High Sensitivity Explosives Detection using Dual-Excitation-Wavelength Resonance-Raman Detector

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ABSTRACT

A key challenge for standoff explosive sensors is to distinguish explosives, with high confidence, from a myriad of unknown background materials that may have interfering spectral peaks. To meet this challenge a sensor needs to exhibit high specificity and high sensitivity in detection at low signal-to-noise ratio levels. We had proposed a Dual-Excitation-Wavelength Resonance-Raman Detector (DEWRRED) to address this need. In our previous work, we discussed various components designed at WVHTCF for a DEWRRED sensor. In this work, we show a completely assembled laboratory prototype of a DEWRRED sensor and utilize it to detect explosives from two standoff distances. The sensor system includes two novel, compact CW deep-Ultraviolet (DUV) lasers, a compact dual-band high throughput DUV spectrometer, and a highly-sensitive detection algorithm. We choose DUV excitation because Raman intensities from explosive traces are enhanced and fluorescence and solar background are not present. The DEWRRED technique exploits the excitation wavelength dependence of Raman signal strength, arising from complex interplay of resonant enhancement, self-absorption and laser penetration depth. We show measurements from >10 explosives/pre-cursor materials at different standoff distances. The sensor showed high sensitivity in explosive detection even when the signal-to-noise ratio was close to one (~1.6). We measured receiver-operating-characteristics, which show a clear benefit in using the dual-excitation-wavelength technique as compared to a single-excitation-wavelength technique. Our measurements also show improved specificity using the amplitude variation information in the dual-excitation spectra.

Keywords: Deep Ultra Violet, Resonance Raman Spectroscopy, Dual Excitation Wavelengths, Explosive Detection, Detection Algorithm.

1. INTRODUCTION

The Dual-excitation-wavelength (DEW) resonance Raman technique uses a laser source with two deep-ultraviolet excitation-wavelengths. The source wavelengths are chosen so that the Raman spectrum in the fingerprint region of the lower excitation wavelength is well separated from the second excitation laser wavelength. Raman scattered photons from the sample are simultaneously measured using a dual-band detection spectrometer. An important requirement for a Dual-Excitation-Wavelength Resonance-Raman Detector (DEWRRED) is the simultaneous detection of the two excitation spectra from a single interrogation area. This ensures that any spatial variation of explosive fill-factor in the sample, or any time-dependent phenomena, such as motion or degradation present in a real detection scenario contribute equally to measurements at both of the excitation wavelengths.

The main reason for using two excitation wavelengths is to make use of Raman spectral intensity variation as an additional orthogonal signature. The Raman scattering intensity from an explosive depends on its Raman cross-section, laser penetration depth and the resonance Raman self-absorption. Resonance Raman cross-sections and the absorption of both the excitation and scattered light vary strongly with excitation wavelength in the DUV region. This results in detected Raman band intensities that depend on excitation wavelength in a complex way, forming unique signatures for different compounds. As an example, DEW signatures can be constructed as a combination of spectral peak positions

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(i.e. Raman frequency shifts) and the ratio of the Raman band intensities measured at the two-excitation-wavelengths. In addition to high signal strengths, Raman signatures in the DUV region are free from solar radiation and have minimal interference from fluorescence.

The main advantages of using a Raman spectroscopy approach with two or more excitation wavelengths are a) improved specificity compared to single excitation wavelength and b) higher sensitivity. Improved specificity was experimentally studied in our previous work where we thoroughly characterized the DUV Raman responses of fifteen explosives and sixteen background materials at multiple DUV wavelengths (213 nm, 229 nm, 238 nm, 244 nm, 248 nm, and 266 nm) to better understand the potential performance of multiple-excitation-wavelength Raman standoff explosives sensors. Improvement to specificity was also seen when only two excitation wavelengths were used.

WVHTC Foundation has developed a laboratory prototype of a DEWRRED sensor that detects explosives using simultaneously-measured Raman signatures with 236.5 nm and 257.5 nm laser excitations. We show results of detection of several bare bulk explosives or small quantities of explosives of ~50 µg from distances of 3.5 ft and 14 ft using a low laser power of <250 µw. The exposure time for detection varied from 0.1 s to 60 s.

2. DUAL EXCITATION WAVELENGTH RESONANCE RAMAN DETECTOR

The laboratory prototype of the DEWRRED sensor used two laser beams at 236.5 nm and 257.5 nm as shown in the schematic of Figure 1. The DUV wavelengths were generated by doubling blue (473 nm) and green (515 nm) lasers. Ideally, the two laser beams would have similar divergence, similar beam profile and copropagate towards the test sample. However, in the current implementation, the two beams travelled at an angle and overlapped on the target. The 257.5 nm beam was aligned to travel along the optical axis of the collection system. In the future, we plan to combine both the laser beams and copropagate them along the optical axis of the collection system. The Raman scattered light from the excitation region was collected using a 6 inch primary mirror. Raman filters were used in the collection system to attenuate the Rayleigh scatter from the two lasers. We designed the collection system to image an illuminated target spot from distances of 3 ft to greater than 50 ft.

Figure 1: Schematic of dual-excitation-wavelength resonance Raman detector setup.
A DUV fiber bundle (spot-to-line converter) delivered the Raman light from the collection system to the input of a dual-band spectrometer. The spectrometer output was separated into two Raman bands and analyzed using a highly sensitive algorithm. Details of the algorithm are described in Reference [8].

Figure 2: Laboratory prototype DEWRRED sensor system consisting of two DUV laser sources, illumination and collection optics, and a dual-band detection spectrometer.

A picture of the sensor system is shown in Figure 2. As part of the DEWRRED sensor, we have built two power-scalable, turnkey, DUV lasers that have the potential to be made compact. The laser technology also has the potential for field use and can be battery operated. These lasers produce narrow line-width DUV light at 257.5 nm and 236.5 nm by coupling diode-pumped solid-state CW blue/green laser sources at 515 nm and 473 nm wavelengths to external second harmonic generation (SHG) units. The 257.5 nm laser produced >2 mW of DUV light with a conversion efficiency of ~2%. The 236.5 nm laser produced <250 μW of light at an efficiency of 0.5%. Lower efficiency at 236.5 nm was partly due to lower power at 473 nm. Each of the laser heads occupied a footprint of 18”x18” on an optical bread board. We are currently developing second generation prototypes which are anticipated to be compact, more efficient (>15%) and produce higher power than the current laboratory prototype. For the explosive detection experiments presented here, the lasers were typically operated at nearly equal power levels from 20 μw to 250 μw. Both the DUV laser powers were continuously monitored in order to normalize the measured relative intensities of the Raman bands.

The two laser beams were collimated with an identical set of optics. Owing to differences in refractive indices of optics at different wavelengths and wavelength dependence of divergence, the beams had slightly different shapes on the sample. This beam mismatch limited the application of the full DEW technique in these lab measurements to uniform samples (bulk or traces) with 100% fill-factor. For samples with a lower fill factor, the sensor functioned as two single wavelength detectors. In the future design we plan to remove this limitation using custom designed optics with focus control, if necessary, to better match the beam shapes to one another.

A picture of the spectrometer used in the current DEWRRED sensor along with the input fiber bundle are shown in Figure 2. The mechanical design of the spectrometer housing was not optimized for size and weight in this phase of the project. The optics (not including the CCD) can potentially be housed in a size of 10 x 12 x 4 cm³. The spectrometer has an unoptimized weight of 6.6 lbs. This design covers a spectral range from 241 nm to 272 nm and is based on gratings and fused silica optics. The design resolution of the spectrometer varied between 29 cm⁻¹ to 34 cm⁻¹ in the
usable Raman spectral regions. Spectral regions near both the laser wavelengths were blocked by Rayleigh filters in the collection system. The remainder of the range was sufficient to cover the fingerprint regions of the Raman spectra for both the excitation wavelengths. All optics, including the gratings in the spectrometer, were built based on a custom design. Although the spectrometer showed low scattering and could be operated in the presence of the room lights, a short-wavelength-pass filter with an edge around 300 nm was used to reject any scattering from laser induced fluorescence arising from sample background. This filter would also allow the system to operate in sunlight. Combined throughput of all the optical components in the spectrometer, and the input fiber (not including the laser rejection and LIF filter) is greater than 55%. The overall efficiency of the entire spectrometer including quantum efficiency of the CCD is around 25%.

3. RESULTS

Typical detection results with the software used to control the DEWRRED sensor are shown in Figure 3. Detection of potassium chlorate (PC) with 1 second exposure time is shown in the Figure. The sample was located at a distance of 1 m from the collection mirror and the laser average powers used in the experiment were 26.5\(\mu\)w and 10.2\(\mu\)w at 236.5 nm and 257.5 nm respectively. PC was detectable even at the lowest exposures of 0.1 sec using these power levels.

![Figure 3](image_url)

Figure 3: (a) Dual-excitation-wavelength Raman spectra of potassium chlorate. The data on the left is from 236.5 nm excitation and on the right is from 257.5 nm excitation. The x-axis was calibrated in wave numbers relative to each laser wavelength. (b) Scores obtained from the DEWRRED sensor algorithm.
3.1 Bulk detection at 3.3 feet and 14 feet

We created a target library using high signal-to-noise (SNR) spectra measured from 3.3 ft distance. The target library included Potassium Chlorate, Sodium Chlorate, Potassium Perchlorate, Ammonium Perchlorate, Sodium Nitrate, Urea Nitrate (UN), Ammonium Nitrate, Ammonium Nitrate in Fuel Oil (ANFO), Dyno AP, Watergel, PETN, Semtex, TNT, and Black Powder. Bulk materials used in the detection were uniform samples that were > 10mg in weight. All pure bulk explosive materials were positively detected with the sensor by using a novel algorithm developed for the sensor. The novel algorithm is based on a combination of a) correlation information between target and library spectra and b) ratiometric information between the two excitation wavelength signatures. The algorithm produces a score by comparing the test spectrum with each target library spectrum. If the scores are below a certain threshold they are discarded and assumed to have no explosive signature. The scores indicate fractional resemblance of the measured spectrum to target library spectra. If multiple scores from closely related groups of explosives are above the threshold, then the material is identified as the library material with the highest score. For example in Figure 3b, Chlorates and Perchlorates have scores above the threshold and the highest scoring target library material is PC. Therefore, the sample was identified as PC.

A key advantage of the DEW technique is improved specificity at lower signal levels. When the algorithm operated on Raman spectra from any one of the two excitation wavelengths alone, it produced high scores for a group of materials with closely resembling spectra (e.g. chlorates/perchlorates or nitrates), and they could not be separated. However with the DEW technique the algorithm was able to distinguish different materials with closely resembling spectra even at SNR=4.

Several background materials and interferant materials were also tested and they typically produced scores below the threshold. Examples of these substances included dry wall, cardboard, various colored plastics, dirt, concrete, asphalt, sugar, salt, creams, cleaning agents etc. We also tested and successfully detected explosives on top of a few representative background materials (tiles, cardboard and dirt).

The DEWRRED system was also tested with samples located at 14 ft distance. Laser power used for these experiments was around 200-250 μw for each excitation wavelength. The spot sizes at this distance were approximately 2.5 mm. We were able to successfully detect explosive samples and samples on top of background surfaces.

3.2 Detection of small quantities of explosives

In order to check the performance of the DEWRRED system in detecting small quantities of explosives, we prepared two samples using PC and UN and measured them from a 3.3 ft distance. Examples of samples used in the experiments and scores are shown in Figure 4. The PC sample was prepared by dissolving PC in water. A single droplet of water was placed on a black aluminium foil and dried. A second sample was prepared with a UN fingerprint on aluminum foil and gently wiped-off with a lens tissue. We estimate the sample quantities exposed to the laser excitation to be less than 50 μg. Because our two laser beams had slightly different sizes on the sample, a limitation with our current setup, we could not take advantage of the ratio variations to achieve higher specificity. Therefore, the PC and UN samples were identified as chlorates/perchlorates and nitrates respectively. Exposure times used in the experiments were 1 to 5 s for PC and 20 to 30 s for UN. The limitation from beam overlap will be addressed in our future design.

Figure 4: Example of small quantity (<50 μg) of explosives or precursors detected from 3.3 ft distance.
3.3 Detection at very low SNR levels

The algorithm developed for the sensor showed high sensitivity even at low signal-to-noise ratios. Figure 5 illustrates the performance of the algorithm. Measurements at two different exposure times (1.0 s and 0.1 s) are shown in the chart. Even when the SNR was close to 1, for the measurement shown in Figure 5(b), high scores were obtained for Ammonium perchlorate. We analyzed 2000 measurements of the sample and background with the algorithm and studied ROC statistics (more details in [8]). The ROC statistics clearly showed that Ammonium Perchlorate, measured at low SNR of 1.6, could be separated from the background. For the same true-positive-rates, significantly lower false-positive-rates were seen with DEW technique as opposed to the two single-wavelength measurements, suggesting that DEW technique is advantageous over single-excitation-wavelength techniques.

![Figure 5: Illustration of algorithm sensitivity.](image)

(a) Ammonium Perchlorate 1 sec

(b) Ammonium Perchlorate 0.1 sec

(c) Noise 1 sec

(d) Noise 0.1 sec

Figure 5: Illustration of algorithm sensitivity. (a), (b) Bulk Ammonium Perchlorate measured at exposure levels of 1 sec and 0.1 sec respectively. The algorithm produced a high score of 1.98 and 1.6 respectively. (c), (d) Background noise from a black Aluminium substrate obtained with the same exposure times (1s and 0.1s). The algorithm produced a low score of 0.2 and 0.8 respectively. Sample to collection mirror distance was 1m and the laser power used was ~20µw at each wavelength.

4. SUMMARY

We have built a laboratory prototype of a dual-excitation-wavelength resonance Raman detector. The sensor consists of two CW DUV lasers at 236.5 nm and 257.5 nm, a dual-band spectrometer covering 241 nm to 272 nm and a very sensitive algorithm. The sensor was tested by measuring samples from a distance of 3.3 ft and 14 ft. Test materials include fourteen explosive/precursor materials, several background materials and interferents. Bulk explosives were
correctly detected and identified using the DEW signatures. The sensor was also able to detect groups of explosive/precursors when presented in small quantities of ~50 μg. The algorithm developed for the sensor showed high sensitivity and was able to separate target materials from noise even at a low SNR of 1.6.

5. ACKNOWLEDGEMENT

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