical and biological threat agents possible at tens of meters from the source [24 and 25].

Furthermore, QCLs can be operated in field conditions, allowing for the sensitive detection of HMEs such as triacetone triperoxide (TATP), of aliphatic nitrate esters such as pentaerythritol tetranitrate (PETN), of aliphatic nitramines as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and of nitroaromatic HEMs as 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (TNT) in the vapor phase using photoacoustic spectroscopy [26-28]. The detection of TATP and TNT in the vapor phase has also been achieved using infrared absorption spectroscopy with satisfactory results [28 and 29]. Moreover, the use of QCL sources has been useful for remote detection of HEMs deposited on surfaces using photoacoustic and traditional infrared absorption spectroscopies [30-35]. Thundat's group recently reported that nanomechanical infrared spectroscopy 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].

However, the majority of previous investigations focused on the detection of HEMs deposited on nearly ideal, highly reflective substrates, such as highly polished metallic surfaces [33]. There are few published reports on the effects of non-ideal, low reflectivity substrates on the spectra of the analyzed target HEM [35]. The work by Suter and collaborators (2012; PNNL) in which they measured the spectral and angular dependence of MIR diffuse scattering from explosives residues for deposited on a painted car door using an external cavity QCL (EC-QCL) laid the foundations for part of the work that this research group pursues [34]. However, our approach is significantly different since it comprises detection, identification and discrimination of explosives on highly interfering backgrounds, such as a cotton shirts or pants, nylon and black polyester from laptop bags or travel cases, simulated human skin, and other compacted solid mixtures [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 a few milliseconds to less than 1 s. The main difference between the expected contributions of this research and the current state of the art is in bridging the gap between lab experiments under well controlled conditions and the real-world detection of explosives residues [36]. Angular dependence of source-target-detector in active mode SO-IRS [37] and dependence of detection limits on angular alignment, substrate type and surface concentration in active mode SO-IRS [38], using both thermal sources (globars), modulated and non-modulated have also been measured as part of the group contributions.

C.   Major Contributions

C.1.   QCL spectroscopy-least squares detection of HEMs on cotton

Remote sensing using IRS depends on the observer-target distance and on the angle between source, target and detector. Another important factor is the reflectivity of the target. In the search for attaining higher return signals in back reflection mode, a QCL was used to determine the presence of HEM on cotton. The identification of vibrational signals was generated by a simple spectral comparison using classical least squares in the minimization of the difference between real spectra (RS) and calculated spectra (CS). The models used for obtaining CS were based on linear combinations of HEM spectra, cotton spectra and biases. As shown in Figure 1, the setup consisted of a 3 in. diam. ZnSe lens, which was used to focus the MIR beam, to collect the reflected light and to focus the light onto the a thermoelectrically cooled mercury-cadmium-telluride detector. The wavenumber accuracy and precision were 0.5 cm^{-1} and 0.2 cm^{-1}, respectively. The spectroscopic system worked best at a head to target distance of 15 ± 3 cm, each laser producing a spot of 2 mm in diam. at 15 cm of distance.
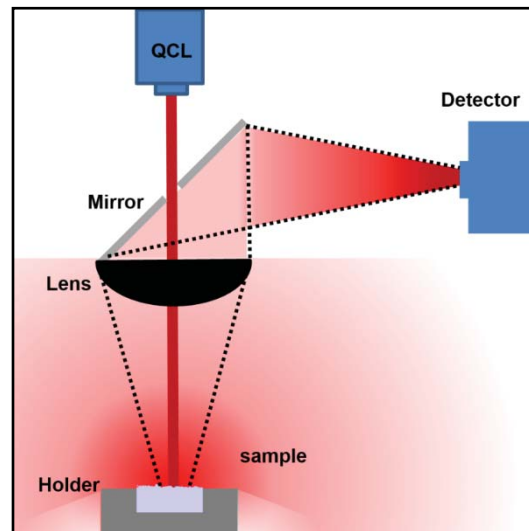

Figure 1: Setup: QCL source, MCT detector, lens, mirror and sample holder for powder samples.

A linear model was assumed, such that:

$$f(\varphi_j, \beta_j)_i = \beta_0 + \beta_1 \varphi_1(\omega_i) + \cdots + \beta_j \varphi_j(\omega_i) \quad (1)$$

Where $f(\varphi_i, \beta_i)$ are the i normalized intensities of the spectrum calculated for a mixture of different components (j), $\varphi_j(\omega_i)$ is the normalized intensity at each wavenumber (ω) of the spectrum of the component and β is a parameter that indicates the fraction of spectrum of a component in the spectral mixture. This model assumes that there are no interactions between the mixture components leading to bond formation and vibrational mode shifting and that the intensities are additive. The parameter β_i was found by minimizing the

least squares of the difference or subtracted between the real spectrum (y_i) and the calculated spectrum:

$$d_i = y_i - f(\varphi_j, \beta_j)_i \quad (2)$$

The minimum of the sum of squares is found by setting the gradient to zero. Since the model contains "n" parameters, there are "n" gradient equations:

$$\frac{\partial d}{\partial \beta_j} = -2 \sum_i d_i \frac{\partial f(\varphi_j, \beta_j)_i}{\partial \beta_j} = 0, j = 1, 2, \cdots, n \quad (3)$$

It is possible to extract signals of interest of the components from the model. For example, if the component of interest is 1. The extracted spectrum (ψ) is:

$$\psi_{1(\omega_i)} = y_i - \beta_0 - \beta_2 \varphi_2(\omega_i) - \cdots - \beta_j \varphi_j(\omega_i) \quad (4)$$

In this work the components were cotton, trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN) and cyclotrimethylenetrinitramine (RDX). The HEM were deposited on cotton by thumb printing the solid. An amount was deposited on glass, fabric was then placed on the explosive and then the HEM were finger print-ed by using pressure to force the explosive to transfer to the substrate. The fabric was weighed before and after the deposition in order to determine the amount deposited. The weighing was carried out using two balances. The first balance had a precision of ± 0.1 mg and was used for depositions of 0.1 to 5 mg. The second balance had a precision of ± 0.1 µg (thermogravimetric balance). The obtained spectra were converted from reflectance units to the negative of logarithm of reflectance because this unit is proportional to the concen-tration. The normalization was done using vector normalization (VN) pre-processing. This was done on the complete spectral region for the analyses. When applying VN, the average intensity was calculated first and then this value was subtracted from the spectrum. Next, the sum of the intensities squared was calculated, and the spectrum was divided by the square root of this sum. Twenty samples of TNT on cotton were pre-pared by depositing 3, 1, 0.5, 0.1 mg (5 replicas of each). QCL spectra were measured and β_{TNT} parameter was calculated from the spectra of the 5 replicas. Then, the probability of detection was estimated (see Fig. 2a). The model for two component mixtures was based on:

$$f = \beta_0 + \beta_{cotton} \varphi_{cotton}(\omega_i) + \beta_{TNT} \varphi_{TNT}(\omega_i) \quad (5)$$

In Figure 2b, the spectrum of 0.1 mg TNT on cotton is shown together with the predicted spectrum from Eq. 5 and the QCL cotton spectrum. The TNT subtracted spectrum calculated from Eq. 4 is also shown. Spectra were compared with the solid TNT spectrum (reference) in order to verify the presence of the important vibrational signatures of the target HEM.
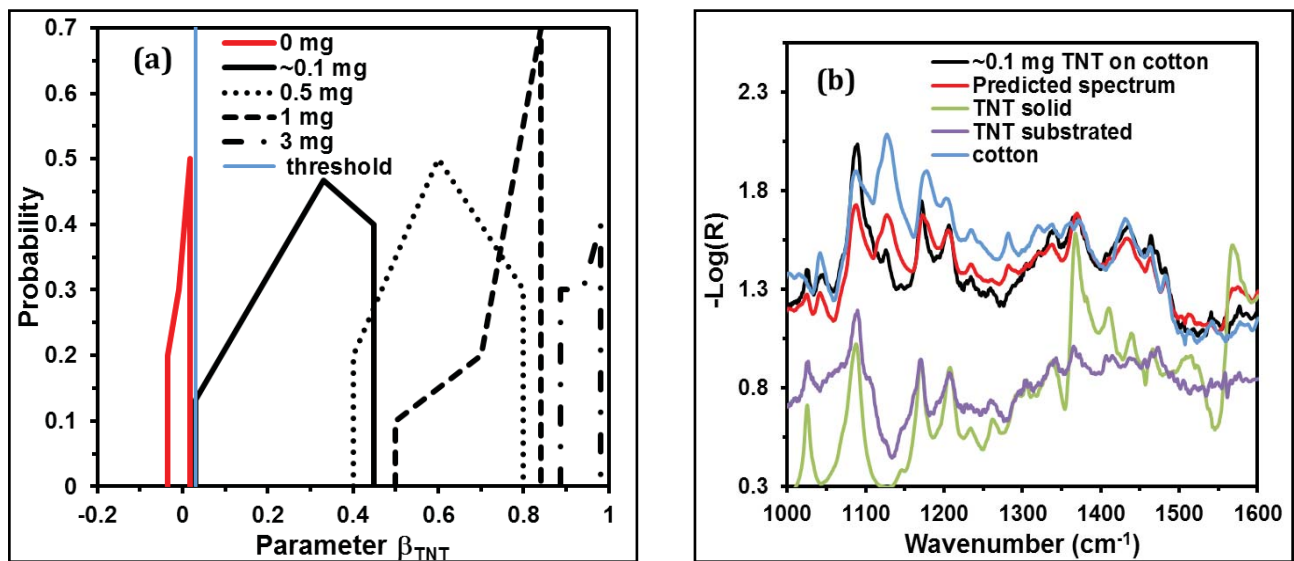

Figure 2: (a) Probability of detection; and (b) spectra: TNT on cotton, predicted, TNT solid, subtracted and cotton.

A second model for three component mixtures was based on the following:

$$f = \beta_0 + \beta_{cotton}\varphi_{cotton}(\omega_i) + \beta_{TNT}\varphi_{TNT}(\omega_i) + \beta_{RDX}\varphi_{RDX}(\omega_i) \qquad (6)$$

Different amounts of TNT, RDX and a mixture of 50% TNT and RDX (134 samples) were deposited on cotton from 0.1 to 3 mg and β_{TNT} and β_{RDX} were calculated. Then the distribution of each sample was plotted for the values calculated of β_{TNT} and β_{RDX} by means of Eq. 7 (see Fig. 3).
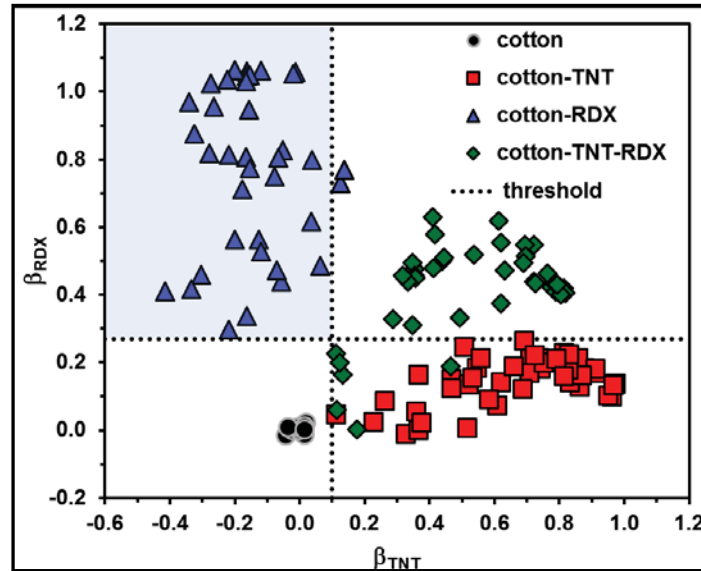

Figure 3: Distribution of samples on β_{TNT} and β_{RDX} parameters.

A third model for four components was tested:

$$f = \beta_0 + \beta_{cotton}\varphi_{cotton}(\omega_i) + \beta_{TNT}\varphi_{TNT}(\omega_i) + \beta_{RDX}\varphi_{RDX}(\omega_i) + \beta_{PETN}\varphi_{PETN}(\omega_i) \qquad (7)$$

Different amounts of TNT, RDX, PETN, a mixture of 50% TNT and RDX, a mixture of 50% TNT and PETN, a mixture of 50% PETN and RDX and a mixture of 33.3% TNT, PENT and RDX (252 samples) were deposited on cotton from 0.1 to 3 mg. β_{TNT}, β_{RDX} and β_{PETN} were calculated and the distribution of each sample was plotted for the values calculated of β_{TNT}, β_{RDX} and β_{PETN} by Eq. 7 (see Fig. 4).
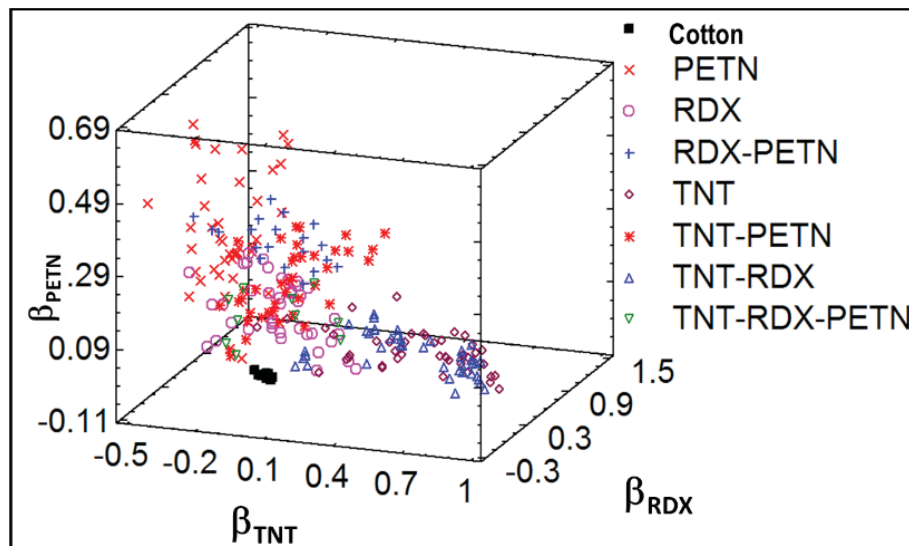

Figure 4: Distribution of samples on β_{TNT}, β_{RDX} and β_{PETN} parameters.

In order to evaluate statistically the discrimination power of the β parameters, a discriminant analysis was carried out. Two statistically significant discriminating functions were obtained. These functions contained nearly all of the statistically relevant information as they contributed to 95.3% of the discrimination capability. As shown in Table 1, the eigenvalues for the discriminant functions were highly significant ($p < 0.0001$). According to the canonical correlation coefficient, which is indicative of the ability or effectiveness for the discrimination capability of new samples, the functions have excellent capacities for determining group differences 93% and 87%, respectively (see Fig. 5). Function three (F3), with a 77% capacity for determining group differences, was not as effective as F1 and F2 in the sought discrimination model and was not used. The detection limit of (LOD) was calculated from different spectra of RDX at low amounts (< 0.1 mg). Eq. 4 was applied to the spectra and the signals of RDX were validated (see Fig. 6a on the next page). Next the signal to noise ratios (S/N) were calculated for two signals (1040 and 1463 cm^{-1}). An S/N of 3 was found for a mass of 22 ± 6 μg. Based on the IUPAC definition, this is the LOD.
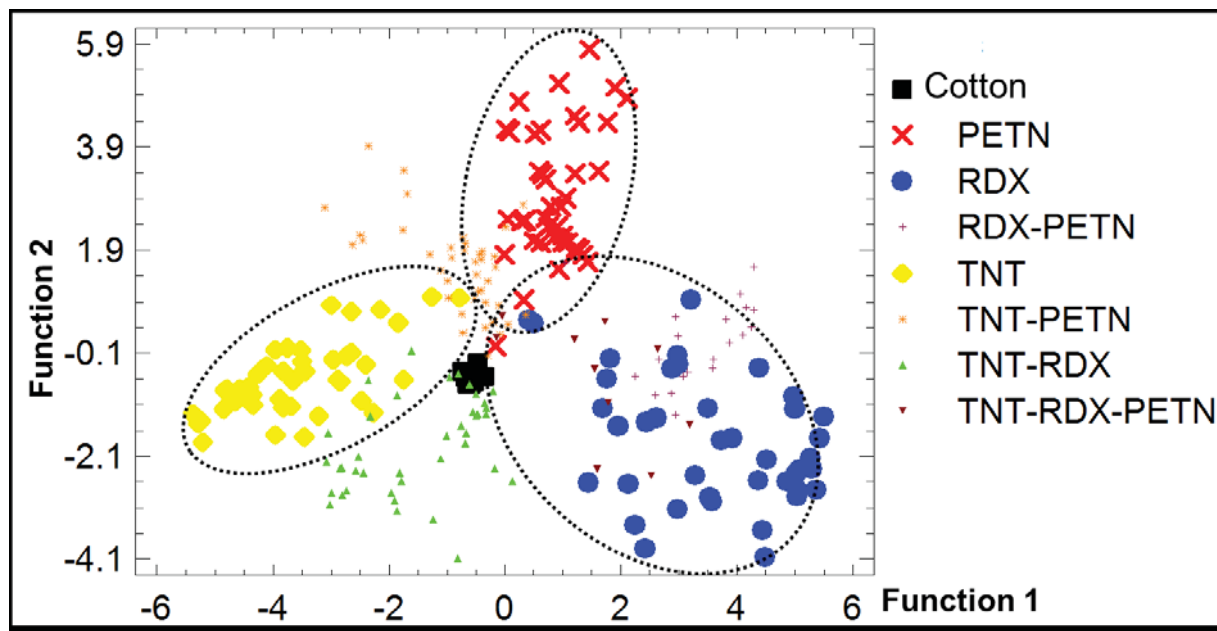

Figure 5: Discriminant plot of F1 and F2.

Discriminant function	1	2	3
Eigenvalue	6.2	3.2	0.5
Relative %	63 %	32 %	5 %
Canonical Correlation	0.93	0.87	0.56
Wilks Lambda	0.02	0.16	0.68
Chi-squared	901.9	431.7	90.6
p value	< 0.0001	< 0.0001	< 0.0001

Table 1: Values of statistical parameters of functions derived from the β parameter.
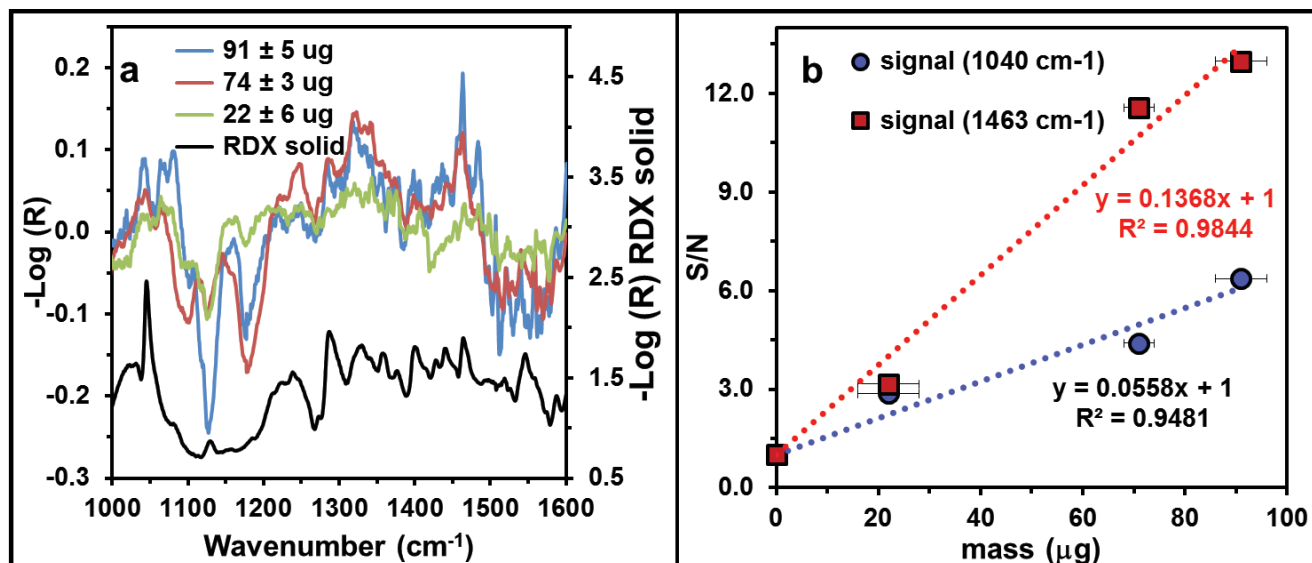
Figure 6: (a) Extracted spectra of RDX particles on cotton; and (b) plot of S/N vs. mass for two RDX signals.

C.2.   QCL spectroscopic library of explosives

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. An addressable QCL Spectral Library was started by measuring vibrational signatures of explosive samples deposited on aluminum using QCL spectroscopy. QCL reflectance spectra were compared with reference spectra acquired in KBr matrices in transmission mode. The reagents used include DNT, RDX and PETN, synthesized at micro scale in the lab. Acetone was used to deposit explosives samples with different surface concentrations on to a travel bag (TB) and on aluminum (Al) used as substrates. Detection of PETN, RDX and DNT deposited on selected substrates was carried out using a QCL spectrometer. All spectra were taken with 5 co-adds and 4 cm^{-1} resolution. In addition, 5 spectra were taken for each sample. The spectral range was 1600 - 1000 cm^{-1}. Table 2 on the next page contains the list of chemicals that have been used to build the QCL library of 46 common (and not so common) explosives. RDX, PETN and TNT have been measured on all substrates: Al (highly reflective metal surface; M), wood (plywood; W), cardboard (CB) and travel bag materials (plastic polymer, black polyester, TB). Their spectra has been included in the QCL spectral library.

#	Status	Explosive	#	Status	Explosive
1	A	RDX	24	M	3,5 dinitro-4-methylbenzoic acid
2	A	PETN	25	M	4- nitrosoresorcinol
3	A	2,4,6-TNT (TNT)	26	M	m-nitroanisole
4	M	2,4-DNT	27	M	p-nitroanisole
5	M	TATP	28	M	3-methyl-2-nitroanisole
6	N	HMX	29	M	4-nitrobiphenyl
7	N	urea nitrate	30	M	5-chloro-2-methylaniline
8	M	p-nitrotoluene	31	M	5-nitro-4-amino-1,3-dimethylbenzene
9	M	p-dinitrobenzene	32	M	m-methylnitrobenzoate
10	M	o-dinitrobenzene	33	M	m- nitrodimethylanaline
11	M	5-nitro-2-aminotoluene	34	M	n(2,4-dinitro-1-napthyl)
12	M	N-nitrosarcosine	35	M	n-methyl-p-nitroanaline
13	N	m-nitroaniline	36	M	n-nitrosodiphenylamine
14	M	2-nitrobiphenyl	37	M	p-nitroanaline
15	M	3-nitrophenol	38	M	n-nitroso-n-ethylurea
16	M	2-methyl-2-nitro-1-propanol	39	M	2-methyl-5-nitroimidazole
17	M	2-methyl-4-nitrophenyl isocyanate	40	M	p-nitrobenzyl chloride
18	M	2,4-dinitrophenol	41	M	p-nitrodiphenylether
19	M	2,4-dinitrophenyl hydrazine	42	M	TMDD
20	M	2,4-dinitro-fluoroanaline	43	M	HMID
21	N	2,4-dinitrophenol	44	N	magnesium perchlorate
22	M	3,4 dinitrotoluene	45	N	ammonium nitrate
23	M	2-nitrodiphenylamine	46	N	black powder

Table 2: Explosives contained in the QCL spectral library. Status: all substrates (A); metallic substrate (M); not measured (N).

Figure 7a on the next page shows QCL spectrum of PETN deposited on Al. Samples were prepared by the smearing deposition method. The most prominent signal is at 1280 cm^{-1}, which corresponds to one of the vibrational signatures of the -NO$_2$ group. Figure 7b on the next page shows QCL spectra of PETN/TB and TB without explosives. Samples with PETN were prepared by the smearing method. Higher signals were achieved by the PETN/TB samples. -NO$_2$ group vibration at 1280 cm^{-1} can be clearly distinguished on top of synthetic fibers of TB. The PETN/TB spectrum reveals to have higher intensities than TB without explosives. The spectra were subjected to various preprocessing steps such as baseline correction and smoothing. Difference spectrum (PETN/TB - TB) should result in the clear identification of targeted explosives, even in reflectance mode.

Sample smearing deposition proved to be an effective sample transfer method on TB and Al substrates. QCL identification was demonstrated to be effective in explosives detection, even in the presence of highly interfering substrates, such as TB. In summary, QCL-MIR spectroscopic detection of explosive samples on common substrates such as TB and Al was demonstrated. Explosives compounds such as PETN, 2,4-DNT and RDX were detected at significant vibration regions at 1300 to 1500 cm^{-1} and identified at near trace level quantities.
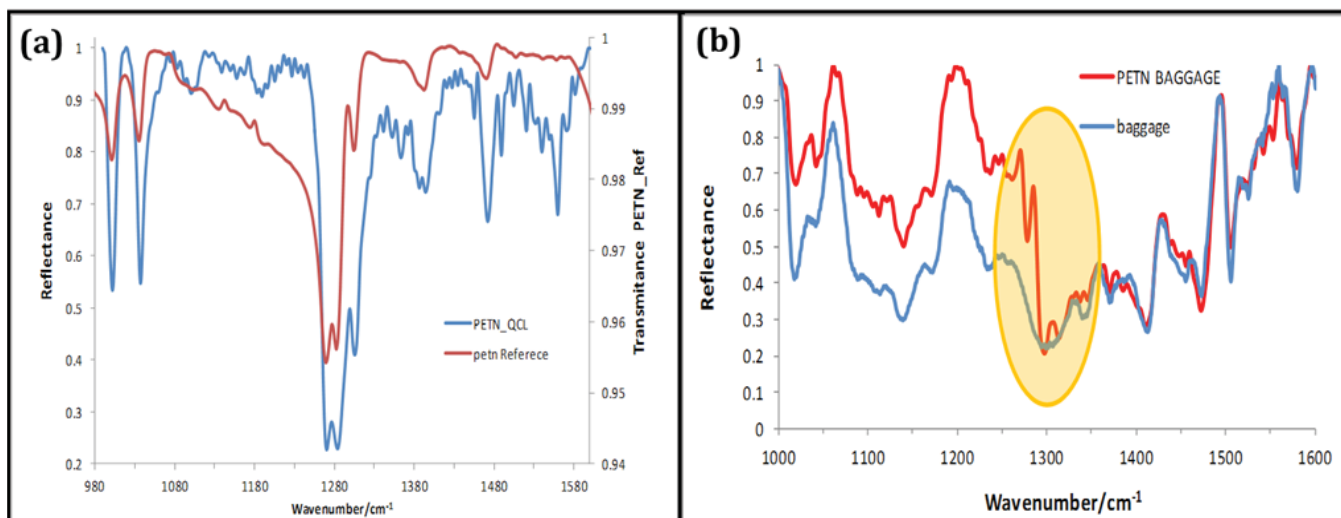
Figure 7: (a) MIR spectra of PETN: blue trace reflectance QCL, and red: transmittance FT-IR; (b) QCL spectra of PETN, red: explosive on TB, and blue: TB without explosive.

D.   Milestones

- Achieved ~ 1 μg/cm^2 detection limit of PETN, RDX and TNT on cardboard, plywood and travel bag materials.
- Began QCL library of explosives on various targets; nearly completed metallic substrates (Al)
- Began addressing discriminating mixtures of explosives and highly interfering background (rag)

E.   Future Plans

Several projects have been planned as a continuation of the efforts in vibrational-spectroscopy-based chemical detection of explosives. These include MIR-spectroscopy-based detection of explosives (using thermal and laser excitation sources) and nanotechnology-based detection of explosives. Plans for next year include continuing to build the addressable library of HE/HEM independent of substrate type. Another relevant project deals with the characterization of HMEs, their detection and their precursors. Upcoming work will include standoff detection of HEM/HME on other substrates such as plastic, wood, leather, cloth, and other metallic surfaces in order to quantify and obtain chemometrics models that can be applied in real-world environments. Detailed theoretical study of optical processes on these surfaces is required to understand the nature of the results of the experiments. We will also study the transition of QCL signatures of explosives to real-world substrates using complex matrices such as sand, plastic, wood, leather, cloth, and other metallic surfaces.

III.   EDUCATION AND WORKFORCE DEVELOPMENT ACTIVITY

A.   Interactions and Outreach to K-12, Community College, Minority Serving Institution Students or Faculty

1. Served as host for 3 high school/junior high school students participating in Science Fair projects.
2. Established first web-based demonstration and experiments with Metropolitan University – Ana G Mendez University System (AGMUS) Institute of Mathematics. Science and technology students used the facilities of the Center for Chemical Imaging and Surface Analysis via web based instruction.

IV. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

The results of ongoing studies demonstrate that the preceding experimental setups can be used in many applications for the detection of explosives and other threat chemicals and biological threat agents. These set ups and applications have already resulted in transition to other US defense and security agencies (as is the case with the collaborative effort with Hughes Research Labs (HRL) to address IARPA's needs as per the SILMARILS program). The results of this study indicates that explosives, as well as illegal drugs can be detected even if they are strategically mixed with innocuous compounds with similar chemical and physical properties, purposely attempting to disguise them from security personnel and using them for criminal or terrorist acts.

This project also intends to expand the knowledge in the field of preparation and characterization of samples and standards based on thin films and islands of HEM/HME for both basic and applied research; depositing traces of target analytes on substrates of high interest using spin coating technology to develop the mentioned assemblies and of thumb prints of HEM/HME that simulate finger prints of explosives on substrates.

A recently acquired Confocal Raman-AFM-SNOM Imaging Spectroscopic System will be used for characterization studies. The specific deliverables are relevant to the DHS Enterprise. Development and the use of QCL MIR portable standoff detection system coupled to multivariate analysis routines, capable of detecting, identifying, and discriminating for HEM/HME. The main use of these systems is as confirming sensors for explosives residues on cloth, luggage, and other substrates down to ng/cm^2. These systems should provide First Responders with a highly versatile tool for explosives detection at close range.

B. Potential for Transition

This project is already transitioning to industry. A collaborative proposal was submitted together with a potential commercialization partners, Hughes Research Labs (HRL), Malibu, CA, and Exelis Geospatial Systems, Rochester, NY (now part of Harris Corp, Melbourne, FL). The proposal was submitted to the Intelligence Advanced Research Projects Activity (IARPA) and was entitled: Standoff Illuminator for Measuring Absorbance and Reflectance Infrared Light Signatures (SILMARILS BAA-15-07 program). Although UPRM received invitations from 3 private companies to be the lead chemical detection partner, HRL contacted us first and the collaboration efforts flourished without significant hurdles. This is a 4.5 yr. program.

A white paper was sent for DHS SED-V program: Standoff Explosives Detection on Vehicles (BAA HSHQDC-15-R-B0003). The pre-proposal is in collaboration with HRL.

C. Data and/or IP Acquisition Strategy

Possible IP and disclosures are in the area of spectral libraries. Our research group has been very active in protecting IP with 3 invention disclosures and 1 patent awarded:

- Awarded: Patent: US 8,932,384B1, 01/13/2015 Surface Enhanced Raman Spectroscopy Gold Nanorods substrates for detection of 2,4,6-trinitrotoulene and 3,5-dinitro-4-methylbenzoic acid explosives.
- Pending: Application number: 61/471,478 of April 4, 2011. Synthesis of Ag, Cu, Pt and Au Nanostructures for Continuous Deposits on Surfaces by Micro-Patterned Laser Image Formation.
- Working on: Applications of QCL in forensic detection of explosives.

V.   PROJECT DOCUMENTATION

A.   Peer Reviewed Journal Articles

1. Figueroa-Navedo, A.M., Galán-Freyle, N.Y., Pacheco-Londoño, L.C. and Hernández-Rivera, S.P., "Chemometrics Enhanced Laser Induced Thermal Emission Detection of PETN and RDX", 2015. J. Chemometrics, 29(6): 329- 337. DOI: 10.1002/cem.2704

2. Galán-Freyle, N.J. Pacheco-Londoño, L.C., Figueroa-Navedo, A. and Hernández-Rivera, S.P., "Standoff Detection of Highly Energetic Materials by Laser Induced Thermal Excitation of Infrared Emission", 2015. Appl. Spectrosc. 69(5): 535-544.

Pending -

1. Castro-Suarez, J.R., Hidalgo-Santiago, M., Hernández-Rivera, S.P., "Detection of highly energetic materials on non-reflective substrates using quantum cascade laser spectroscopy", 2015. Appl. Spectrosc., accepted for publication.

2. Castellanos, J., Betancourt-Pagan, S. A., Robledo-Ortiz, E. J., Pacheco-Londoño, L. C., De Jesús M. A., Hernández-Rivera, S. P., Fabrication of Columnar Sub-microstructures using a Q-switched Nd:YAG Laser in the Nanosecond Time Regime, 2015. Journal of Laser Micro/Nanoengineering, accepted for publication.

B.   Technology Transfer/Patents

1. Patents Awarded

   a. Patent #US8,932,384B1, 01/13/2015 Surface Enhanced Raman Spectroscopy Gold Nanorods substrates for detection of 2,4,6-trinitrotoulene and 3,5-dinitro-4-methylbenzoic acid explosives. Inventors: O.M. Primera-Pedrozo.; A.N. Chamoun-Emanuelli.; W. Medina-Ramos.; and S.P. Hernández-Rivera.

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