# STANDOFF LASER-INDUCED THERMAL EMISSION OF EXPLOSIVES

By

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#### ABSTRACT

A laser mediated methodology for remote thermal excitation of analytes followed by standoff infrared (IR) detection is proposed. The goal of this study was to determine the feasibility of using laser induced thermal emission (LITE) to vibrationally excite explosives residues deposited on surface to detect the compounds remotely. Telescope based Fourier Transform IR (FT-IR) spectral measurements were carried out to examine substrates containing trace amounts of threat compounds used in explosive devices. Highly energetic materials (HEM) used as targets were pentaerythritol tetranitrate (PETN), triacetone triperoxide (TATP), 1,3,5trinitroperhydro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT) and ammonium nitrate (AN) at concentrations from 5 to 200 µg/cm<sup>2</sup>. Target substrates of various thicknesses were remotely heated using a high power CO<sub>2</sub> laser, and their mid-IR (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 distances from 4 to 64 m with an FT-IR interferometer at 4 cm<sup>-1</sup> resolution and 10 scans. Laser power was varied from 4-36 W at radiation exposure times of 10, 20, 30 and 60 s.  $CO_2$  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 the surface concentration), as well as the laser power and laser exposure time. The limits of detection for the different explosive were from 21 to  $1 \mu g/cm^2$  at 4 m. The detection was possible at 64 m for 200  $\mu g/cm^2$  of RDX.

#### RESUMEN

Se propone una metodología mediada por láser para la excitación térmica remota de analitos seguido por la detección infrarroja (IR) a distancia. El objetivo de este estudio fue determinar la viabilidad de la utilización de emisión térmica inducida por láser (LITE) para excitar vibracionalmente residuos de explosivos depositados sobre superficies para detectar los compuestos remotamente. Mediciones espectrales basadas en un telescopio infrarrojo de transformada de Fourier (FT-IR) se llevaron a cabo para examinar sustratos que contienen cantidades traza de compuestos peligrosos utilizados en dispositivos explosivos. Los materiales de alta energía utilizados fueron tetranitrato de pentaeritritol (PETN), triperoxido de triacetona 1,3,5-trinitroperhidro-1,3,5-triazina (RDX), 2,4,6-trinitrotolueno (TNT), (TATP), 2.4dinitrotolueno (DNT) y nitrato de amonio (AN) a concentraciones de 5 a 200 µg/cm<sup>2</sup>. Sustratos que sirvieron de blanco de diversos espesores se calentaron a distancia usando un láser de  $CO_2$ de alta potencia, y se registraron sus espectros de infrarrojo medio (MIR) de emisión estimulada térmicamente. El telescopio se configuró a partir de elementos ópticos reflectivos con el fin de minimizar las pérdidas de emisión en las frecuencias MIR y para proporcionar un rendimiento óptimo. Réplicas espectrales se adquirieron a distancias de 4 a 64 m con un interferómetro FT-IR de 4 cm<sup>-1</sup> de resolución y 10 scans. La potencia del láser se varió de 4 a 36 W y los tiempos de exposición de radiación fueron 10, 20, 30 y 60 s. La potencia de láser de CO<sub>2</sub> se ajustó para mejorar la detección y la identificación de las muestras de HEM. Las ventajas de aumentar la emisión térmica se observan fácilmente en los resultados. Intensidades de señal fueron proporcionales al espesor de la superficie revestida (una función de la concentración superficial),

así como la potencia del láser y el tiempo de exposición al láser. Los límites de detección para los distintos explosivos fueron desde 21 a 1  $\mu$ g/cm<sup>2</sup> a 4 m. La detección fue posible a 64 m para 200  $\mu$ g/cm<sup>2</sup> de RDX.

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To Almighty God, to my parents Francisco and Carmen and to my new small family Leo and Leah.

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# **CHAPTER 1**

# **1.1 INTRODUCTION**

There is a wide variety of techniques suitable for hazardous chemicals detection, identification and discrimination using lab based experiments and controlled environments that are not appropriate for detection of small amounts of hazardous material at safe distances in field operations.<sup>1-3</sup> However, remote detection of explosive materials using vibrational spectroscopy: IR and Raman, has been demonstrated to be well applicable for this type of study.<sup>4,5</sup> It is significant to note that Raman, a scattering-based technique, is expected to be less sensitive than techniques based on infrared (IR) absorption as reported Kumar et al., 2010.<sup>6</sup> The two principal reasons for this fact are a far weaker Raman scattering cross section (~10<sup>-29</sup> cm<sup>2</sup> molecule<sup>-1</sup>) than an IR absorption cross section (~10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup>), and their frequency dependences. The wavelength dependence of a Raman-scattering cross section,  $\lambda^{-4}$ , requires the use of short wavelength laser excitation sources, often at non-eye-safe wavelengths and not appropriate for atmospheric propagation over long distances. On the other hand, strong optical absorption features of many explosives occur in the long wavelength atmospheric window from 8–12 µm in the mid-IR (MIR).

Patel and collaborators demonstrated the detection and identification of small amounts of TNT at distances of 150 m illuminated with tunable infrared radiation (a  $CO_2$  laser) because laser radiation at this wavelength is strongly absorbed in the fingerprint region of the target explosives.<sup>6</sup> Accordingly, the use of a  $CO_2$  laser to induce thermal emission of the target explosive is highly suitable in promoting the strong IR process. Thus, in this work the main

motivation to use a  $CO_2$  laser was that is an excellent source of remotely heating the hazardous chemical samples and inducing strong MIR emissions.

Infrared emission spectroscopy is a technique that is not commonly used. One of the principal reasons for the unpopularity is the very low intensity of the infrared emission signal for non-heated samples, when compared with its complementary modalities: IR absorbance, transmission or reflectance spectroscopy. Also, another disadvantage of this technique is the so called "self-absorption" of the sample. This effect is due to the thicknesses of the various layers within the composite sample since a cooler surface layer can absorb radiation emitted by the inner parts or deeper-lying warmer layers.<sup>7</sup> Nevertheless, the evolution to high-sensitivity instruments based on Fourier transform infrared (FT-IR) spectroscopy in combination with the appropriate use of means for temperature increases and sample thickness has been responsible for the improvement of weak signal intensity in MIR emission spectroscopy (MIRES) modality. Therefore, interest in MIRES has been gradually increasing. In fact, interest in MIRES has resulted in numerous contributions dealing with developmental research in thermal emission of radiation.<sup>8-14</sup> In these studies, a sample is thermally excited to higher vibrational energy levels, and the radiant relaxation process is monitored by a spectrometer or interferometer.<sup>15</sup>

Provided that the sample can be heated, regardless of the background material, the thermal emission spectra of the samples should be measurable. Therefore, the use of a laser to induce thermal emission remotely has generated a practical method known as laser-induced thermal emission (LITE) spectroscopy.<sup>12</sup> In this technique, a laser beam is used to heat locally the sample by laser absorption, regardless of the size, shape, and components of the background material, leading to the MIR thermal emission.<sup>16</sup> At the same time, this emission method presents a

potential advantage: the sample itself is the source of the analytical information. For that reason, the emission spectra can be monitored directly in processes where the sample is heated.<sup>13,14,17-19</sup> Also, due to the intrinsic strength of the emission process, smaller amounts of samples and surface concentrations are required in investigations of thermal emission.<sup>15</sup>

On the other hand, studies in standoff detection of explosives using vibrational spectroscopy have shown the importance of the remote detection when performing research using hazard materials.<sup>20,21</sup> Standoff detection of hazardous materials is defined as making measurements at a distance for safety reasons.<sup>22</sup> In IR standoff spectroscopy explosives detection, vibrational signatures can be recorded from several meters to hundreds of meters in the range between the target and the instrument, thus preventing or minimizing the damage caused by terrorist action in the case of detonation.

In this research, a combination of modified open path FT-IR (OP/FTIR) and an appropriate means of heating the target remotely using a CO<sub>2</sub> laser made feasible the detection by emission of explosive traces in the order  $\sim 7 \ \mu g/cm^2$  or 5.5  $\mu g$  (total mass) in the field of view of the instrument at 4 m. We report on the advantages of LITE spectroscopy for standoff explosives detection using a CO<sub>2</sub> laser. Furthermore, this innovative standoff detection system using CO<sub>2</sub> lasers have been designed at a standoff distance of 4 m, with the main goal of controlling the size of the laser heating spot (0.8 cm radius) to compensate losses in emission signal intensity of the target, due to the surrounding emission signal. In addition, tolerances of sample thickness, maximum increase in temperature and the effectiveness of the emission signal were investigated to provide useful analytical information.

#### **1.2 PROBLEM, OBJECTIVES AND HYPOTHESIS**

Spectroscopic emission systems for standoff detection have been configured for passive mode measurements using unsuitable thermal excitation sources on the sample that do not enable the detection to take place further away from people and vital assets and reduce the potential for severe damage. For example, studies where aluminum plates with traces of explosives were heated by a tungsten lamp that was placed on back of the plates to recording the emission spectra. Based on this problem we proceeded to make the following hypothesis: *"Is it possible to induce heating a sample at a distance using a remote source by increasing the emission of the sample?"* 

On the other hand, the acquisition of emission spectra using a telescope that focuses at infinity (open path FT-IR spectrometer) adds surrounding emission noise. "Is it possible that the modification of an open path FT-IR spectrometer could have the capability of minimize collection of surrounding ambient emissions in the MIR wavelengths range to provide optimal performance in the collected emissions of the targets?"

Throughout this work a  $CO_2$  laser was selected as a remote heating source generating an additional problem: since the  $CO_2$  laser emission is in the spectral window where the samples were analyzed (600 to 1400 cm<sup>-1</sup>), will this interference make impossible the acquisition of the sample spectrum? In order to solve this problem the emission from the sample was collected after thermal induction.

The research objective was to make feasible the detection of HEM by emission of explosive traces using the combination of a modified OP/FT-IR and an appropriate means of heating the target remotely using a  $CO_2$  laser in the field of view of the instrument at 4 m. The advantages of LITE spectroscopy for standoff explosives detection using a  $CO_2$  laser are

presented. Furthermore, this innovative standoff detection system using  $CO_2$  lasers have been designed to standoff distance of 4 m, with the main goal of controlling the size of the laser heating spot (0.8 cm radius) to compensate losses in emission signal intensity of the target, due to the surrounding emission signal. In addition, tolerances of sample thickness, maximum increase in temperature and the effectiveness of the emission signal were investigated to provide useful analytical information.

# **CHAPTER 2**

# THEORY

A brief overview of the theory to be driving in this work will be presented below.

# 2.1 Infrared Spectroscopy

Infrared spectroscopy (IRS) over time has undergone many changes since the discovery of infrared range by Sir William Herschel until the appearance of the Fourier transform which has become so dominant that nowadays only the term FT-IR is mentioned. IRS is an important analytical technique, since a variety of samples (organic compounds, inorganic compounds, plastics, solids, liquids, gases, etc.) can be studied due to the high spectral information content and its variety of possibilities for sample measurement and substance preparation. In addition, the IR spectrum is highly characteristic for a substance and can be used for identifying it, specifically in the fingerprint region about 1500 and 650 cm<sup>-1</sup>.

All the molecules vibrate. The vibrations may be quite simple when a molecule consists of only two atoms, with one vibrational mode. When three atoms are involved, however, several vibrations are possible. In larger molecules, all bonds vibrate at the same time and the combinations become still more complex. The good news is that vibrations of key functional groups occur at characteristic frequencies. In IR spectroscopy infrared radiation is passed through the sample and the frequencies absorbed are monitored. Energy from the absorbed radiation causes bonded atoms to vibrate.

Based on Bohr's atomic model and the observed emission line spectra for hydrogen, it is obvious that electromagnetic radiation can interact with an electron. Consequently, electromagnetic radiation of the corresponding frequency can only then be absorbed by a molecule if a change in the dipole moment is associated with vibrational excitation of the atomic group concerned. The motion of the atoms during the vibration is usually described in terms of the normal coordinate,  $Q_i$ . The molecule is promoted to the excited state only if its dipole moment,  $\mu$ , changes during the vibration [i.e., provided that  $(\partial \mu / \partial Q_i) \neq 0$ ]. For molecules with certain elements of symmetry, some vibrational modes may be degenerate, so that more than one mode has a given vibrational frequency whereas for others vibrational transitions may be completely forbidden.

The IR spectra consist in three regions: the *far-infrared* region of the spectrum (~10 to 400 cm<sup>-1</sup>) is rarely used for structural elucidation but contains useful information on the vibration of heavy atoms (especially for inorganic compounds) and/or weak bonds such as hydrogen bonds. The *mid-infrared* spectrum (400 to 4000 cm<sup>-1</sup>), where of most vibrational modes are located. Measurement of the *near-infrared* spectrum from ~4000 to 12500 cm<sup>-1</sup> may prove advantageous for measurement of overtones and combination bands, which are usually much weaker than the fundamental modes from which they are derived.

#### 2.2 Fourier Transform Spectrometer

The invention of an interferometer used for IR spectrometry which was originally designed by Michelson in 1891, generated an increase in the use of this instrument for IR emission spectroscopy (IRES) as an alternative spectroscopic technique for condensed materials and bulk. The Michelson interferometer is a device that can divide a beam of radiation into two paths and then recombine the two beams after a path difference has been introduced. A condition is thereby generated under which interference between the beams can occur. The variation of intensity of the beam emerging from the interferometer is measured as a function of path difference by a detector. The simplest form of the Michelson interferometer is shown in Figure 1. It consists of two mutually perpendicular plane mirrors, one of which can move along an axis that is perpendicular to its plane and the other mirror remains fixed.



Figure 1. Schematic illustration of a FT-IR system.

Bisecting the fixed mirror and the movable mirror is a beamsplitter, where a collimated beam of radiation from an external source can be partially reflected to the fixed mirror (at point F for the median ray) and partially transmitted to the movable mirror (at point M). When the beams return to the beamsplitter, they interfere and are again partially reflected and partially transmitted. Because of the effect of interference, the intensity of each beam passing to the detector and returning to the source depends on the difference in path of the beams in the two arms of the interferometer. The variation in the intensity of the beams passing to the detector and returning to the source as a function of the path difference ultimately yields the spectral information in a Fourier transform spectrometer.

The beam that returns to the source is rarely of interest for spectrometry, and usually only the output beam traveling in the direction perpendicular to that of the input beam is measured. Nevertheless, it is important to remember that both of the output beams contain equivalent information. The main reason for measuring only one of the output beams is the difficulty of separating the output beam that returns to the source from the input beam. On rare occasions, both output beams are measured with the use of two detectors or by focusing both beams onto the same detector.<sup>23</sup> Therefore, as the monochromator is the heart of a dispersive spectrometer, the interferometer is the heart in FT instruments. Finally, the symmetrical interferograms obtained can be converted into the spectrum by applying the Fourier transform, as shown in the schematic illustration of FT-IR system (Figure 1).

The spectrometer that was used to accomplish the research was a FT instrument. However, a new FT-IR emission system was used (see schematic illustration, Figure 2). Some differences are observed in comparison with the schematic illustration shown in the Figure 1, because in this work we used a FT-IR emission system that should keep two principal conditions: a) sample is the source and b) the sample must be at higher temperature than the surrounding medium.



Figure 2. Schematic illustration of FTIR emission system.

## **2.3 Infrared Emission**

When the temperature of any sample is raised above ambient temperature the Boltzmann distribution of the population of vibrational energy states is altered, and the IR radiation emitted can be monitored by a detector at ambient temperature. Bands or lines which are strong in emission spectra are just as characteristic as absorption spectra for determining molecular structure. Since the intensity of emission bands is usually low, most measurements to date have been made either using nondispersive means or FT spectrometers.<sup>9</sup> Emission spectroscopy is based on a few basic equations and principles such as the laws of Kirchhoff (absorption = emission), Stefan-Boltzmann (total radiation is proportional to  $T^4$ ), Planck (distribution of spectral emission) and Wien (radiation maximum is proportional to  $T^{-1}$ ) with the added constraint that the radiation balance is has to comply with conservation of energy: the sum of the emittance  $\epsilon$ , reflectance R, and transmittance T is unity, i.e.

#### $\varepsilon + \mathbf{R} + \mathbf{T} = \mathbf{1}$

This last relationship implies that high-reflecting substances do not show any emission.

A few particularities must be accounted for in measuring the sample emission: the emission spectrum also depends on the thickness. Normally, the sample is present as a thin layer on a base. For thicker samples, re-absorption may occur thereby causing the emission spectrum to be definitely more complicated, have less structure and to resemble the emission curve of a black body (black radiator). The sample can also form gases, which re-absorb the radiation, or it can simply be thermally degraded. In practice, an emission spectrum is acquired by using the heated sample, located in the emission port of the FT spectrometer, as the radiation source. A black radiator, having the same temperature as the sample, acts as the reference. Spectra, which are represented as the quotient of the emission of the sample and of the black radiator, however, contain emission contributions from the sample environment and from fractions reflected by the sample.<sup>24</sup>

#### 2.4 LITE Spectroscopy

LITE spectroscopy is introduced as an analytical technique for condensed-phase specimens. In this technique, a laser beam is used to locally heat the specimen, and the MIR thermal emission is observed. Many of the problems of thermal emission spectroscopy can be solved by using a laser to induce emission. Unlike the IR fluorescence experiments the laser energy input into the sample transfers predominantly by intramolecular motions or intermolecular collisions. Thus, in the liquid or solid state, a Boltzmann distribution of energy is rapidly achieved. This higher macroscopic temperature results in emission spectra which are essentially the same as those obtained in a conventional heated cell. This technique was entitled LITE spectroscopy. LITE spectroscopy differs from conventional emission spectroscopy in its simplicity and in the various dimensions of information extractable.

Similar to Raman and electronic fluorescence measurements, spatial resolution can be easily achieved with LITE because the exciting laser can be directed onto a certain spot on the specimen or scanned across its surface. Processes removing heat from the excitation volume of the specimen will ultimately limit the spatial resolution achievable with LITE. However, high spatial resolution should be possible with LITE, as it is technologically comparable to laser surgery, in which a small region of material can be heated to a high temperature without damaging nearby tissue.

In contrast to the circumstances with FIR and MIR absorbance and reflectance measurements, with LITE the photon flux onto the detector is relatively small and the background is dominated by thermal emission from optical components and surroundings. Because of the low photon flux, the detection electronics could be configured for maximum sensitivity, because the dynamic range need not be great. In addition, the LITE spectrometer can be designed so that the laser-induced emission can be readily discriminated from background emission.

The potentially high sensitivity, along with the simplicity and accuracy with which one can direct the excitation, makes LITE a powerful way to obtain vibrational spectra of microscopic regions of condensed phases. Another advantage of LITE over conventional IR microscopy is that the light scattering properties of the specimen will not easily introduce spectral anomalies. The dependence of LITE on the thermal properties of the specimen could also be used to the researcher's advantage. The microscopic measurement of these thermal properties could be established by spectroscopic monitoring of the time evolution of heating or cooling of the material.

Again, analogous to Raman spectroscopy, LITE spectroscopy can be used as a means of obtaining spatially resolved vibrational spectra from a condensed phase. Although the limits of spatial resolution will not be as good as those for Raman, LITE intensities are much stronger than Raman intensities, particularly in the low-frequency region, where emission intensities are strongest. This region of the spectrum is difficult to measure with Raman spectroscopy, because stray light from the Rayleigh line is a significant interference for low-wavenumber shifts. Similar to electronic fluorescence spectroscopy, LITE spectroscopy allows one to achieve a certain degree of selectivity through choice of the exciting laser wavelength.

The same way that lasers can be chosen to excite electronic transitions in the visible region of the electromagnetic spectrum, vibrational overtones in the NIR or in fundamental vibrational bands in the MIR and FIR. Because the absorbed laser energy is quickly redistributed from the excited molecule to nearby molecules, selectivity for single molecules is not possible with LITE. However, if the specimen has macroscopic regions of different chemical composition, it is possible that one may be able to choose a laser wavelength that heats one area selectively over another. In this way, one could record the emission spectrum of a specimen through a thin layer of material on the surface of that specimen. This procedure can be most easily applied to analysis of composite materials whose constituents are known. With a tunable laser, one could perform an absorption experiment on the specimen in much the same way that thermal lens or photoacoustic spectroscopy experiments are performed. In those experiments, a physical property is measured that is modulated by the photon heating of the specimen. In the thermal lens experiment that property is refractive index; in the photoacoustic experiment that property is thermal expansion. The absorption of a specimen can also be detected by monitoring the IR emission intensity. Thus another dimension of information is obtainable by measuring the total IR emission intensity as a function of laser wavelength<sup>12</sup>.

#### 2.5 CO<sub>2</sub> Laser

The carbon dioxide (CO<sub>2</sub>) laser, a gas laser, is one of the most powerful lasers today. A gas laser is a laser in which the gain medium is a gas, which is used to produce laser light through excitation by an external source such as an electrical discharge. The first CO<sub>2</sub> laser was developed by Patel in 1964 at Bell Labs.<sup>25</sup> The carbon dioxide the gas medium that becomes excited and emits laser light that can be used for numerous applications. There are various configurations that will allow various powers at continuous or pulsed and tunable operation for many uses.

Other gases can be mixed with  $CO_2$  to help excite the  $CO_2$  molecules as well as to help improve other parameters. Gases such as nitrogen and helium are introduced to help excite the  $CO_2$  molecules and to increase the efficiency of the laser. Instead of exciting atomic energy levels to produce light, the  $CO_2$  laser uses the vibrational modes (symmetric, bending and asymmetric) of the  $CO_2$  molecule.

Typically an electric discharge is used to excite the  $CO_2$  molecules. The electrons from the discharge collide with the nitrogen molecules mixed in with the carbon dioxide molecules. These collisions transfer energy from the electrons to the nitrogen molecules thereby exciting nitrogen

molecules into a low lying triplet excited state. This excited state of the nitrogen is long lived because of a forbidden  $T \rightarrow S$  transition which means that a large portion of the nitrogen molecules will stay in this excited state for a long time. These excited nitrogen molecules will then start to collide with the carbon dioxide molecules, which are sharing the same space. The collisions will then provide the CO<sub>2</sub> molecules with enough energy to vibrate at one of their vibrational modes and therefore become excited. An energy level diagram showing the involved energy levels of carbon dioxide and nitrogen is shown in figure 3<sup>26</sup>.



Figure 3. Schematic of (a) CO<sub>2</sub> energy levels and (b) nitrogen energy levels.

The CO<sub>2</sub> energy level 001 is the state where the CO<sub>2</sub> molecules will collect, which is desirable because it is a long-lived state (lifetime: ~0.4 ms) and helps to increase the efficiency of the laser. If there is still any excitation left in the CO<sub>2</sub> molecules after they decay and produce light, they will collide with helium atoms, which will help to remove any of the excess energy by removing excess energy from CO<sub>2</sub> molecules, moving to the gain tube wall and releasing the energy there through more collisions.<sup>27</sup>

# **CHAPTER 3**

# **PREVIOUS WORK**

Explosives are commonly used for different purposes: ordnance, demolition of buildings, mining, fireworks, and avalanche control among others. In recent years explosives began to be used by terrorists as weapons mass destruction (WMD). Therefore controlling the use and the abuse of these are of utmost priority to Homeland Security and other security enforcing federal agencies. Consequently many researchers have been pursuing knowledge of standoff detection of threat materials and methods to improve trace explosive detection, among these LITE spectroscopy.

In **1988 Lin, et al.** presented preliminary studies of laser-induced thermal emission spectroscopy of condensed phases. In this technique, a laser beam was used to locally heat the specimen, and the MIR thermal emission was observed

In **1989 Tsuge, et al.** investigated the applications of LITE spectroscopy for analysis of various samples such as of potassium dichromate powder, molybdenum trioxide on molybdenum powder, red ink on a stainless steel bolt and green insulating coating on the copper of a printed circuit board.

In **1995 Keresztury, et al.** advocated the use of a linear intensity scale, emissivity, for quantitative work and drew attention to potential sources of spectral distortions or errors in quantitative applications stemming from improper operations over emittance spectra.

In **2009 Pacheco-Londoño, et al.** used vibrational spectroscopy for standoff detection of explosives (RDX, TNT, DNT and TATP) and proved that standoff detection in IR and Raman was viable.

In **2008 Furstenberg, et al.** studied the standoff detection of 2,4,6-trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX) traces on transparent, absorbing, and reflecting substrates via resonant infrared photothermal imaging.

In **2012 Mukherjee, et al.** performed the standoff detection of trace of explosive at distances of up to 150 m, illuminating the target object with a tunable  $CO_2$  laser that was strongly absorbed by the target.

# **CHAPTER 4**

# **METHODOLOGY**

### 4.1 Apparatus

The spectrometer used for recording MIR spectra of highly energetic materials (HEM) samples deposited on Al plates was an OP/FT-IR, model EM27 (Bruker Optics, Billerica, MA, USA). The optical bench consisted of a compact, enclosed and desiccated Michelson type interferometer equipped with ZnSe windows, an internal blackbody calibration source, a KBr beamsplitter, a very fast native focal ratio of f/0.9 and a field of view (FOV) of 30 mrad (1.7°). The target surface was heated using a high power carbon dioxide laser (Firestar, vi30, Synrad, Inc., Mukilteo, WA, USA) with an emission range from 10,200 to 10,800 nm.

#### 4.2 Samples

The reagents used included HEM and solvents. TNT and 2,4-dinitrotoluene (DNT) were acquired from ChemService, Inc. (West Chester, PA) as crystalline solids (99%). Pentaerythritol tetranitrate (PETN), triacetone triperoxide (TATP), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) were prepared in the lab. Ammonium nitrate (AN) was purchased from Fisher Scientific International (Pittsburg, PA, USA). Acetone (99.5%, GC grade) and methanol (99.9%, HPLC grade) were purchased from Aldrich-Sigma Chemical Co. (Milwaukee, WI, USA) and were used as solvents. HEM samples were deposited on aluminum (Al) plates used as substrates at several surface concentrations.

#### **4.3 Sample Preparation**

Sample preparation is an important task in validation runs in standoff detection experiments of threats chemicals present as trace deposits on metallic substrates. A sample smearing technique<sup>28</sup> was used to deposit the HEM from 5 to 200  $\mu$ g/cm<sup>2</sup> on Al substrates. These mass transfers resulted in films of ~ 0.3-1.1  $\mu$ m thickness. Al plates of sizes 3.0 cm x 3.0 cm were used as material support for the samples. Plates were first cleaned with neat acetone. This was followed by air-drying before depositing the desired HEM surface loading.

#### 4.4 Setup

Spectra were acquired at a distance of 4 to 64 m with an FT-IR interferometer in the 5 to 16.6  $\mu$ m of wavelength at 4 cm<sup>-1</sup> resolution, 10 scans and 10 repetitions. The target surface was heated using a CO<sub>2</sub> laser. Laser power was varied from 4 to 36 W at radiation exposure times of 10, 20 and 60 s. CO<sub>2</sub> laser powers were adjusted to detect and identify the HEM under maximum signal/noise (S/N) conditions. A commercial receiver telescope 15 cm in diam. and focal ratio f/3 with gold coated mirrors and a field of view (FOV) of 10 mrad (0.57°) configured from reflective optical elements and designed for open path IR measurements was used to collect emitted MIR light (Figure 4). The telescope was modified by allowing the secondary mirror (represented by dotted arrows) to become a movable optical element allowing for a decreased controllable focus. This modification was done in order to minimize collection of surrounding ambient emissions in the MIR wavelengths range examined and to provide optimal performance of the collected emissions of the targets. Also, this modified OP/FTIR spectrometer had the additional capability of compensating for losses in signal intensity of the target.



Figure 4. Experimental set-up details of the standoff laser induced thermal detection of HEM (explosives). Movable optical elements are represented by dotted arrows. Inset: scheme for data acquisition time.

# 4.5 Data acquisition: spectra

The data acquisition of emission spectra in standoff IR detection is described in three steps. First, the sample was heated using a  $CO_2$  laser at a specific power for a given lapse of time (induction, see dot line in Figure 4). Second, the  $CO_2$  Laser was turned off. Finally, the thermal emission spectra were acquired by a telescope enabled spectroscopic system in a time interval while the sample is cooling, as shown in the timing-temperature schematic inset in Figure 4.

# **CHAPTER 5**

# **RESULTS AND DISCUSSION**

Molecular emission spectra were recorded from thermally excited samples. Their emission maxima agree with the absorption maxima of conventional spectra in terms of wavelength position. Figure 5 shows typical MIR thermal emission of explosives investigated in the spectral range of  $600-1660 \text{ cm}^{-1}$ .



Figure 5. Standoff thermal emission spectra of PETN, TATP, RDX, TNT, DNT and ammonium nitrate (A.N) at surface concentration of 200  $\mu$ g/cm<sup>2</sup>. Conditions for thermal induction by CO<sub>2</sub> laser were to 36 W of power and 20 s of exposure time.

Samples of HEM: PETN, TATP, RDX, TNT, DNT and AN used as targets were thermally excited by the  $CO_2$  laser adjusted to 36 W of power and 20 s of exposure time. Emission spectra were recorded for each HEM and fingerprint signals were identified. Results show that the experimental setup had good control of ambient variables, such as humidity, temperature changes, homogeneity of samples on Al plates, and others at a distance of 4 m and surface loadings of 200  $\mu$ g/cm<sup>2</sup>.

Most of the characteristic vibrational signatures of DNT, AN, RDX, TATP, TNT and PETN are well defined when the sample is heated. The most important vibrational band for PETN at 851 cm<sup>-1</sup> and 870 cm<sup>-1</sup> were tentatively assigned to O-N stretching, combination band at 1003 cm<sup>-1</sup> was tentatively assigned to C–O stretch + CCC deformation and combination band of C-O stretching + C<sub>5</sub> skeletal + NO<sub>2</sub> rock appeared at 1038 cm<sup>-1</sup>, results agree with reported values.<sup>29</sup>

Spectroscopic signatures of TATP were tentatively assigned by Brauer et al.<sup>30,31</sup> as combination bands OCOO shearing (sh) + CCO sym stretching (st) at 785 cm<sup>-1</sup>, CCO bending (b) + CCC st at 937 cm<sup>-1</sup>, CO st + OCO b + CCC b at 946 cm<sup>-1</sup>, CC st + CCO b at 1186 cm<sup>-1</sup>, CCC b + OCO b at 1202 cm<sup>-1</sup>, CC st + CCO b at 1234 cm<sup>-1</sup>, CO b + CO st at 1275 cm<sup>-1</sup>. Also other bands detected included OCOO shearing at 842 cm<sup>-1</sup>, CCO stretching (st) at 885 cm<sup>-1</sup> and degenerated band CCC asym st, CCO b at 1369 cm<sup>-1</sup>. All these bands were recognized in TATP LITE spectra.

For DNT and TNT the prominent signal located at 1343 cm<sup>-1</sup> is tentatively assigned to C-No vibration coupled to C-N stretch.<sup>32</sup> Tentative assignments for IR signals of RDX included

the band at 1264 cm<sup>-1</sup> and the band at 1321 cm<sup>-1</sup> for N-NO<sub>2</sub> symmetry stretch and for the 1593 cm<sup>-1</sup> band, N-NO<sub>2</sub> asymmetry stretch.<sup>33-35</sup>

HEM samples at various surface concentrations: 200 to 5  $\mu$ g/cm<sup>2</sup> were deposited on the AI supporting plates, heated with the CO<sub>2</sub> laser and then the remote emission spectra were acquired. The detection was achieved at concentrations as low as 5  $\mu$ g/cm<sup>2</sup> for PENT, TNT and RDX. Therefore, a combination of modified open path FT-IR and appropriate heating of the target using CO<sub>2</sub> laser made feasible the detection by emission of explosive traces in the order ~ 7  $\mu$ g/cm<sup>2</sup> in average for all HEM, equivalent to 5.5  $\mu$ g (total mass) in the field view of the instrument at 4 m. However, when the samples were not heated representative signals of the samples could not be distinguished to identify the substances that were deposited on the AI support plates at 4 m from the detector.

Signal intensities were proportional to the thickness of the coated surfaces (a function of the surface concentrations), as well as the laser power and laser irradiation time. Therefore, it was possible to determine the qualitative potential of the proposed setup.

#### 5.1 Variation of the remote emission spectra with the laser power and time of irradiation

Figure 6 shows the effect of the laser power and laser irradiation time on the remote emission spectra. An exponential increase of the emission intensity of RDX was observed. A well selected combination of laser exposure time and power was able to enhance the signal-tonoise ratio at higher laser power and time of induction. A clear thermal induction effect on a sample measured remotely is represented in Figure 6, which compares an unheated sample of  $200 \ \mu/cm^2$  RDX i.e. laser power of 0 W and a sample heated with infrared laser radiation at the conditions which obtained at highest signal intensities: laser power ranged from 4 to 36 W of and from 10 to 60 s of irradiation.



Figure 6. Remote emission spectra of 200  $\mu$ g/cm<sup>2</sup> RDX from 600 to 1660 cm<sup>-1</sup> with exposure time of 10-60 s at laser powers from 4-36 W. Inset: 3D representation of variation of peak height of asymmetric -NO<sub>2</sub> vibration in RDX [1556-1623 cm<sup>-1</sup>] with respect to laser power and irradiation time.

The upper left corner inset of Figure 6 shows a 3D representation of the effect of the laser power and time of induction over the emission intensity for a selected RDX emission peak. The asymmetric NO<sub>2</sub> band of RDX [1556-1623 cm<sup>-1</sup>] was used, showing the variation of the peak height with the effect of the several power levels and thermal induction times. The most intense signal of the peak at 1556 to 1623 cm<sup>-1</sup> was reported to the highest condition of power laser 36 W and the most time of exposition 60 s of the laser. These data permit concluding that the principal differences in the emission spectrum coming from the laser power and time of induction conditions.

#### 5.2 Determination of emissivity spectra

There are different ways of representing the intensity scales of thermally excited FT-IR emission recorded spectra: a) single-beam emission spectrum, b) emittance (relative to the blackbody or relative to the background), d) reflection-correction emittance and finally in order to have a linear scale with the concentration in consideration e) emissivity. The emissivity has to be obtained using the Beer-Lambert law of emission spectroscopy as is shown in the follow Eq.  $2.^{7}$ 

$$Emissivity = -log_{10}[1 - Emitance] = Absorbance$$
<sup>(2)</sup>

Emissivity spectra of PETN, TATP, RDX, TNT, DNT and AN samples were determined with recorded blackbody spectra, which were acquired by a Fluke - Hart Scientific 4180/4181 Infrared Calibrator (Fluke Electronics Corp, Everett, WA, USA) at the same temperature of the samples.



Figure 7. Remote emissivity spectra of 100µg/cm<sup>2</sup> PETN, TATP, RDX, TNT, DNT and A.N to measured heating temperature from 41°C to 44°C by CO<sub>2</sub> laser, to the conditions of 36W-60s.

On the other hand, the temperature of the sample was calculated through a thermocouple attached to the aluminum surface where the sample was deposited. Finally, the single-beam emission spectrum of each sample was divided by the measured blackbody spectrum to determine the emittance, followed by the respective calculation of the Eq. 2 to produce the emissivity spectra of each sample. The calculated emissivity spectra of samples of  $100 \ \mu\text{g/cm}^2$  PETN, TATP, RDX, TNT, DNT and AN are shown in Figure 7. LITE spectra were measured heating with CO<sub>2</sub> laser at 36 W for 60 s obtaining temperatures that ranged from 41°C to 44 °C.

Based on the emissivity spectra a quantitative analysis could be performed to calculate the values of S/N for the different HEM concentrations. The limit of detection (LOD) for the HEM studied were calculated by estimation of the concentration equivalent to S/N of 3 as suggested by International Union of Pure and Applied Chemistry (IUPAC).<sup>36</sup> This estimate was made by extrapolating linear fittings of the concentration data. Two spectral regions selected were: from 600 to 1100 cm<sup>-1</sup> and 1100 to 2000 cm<sup>-1</sup>. Investigating the spectral behavior at these two regions served to understand how the S/N and LOD values varied with the different selected regions of the spectra due to environmental interferences.

Table 1 contains the calculated S/N and LOD values for each HEM. The spectral range that showed better results was the region from 600 to 1100 cm<sup>-1</sup>. Both the S/N value as the value of LOD were improved compared to the region from 1100 to 2000 cm<sup>-1</sup>, these are because the interferents signals of carbon dioxide and water affect the calculated values of S/N and LOD. This analysis can be also clearly observed in the emissivity spectra for the HEM (Figure 7). The best results were S/N values of 378 and 241 for PETN and RDX in R<sub>2</sub> (second range of the spectra, see Table 1) respectively and LOD values of 1 and 2  $\mu$ g/cm<sup>2</sup> for PETN and RDX.

	S/N for 100 $\mu$ g/cm <sup>2</sup>		LOD µg	g/cm <sup>2</sup>
	<b>R</b> <sub>1</sub>	$R_2$	$R_1$	$R_2$
DNT	8	18	71	21
AN	5	76	127	8
PENT	10	378	61	1
RDX	33	241	18	2
TATP	6	80	94	7
TNT	12	143	51	4

Table 1. The corresponding values of S/N and LOD calculated to each HEM using two different range of the spectra.<sup>a</sup>

<sup>a</sup>Note:  $R_1$  is the range from 2000 to 1100 cm<sup>-1</sup> and  $R_2$  from 1100 to 600 cm<sup>-1</sup>

#### **5.3 Range Effect**

There are many methods of sensing explosives; most of these require transport of the sample to the instrument inlet port or to be at close range in order to collect the sample. In order to enable that detection to take place further away from people and protect vital assets and reduce the potential for severe damage is the objective of standoff detection. In this study evidence is presented to demonstrate that LITE signals can be collected at very long distances from the detector. The spectroscopic system was configured for detection in passive mode measurements using thermal excitation of the sample to 4 m of distance as is shown in Figure 4, but this distance is not enough to keep the security of the analyst. In addition, measurements for remote distances from 4 to 64 m were done. The experimental arrangement was adjusted for each distance. This was made moving the secondary mirror of the reflective IR telescope.

Remote LITE spectra of 200  $\mu$ g/cm<sup>2</sup> RDX deposited on Al substrates at various standoff distances using exposure time of 60 s and laser power of 36 W were acquired as shown in Figure

8A. The RDX signals were clearly observed up to 64 m but with a decrease in the intensity of the LITE emission intensity, as illustrated in Figure 8B.



Figure 8. A) Remote emission spectra of 200  $\mu$ g/cm<sup>2</sup> RDX in different standoff distances with exposure time of 60 s to laser power from 36 W. B) Effect of the distance in the variation of the intensity of emission of the selected RDX peak height [1000-1100 cm<sup>-1</sup>] and the laser spot on the target surface.

In this experiment, careful alignment of the angle between the laser, target and detector is not critical while spectrum is recorded. Nevertheless, the size of the laser spot on the target surface in the moment of the thermal induction is very critical to get a good signal of target emission. The band between 1000 to 1100 cm<sup>-1</sup> was selected in order to observe the exponential decay of the peak height as the distance increased, owing to laser spot increase at longer

distances as shown in the Figure 8B. For future studies the spectroscopy system focusing the laser spot on the sample will be configured to maintain constant diameter laser spot on the sample with the central aim to allow higher intensities of emission in order to further increase the detection distances.

# CHAPTER 6

# CONCLUSIONS

A prototype vibrational spectroscopy based standoff system based on thermal excitation of traces of threat chemicals deposited on substrates has been designed, assembled and tested by coupling a CO<sub>2</sub> laser with a modified commercial open-path FT-IR spectrometer. The CO<sub>2</sub> laser source: 926-980 cm<sup>-1</sup> was operated at varying powers (4 - 36 W) which caused a thermal induction of stimulated emissions on the target samples. The remote system was used in the remote detection of PETN, RDX and other explosives at 4 m and at varying distance for RDX (4 to 64 m range). The S/N was calculated for different distances in order to obtain the dependence of the detection with distance. The advantage of this standoff detection scheme is the high specificity obtained when measuring the stimulated molecular fingerprint emissions. The expected interferences from back-reflection of the laser source were not observed due to the experimental setup in which spectra were collected after turning off the laser. In this modality, the measured emissions of the samples were done in passive mode, but the emission levels were increased by thermal excitation to a temperature higher than local temperatures. Therefore, the increase of thermal emission and sensitivity depended on sample exposure to the laser action: power and irradiation time.

### CHAPTER 7

# ACOMPLISHMENTS AND SCIENTIFIC CONTRIBUTIONS

This investigation focused on standoff detection of explosives using infrared emission induced by a CO<sub>2</sub> laser. The standoff IR system was designed, developed, tested and used successfully. The system was developed from commercial off-the-shelf (COTS) components. The objective was to establish the feasibility of thermally increasing IR emission signal of a target by using a suitable remote heating source, of in this case a CO<sub>2</sub> laser that is a source that can be used in standoff mode allowing a safe operational distance between the sample and the investigator to reduce the potential damage posed by potential chemical and biological threats. Second the combination of optically modified telescope that allowed the reduction of interfering surrounding ambient emissions, helping to improve the recorded emission spectra.

This is the first published application of LITE in standoff emission of explosives residues. The study is closely related to the work of Patel and collaborators in 2012. Even though a direct comparison between this study and Patel's work because the methodologies are different establishing the similarities and differences aids in validating this contribution to a significant contribution available in the open literature. The principal advantage of this standoff detection is the high specificity obtained when measuring the stimulated molecular fingerprint emissions, because is possible to analyze a higher region of the spectra to difference of the Patel study where a unique band of the TNT spectra is analyzed.

The main accomplishment of the work was in obtaining a significant increase in the thermal emissions of the sample by the laser action (power and irradiation time), the possibility of detection by emission of explosives traces up to 64 meters, made this study an excellent contribution in the development of sensors and standoff (or non-contact) detection systems for use in National Defense and Security applications.

This research will be much closer to completion when the intensity of the laser power on the sample surface after thermal induction is measured. Investigating the effects of IR emissions enhancements with others sources of heating such as microwave emitter or telecommunication laser in the NIR infrared would also help in comparing and benchmarking this technology to others. Finally, for future studies the spectroscopic system could be improved by focusing the laser spot on the sample would be configured to maintain constant diameter laser spot on the sample with the central aim to allow higher intensities of emission in order to further increase the detection distances.

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