

Multiple-Excitation-Wavelength Resonance-Raman Explosives Detection

Balakishore Yellampalle*^a, Mikhail Sluch^a, Sanford Asher^b, and Brian Lemoff^a

^aAdvanced Technologies Group, West Virginia High Technology Consortium Foundation, Fairmont, WV, USA, 26554

^bDepartment of Chemistry, University of Pittsburgh, Pittsburgh, PA, USA, 15260

ABSTRACT

Deep-ultraviolet resonance Raman spectroscopy (DUVRRS) is a potential candidate for stand-off detection of explosives. A key challenge for stand-off sensors is to distinguish explosives, with high confidence, from a myriad of unknown background materials that may have interfering spectral peaks. To address this, we have investigated a new technique that simultaneously detects Raman spectra from multiple DUV excitation wavelengths. Due to complex interplay of resonant enhancement, self-absorption and laser penetration depth, significant intensity variation is observed between corresponding Raman bands with different excitation wavelengths. These variations with excitation wavelength provide a unique signature that complements the traditional Raman signature to improve specificity relative to single-excitation-wavelength techniques. We have measured these signatures for a wide range of explosives using amplitude-calibrated Raman spectra, obtained sequentially by tuning a frequency-doubled Argon laser to 229, 238, 244 and 248 nm. For nearly all explosives, these signatures are found to be highly specific. An algorithm is developed to quantify the specificity of this technique. To establish the feasibility of this approach, a multi-wavelength DUV source, based on Nd:YAG harmonics and hydrogen Raman shifting, and a compact, high throughput DUV spectrometer, capable of simultaneous detection of Raman spectra in multiple spectral windows, are being investigated experimentally.

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

INTRODUCTION

Standoff detection of traces of explosives is of great interest due to recent increase in threats from terrorist bombings and improvised explosive devices. Standoff trace detection is a challenging problem [1,2] because of the variety of available explosives, myriad of unknown background materials and the minute quantities involved. These challenges place a high demand on the stand-off sensor performance metrics such as selectivity and sensitivity. Raman spectroscopy is well-suited for stand-off detection of explosive traces. In particular, explosives spectra have narrow, distinct Raman bands that are highly enhanced in the DUV due to: 1) resonant enhancement of Raman cross-section [3], and 2) λ^{-4} cross-section increase [4], thus providing good selectivity and sensitivity. An added advantage of DUV excitation is that Raman signatures are free from fluorescence [5] and solar background. Although visible and IR wavelength excitation show deeper sample penetration in thick explosive materials, the DUV resonance Raman enhancement allows for higher signal levels in very thin, trace explosive samples. Thus, DUV resonance Raman spectroscopy (DUVRRS) [6,7] is a promising potential method for standoff detection of explosive traces. Despite its potential, in a real detection scenario, achieving specificity is a challenge because Raman bands from non-explosive background materials can interfere due their proximity to the explosive bands. In order to address this, we introduce a new technique based on Raman spectra simultaneously obtained from multiple DUV excitation wavelengths.

1.1 Multiple excitation wavelength concept

The Raman scattering intensity from explosives 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 varies strongly with excitation wavelength. This results in Raman band intensities that depend on excitation wavelength in a complex way, forming unique signatures for different compounds. We have measured these signatures for a variety of explosives and demonstrate the utility of multi-excitation-wavelength resonance Raman measurements for explosive detection.

An ideal implementation of the multiple-excitation-wavelength (MEW) resonance Raman detection technique consists of a multiple-wavelength DUV source that simultaneously generates collinear excitation beams directed onto a sample, and a multiple-band detection spectrometer that measures the multiple Raman spectra simultaneously. The simultaneous detection of spectra from a single interrogation area ensures that any spatial inhomogeneities of explosives in the sample, or any time-dependent phenomena, such as motion, degradation present in a real detection scenario contribute equally to all the excitation wavelengths measurements. Figure 1 shows the schematic of an ideal implementation of the MEW concept.

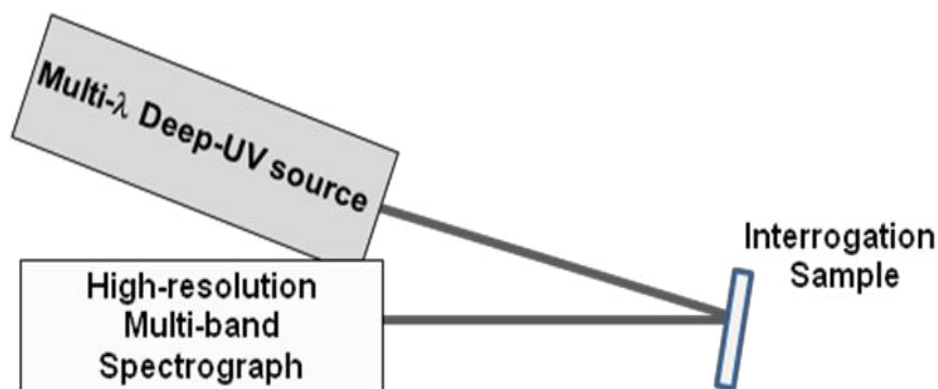


Figure 1: Concept of multiple-excitation-wavelength deep UV resonance Raman detection scheme.

The main benefit envisioned from the approach is improved specificity in detection due to the presence of additional band intensity variation information. In this work, we demonstrate the benefit of this technique making use of experimentally measured MEW signatures of several explosives.

1.2 Experimental verification of the concept

Since a multiple-excitation-wavelength source and a multiple-band spectrometer were not available, we measured these signatures by using a sequentially tuned DUV laser source and spectrometer. Because the measurements were performed sequentially, the samples were prepared identically for each excitation wavelength measurement. In addition, at each excitation wavelength, the spectral intensities were normalized. The normalization constant was derived using a) the spectral intensities of a separately measured acetonitrile reference positioned at an identical location as the sample, b) known wavelength dependence of Raman cross-section of acetonitrile [8] and c) spectral dependence of spectrometer efficiency. Spectral dependence of the spectrometer was determined using a standard Deuterium lamp.

A schematic of our experimental setup is shown in Figure 2. An intra-cavity frequency doubled Argon ion laser is reflected off of a Pellin-Broca prism to remove fundamental light frequency. The DUV light is directed towards a sample that is located approximately one meter from the entrance slit of a SPEX 300 spectrometer. The spectrometer is located in the back-scattering direction to mimic a typical stand-off detection scenario. An imaging lens collects light from the sample on to the spectrometer. The main advantage of our experimental setup is the long depth-of-focus (9 mm) of the collection system, which allows low error from sample positioning and from thickness of reference acetonitrile solution cuvette.

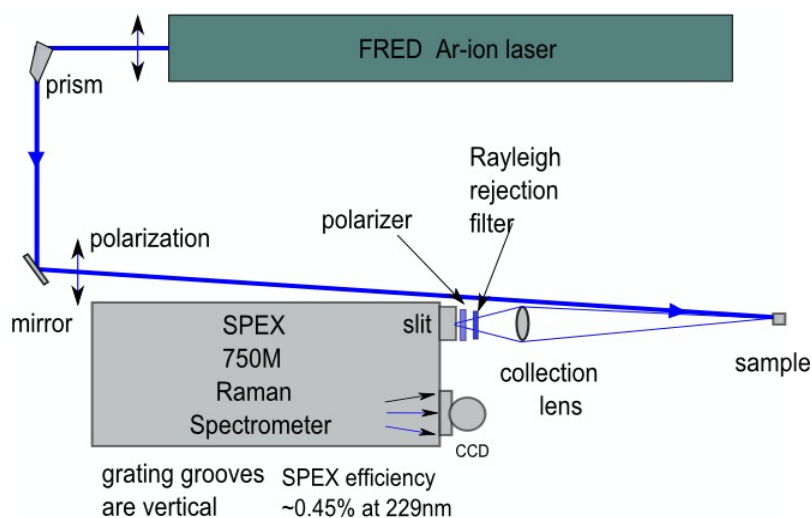


Figure 2: Schematic of the experimental setup used in the measurement of MEW Raman spectra of explosives.

A BBO crystal polarizer was positioned in between the Raman filter and the spectrometer slit. In our setup, spectrometer grating and angled dielectric Raman filter, whose orientation is adjusted depending on the excitation wavelength, result in varying polarization response. The purpose of the polarizer was to correctly account for these polarization dependent effects across each excitation-wavelength measurements. Raman intensity of parallel polarization was measured in our experiments since generally it has the maximum Raman signal.

A total of fifteen different explosives and sixteen different interferent materials were characterized at four different excitation-wavelengths (229 nm, 238 nm, 244 nm, 248 nm) from the laser source. The characterized explosives are listed in Table 1. The materials were identically prepared and were stationary during the characterization.

Table 1: List of measured explosives

Ammonium Perchlorate	HMX	TNT	Semtex A1	Nitromethane
Black Powder	Watergel	Dyno-AP	PETN	C4
Potassium Perchlorate	Urea Nitrate	Ammonium Nitrate	RDX	ANFO

RESULTS

1.3 Measurement of DUV Resonance Raman Spectra

Figure 3(a)-(c) show measurement of Raman spectra of three explosives containing nitrates using the 248 nm excitation wavelength. All three explosives have a very prominent and characteristic nitrate band at 1042 cm^{-1} . In addition, less prominent common bands can be seen at 1290 cm^{-1} , 1410 cm^{-1} , 1460 cm^{-1} , 1655 cm^{-1} and 2082 cm^{-1} . ANFO has a distinct frequency band at 1378 cm^{-1} probably arising from naphthalenic-type derivatives in fuel oil. Although these spectra share six common bands, the spectral features contain sufficient variation among band intensities within each spectrum. This allows clearly distinguishing the three spectra from one another. Similarly, if a Raman spectrum of

nitrate containing fertilizer is presented, it may be possible to distinguish it from nitrate explosives using a single-excitation-wavelength DUV resonance Raman spectroscopy. However, if there is noise present in the measurement, like in a typical stand-off detection scenario, then the subtle features and less prominent peaks are less likely to be detected.

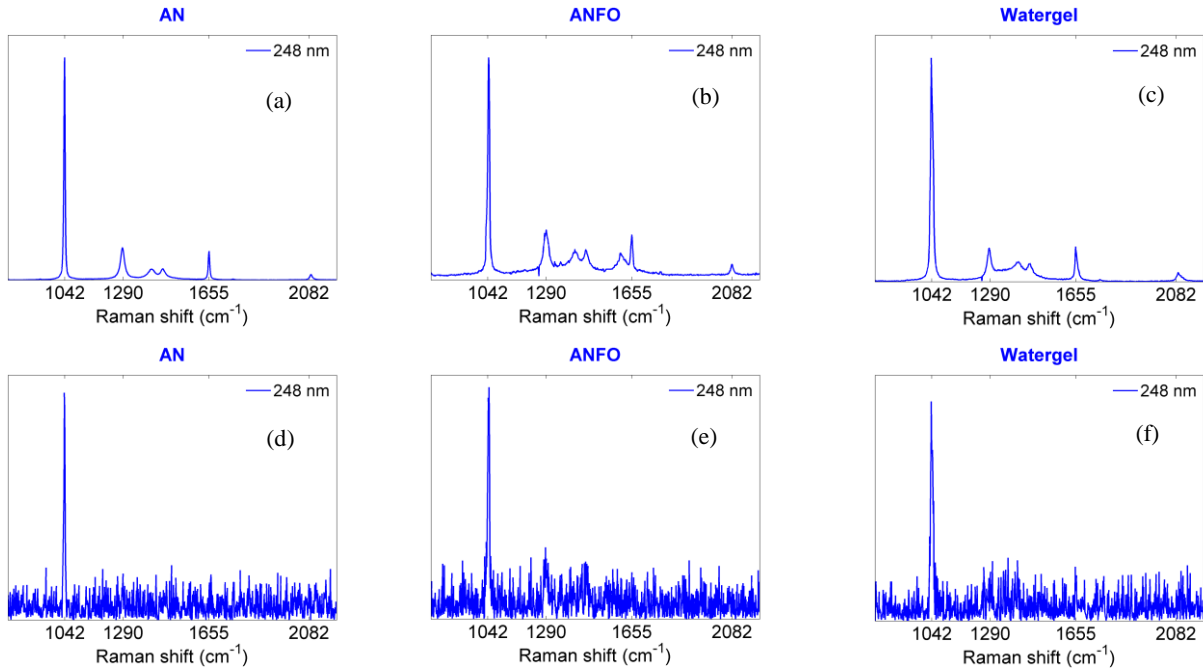


Figure 3: (a)-(c) DUV resonance Raman measurements of three different nitrates. (d)-(f) Nitrates spectra in presence of noise.

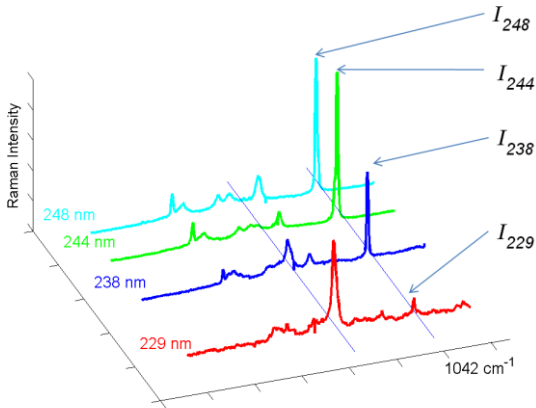


Figure 4: Multiple-excitation-wavelength Raman spectra of ANFO.

determine a vector of ratios by normalizing the band intensities with the band intensity at 229 nm. Such ratios for optically thick solid explosives are unique signatures. This is because solid explosives in the DUV wavelengths have a penetration depth of less than 50 nm. Therefore, detecting explosive traces with thickness greater than this penetration depth always results in the same ratios.

Figure 3(d)-(f) show Raman spectra of the three nitrates with the addition of Gaussian random noise. The subtle spectral features are not easily seen and all the three spectra look nearly the same. Obviously by trading-off integration time during detection, the single-to-noise ratio can be improved. We would like to show that without such trade-offs, a MEW technique can distinguish the three explosives from one another and other interferences. Figure 4 shows MEW spectra of ANFO measured at the four different excitation-wavelengths. Between the different excitation-wavelengths, there is a significant variation in the band intensities. At 229 nm, the nitrate band at 1042 cm⁻¹ has significantly small band intensity and is less prominent than the 1378 cm⁻¹ band. This rich variation of spectral features is a unique signature of ANFO. The band intensities of the 1042 cm⁻¹ band are illustrated in the figure. We

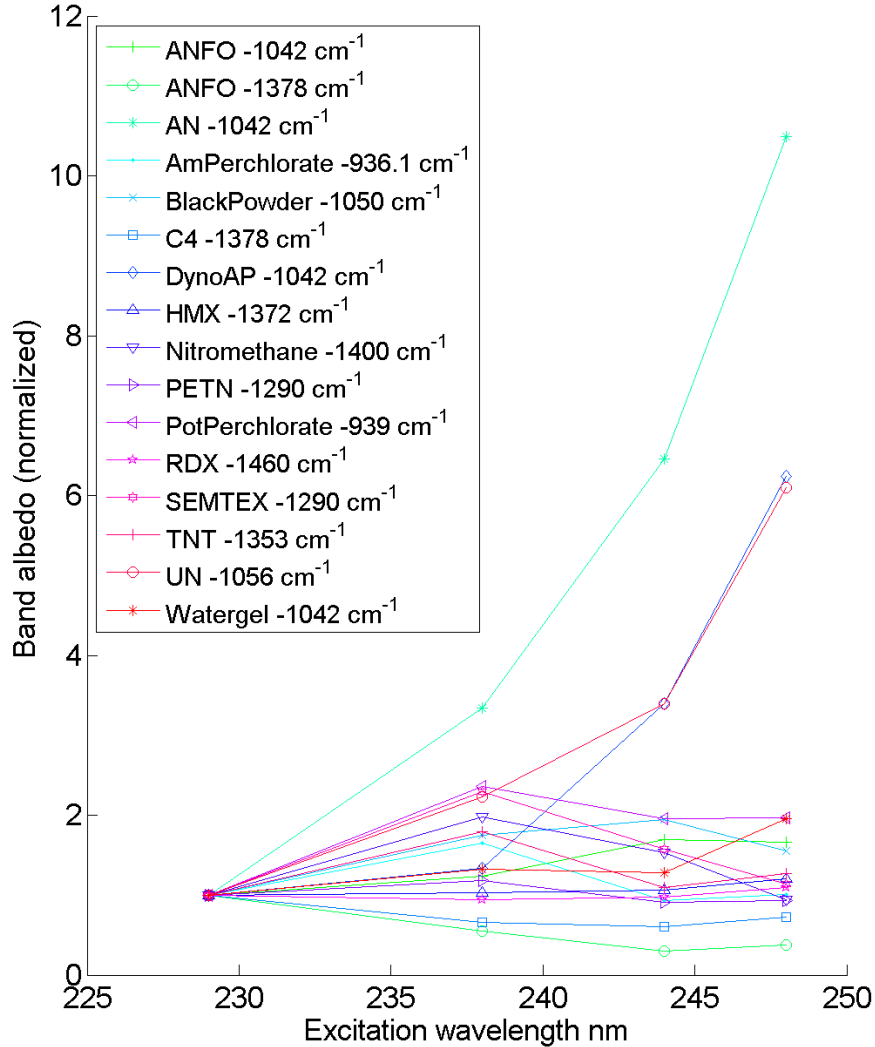


Figure 5: Ratios of band intensities of prominent bands normalized to the band intensity at 229 nm wavelength-excitation.

Figure 5 shows a plot of ratios of band intensities of prominent bands of all the measured explosives. A wide range of variation in the ratios of band intensities as a function of excitation wavelength is noticed. Nearly all explosives, with the exception of RDX and HMX, show a variation greater than 50%. Therefore, these signatures will be noticed even when the signal-to-noise ratio is as small as 5. RDX and HMX in our experiments were degraded due to long exposure time and showed small variation (<20%). A sensitive detection instrument will overcome degradation and produce better ratio signatures.

SPECIFICITY ENHANCEMENT

For each explosive, we use the ratios and the corresponding band position as a unique signature. As an example, we plot the signatures derived from spectra obtained using dual-excitation-wavelengths (DEW) in Figure 6(a). The ratio of band intensity at 244 nm to the band intensity value at 229 nm is plotted as a function of band position in the two dimensional plot. The signatures show a very clear separation even with just two excitation wavelengths. On the contrary, single-excitation-wavelength (SEW) signatures of explosives lack the y-axis (ratio axis) which results in signature overlap

among similar species. Hence SEW technique lacks specificity. In order to quantify the specificity of the technique in distinguishing explosives and interferences, we developed a similarity score. The score is formed from the product of a window function applied to the frequency position and a metric based on the difference between the target and sample band intensity ratios. A score of one implies a perfect match. Figure 6(b) shows similarity maps of DEW and SEW techniques. A dramatic enhancement in specificity from the DEW technique is noticeable in the figure. Since only the most prominent peaks are used in the signatures, the specificity enhancement is retained even at the sensitivity limit of a DEW instrument, where the noise level is just below the strongest peak.

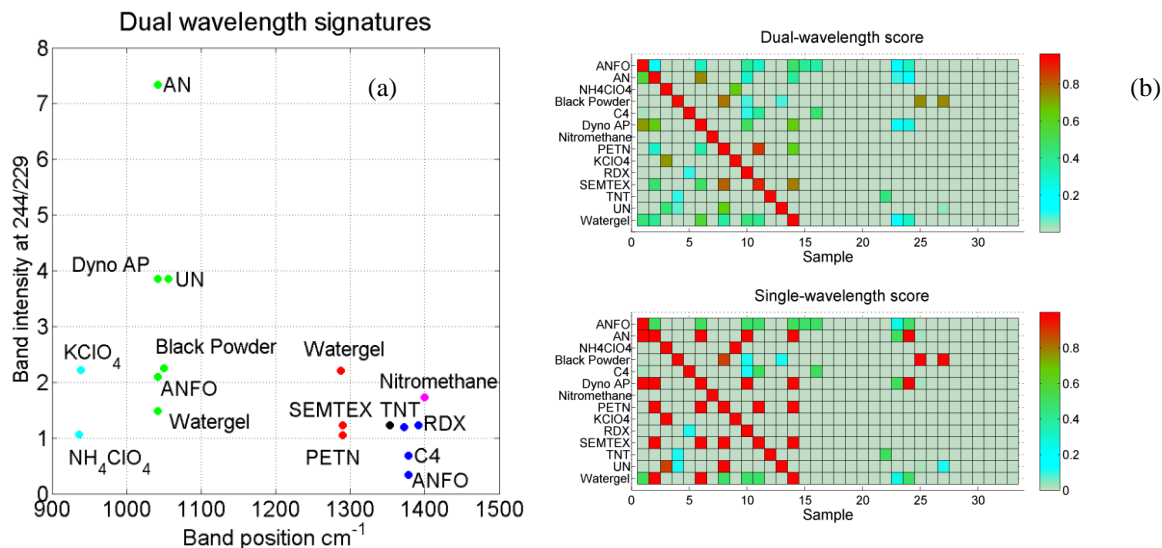


Figure 6: (a) Dual-excitation-wavelength signatures of measured explosives. (b) Similarity score maps derived using the Raman spectra measured at 229 nm and 244 nm. First fifteen materials on the x-axis are the same as target explosives shown on the y-axis. Number 16-33 on the x-axis are interferences.

SUMMARY

We presented the concept of multiple-excitation-wavelength DUV resonance Raman technique for the detection of trace amounts of explosives. MEW DUV Raman spectra of several explosives and interferent materials were measured. MEW signatures were derived using the band frequency and band intensity ratios from these spectra. Plots of these signatures show a clear separation among all explosives, where as single wavelength signatures overlap. A dramatic improvement in specificity is noticed in the MEW technique.

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