F2-F: Remote Vibrational Spectroscopy
Detection of Highly Energetic Materials

Abstract—The main objective of the ALERT F2-F component is to develop Vibrational Spectroscopy for photonic detection of highly energetic materials (HEM) and homemade explosives (HME). The expected outcome of the project is to improve significantly the current state of development of vibrational standoff detection of HEM/HME in terms of: range (target-observer distance), detection limits, discrimination capabilities and quantification of HEM/HME from interferents (background and matrices). During Year 5 significant improvements were made in the development of remote mid-infrared (MIR) sensing of explosives using QCL, thermal and CO$_2$ laser based methods.

I. PARTICIPANTS

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II. PROJECT OVERVIEW AND SIGNIFICANCE

The need for rapid detection and identification instrumentation for explosives threats in homeland security and defense applications has become a concern of vast importance in modern society. From military, security and anti-terrorist personnel, to first responders and law enforcing employees such as police officers, airport screeners, and border patrols personnel, to Navy, Army, Air Force, and National Guard workforces, the possibility of coming in contact with an explosive threat agent is high. To achieve the required countermeasures in explosives threats mitigation, vibrational spectroscopic techniques are frequently used. Detection of highly energetic materials (HEMs) at trace levels in air and on substrates remains a subject of great importance. In the past few years, many of the published reports have focused on the detection of these important chemical compounds. However, the majority of them require some type of sampling. Obtaining samples in the field is the principal disadvantage of most explosive detection devices because the person doing the sampling is at risk.

Vibrational spectroscopy based standoff detection has been used for sensing highly energetic materials (explosives, HEM) and homemade explosives (HME) as part of the ALERT F2-F component at the University of Puerto Rico-Mayagüez. During the last year, research has covered applications at close distances (0.1 m to 4 m) and long ranges (5 to 65 m) in the case of standoff IR, not limited by range but rather by source; and up to 140 m (in the case of standoff Raman spectroscopy). Synthesis, characterization and samples and standards preparation studies have also been conducted as part of the point detection (Raman and IR) and wide area detection (IR studies).

III. RESEARCH AND EDUCATION ACTIVITY

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

Rapid and precise identification of high explosives (HE), as well as homemade explosives (HME), is one of the central tasks of security and public safety personnel, particularly with the recent proliferation of improvised explosive devices and other explosives threats worldwide. Instruments that can be used in the field to rapidly and accurately detect and identify explosives and their precursors should form part of checkpoint security stations in airports, seaports and government buildings. Infrared spectroscopy (IRS) in the mid-infrared (MIR) region has played an important role in the characterization of highly energetic materials through persistent characteristic signatures. These signatures can be universally used to detect these compounds from a distance.

B. Major Contributions

Project I: Dependence of Detection Limits on Angular Alignment, Substrate Type and Surface Concentration in Active Mode Standoff IR

A standoff multivariate calibration for detection of highly energetic materials (HEM) using Fourier transform infrared spectroscopy is presented in this report. The procedure consists in standoff sensing at 1 m distance and the variation of three parameters of detection. The first variable considered was the angular dependence: 0° to 45° from source-target with respect to alignment of target-detector. The second variable consisted of the use of several surfaces on which the material was deposited. The substrates used were polished aluminum and anodized aluminum. The third variable studied was the dependence on some specific analyte loading surface concentration: from 10 μg/cm² to 200 μg/cm². The HEM used in this work was PETN, synthesized in our lab. Calibration curves were based on the use of chemometrics routines such as partial least squares (PLS) regression analysis. This algorithm was used to evaluate the impact of the angular dependence about the limits of detection of different HME loadings on aluminum substrates (see Figure 1 on the following page).
Project II: Angular Dependence of Source-Target-Detector in Active Mode Standoff Infrared Detection

In active mode infrared standoff detection the signal is presumed to be highly dependent on the alignment of the light source, the target and the collector. This is particularly critical in detection of the back reflected light. In fact, many authors presume that off normal geometries are completely forbidden in active mode experiments. Signals can be obtained at high angles of “misalignment” (off surface normal geometries) but the question arises: are the signal intensities that can be measured higher than the experimental noise? In other words is the signal to noise ratio (S/N) greater than 3 at these angles of “misalignment” from conventional setup geometries?

Another important question that can be brought to the discussion is: are there differences in the spectral features between specular reflections and diffuse reflection (scattering) at different angles of off target surface normal geometry? How is the surface deposition of analyte affected by detection at these off surface normal angles and how do these measurements complicate the material identification? Is it possible to achieve detection using conventional sources at long distances or are collimated and coherent sources (lasers) required for these tasks?

The brightness of the light used in active mode standoff detection experiments is essential for achieving the sought results. This has been demonstrated in literature and a high dependence of detection with brightness and distance has been shown. If active mode standoff detection is highly dependent on light sources brightness (power; in the case of laser sources) this should be a critical factor in the detection at off-surface normal standoff geometries.

Active mode standoff measurement using infrared spectroscopy were carried out in which the angle between target and the source was varied from 0-70° with respect to the surface normal of substrates containing traces of HEM (explosives). The experiments were done using three infrared sources: a modulated source (Mod-FTIR), an unmodulated source (UnMod-FTIR) and a scanning quantum cascade laser (QCL), part of a dispersive mid infrared (MIR) spectrometer. The targets consisted of PETN 200 μg/cm² deposited on aluminum plates placed at 1 m from the sources. Evaluation of the three modalities was aimed at verifying the influence of the highly collimated laser beam in the detection in comparison with the other sources. Mod-FTIR performed better than QCL source in terms of the MIR signal intensity decrease with increasing angle.

Figure 2 on the following page shows the schematic diagram of the experimental setup used in the investigation. Three types of experiments were performed. The setup for the first and second experiments is shown on the left. The setup consisted of three lenses, one ZnSe lens 2 in. diameter and 1 m of focal length used to focus the light from the FTIR spectrometer (Mod-FTIR source) or the QCL spectrometer to the sample target. Two ZnSe 4 in. diameter lenses, one 1 m focal length used to collect the light reflected from the sample and other 0.1 m focal length used for focus the light to the detector (MCT). The setup for the third experiment is
shown in part B. The assembly consisted of three ZnSe lenses, two lenses of 4 in. diameter, one of 10 m and other 1 m of focal length used for focus the light from the source (unmodulated source) to sample and other of 0.1 m and 2 in. diameter used to collect and focus it onto the OP-FTIR spectrometer.

The view angle \( f \) for the setup was calculated using the following equation, where \( d \) is the diameter of the collection lens and \( L \) is the experimental distance (range or standoff distance):

\[
f = 2 \cdot \arctan \left( \frac{d}{2L} \right)
\]

Figure 3 shows the spectra of 200 \( \mu g/cm^2 \) of PETN at 1 m \( f = 5.8^\circ \) at an angle of 60\(^\circ\). PETN spectra are well defined from 0\(^\circ\) to 20\(^\circ\) for the QCL spectroscopic system, however at 60\(^\circ\) the signals are not observed. When the experiment was done at 20 cm the signals were observed for all angles (0\(^\circ\)-80\(^\circ\)). Similar behavior was found for Mod-FTIR and UnMod-FTIR. Stronger signal intensities for PETN were observed.

The signature bands of PETN were present in all the spectra acquired by the three techniques investigated. These vibrational signatures for PETN were assigned as follows: 1003 cm\(^{-1}\) was assigned to C–O stretch + CCC deformation and 1300 cm\(^{-1}\), 1400 cm\(^{-1}\) and 1500 cm\(^{-1}\) was assigned to NO\(_2\) stretch.

The dependence of the signal intensity and S/N with \( \Theta \) can be observed. Only for the experiment of QCL for \( f = 5.8 \) can observed an S/N lower than 3 for 20\(^\circ\) to 80\(^\circ\). This can be attributed to the low QCL laser power (0.5-10 mW). Therefore, it is suggested that for distances > 1 m laser powers must be much higher than 10 mW. Detection was better in the Mid-FTIR than Un-mod-FT-IR for all angles, although that Mid-FTIR has a lower viewing angle than UnMod-FTIR. This can be explained due to modulation of the light. The detector is more sensitive to this light and can differential
this of surrounding noise. This is indicated that the modulation of light before reaching the sample increases the sensitivity compared to an unmodulated source FT-IR where the light first interacts with the sample prior to entering the interferometer.

For the QCL experiments, minor changes at the initial angular values generate a sharp fall in the S/N. Then a rapid exponential decay of the S/N with the angle is observed. For Mod-FTIR and UnMod-FTIR the S/N do not decay considerably with increasing angle but are rather stable at all angles. An advantage in the mod-FTIR is that the signs are more defined than in others. This is due to the form of acquisition of the spectra; the detector is more sensitive to this modulated light to the ambient light.

The detection limits were calculated by making an extrapolation a S/N = 3 for each method and each angle. For Mod-FTIR the LOD at angles of 0-80° were 4-20 μg/cm². For UnMod-FTIR the corresponding values were 2-100 μg/cm². For the QCL based methodology (f=5.8) LOD values ranged from 0.1 to 600 μg/cm² and for the QCL (f=17.6) LOD values were 0.01-6 μg/cm².

**Project III: Detection of HEM using Quantum Cascade Laser Spectroscopy**

An infrared spectroscopy based explosives detection system using a quantum cascade laser (QCL) as excitation source was used to record mid infrared spectral signals of highly energetic materials (HEM) deposited on real world substrates such as travel baggage, cardboard and wood. As indicated in Figure 4, the HEMs used were nitroaromatic military explosive trinitrotoluene (TNT), aliphatic nitrate ester pentaerythritol tetranitrate (PETN) and aliphatic nitramine hexahydrotrinitroazine (RDX).

Various deposition methods including sample smearing, spin coating, spray deposition and partial immersion were evaluated for preparing samples and standards used as part of the study. Chemometrics statistical

![Figure 4: (A) Experimental setup: PETN, TNT and RDX explosives detection using QCL spectroscopy on real substrate such as wood, cardboard and travel baggage. (B) PETN spectra deposited on TB and CB substrates and detected in back reflection mode using QCL spectroscopy. (C) PCA regression QCL spectra for PETN, RDX and TNT deposited on CB substrates using QCL. Preprocessing steps applied were: 1st deriv (15 pt.) + Mean Centering.](image)
routines such as principal component analysis (PCA) regression with various preprocessing steps were applied to the recorded infrared spectra of explosives deposited as trace contaminants on target substrates. The results show that the dispersive infrared vibrational technique investigated using QCL is useful for detection of HEMs in the types of substrates studied.

**Project IV: Detection of Homemade Explosive in gas phase using quantum Cascade Laser Spectroscopy**

In this project, we investigated infrared vibrational detection of high energetic materials such peroxide triacetone triperoxide (TATP) in the gas phase present in the air. The detection experiments were carried out in active mode using a quantum cascade laser (QCL) IR source for detections by dispersive spectrometer. Partial Least Squares-Discriminant analysis (PCA) was used to generate pattern recognition schemes of traces of explosive in the air from IR spectra obtained. Classificatory capacities from the different models of PCA were used to establish the best experimental setup for the detection and classification of this explosive in the gas phase.

Three types of experiments were performed (see Figure 5). The HEM samples were placed on the bottom of 500 mL Erlenmeyer flasks. A flow of dry air (1-16 mL/s) at several temperatures (0-38°C) was used. The temperature was regulated by either scanning in the range of temperature or by using point-by-point fixed temperature measurements. Trace amounts of explosives in the gas phase were dragged from the surface by the air flow and transported to an IR gas cell for detection. Spectra were recorded using the instrument at 4 cm⁻¹ of resolution and 25 scans. The spectral range was from 400-4000 cm⁻¹.

The frequency distribution for the CV of air with TATP and DNT is shown in Figure 6 on the following page. The solid line represents the data for air with the analyte of interest, and the dotted line represents the data for clean air and air with other analytes. Good discrimination was obtained in all of the statistical experiments. The evaluation is shown in Table 1 on the following page. The PCCC for all of the models was 100.0%, and complete classification is observed. However, the cross-validation PCCC was not 100.0% for DNT samples.

In the FT-IR model with a modulated Globar source, the PCCC for TATP was 100% but was lower for 2,4-DNT. This result can be attributed to the fact that pure air was only analyzed at 25°C whereas 2,4-DNT was analyzed from 0°C to 38°C. In this model for 2,4-DNT, 0.25% of the sample was not correctly classified. These data missed the detection of or indicated a false negative for air with 2,4-DNT at low temperatures where the sublimation of DNT is very small. For this model of 2,4-DNT, the sensitivity was 100.00%, the specificity was 99.75% and the false alarm rate was 0.00%.

In the second model (unmodulated FT-IR), the PCCC for all of the models constructed were also 100.0%, but the PCCC for 2,4-DNT was 99.67%. In these cases, the false alarm rates were 0.50%, and the sensitivities were 99.50%. This result is an indication that samples of air or air with TATP were discriminated better than air with 2,4-DNT. In these cases, one of the air samples was poorly discriminated because this experiment was open to the surroundings resulting in possible contamination in the lab. In this setup interferences from
ambient water vapor and CO$_2$ were high.

In the third model (QCL scan), all of the samples were correctly classified. However, the number of samples analyzed must be considered, and the number of variables in this experiment is lower compared to the other experiments. The experimental conditions are not fully comparable because the intensity of this source is much higher than those of the other experiments and the sampling path is smaller for this system.

For the models to have highly significant statistical merit according to the canonical correlation coefficient ($p < 0.0001$), the functions must have an excellent ability to determine the group differences. Wilks' Lambda value indicates how many times the variance is not explained by group differences. Because these values were small, highly correlated differences were established. Other models were generated using only the region of 873-1400 cm$^{-1}$ or the region of emission of the QCL to compare the technique with the FT-IR based experiments. The QCL-based experiments were better than the modulated source FT-IR setup, which, in turn, were better that the non-modulated source FT-IR setup. The validation information is shown in Table 1. A high significance ($p < 0.0001$, equivalent to > 99.99% confidence level) for all of the models were found, indicating that the resulting parameters are highly reliable and the comparison between techniques is highly dependable. The high power QCL scan produces a high sensitiv-

![Figure 6: (A). Histogram for discrimination using modulated source FT-IR. (B). Histogram for discrimination using non-modulated source FT-IR. (C). Histogram for discrimination using QCL.](image)

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Table 1. Validation Parameters for the various models constructed
ity for trace level detection in air but the modulated source FT-IR is close in performance to the QCL-based methodology. This result indicates that the modulation of light (using an interferometer) before reaching the sample increases the sensitivity compared to a non-modulated source FT-IR where the light first interacts with the sample prior to entering the interferometer.

The loading for models of the region (870-1400 cm\(^{-1}\)) are shown in Figure 7. The band observed for TATP at 1200 cm\(^{-1}\) that was tentatively assigned to C-O stretching is the largest contributor to the loadings calculated by the models for modulated source FT-IR and QCL source. However, in the unmodulated source FT-IR experiments, the same result was not found: the first loading has the spectral information shifted. Other bands that contribute occur at 890 cm\(^{-1}\) and 939 cm\(^{-1}\) which are tentatively assigned to O-O stretching. The same analysis applies for all of the other loadings (data not shown). This indicates that the discrimination is generated by a combination of all of the loadings. The QCL model requires only 5 loadings; FT-IR based models require 7 (full spectrum) or 10 (spectral width) loadings.

**Project V: Standoff Laser-Induced Thermal Emission of Explosives**

A laser mediated methodology for remote thermal excitation of analytes followed by standoff IR detection is investigated. The goal of this study was to determine the feasibility of using laser induced thermal emission (LITE) from vibrationally excited explosives residues deposited on surfaces to detect explosives remotely. Telescope based FT-IR spectral measurements were carried out to examine substrates containing trace amounts of threat compounds used in explosive devices (See Figures 8 and 9).

The highly energetic materials (HEM) used were PETN, TATP, RDX, TNT, DNT and ammonium nitrate (AN) at 200 μg/cm\(^2\). Conditions were to 36 W of power and 20 s of exposure time.
laser, and their mid-infrared (MIR) thermally stimulated emission spectra were recorded. The telescope was configured from reflective optical elements in order to minimize emission losses in the MIR frequencies and to provide optimum overall performance. Spectral replicas were acquired at a distance of 4 m with an FT-IR interferometer at 4 cm⁻¹ resolution and 10 scans. Laser power was varied from 4-36 W at radiation exposure times of 10, 20, 30 and 60 s. CO₂ laser powers were adjusted to improve the detection and identification of the HEM samples. The advantages of increasing the thermal emission were easily observed in the results. Signal intensities were proportional to the thickness of the coated surface (a function of surface concentration), as well as laser power and laser exposure time. For samples of RDX and PETN, varying the power and laser exposure, calculated limits of detection were 2 and 1 μg/cm², respectively.

**Project VI: Improved Detection of Highly Energetic Materials Traces on Surfaces by Standoff Laser Induced Thermal Emission Incorporating Neural Networks**

Infrared emissions (IREs) of substrates, with and without HEM, were measured to generate models for detection and discrimination. Multivariate analysis techniques such as principal component analysis (PCA), soft independent modeling by class analogy (SIMCA), partial least squares-discriminant analysis (PLS-DA), support vector machine (SVM) and neural networks (NN) were employed to generate models, in which the emission of IR light from heated samples was stimulated using a CO₂ laser giving rise to laser induced thermal emission (LITE) of HEMs.

![Figure 10: (A) Custom built experimental setup for measuring PETN emissions on: PVC, aluminum, wood, acrylic, Teflon, rubber and blended leather; (B) PETN on acrylic surface and thermal emission (B-b) shows a prominent PETN band (B-c) in the region from 800 to 900 cm⁻¹ which contrasts greatly from the spectra of the substrate without the HEM (B-a)](image)

Traces of a specific target threat chemical explosive: PETN in surface concentrations of 10 to 300 μg/cm² were studied on the surfaces mentioned. A custom built experimental setup (Figure 10) used a CO₂ laser as a heating source positioned with a telescope, where a minimal loss in reflective optics was reported, for the Mid-IR at a distance of 4 m and 32 scans at 10 s. As shown in Figure 11, SVM resulted in the best statistical technique for a discrimination performance of 97%. PLS-DA accurately predicted over 94% and NN 88%. Figure 12 on the following page shows the receiver operating characteristic (ROC) space in which the best discrimination of efficiency was demonstrated by SVM for discrimination of one HEM (PETN) on various substrates. Figure 12-B on the following page is a radar plot comparing the overall performance of the various multivariate methods used.

**Project VII: Synthesis and Characterization of Homemade Explosives, Precursors and Binary Mixtures with other explosives, accelerators and retardants**

A novel method to synthesize diacetone diperoxide (DADP) from acetone and hydrogen peroxide without the presence of a catalytic agent and synthesis improving of yields of HME was examined. This synthet-
ic route can be useful for preparing reliable standards samples for GC/MS and detection experiments.

Many researchers have proposed reaction mechanisms for the formation of cyclic acetone peroxide products, agreeing that triacetone triperoxide (TATP) is the main reaction product. Diacetone di-peroxide (DADP) is formed in low proportions. One way of preparing DADP in high proportions is by acid-catalyzed isomerization of TATP in organic solvents. An alternative procedure involves the slow addition of hydrogen peroxide (30%) to a cold (-5°C), stirred mixture of acetone and catalytic m-sulfonic acid in dichloromethane. All previously reported methods to synthesize DADP involved the use of a catalyst. The drawback of this approach is that the purity of the product is compromised. In this study, a new method for synthesizing DADP with a nearly 100% purity without the presence of a catalysts is presented. High-purity synthetic DADP can be used in the preparation of chromatographic and mass spectrometric standards, for characterization studies, for bioassays, in fundamental and applied studies, among other uses. In brief, the experiment consisted in the following: in an attempt to reduce the formation of the TATP, which is the predominant product of the reaction between acetone and hydrogen peroxide, and to isolate the linear polymer precursors of cyclic acetone peroxides, hydrogen peroxide and acetone were mixed in molar ratios of 1:2, 1:3 respectively giving the same yields in both cases. To prevent evaporation of the solvent, a reflux condenser was placed over the reaction mixture and was kept at temperatures below room temperature. White crystals formed from direct gas phase condensation were washed and recrystallized using water and dichloromethane.

Determination of sublimation enthalpies of homemade cyclic acetone-peroxide explosives and homemade amino-peroxide explosives using thermogravimetry analysis and FT-IR grazing angle techniques was also carried out. This study is important for the determination of thermodynamic parameters of Temperature dependence-analysis.

The thermal study deals with a non-linear thermal fitting, theoretically-supported to determine sublimation enthalpies of cyclic organic peroxides explosives using thermogravimetry analysis and FT-IR grazing angle techniques. TGA and FT-IR-GA experiments consisted in the determination of mass loss rate at several isothermal points under the sample melting point and/or decomposition point; these measurements were carried out using a TA Instrument Q-500 Thermal Gravimetric Analyzer. The thermal conditions were as follow: (1) Temperature Range: 294.17 K to 344.15 K (for DADP and TATP) and 334.15 K to 400.15 K (for TMDD and HMTD). The temperature ranges were chosen according to melting and decomposition point of each explosive. The sublimation and decomposition enthalpies values were comparable with previously reported.

Project VIII: Standoff Raman Detection, Identification and Discrimination of Mixtures of HEM/HME with Non-Explosives

Remote Raman detection has become a powerful analytical technique for detection of hazardous compounds in situ and without sample preparation at distances away from the observation site.

Recently, our research group has been working on the design and development of approach for detection and classification of hazardous compounds such explosives, chemical warfare agents simulants and toxic industrial compounds based on remote Raman system.
In the current study we have demonstrated the capability, of remote Raman system for the quantification and prediction of explosives (TNT and PETN) and non-explosives (4-nitrobenzoic acid and acetaminophen) compound present within mixtures. Partial least squares (PLS) regression was used as chemometrics tool to perform quantification and prediction studies of explosives in different mixture compositions at 8 m of remote distance. The determination coefficients (R²) of the calibration models of Explosives and non-explosives were around 99% respectively with LOD below 9% with values of RMSECV and RMSEP were below of 3% for all components (see Figure 13).

Project IX: SERS based vapor sensor for volatile explosives

A prototype apparatus for testing vapor samples by using a SERS probe head was designed or adapted of a commercial micro vacuum cleaner (Figure 14). The design, places the SERS substrate at the focal point of the vacuum probe. The air is drawn into the chamber using a fan. This fan forces the turbulent flow over the substrate placed in the pass of the air from exterior to the chamber. The substrate is easily removable for SERS assay and quickly changeable for new one. We demonstrate the capabilities of our SERS-active substrates to detect the chemical vapor signature emanating from a possible explosive artifact or containers contaminated with harmful substances.

Spectra collected over SERS-active substrates after vacuum process demonstrate high signal-to-noise ratios obtained in 30 s with vapor concentrations. The results (Figure 15) indicate sensitive detection at sub-picogram levels. Combining SERS substrates with a vacuum demonstrate the potential of our design as a vapor-phase “sniffer” apparatus.

In the other work we developed a novel methodology for the deposition of a highly

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**Figure 13:** PLS models and Loading plots for the Quantification and Prediction of HEM in mixtures.

**Figure 14:** SERS probe head for ultrasensitive vapor detection. a) Micro vacuum cleaner, b) chamber showing the location of the substrate, c) sampling of 2,4-dinitrotoluene vapors.

**Figure 15:** Raman and vapor SERS spectra of: 2,4-dinitrotoluene, Substrate: filter paper coated gold nanoparticle. Laser: 785 nm. Power: 0.75 mW. Sampling was done at room temperature.
sensitive surface-enhanced Raman scattering (SERS) active gold substrate inside the surface of a quartz capillary (Figure 16). First, a ZnO thin film was grown on the inner surface of the capillary by mean of a chemistry reaction. This ZnO film serves as support for the posterior deposition of the gold nanoparticles film. Gold nanoparticles were prepared filling the capillary tube with a gold salt solution and exposing to direct UV light by various hours. This procedure permits the reduction of the gold ions to metallic gold and at the same time attached the gold nanoparticle on the ZnO film previously deposited. These substrates were assays for SERS activity using 4-nitrobenzoic acid (PNBA) as probe molecule. The results suggest that the Au-ZnO coated capillary is a promising tool for microanalysis of effluents by SERS.

Enhanced Raman spectra were taken making flow a PNBA solution at milimolar concentration through the SERS-active capillary using a mini-pump variable flow. The SERS signals were monitored in real time taking the SERS spectrum with a Renishaw Raman microspectrometer RM2000 system while liquid flowing through the capillary. All SERS spectra were taken using 785 nm excitation line (Figure 17).

**Project X: Preparation and Characterization of Thin Films of HEM**

To manipulate quantities of HEM to develop thin films standards it is important to know the quantity of HEM dissolving in appropriated solvent. The solubility of hexahydro-1,3,5-trinitro-s-triazine (better known as RDX or Cyclonite) in alcohols is of both fundamental and practical importance to such scientific disciplines as chemical engineering, materials science, geology, and environmental science. This data is also important for people to understand the characteristics and intermolecular or intramolecular interactions of solute-solvent in various organic alcohols solvents. In fact, the solubility data could be used to separate mixtures, and make standard solutions. In particular, the solubility of RDX in those solvents is not known; the properties of these volatile solvents are important for detection of chemical on surfaces or standoff. In 1986, Griffiths and Haseth have been operating mid infrared (MIR) spectroscopy at the “grazing angle” of incidence (~80° from the surface normal), which is considered one of the most sensitive optical absorption techniques available for measuring low concentration of chemical compounds deposited on surfaces such as plastics, metals, and glasses. Following the same principles, recently Primera-Pedrozo et al. enhanced this technique using fiber optics coupled: grazing angle probe/ Fourier transform reflection absorption infrared spectroscopy. They have been developing new methodologies for detecting traces of materials explosives, using a standard solution of high
energetic materials (HEM) such as TNT, 2,6-DNT, HMX, TATP, and PETN, deposited on metal surfaces. By the way, measurements of solubility of HE such as 2,6-DNT, PETN, TNT have been studied not only in solvents mentioned previously, but others such as water [14], seawater, and organic mixtures such as stearic acid and alcohol ethylic and aniline. Another important HEM to consider is RDX, which is a powerful secondary explosive that has attracted considerable attention due to its interesting structure and unique properties. It is also an important ingredient in military shells, bombs, landmines, grenades, demolitions operations and underwater blasting. To make solubility measurements of RDX in alcohols, the analytical technique of high-performance liquid chromatography (HPLC) was used. This technique was used because explosives materials (including nitro aromatic and nitramines) absorb in ultraviolet (UV) spectral region, allowing their detection. This technique has become an indispensable analytical tool and is usually employed by researchers to separate species in a variety of matrices.

Solid-Liquid equilibrium data of organic nonelectrolyte systems have been important, particularly in the evaluation of HEM that are still undetonated in sea water. This equilibrium allows an analysis about the solvation free energy of nonelectrolyte organic systems. Solvation free energy (ΔGs) depends on: (a) the solvent type, (b) their spatial characteristics, which affects the structure of solvation in solvent, and (c) electronic structure which contributes to: the electrostatic interaction, dispersive interaction, formation of the hydrogen bonds, etc. The standard thermodynamic properties of this energetic material (RDX) for those solvents at the temperature range of 15°C to 40°C, and have solubility data, are areas that has received little attention from the scientific community, therefore are not easily obtained. Despite efforts by experimental and scientific organizations, in terms of both new experimental measurements and critically evaluated data compilations, there still exist numerous systems for which solubility data is not readily available. The purpose of this work is to determine solubility measures of RDX in four alcohol solvents. In addition, the concentration of RDX dissolved in the selected alcohols on equilibrium by HPLC using a suitable methodology has been analyzed. In fact, many applications need the solubility information to make standard solution to enhance sensors that detect materials explosive using techniques such as grazing angle, standoff, and SERS analyses, among others. As a matter of fact, thermodynamic functions such as enthalpy, entropy and free energies of solutions were derived from the solubility data obtained.

An important aspect is that IR spectroscopy is one of a few physical methods that can be used for both in situ studies of various processes on surface and at interfaces, and technological monitoring of thin-film structures in fields such as microelectronics or optoelectronics under serial production conditions. The versatility of modern FTIR spectroscopy provides means to characterize ultrathin coatings on both oversized objects (e.g., works of art) and small (10–20-μm) single particles, substrates with unusual shapes (e.g., electronic boards), and recessed areas (e.g., internal surfaces of tubes). It should be emphasized that IR spectroscopy can be highly sensitive to ultrathin films: Depending on the system the sensitivity is 10−5–10% monolayer. However, the various IR spectroscopy techniques must be adapted to measure spectra of very small amounts of substance in the form of ultrathin films.

Investigative methods that use knowledge of the material optical constant include laser pyrolysis, for determining energetic material decomposition chemistry, and laser-augmented combustion and ignition, knowledge of the optical constant allows estimation of surface (Fresnel) reflection losses and spatial distribution of radiation absorption. To determine the intensity of the reflected and refracted rays, the treatment of Fresnel is employed. Fresnel, in the late eighteenth century, considered the interaction of the electromagnetic wave with the surface between the two media as involving two extreme orientations or polarizations of the electric vector—light polarized in the plane of incidence, p-polarization and light polarized perpendicular to the plane of incidence, s-polarization.

Another important aspect of the adsorption process is the nature of the site in which the adsorbate is bound. The sites available have considerable influence on the binding of an adsorbate and on the charges transfer that takes place between the adsorbate and the surface. Indeed, different faces of the same crystal might exhibit different behavior with respect to certain adsorbate because not only might one be more open in
structure than another (with associated differences in electron density in the valence band) but also, in some cases, one might offer less favorable sites for binding than the other.

The fact that infrared spectroscopy provides specific information on the types of bonds present in a molecule, is non-destructive, and does not require UHV has made it a highly versatile technique for surface analysis. However, many samples are effectively opaque to the IR radiation and thus cannot be studied in transmission mode. Reflectance methods are particularly useful here and have found wide application in both routine and research surface analysis. In order to be able to optimize the efficiency of a reflectance experiment it is necessary to understand the equations governing the reflectance process. Hence, most studies use so-called reflection mode as reflection-absorption infrared spectroscopy (RAIRS). The setup is shown in Figure 18.

The compound studied is the cyclic nitramine hexahydro-1,3,5-trinitro-s-triazine, as well known as RDX, in solid state, has preferentially conformed in chair configuration by six-member ring. However, its polymorphism is referred to NO2 groups in either equatorial or axial position respect to the triazine ring. Some symbolism is used to discriminate these orientations. As summary, α-RDX has established as the stable form at room temperature, where two of NO2 groups are axial and the third equatorial with Cs symmetry, (AAE-RDX). The molecular conformation referred β-RDX which has the NO2 groups occupying all axial with respect to the triazine ring. (AAA-RDX) and it has a molecular symmetry C3V. RDX in its polymorphic phases termed α, β and γ has been studied in detail.

A variety of results from different techniques were used to determine the optical constant for RDX. The methods included HPLC, and also Reflection-Absorption Infrared Spectroscopy coupled to Fourier transform (FT-RAIRS) with polarized light as perpendicular as parallel to the plane of incidence in conjunction with Kramers-Kroning Transformation, and also the Poynting Theorem.

### IV. EDUCATION ACTIVITY

The ALERT F2-F component has had a strong commitment to education and training at all levels from high school to post-doc trainees. Table 2 illustrates the main factors used to measure productivity and effectiveness.

<table>
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<th>PRODUCTIVITY</th>
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<th>YR-3</th>
<th>YR-4</th>
<th>YR-5</th>
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<td>P</td>
<td>PI</td>
<td>PI</td>
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<tr>
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<td>13</td>
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<td>0 / 2</td>
<td>0 / 4</td>
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<tr>
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<td>3</td>
<td>3</td>
<td>2</td>
<td>12</td>
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<tr>
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<td>0</td>
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<td>2</td>
</tr>
</tbody>
</table>

Table 2: Productivity factors on F2-F ALERT component at UPR-M: 5 years of project operation.
During the summer of 2013 the Research Experiences for Undergraduates was extended to host 6 undergraduate students: two (2) from the DHS ALERT-COE; one (1) from DOD HBCU-MI program and two (2) from a recently awarded NSF-REU grant in which Metropolitan University. The students are listed in Table 3.

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
<th>Sponsor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eric Warren</td>
<td>U. Iowa</td>
<td>ALERT</td>
</tr>
<tr>
<td>Natalia Santiago</td>
<td>Metropolitan U. AGMUS-PR</td>
<td>ALERT</td>
</tr>
<tr>
<td>Doris Laguer</td>
<td>UPRM</td>
<td>EPA</td>
</tr>
<tr>
<td>Andrea Flores</td>
<td>Metropolitan U. AGMUS-PR</td>
<td>NSF-REU-MET. U.</td>
</tr>
<tr>
<td>Edgar J. Trujillo</td>
<td>Metropolitan U. AGMUS-PR</td>
<td>NSF-REU-MET. U.</td>
</tr>
<tr>
<td>Amanda Figueroa</td>
<td>UPR-Mayaguez</td>
<td>DOD-HBCU/MI</td>
</tr>
</tbody>
</table>

Table 3: F2-F Year 5 REU Participants

V. FUTURE PLANS

Several projects have been planned as 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. Another relevant project deals with characterization of homemade explosives (HMEs) and 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 about optical processes on these surfaces is required to understand the nature of the results of the experiments. Transition of standoff laser induced thermal emission (LITE) of explosives to real world substrates using complex matrices such as sand, plastic, wood, leather, cloth, and other metallic surfaces.

Future work will also be performed for detection of HME and other harmful substances in vapor phase combining with statistical analysis in order to obtain a quantification model using chemometrics. In addition, will be performing research in order to optimize the overall process in the fabrication of our capillary SERS substrate and fully characterize the obtained microdevices.

VI. RELEVANCE AND TRANSITION

The results of studies completed and ongoing indicate that the experimental setups can be applied in other experiments such as screening for explosives on real world substrates. The results of this study indicate that Explosives as well as illegal drugs can be strategically mixed with other compounds with similar chemical structure in order to confuse the authorities and make criminal or terrorist episodes. Therefore the detection of hazardous compounds such as explosives, chemical and biological agents employed by terrorist are considered interest area of research for federal government (Homeland Security and Forensic Agencies).

This project intends to expand the knowledge in the field of preparation of samples and standards based on thin films of HEM also HEM for both basic and applied research by depositing traces of target analytes on substrates of high interest using spin coating technology to develop the mentioned assemblies. The two main goals of this project are related to the study of solid-substrate interactions. The first and primary goal is to develop methodologies capable of producing solid samples deposited on substrates in controlled size and distribution modes deposited on selected surfaces to generate specimens that would reproduce real contamination samples. In a second closely related aim, the prepared samples will be used to analyze-substrate interactions, physical and chemical properties derived from these interactions, including, but not limited to, particle sizes and shapes, polymorphism at the sub-micro range, optical and spectroscopic properties,
thermal properties, and others. At the micron and sub-micron ranges, the residence time of these adsorbate-substrate assemblies becomes an important property for study, since behavior at the microscopic scale is very different from bulk phase characteristics. Finally, the applications of these well-characterized samples include use in experiments that require fine control of the distribution of loadings of analytes on surfaces.

VII. LEVERAGING OF RESOURCES

Work on QCL based detection of explosives is being pursued in collaboration with Eos Photonics and Thermo-Fisher Scientific (formerly Ahura) for development of hand-held MIR explosives detection equipment. Other companies (such as United Technologies Research Center) are being considered as partners for collaborative and transitioning work. The commercial applications have been envisioned in the standards market for cyclic organic peroxides (CAP) HME, including DADP, HMTD and TMDD.

The NSF Chemical Measurement and Imaging Program supports research focusing on chemically-relevant measurement science and imaging, targeting both improved understanding of new and existing methods and development of innovative approaches and instruments. For which the primary focus is on development of new instrumentation enabling chemical measurements likely to be of wide interest and utility to the chemistry research community.

VIII. PROJECT DOCUMENTATION AND DELIVERABLES

A. Peer Reviewed Archival Publications


B. Conference Proceedings


C. Other Presentations

Invited Presentations


Presentations


Continued Education Courses:

Grants:
Approved: $450,000 3 years co-Funded by DOD
Title: Puerto Rico REU: Research Training in Cross-disciplinary Chemical Sciences
Funding agency: NSF
PI: Dr. Osvaldo Cox
Co-PI: Dr. Beatriz Zayas

Research Mentors: Dr. Ajay Kumar; Dr. Mith’El B. Santiago, Dr. Oliva M. Primera-Pedrozo, Dr. Jonathan Friedman, Dr. Shikha Raizada, Dr. Antonio Alegria, Dr. Carlos Cabrera and Dr. Samuel P. Hernandez.

Description: The goal of this project is to build a cross-disciplinary research community in chemistry to increase the competitiveness of chemistry majors in Puerto Rico and thereby increase their preparedness and enthusiasm to continue to graduate school. The project will recruit students at Universidad Metropolitana, a Hispanic Serving Institution in San Juan, Puerto Rico and offer a program during the academic year followed by a summer component at four (4) partner institutions which are research intensive institutions.

VIII. REFERENCES


